Maximum Allowable Concentration, Residual Saturation, and Free-Product Mobility

Technical Background Document and Recommendations

Prepared for

Alaska Statement of Cooperation Working Group

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Preface

This document was created under the Alaska Statement of Cooperation (SOC), which is an agreement between the Alaska Department of Environmental Conservation (ADEC), the U.S. Environmental Protection Agency (EPA), the Departments of the Army, Air Force, Navy, Military and Veterans Affairs (Army National Guard), Interior, and the Federal Aviation Administration (FAA) and U.S. Coast Guard. The objective of the agreement is to work cooperatively to identify and resolve issues affecting human health and the environment through promoting compliance with environmental laws, preventing pollution, creating partnerships to identify and cleanup contaminants and pollution, promoting training and coordinating with affected Tribes. A subcommittee or "working group" was formed under the SOC to evaluate the characterization and fate and transport of petroleum hydrocarbons spilled in the environment, and the risks posed by petroleum contamination. FAA contracted with Geosphere and CH2M Hill to research the issues and develop eight technical issue papers. The paper titles are listed below. Staff from ADEC, FAA, the Army and Army Corps of Engineers, and the Army National Guard reviewed and provided feedback on the draft papers. These papers provide sound scientific and technical information along with recommendations for use and/or future consideration.

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Statement of Cooperation Working Group Paper Titles

1. Three- and Four-Phase Partitioning of Petroleum Hydrocarbons and Human Health Risk Calculations, Technical Background Report Document and Recommendations
2. Hydrocarbon Characterization for Use in the Hydrocarbon Risk Calculator and Example Characterizations of Selected Alaskan Fuels, Technical Background Document and Recommendations
3. Dilution-Attenuation Factors at Fuel Hydrocarbon Spill Sites, Technical Background Document and Recommendations
4. Maximum Allowable Concentration, Residual Saturation, and Free-Product Mobility, Technical Background Document and Recommendations
5. Groundwater Sampling Techniques for Site Characterization and Hydrocarbon Risk Calculations, Technical Background Document and Recommendations
6. Migration to Indoor Air Calculations for Use in the Hydrocarbon Risk Calculator, Technical Background Document and Recommendations
7. Site Conditions Summary Report for Hydrocarbon Risk Calculations and Site Status Determination, Technical Background Document and Recommendations
8. Proposed Environmental Site Closeout Concepts, Criteria, and Definitions, Technical Background Document and Recommendations

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Acronyms and Abbreviations

AAC	Alaska Administrative Code
ADEC	Alaska Department of Environmental Conservation
API	American Petroleum Institute
CONCAWE	Conservation of Clean Air and Water in Europe
DRO	diesel-range organics
GRO	gasoline-range organics
L/m^3	liters per square meter
LNAPL	light nonaqueous phase liquid
mg/kg	milligrams per kilogram
mm	millimeter
NAPL	nonaqueous phase liquid
psi	pounds per square inch
RRO	residual-range organics
SOCWG	Alaska Statement of Cooperation Working Group

SECTION 1

Introduction

As part of a broad policy of protecting human health and the environment, the Alaska Department of Environmental Conservation (ADEC) requires the recovery of free product to the extent practicable, and has incorporated "maximum allowable concentration" criteria for petroleum hydrocarbons into Table B2 of the contaminated sites regulations (18 Alaska Administrative Code [AAC] 75). The free product recovery requirement is described in Section 18 AAC 75.325(f) as follows: *"A responsible person shall (1) to the maximum extent practicable, (A) use permanent remedies; (B) recover free product in a manner that (i) minimizes the spread of contamination into an uncontaminated area by using containment, recovery, and disposal techniques appropriate to site conditions; (ii) avoids additional discharge…."*. The "maximum allowable concentration" criteria place a cap or ceiling on the gasoline range organics (GRO), diesel range organics (DRO) and residual range organics (RRO) concentrations that may remain at a site, which may be below the risk based concentration calculated for the site. As described in footnote 14 to Table B2, the maximum allowable concentration "*is the concentration of C_6 - C_{10}, C_{10} - C_{25}, or C_{25} - C_{36} petroleum hydrocarbon range in surface and subsurface soil that, if exceeded, indicates an increased potential for hazardous substance migration or for risk to human health, safety, or welfare, or to the environment; the level of a petroleum hydrocarbon may not remain at a concentration above the maximum allowable concentration unless a responsible person demonstrates that the petroleum hydrocarbon will not migrate and will not pose a significant risk to human health, safety, or welfare, or to the environment."* As described here the maximum allowable concentration criteria emphasizes contaminant mobility issues; however, the ADEC points out that the maximum allowable criteria are also intended to address other environmental criteria, including but not limited to, aesthetic criteria such as soil staining and/or noxious odors, anti-degradation, public opinion that pollution is bad (e.g. a public outrage factor), pollution prevention issues, and phyto-toxicity issues (ADEC, 2005).

Because the above description relates the maximum allowable concentration to "the concentration above which there is an increased risk of hazardous material migration" and because the numerical values chosen for GRO, DRO and RRO maximum allowable concentrations are drawn or modified from a section of an American Petroleum Institute (API) publication (API 1628) dealing with the concept of residual saturation, the term "maximum allowable concentration" could be interpreted to be related to the concentration at which the hydrocarbon product becomes mobile as a separate phase (i.e., the oil can flow through the soil) and to be similar to the term "residual saturation." The terms residual saturation and residual concentration may be described as the hydrocarbon concentration remaining in a soil after oil has flowed through a vadose zone soil, or after water has displaced oil from a saturated zone soil. At concentrations below residual levels hydrocarbon product is not mobile as a separate phase. The terms residual saturation and residual concentration are commonly used in soil physics, petroleum engineering, and environmental engineering; however, the details or implications of the terms' meanings may vary slightly. The API 1628 document lists example residual saturation concentrations for soils with differing textures. ADEC considered API 1628 values when establishing the maximum allowable concentration values.

The requirement to recover free product is commonly interpreted to refer to free product that collects on the groundwater surface in monitoring wells, although phase partitioning relationships show that free product is present at relatively low GRO, DRO and RRO concentrations (e.g., 30 milligrams per kilogram [mg/kg] DRO). Note that in this report, the terms "oil phase," "oil," "free product," and "nonaqueous phase liquid (NAPL)" are used synonymously and do not necessarily indicate that oil has been observed in a monitoring well or that the oil phase is mobile. A key part of the free product recovery requirement is the phrase "to the extent practicable." The ADEC and U.S. Environmental Protection Agency (EPA) define "practicable" with the statement that a remedial "*alternative is not practicable if the incremental cost of the alternative is substantial and disproportionate to the incremental degree of protection afforded by the alternative as compared to another lower cost alternative.*" Therefore, the benefit or risk reduction provided by free product recovery must be understood to assess if free product recovery is practicable.

The risk-screening levels for the migration-to-groundwater, outdoor-air-vapor-inhalation and soil-ingestion pathways calculated by using Raoult's Law show that, depending on site conditions, GRO, DRO, and RRO concentrations higher than the current ADEC maximum allowable concentration may remain in soils without creating a human health risk.

This document presents background information on oil mobility in soils, background information regarding the API 1628 document, and information on the significance of oil in monitoring wells. The information in this paper may be used to help a responsible person assess if the hydrocarbon concentrations measured at a particular site pose an increased migration risk, and depending on the assessment results, *demonstrate that the petroleum hydrocarbon will not migrate* as required in footnote 14 to Table B2. The hydrocarbon risk calculator (described in another Alaska Statement of Cooperation Working Group [SOCWG] paper) will help assess if the *petroleum hydrocarbon poses a significant risk to human health, safety, or welfare* as required in footnote 14 to Table B2. This document proposes use of the "Charbeneau Equation" to help assess if NAPL discovered in monitoring wells is mobile at the site scale, which is key to assessing if free product recovery is practicable as required in 18 AAC 75.325(f). Other calculation tools or models are available to help assess the reduction in source area longevity facilitated by free product recovery. The paper does not directly address the aesthetic, public opinion, anti-degradation, and phyto-toxicity environmental issues incorporated into the maximum allowable concentration concept. However, by providing a tool to directly address the free product mobility issues, this paper allows the other criteria to be separated and addressed independently.

SECTION 2

Units Used to Describe and Quantify Water and Oil in Soil

Residual saturation terminology and concepts have been primarily developed in the fields of petroleum engineering and soil science. In these fields, it is necessary to describe the flow of water, oil, and gas through a reservoir and the movement of water and air through a soil. As the field of environmental engineering has developed, the concepts behind multiphase flow and residual saturation have been borrowed and applied to hydrocarbon contamination problems.

Several terms and interrelated units of quantification are commonly used to describe the water and oil content of a soil. Several examples follow:

- Water and oil saturation values refer to the fraction of the soil pore space filled with the fluid of interest (water saturation = volume of water in a given soil volume/volume of soil pores in the same soil volume). These values are unitless or expressed as percentages.
- Water and oil concentration values refer to weight of the water or hydrocarbon in a sample of soil relative to the weight of the solid soil particles in that same sample (oil concentration mg/kg = weight of oil in milligrams in a given soil sample / weight of solid soil particles in kilograms in the same soil sample). These values are commonly expressed on a parts per million or mg/kg basis.
- Gravimetric values for water content refer to the weight of the water in a volume of soil relative to the weight of the solid soil particles in that volume (water content = weight of water in a given soil volume/weight of solid soil particles in the same soil volume). These values are commonly expressed as fractions or percentages.
- Oil-retention capacities refer to the volume of oil in a given volume of soil (oil retention capacity = volume of oil in a given soil volume/volume of soil). These volumes are commonly expressed in units of liters per cubic meter (L/m^3).

The different units used to characterize water or oil in a soil may be related to each other if the fluid densities, soil bulk densities, and specific gravities of the solids are known.

SECTION 3

Water—a Polar Molecule

The two hydrogen atoms that attach to an oxygen atom to form the water molecule are located more to one side of the water molecule than the other, giving the water molecule a side that has a positive charge and a side that has a negative electrical charge (Brady and Weil, 1996; Hillel, 1980). This polar nature of the water molecule causes water molecules to have an affinity for soil particles (described as adhesion) and an affinity for other water molecules (described as cohesion). The water in a soil above the water table tends to coat the soil particle surfaces (hygroscopic moisture) and to fill the small pore spaces where soil grains contact each other (capillary water). Because water will typically cover the soil particles first and then oil will cover the water, with air (in general) not contacting the soil or water, water is called the "wetting phase" and oil and air are referred to as the "nonwetting phases" (in two-fluid systems) (Corey, 1994). In a three-fluid system in which water, oil, and air are present simultaneously, the oil will be the intermediate phase and will tend to cover the water surfaces, which are covering the soil surfaces, and air will tend to occupy the largest soil pores. If only oil and air are present in soil, oil will preferentially coat the soil particles. In this report, water is always considered the wetting phase (wetting phase is synonymous with water) and oil or air will be the nonwetting phase when discussing two-fluid systems.

The cohesive and adhesive properties of water cause complex, but understandable and predictable, interactions between water, oil, and air in the soil environment. Understanding a few details of these interactions will aid interpretation of the test results for residual saturation and the development of appropriate criteria for assessing free-product mobility. The discussion draws from numerous references, including Hillel (1980), Corey (1994), Brady and Weil (1996), and Dullien (1992).

SECTION 4

Soil Moisture Retention

As shown in Figure 1, when the tip of a small-diameter hollow glass tube (called a capillary tube) is immersed in water, the polar water molecule is attracted to the walls of the tube and tends to rise in the tube (Corey, 1994; Hillel, 1980). Because water molecules are also attracted to other water molecules, the water rising on the walls of the capillary tube tends to pull a water surface up the capillary tube until the force of gravity equals the forces of adhesion and cohesion. The height of rise of any fluid in a capillary tube is inversely proportional to the diameter of the tube and directly proportional to the surface tension of the fluid:

$$h = 2T / r_c \rho g.$$

Where h = height of capillary rise

T = surface tension of the water

r_c = radius of the capillary tube

ρ = density of the fluid

g = force of gravity

For an air-water system, the height of water rise in a glass capillary tube reduces to $h = 0.15 / r_c$. Therefore, the capillary rise in a large-diameter tube is less than in a small-diameter tube. The interconnected pores of a soil may be viewed as a "bundle of capillary tubes" of different sizes. The diameters of the capillary tubes in a bundle representing a soil conceptually mirror the distribution of pore sizes in the soil. If the soil has relatively small pores, represented by small capillary tubes, the soil tends to hold water tightly and retain a high moisture content even when the water is under high tension, as shown for a silt in the sketch (upper right) in Figure 1. If the soil has relatively large pores, represented by large capillary tubes, the soil tends to hold water loosely and has a low moisture content when the water is under high tension, as shown for a sand in the sketch (lower right) in Figure 1. Note that the size of the pores in a soil is related to the grain size distribution and the bulk density of the soil, but that the soil pore size and moisture-holding characteristics of a soil tend to be more a function of the finer size fractions than of the largest or median particle sizes.

The amount of water that a soil holds is commonly graphed as a function of the capillary pressure or tension in the water. The left side of Figure 1 provides an example of a graph or curve showing soil-moisture retention. The x-axis displays the amount of water in a given volume of soil and may be expressed in different units, such as percentage of saturation and grams or milliliters of water per cubic centimeter of soil. The y-axis quantifies the capillary pressure (the difference in pressure between the wetting and nonwetting phases in the soil) and is commonly expressed in units of pounds per square inch (psi), atmospheres or bars, and inches, feet, or centimeters of water. Below the water table, water pressures increase with depth; however, above the water table, soil moisture that is in vertical equilibrium is under tension or a negative pressure. Because "capillary pressure" is defined as the nonwetting-phase pressure

minus the wetting-phase pressure, capillary pressures have positive values (even though the water is held in tension). When the water in a small block of soil is in vertical equilibrium, the capillary pressure is equal to the height of the block of soil above the water table. As shown on the soil moisture retention curve (Figure 1) at low-capillary pressures (for example, in a block of soil near the water table), both the sand and silt soils tend to be saturated. As the capillary pressure increases, the soils hold less water (for example, in a block of soil many feet above the water table). However, the sand soil with its larger soil pore and capillary tubes decreases in water content at lower capillary pressures than the silt soil. At very high capillary pressures, the moisture content of both the sand and silt soils does not continue to decrease, but rather stabilizes at an "irreducible" water content and tends to stay at that irreducible water content as the capillary pressure increases.

The moisture-retention curve of a soil sample is generally measured by using a pressure plate apparatus or a centrifuge, and the data generated are characteristic only of a relatively small "representative elemental volume" of soil. In most cases, analysis of many samples and an understanding of site soil stratigraphy are necessary to characterize a site.

SECTION 5

Hysteresis

The void spaces in a soil are incredibly complex. They consist of relatively large pore bodies and narrow pore throats ranging in size over several orders of magnitude, with myriad cross-connections and tiny spaces where soil grains converge and contact each other. Although the simple model of a capillary tube bundle has a limited capacity to represent the complexity of a real soil, by modifying the shape and length of the capillary tubes and adding connections between tubes, the conceptual capillary tube model may be used to illustrate several phenomena displayed by soils.

For example, when a soil undergoes drainage (which is always defined as the decrease in the wetting-phase content of the soil), the saturation-pressure relationship follows the moisture retention curve or "drainage curve" of the soil. However, when the same soil increases in moisture content, the saturation-pressure relationship follows a different curve (top left of Figure 2) (Hillel, 1980; Corey, 1994; Brady and Weil, 1996). This wetting or "imbibition" curve has a lower moisture content at a given capillary pressure than the drainage curve. The difference in the moisture contents at the same capillary pressure may be understood by envisioning capillary tubes that have undulating walls that represent pore bodies and pore throats (top right of Figure 2). As the capillary pressures increase during drainage, the water level in a capillary tube drops. If the capillary pressure is sufficient to allow a narrow pore throat above a wide pore body to remain saturated, however, the pore body below retains water (even if the capillary pressure is not sufficient to allow a continuous capillary tube of the pore body diameter to remain saturated). In contrast, as the capillary pressures decrease during imbibition, the water level in a capillary tube cannot rise through the wide pore-body portion of the capillary tube and into the pore throat until the capillary pressures decrease enough to allow the pore body to become saturated.

The different saturation-pressure relationships that occur when a soil is draining versus wetting are called "hysteresis." Many soil physics textbooks describe the soil-drainage and wetting-curve hysteresis and show the drainage and wetting curves converging at 100 percent saturation (top of Figure 2). After draining significantly, however, a soil is unlikely to become fully saturated with the wetting phase again because of trapping of the nonwetting phase.

SECTION 6

Hysteresis and Trapping

Recognizing the tendency of a soil to not fully resaturate during imbibition is critical to understanding residual saturation and oil mobility in soils.

As indicated above, when developing drainage and wetting curves for soils in the laboratory, the wetting curve generally does not merge with the drainage curve at 100 percent saturation and zero capillary pressure. Rather, at zero capillary pressure, the wetting curve shows that the soil is less than 100 percent saturated with the wetting phase (water) and therefore must contain some nonwetting phase (oil or air) trapped within the pore structure of the soil (as shown on the soil moisture curve in the lower left of Figure 2). The trapping of the nonwetting phase by the wetting phase during imbibition has been studied as it pertains to oil in reservoir rocks and at oil spill sites. Two primary trapping mechanisms have been identified: snap-off, and bypassing (Mohanty et al., 1982). "Snap-off" refers to the break in continuity of the nonwetting phase between adjacent pores. During snap-off, the wetting and nonwetting phases are both flowing through pore throats and pore bodies that have a large difference in diameter (lower right of Figure 2). The differences in the diameters cause a low wetting-phase pressure in the pore throats, which causes a collar of wetting-phase fluid to build in the pore throat. The collar may eventually bridge the pore throat, breaking the continuity of the nonwetting phase. In the "bypassing" process, the myriad connections between pores allow the wetting-phase fluid to follow a flow path that is different from that followed by the nonwetting phase. The wetting phase bypasses and surrounds pores that contain the nonwetting phase. Two pore configurations that allow bypassing are shown in the lower right of Figure 2. Research by Chaztis (1982) shows that the rate of capillary-pressure change and rate of wetting- and nonwetting-phase flow influences which pores that contain the nonwetting phase are bypassed by the imbibing wetting phase (with the result that the same soil may yield different imbibition curves under different flow regimes). Both the snap-off and bypassing mechanisms or processes are caused by *contrasts in pore sizes, shapes, and interconnections* and, presumably, the trapping of the nonwetting phase occurs similarly across a wide range of pores sizes (given that the capillary pressures are sufficient to allow the non-wetting phase to enter a particular pore size range).

Once the nonwetting phase in a given pore becomes physically separated or discontinuous from the nonwetting phase in an adjacent pore, the nonwetting phase can no longer flow as a separate phase (Corey, 1994; Dullien, 1992; Parker and Lenhard, 1987; Lenhard and Parker, 1987). The discontinuous or trapped nonwetting phase is said to become "immobile residual" or "residual saturation." Note that at very high gradients, a portion of the immobile residual may be transported as immiscible globules (Wilson and Conrad, 1984). Groundwater gradients are not typically steep enough to cause migration of the immiscible globules, but pumping and water injection activities may create gradients that promote localized migration of the immiscible globules.

Figure 3 shows details from moisture-retention curves with hysteresis and trapping from several sources (Dullien, 1992; Iwata et al., 1988; Luckner and Schestakow, 1990). In each study,

the authors appeared to follow similar drainage and wetting steps and described the resulting legs of the saturation-pressure curves as follows:

- Step 1 starting with a soil 100 percent saturated with water (the wetting phase) and displacing the water with the air or oil (the nonwetting phase) to the irreducible water content. Morrow and Harris (1965) called the drainage curve that formed during this displacement of the wetting phase from 100 percent saturation to the irreducible water content the "primary drainage curve," and Iwata et al. (1988) called this curve the "first drainage curve."
- Step 2 starting at the irreducible water content and displacing the nonwetting oil or air with water to a capillary pressure of zero. Morrow and Harris (1965) called the resulting curve the "secondary imbibition curve," and Iwata et al. (1988) and Luckner and Schestakow (1990) called the resulting curve the "main wetting curve." This secondary imbibition curve or main wetting curve does not rejoin the primary drainage curve and return to 100 percent saturation with water at zero capillary pressure. *The trapped non-wetting phase (oil or air) content that occurs following wetting from the irreducible water content was defined as the residual saturation in all of the studies.*
- Step 3 starting at residual saturation for the nonwetting phase and again displacing the water with air or oil to the irreducible water content. The drainage curve formed is called the "secondary drainage curve" by Morrow and Harris (1965) and the "main drainage curve" by Iwata et al. (1988) and Luckner and Schestakow (1990).
- Step 4 changes the capillary pressures to cause partial wetting and drainage. The wetting and drainage curves created form a family of "scanning curves" between the secondary drainage curve of Morrow and Harris (1965) or main drainage curve of Iwata et al. (1988) and Luckner and Schestakow (1990) and the secondary imbibition curve of Morrow and Harris (1965) or main wetting curve of Iwata et al. (1988) and Luckner and Schestakow (1990). The graph shows that after drainage to the irreducible water content and imbibition to zero capillary pressure, all subsequent capillary pressure changes will yield saturations between the main drainage and main wetting curves, and that the capillary-pressure and saturation changes will display hysteresis.

The above studies and terms are useful in understanding some of the processes and paths occurring during wetting-phase displacement and imbibition, but they may not be representative of field conditions at an oil spill site. The most important difference between the curves shown in Figure 3 and what occurs in the field is that oil displaces water from 100 percent saturation to the irreducible water content of soils only on rare occasions. In most oil spill situations, the capillary pressures that form limit the water drainage and oil saturation to something less than the irreducible water content. Therefore, some fraction of the soil pores that have the potential to trap oil never become oil-filled and do not trap oil. This concept is illustrated in Figure 4, where oil initially displaces water from 100 percent saturation following the first or primary drainage curve (Curve 1 in Figure 4). Before the irreducible water content is reached, however, the capillary pressure decreases to zero and the soil is re-wet (Curve 2 in Figure 4), but with a trapped oil phase. The trapped oil is immobile residual, but the percentage of saturation or residual concentration is not the maximum that the soil can hold as immobile residual. As depicted in Figure 4, if oil again displaces water but to a higher capillary pressure (and higher oil saturation and lower water saturation) than in the first drainage event, and then

the soil is re-wet to zero capillary pressure, there is a higher residual saturation (Curves 3 and 4 in Figure 4). The additional residual oil saturation represents oil trapped in pores that were not drained in the initial drainage event. Finally, if oil displaces water to the irreducible water content and the soil is re-wet to zero capillary pressure, then the "maximum" residual saturation or concentration for that soil would be measured. The additional residual oil saturation, measured in the third drainage and wetting cycle in this hypothetical example, represents oil trapped in pores that were not drained in the two preceding drainage events. From this discussion, the following conclusions can be drawn:

- The residual saturation or residual concentration measured in a field sample from a contaminated site is a function of the saturation history of the soil and, most importantly, the maximum historical oil saturation of the soil.
- The residual saturation value measured in a laboratory test, in which oil displaces water to the irreducible water content, may commonly be greater than what is observed in the field.

SECTION 7

Relative Permeability

Why drainage does not occur to the irreducible water content at contaminated sites may be explained by considering (1) the magnitude of the capillary pressure required to reach the irreducible water content, and (2) changes in oil and water permeability during drainage and imbibition. The capillary pressure required to reach the irreducible water content varies greatly with soil type, but has been characterized for many types in a database recently prepared by API. Example capillary pressures required to drain a soil to the irreducible water content show that relatively tall oil columns (commonly tens of feet of oil) are necessary to generate the required capillary pressures.

The permeability of a soil is a measure of the ability of the soil to transmit fluid when saturated with that fluid. (Hydraulic conductivity describes the flow of water through a soil.) During drainage and imbibition the soil is not saturated, and the presence of water and oil, water and air, or all three in the soil pores dramatically changes the permeability of the soil to each fluid. A typical "relative permeability" graph (Figure 5) shows characteristic changes in the permeability of the wetting and nonwetting phase as a function of the saturation of each phase (assuming only two phases are present). The dual x-axes in Figure 5 show the wetting-phase saturation and the nonwetting-phase saturation. (The sum of the wetting and nonwetting phases must always be 100 percent.) The y-axis of the graph is the relative permeability, which is the fraction of the saturated permeability (relative permeability = permeability at some saturation x/saturated permeability). As shown in Figure 5, when either fluid is at 100 percent saturation, the relative permeability of that fluid is 1; however, as the saturation of either fluid drops from 100 percent, the relative permeability changes in a very nonlinear fashion. Examining Figure 5 in greater detail, and assuming that water is the wetting phase and oil is the nonwetting phase, the water permeability can be observed to decrease dramatically as the water saturation drops below 100 percent. For example, at about 92 percent water saturation, the water permeability is less than 40 percent of the saturated permeability (in the hypothetical soil represented by the diagram). This rapid decrease in permeability results from the largest-diameter pores, which are responsible for most of the permeability of the soil, being the first pores dewatered by the invading oil. According to Poiseuille's Law, the flow through a capillary tube is a function of the fourth power of the radius of the tube. This indicates that a single 4-millimeter (mm) capillary tube can transmit as much fluid as sixteen 2-mm tubes and two hundred fifty-six 1-mm tubes (holding all other variables constant). It should also be noted that at about 92 percent water saturation and 8 percent oil saturation, the oil permeability is still zero. This permeability value results because at about 8 percent saturation, the oil is not yet continuous through the soil volume represented by the diagram. As the oil saturation increases above about 8 percent (in the hypothetical soil represented by the diagram), the oil phase becomes continuous through the soil and develops permeability that increases relatively quickly as the oil saturation continues to increase. As the water content decreases to the irreducible water content, the water relative permeability asymptotically approaches zero. As the water content approaches the irreducible water content, the oil relative permeability approaches 1 but, because water still occupies some soil pores, the oil relative permeability never reaches 1 in a soil that was originally water wet

Achieving the capillary pressure necessary to dewater a soil to values near its irreducible water content requires a large oil head. Figures 4 and 5 show that as capillary pressures increase, a corresponding increase in saturation and relative permeability would result. The combination of an increasing oil pressure and increasing oil permeability would tend to promote rapid flow away from the high-pressure area (the center of the spill), which would naturally tend to limit the capillary pressures achieved in the field. The limited capillary pressures would limit the maximum oil saturation achieved and, in turn, limit the residual saturation or residual concentration measured in field samples to values below those measured in laboratory tests.

During imbibition, the water and oil relative permeability curves follow a slightly different path than during drainage (Figure 5). This hysteresis is a result of the trapping of oil and the displacement of water into larger-diameter pores during imbibition. It should also be noted that the oil permeability decreases to zero when the oil reaches residual saturation, and that the distribution of the trapped oil at residual saturation is very different than the distribution of oil when the oil first becomes continuous through the representative elemental soil volume. (When oil first becomes continuous through the soil, during oil invasion and water drainage, the oil occupies only the largest interconnected pores. In contrast, when the oil becomes discontinuous during water imbibition, the residual oil is trapped in a cross-section of soil pore sizes.)

SECTION 8

Residual Saturation Trends

As described by Schwille (1984) and suggested by the preceding discussion, the distribution and concentration of oil in the soil at a spill site are influenced by the rate of hydrocarbon release; the total oil volume released; oil properties such as density and viscosity; soil properties such as porosity, grain size distribution, permeability, and moisture content at the time of release; soil stratigraphy and structure; depth to groundwater; and the magnitude and timing of water table fluctuations. Despite this large number of variables, the large range in values for many of the variables, and the difficulty in measuring the values of many variables, the distribution of hydrocarbon follows general patterns at most spill sites and, with careful study, the distribution and migration may be quantitatively assessed. Mercer and Cohen (1990) published a review on immiscible fluids in the subsurface. In the section of the paper describing residual saturation, they point out the following observations and conclusions about the trends in residual hydrocarbon distribution at spill sites:

- At the irreducible water content, the water phase is continuous, but at residual saturation the nonwetting phase is not continuous.
- In the vadose zone, infiltrating oil may not have to significantly displace water because the soil is likely unsaturated and oil is more wetting than air and therefore is drawn into the soil pores. (Some residual oil in the vadose zone may be present as a continuous film covering the wetting phase.)
- The residual concentration in the vadose zone tends to increase with decreasing intrinsic permeability, effective porosity, and soil moisture content.
- Higher residual concentrations may be expected in the saturated zone, in part because the fluid density ratio favors greater drainage in the vadose zone.
- Residual saturation tends to increase with increasing differences in the pore throat to pore body sizes and pore size heterogeneity, and with decreasing porosity.

SECTION 9

Rate of Oil Infiltration

The rate of oil infiltration is of interest when assessing residual saturation concentrations to help answer the question, "are the oil concentrations measured at the site the residual concentration, or is the oil still draining?" A few published papers help address this issue:

- A paper by Hoag and Marley (1986) describes the technique they used to establish residual saturation in prepared soils in the laboratory. They note that the majority of gravity drainage occurs in a period of hours after introducing fluids into the soil column and not in periods of months or years.
- A 1974 Conservation of Clean Air and Water in Europe (CONCAWE) document also describes in general terms the rate of hydrocarbon infiltration and spreading following a spill, stating that "40 to 70 percent of the maximum spread is obtained in the first 24 hours, and 60 to 90 percent in one week." (CONCAWE is the health, safety, and environment organization for European oil companies.)
- A U.S. Geological Survey paper by Prill et al. (1965) evaluated the effect of time on soil column drainage and found that most of the gravity drainage occurred in a period of hours or days and that moisture redistribution later in time occurred by vapor migration and not mass flow.

Most contaminated site investigations are conducted relatively long after the spill has occurred, given the drainage rates listed in the literature (typically months or years after the spill). Therefore, it is logical to assume that the vadose-zone soil concentrations measured during these site investigations are the residual saturation concentrations, given the history of that particular soil. Intuitively, if oil was mobile in the vadose zone it would drain, and if oil in the vadose zone did not drain over the course of months or years, it is immobile by definition.

SECTION 10

Free Product on the Water Table and Product Mobility

Oil that infiltrates through the vadose zone to the saturated capillary fringe tends to displace water from the water-saturated pores until the weight of the oil balances the weight of the displaced water. If sufficient oil infiltrates to the water table, the oil saturation in the vicinity of the capillary fringe will increase until the oil pressure is sufficient to collapse the capillary fringe and reach the water table. At the water table, the oil tends to form a low free-product mound and spread laterally or semiradially (especially in the immediate vicinity of the infiltrating oil). When the movement of free product to the water table is terminated, the oil in the vicinity of the water table will tend to continue to spread laterally until "the resisting forces in the water wet sediments balance the driving forces in the NAPL pool" (Huntley and Beckett/API, 2001). Without water table fluctuation, the rate of spreading will tend to decrease asymptotically as the oil head dissipates, and as continuous mobile oil becomes trapped residual oil (McWhorter and Sunuda, 1990). Rising or falling water table conditions will tend to accelerate the decrease in the mobile oil volume and the increase in residual oil volume by increasing the volume of soil contacted by the oil. However, continuous free product may persist in monitoring wells at a contaminated site for an extended period.

Monitoring wells installed in the core of the contaminated zone and with screened intervals bridging the water table are the best tools to discern whether continuous free product, mobile free product, or both are present at a site. Research papers by Charbeneau et al. (1999), Huntley and Beckett (2001), Lenhard and Parker (1990), Farr et al. (1990), and others have provided a technical basis for understanding free-product migration and support the following conclusions:

- If oil does not collect in properly installed monitoring wells during periods of low water levels, "continuous" oil is not present at the spill site, and any oil present is immobile residual.
- If oil does collect in a monitoring well, oil is continuous in the soil near the monitoring well, but may or may not be mobile at a site scale.
- For the continuous oil to be mobile, the oil thickness, measured in monitoring wells near the downgradient edge of the free-product footprint area, must be great enough to overcome the water-displacement pressure (or pore-entry pressure) of the uncontaminated soils adjacent to the soil containing continuous free product.
- Example water-displacement pressures for several soils types are expressed as thickness of oil in Table 2. (The oil thickness values are the approximate minimum oil thicknesses that must be present in a monitoring well to cause oil to migrate into uncontaminated soils.) According to the Charbeneau et al. (1999) data in Table 2, about 1 foot of oil must be present in monitoring wells for oil (with a specific gravity of 0.85) to displace water and invade uncontaminated adjacent sand soils, and up to about 6 feet of oil must be present in

monitoring wells for the oil to be able to displace water and invade uncontaminated silty soils. *Mobile oil will stop migrating when the oil pressures in the continuous oil body are insufficient to overcome the water-displacement pressure in adjacent soil pores.* When the oil pressures in the oil body become insufficient to cause migration of oil, the oil pressures are typically still sufficient to allow the oil to enter a monitoring well (which acts as a large pore with a very low displacement pressure). Therefore, oil will enter monitoring wells, creating a measurable oil thickness or sheen in the well, when it is not mobile in the formation. When continuous oil has insufficient pressure to migrate farther downgradient, the immobile continuous oil will tend to be smeared through water table fluctuation and become discontinuous. This immobile continuous oil will also tend to dissolve, biodegrade, or volatilize. However, immobile continuous oil may persist in monitoring wells at a contaminated site for an extended period. The thickness of oil equivalent to the water-displacement pressure may be calculated on a site basis by using the following equation (Charbeneau et al., 1999):

$$\Delta\psi = (\{(\sigma_{ow}/\sigma_{aw})/(1-(\rho_o/\rho_w))\} - \{(\sigma_{ao}/\sigma_{aw})/(\rho_o/\rho_w)\}) \psi_{baw}$$

Where:

$\Delta\psi$ = Light nonaqueous phase liquid (LNAPL) thickness equivalent to entry pressure

σ_{ow} = interfacial tension of the oil/water pair

σ_{aw} = interfacial tension of the air/water pair

σ_{ao} = interfacial tension of the air/LNAPL pair

ρ_o = LNAPL density

ρ_w = water density

ψ_{baw} = air-water bubbling pressure

The oil thicknesses listed in Table 2 also help explain the observation of oil in monitoring wells at many sites without apparent migration of oil at the site

- For continuous oil to be mobile, there must be an oil gradient. In an unconfined aquifer, the oil gradient may be discerned by measuring the elevation of the oil in at least three monitoring wells. If an oil gradient cannot be measured, the oil is likely immobile. If an oil gradient is measured, the velocity of the oil in the area of continuous oil may be estimated by using Darcy's equation as follows (excerpt from Sale, 2002; equation from Huntley and Beckett, 2001):

LNAPL Seepage Velocity = (Conductivity to LNAPL) x (Driving Force)

$$v_{LNAPL} = -\left(\frac{kk_{rLNAPL}\rho_{LNAPL}g}{\mu_{LNAPL}nS_{LNAPL}}\right)\left(\frac{dh_{LNAPL}}{dx}\right)$$

Where: v_{LNAPL} = seepage velocity of the LNAPL

k = permeability of the porous media

k_{rLNAPL} = relative permeability of the porous media to LNAPL

ρ_{LNAPL} = density of the LNAPL

g = gravitational constant

μ_{LNAPL} = viscosity of the LNAPL

n = porosity

S_{LNAPL} = fraction of the pore space filled with LNAPL

h_{LNAPL} = LNAPL head

x = the direction of LNAPL flow

"The terms in the first bracket on the right-hand side describe the formation's capacity to conduct LNAPL. Methods for determining the first bracket terms are described in subsequent text. The inputs in the second bracket describe the driving force. This information can be obtained using the elevation of the top of oil in three or more wells within a body of continuous LNAPL. When applying this technique one often finds that LNAPL moves far slower than groundwater at older releases. Recognizing groundwater flow to be slow (for example, < 1 ft /day) LNAPL seepage velocities can be quite small (for example, < 0.1-0.01 ft/day). On the other hand, observed migration rates from release points suggest that LNAPL may have moved faster than groundwater during the period(s) of active release. This would be consistent with large driving forces associated with LNAPL mounds beneath release points. Lastly, LNAPL seepage velocity is inversely proportional to viscosity."

- Oil that collects in a monitoring well does not fill all pores in the soil outside the well. Rather, the oil displaces water from the largest pores (as discussed in the sections on soil moisture-retention curves), while water remains in the smaller pores of the soil. The distribution of oil and water in the soil pores outside the well and the volume of mobile oil per unit area of aquifer containing continuous oil are functions of the soil properties and the thickness and specific gravity of the oil in the well (Charbeneau et al. 1999; Huntley and Beckett, 2001; Lenhard and Parker, 1990; Farr et al., 1990). The mobile oil volume in the soil outside a well may be estimated by integrating the oil saturation over the free-product interval in the monitoring well and is best expressed as a volume per unit area. In addition, the mobile-product volume at the site scale may be estimated by integrating the mobile oil volume indicated by the monitoring well data over the entire free-product-footprint area. The relationship between the thickness of oil in a monitoring well and distribution of oil in the soil outside the well is described by Sale (2002) in Figure 6.

The soil texture and pore size distribution of the formation soil outside a monitoring well greatly influence the relationship between the thickness of oil observed in the well and volume of product per unit area outside the well. As shown in the example at the top drawing of Figure 7, at a continuous oil volume per unit area of 0.3-cubic meter per square meter, a sandy soil would tend to have a smaller oil thickness (~1 meter) than would a loam soil (~2 meters). The bottom drawing of Figure 7 illustrates that at a given oil thickness in a monitoring well, finer-grained soils have lower volumes of oil per unit area than do coarser-grained soils. Figure 7 also clearly shows that significant oil thicknesses may be present when only relatively insignificant volumes of continuous oil are present in the formation. For example, in a silty sand, a monitoring well may contain a meter of oil, and yet there may be virtually no continuous mobile oil in the formation. Similarly, in a fine to medium sand, a monitoring well may contain a meter of oil, yet there may be less than about 10 cubic centimeters of continuous oil per square centimeter in the vicinity of the well.

As the water table rises and falls, the thickness of oil measured in a monitoring well should be expected to change as oil becomes trapped above and below the water table. (In general, lower oil thicknesses are observed during periods of high water and greater thicknesses of oil are observed during periods of low water.)

SECTION 11

Terms to Describe NAPL Distribution

The definition of several terms may facilitate communication about free product in the soil environment. The free product, or NAPL, exists when the soil concentration exceeds the soil saturation concentration (defined in Section 4), and NAPL or free product likely exists when DRO concentrations exceed about 30 mg/kg in a mineral soil. The oil phase may be divided into several categories that relate to whether the free product is continuously connected through the soil pores, the location of the oil above or below the water table, and the mobility of the oil as described below:

- "Pendular residual free product" is free product immobilized by capillary forces in the soil pores above the water table. Pendular residual free product is under tension, and is commonly described as occurring in the soil pores as "pendular rings" of oil at points where soil grains contact each other. Pendular residual free product is described as being discontinuous because the oil in one soil pore is not connected or continuous with the oil in an adjacent pore. When the oil is not continuous, it cannot be mobile as a separate phase. In addition, some vadose zone oil may be present as immobile films covering the wetting phase.
- "Insular residual free product" is free product immobilized by capillary forces in the soil pores below the water table. Insular residual free product is described as existing in the soil pores as "discontinuous globules," "isolated blobs," or "disconnected ganglia" of oil. The terms discontinuous, isolated, and disconnected are used because the oil in one soil pore is not connected or continuous with the oil in an adjacent pore. When the oil is not continuous, the oil cannot be mobile as a separate phase (although oil droplets or micells may be mobilized under high local-pressure gradients).
- "Continuous" free product is oil that is continuously connected through the soil pores. This continuous free product collects on the water table surface in monitoring wells. Continuous free product may migrate between pores containing oil; however, not all of the continuous free product that collects in monitoring wells is mobile at the site scale. On a site scale, the continuous free product may be further described as immobile and mobile continuous free product, based on the potential to migrate into uncontaminated downgradient soils.
  - Immobile continuous free product has a high enough oil saturation and oil pressure to collect in monitoring wells, but is not present at pressures that are high enough to overcome the displacement pressure or air-entry pressure of the in situ soil at the edge of the free-product footprint area; therefore, the free product cannot migrate farther downgradient. At sites where the spill source has been shut off and where the oil has been through several seasonal water table fluctuation cycles, the majority of the continuous free product is likely present as immobile continuous free product.
  - Mobile continuous free product is present under a positive pressure that exceeds the displacement pressure or air-entry pressure of the soil. As a result, the free-product front may advance farther downgradient. The velocity of the oil through the soil is controlled

by the intrinsic permeability of the soil, the oil saturation (or relative permeability), and the oil gradient.

SECTION 12

Background Information on the API 1628 Residual Saturation Values

To assess the appropriateness or applicability of the API 1628 values to Alaskan soils, it is necessary to understand the background and basis for the API 1628 values (the values that were considered by ADEC to help establish the maximum allowable cleanup levels). The API 1628 document presents the residual saturation values as part of a discussion of general conceptual models for fuel spills. The discussion points out that residual saturation values are generally higher in fine-grained soils than in coarse-grained soils and references the table that includes the numerical residual saturation values which were considered by the ADEC when developing the maximum allowable values. The API 1628 document does not present any background for the residual saturation values, other than listing the oil densities and soil bulk densities assumed for the soil types listed in the table and referencing "de Pastrovich and others, 1979" as the source of the data. Figure 8 is a flowchart that traces the API residual saturation values through a series of references, and Table 3 documents changes in the way the values are displayed in the different references.

The "de Pastrovich and others" paper (1979) is a CONCAWE publication titled *Protection of Groundwater from Oil Pollution* that deals with environmental responses to oil spills. The CONCAWE document presents the residual saturation values in a section of the report dealing with the depth of penetration of spilled oil into the vadose zone. The report lists typical values of the "oil-retention capacity" for several soil textures for a fuel with a viscosity similar to a kerosene, jet, or diesel fuel. The report notes that the oil-retention capacity may be multiplied by 0.5 for low-viscosity fuels, such as gasoline, and by 2.0 for higher-viscosity oils, such as "light fuel oil." The oil-retention capacities have units of liters of retained oil per cubic meter of soil (L/m^3). The retention values listed in the API 1628 document are the same values as those listed in the CONCAWE document; however, the API values have been converted to units of mg/kg by using an assumed typical soil-bulk density and fuel density (as listed in the API document). In addition, the viscosity adjustment factors have been applied so that the API document lists residual concentrations for gasoline, middle distillates, and fuel oil. The 1979 CONCAWE document references a 1974 version of a similar CONCAWE document as the source of the oil-retention capacities and does not provide any details on the soil classification system used to describe the soil textures.

The 1974 CONCAWE document titled *Condensed Inland Oil Spill Cleanup Manual* provides recommendations for oil spill response and presents the same oil-retention information contained in the 1979 report. However, the oil-retention information in the 1974 document is presented as a dimensionless oil-retention constant. The 1974 CONCAWE document also describes in general terms the rate of hydrocarbon infiltration and spreading following a spill, stating that "40 to 70 percent of the maximum spread is obtained in the first 24 hours, and 60 to 90 percent in one week." The 1974 CONCAWE report states that it is based on an ESSO manual for responses to inland oil spills in the United Kingdom. The ESSO manual presumably presents the same oil-retention capacities, and references a 1970 report prepared by the German

Federal Ministry of the Interior as the source of the values for oil-retention capacity. (The German report was also referenced in de Pastrovich, but was not listed as the source of the oil retention values.)

The German report, titled *Evaluation and Treatment of Oil Spill Accidents on Land with a View to the Protection of Water Resources*, was authored by Freidrich Schwille and others. Schwille is a well-published researcher who conducted a number of oil-infiltration studies in tanks containing prepared soils. The 1970 German Federal Ministry of the Interior report presents several drawings from Schwille's research showing the distribution of hydrocarbon during infiltration through different soil types. It also presents an equation for estimating the depth of oil infiltration into vadose soils, given the spill volume, the infiltration area, and an oil-retention capacity for the soil. Appendix 2 of the report provides reference values for the oil-retention capacities (in units of L/m^3) for a cross-section of soil types. The oil-retention capacities listed in the 1970 German Federal Ministry of the Interior report are the same values as those listed in the 1974 CONCAWE report, the 1979 de Pastrovich/CONCAWE report, and the API 1628 paper; however, as described above, the values have been presented in different formats in some of the reports. The values for oil-retention capacity and the relationships between the values presented in the different reports listed above are shown in Table 3. Three important pieces of information can be gained from the 1970 German Federal Ministry of the Interior report:

- The equations for depth of oil infiltration are provided as a tool to estimate the "maximum" potential depth of oil infiltration into the vadose zone (to assess whether oil could reach the water table) to help plan emergency response following a release. The authors were not concerned with estimating whether the oil had reached the water table at old spill sites (years after the spill occurred), because this information can readily be measured (rather than being estimated from oil-retention capacities and spill volumes). Because of the intended use of the equations, the oil-retention capacities appear to be conservative (low). The report authors acknowledge that the retention capacities are for making order-of-magnitude estimates of the maximum oil penetration depth and point out that in layered soils higher retention capacities should be expected.

- The Schwille/CONCAWE/API oil-retention capacities and associated soil types are correlated with hydraulic conductivity values and capillary rise heights, and the soil textures associated with the oil-retention values are described in more detail than in subsequent references. The hydraulic conductivity values and correlations for capillary rise height are of much greater value in characterizing the soil types associated with the oil-retention capacities than simple textural descriptions such as sand or gravel. The 1970 German Federal Ministry of the Interior report associates the oil-retention capacity of the API gravel soil with a soil description of "boulders, cobbles, coarse gravel" and describes the next most coarse-grained soil as "gravel, coarse sand." The report also states that 1) the listed oil-retention capacities are for oils with viscosities in the 2- to 6-centistoke range; 2) for products with lower viscosities, such as gasoline, the retention values may be multiplied by 0.5; and 3) for higher-viscosity products such as spindle oil or machine oil, the retention capacities should be correspondingly increased.

- The source of the data on oil-retention capacity is not provided. This is important because the values for oil-retention capacity do not appear to be from well-controlled laboratory

experiments or from a large database of well-documented spill sites. Rather, the listed oil-retention capacities appear to be estimates of the minimum retention capacity by several knowledgeable people provided for the specific purpose of estimating oil-infiltration depths immediately following a spill.

The 1970 German Federal Ministry of the Interior report does provide several general references for the section of the report dealing with the oil-retention capacities. These references include a 1967 report by Schwille, in which he presented oil-retention concepts and gave the equation for estimating the depth of oil infiltration following a spill. The 1967 Schwille report did not provide any oil-retention values or identify a potential source for oil-retention data. Geosphere acquired several other references listed in the 1970 German Federal Ministry of the Interior report and tried to contact Schwille and several of his coworkers. Unfortunately, Dr. Schwille passed away a few years ago; the other references did not provide any oil-retention value,; and Schwille's coworkers (those contacted) did not know the source of the oil-retention capacities listed in the 1970 German Federal Ministry of the Interior report.

SECTION 13

Other Published Values of Residual Saturation

The literature search revealed several documents, in addition to those listed above, that contain data on residual saturation for hydrocarbons. However, only a limited quantity of residual saturation data appears to be available, and it may be difficult to correlate the published values with each other and with geotechnical index parameters because the references often do not completely characterize the soils or their residual saturation test methods. Data contained in a widely referenced paper by Mercer and Cohen (1990), titled *A Review of Immiscible Fluids in the Subsurface: Properties, Models, Characterization and Remediation*, is shown in Table 4 and graphed in Figure 9. The values for residual saturation and oil-retention capacities listed in the Mercer and Cohen table have been changed to residual oil concentrations, and Geosphere estimated the soil and oil properties such as the average grain size, bulk density, and oil densities to make the conversions. Important points concerning the values listed in the Mercer and Cohen report include the following:

- The graphs of the Schwille data on oil-retention capacity show a smooth line (Figure 9), which would not be expected if the data represented real field or laboratory data.
- Because the Schwille/de Pastrovich/Fussel (et al., 1981)/API values for all five soil types and for three fuel types are listed independently (15 data points), they represent most of the values in the Mercer and Cohen table (and in the Brost and DeVaull, 2001, table), even though the values may not be measured from field sites or laboratory experiments. By comparison, the Hoag and Marley (1986) report provides 30 data points, which are summarized by maximum and minimum values in the Mercer and Cohen report and represented by only three data points in Figure 9. (The Hoag and Marley residual saturation values are higher than the Schwille/de Pastrovich/Fussel/API values.)
- Finally and most importantly, the Schwille/de Pastrovich/Fussel/API values for gasoline and diesel fuel appear to be significantly lower than the other residual saturation data presented in the literature (and in Figure 9). This observation is consistent with Schwille's objective, but is not consistent with the use of Schwille's values to identify and regulate the presence of mobile free product years after a spill has occurred.

SECTION 14

Summary of Residual Saturation

Oil migration through soils and the trapping of residual oil in soils has been investigated by reviewing published literature. The literature search has revealed the following:

- The oil-retention capacity values of Schwille (German Ministry of the Interior, 1970) which were later characterized as residual saturation values (API, 1996) and which were considered by ADEC when developing the maximum allowable concentrations were originally intended to help assess whether oil could migrate to the water table at recent spill sites and are likely not based on a large database or controlled laboratory tests.
- Mobile oil in the vadose zone tends to infiltrate through the soil in a period of days or weeks, which leads to the conclusion that NAPL present in a vadose-zone soil months or years after a spill event is by definition immobile residual.
- There is not a change in the dissolved and vapor phase migration processes associated with the concentrations used as maximum allowable criteria (partitioning into the dissolved and vapor phases, and advection and diffusion occur the same at concentrations above and below the maximum allowable concentration criteria).
- If oil does not collect in properly located and constructed monitoring wells screened across the water table during periods of low water, then there is not continuous oil at the spill site, and any oil present is immobile residual.
- If oil does collect in a monitoring well, then oil is continuous in the soil near the monitoring well but may or may not be mobile at a site scale.
- For the continuous oil to be mobile, the oil thickness, measured in monitoring wells near the downgradient edge of the free-product-footprint area, must be great enough to overcome the water-displacement pressure (or pore-entry pressure) of the uncontaminated soils adjacent to the soil containing continuous free product.
- For continuous oil to be mobile there must be an oil gradient. If continuous oil is present, the oil conductivity may be measured by conducting an oil bail down test and reducing the data as described by Huntley (2000).

SECTION 15

Recommended Approach for Assessing Free Product Mobility

The presence of mobile NAPL presents a potential risk to human health and the environment primarily by increasing the footprint area of the NAPL-contaminated soil source area. In general terms, the expansion of the NAPL-contaminated soil source area makes it more likely that the migration to indoor air and the groundwater ingestion route are completed, and causes the margin of the NAPL to become closer to downgradient receptors, which tends to increase the dissolved-phase concentration at the downgradient receptor locations. In addition, if mobile NAPL is present at a contaminated site, then recovery of the mobile NAPL may be an effective remedial approach for the site. To help protect human health and the environment it is desirable to limit the lateral spreading of mobile NAPL at petroleum hydrocarbon-contaminated sites to the extent practicable.

The SOCWG has the following general recommendations regarding the maximum allowable concentration criteria and the requirement to recover free product:

- Use human health and environmental risk as the primary criteria for determining site status.
- Recognize that the maximum allowable criteria as currently applied in 18 AAC 75 is not a risk-based criteria and therefore change the use of the maximum allowable concept to become part of the process of screening for mobile oil.
- When free product is observed in wells, evaluate the free product mobility and the impact of mobility on human health and environmental risk.
- Address free product recovery as part of an overall remediation and risk reduction, or risk management approach to the site.

The SOCWG has the following specific recommendations for assessing the presence or absence of mobile NAPL using several lines of evidence or screening criteria as listed below.

1. *Use the API 1628 residual saturation values as a screening tool to differentiate sites with some potential for mobile NAPL from sites with no or very low potential for mobile NAPL.* If maximum concentrations measured at a site are below API 1628 residual saturation values for the given soil textures and no other conflicting data are available (that is, oil is not observed in wells), then the site meets the "no mobile product" criteria. If the maximum soil concentration measured at a site is above the API 1628 residual saturation values for the soil texture present at the site, then additional study may be necessary to assess if mobile NAPL is present.

   To apply this line of evidence, quality data are required. Mobile oil in the vadose zone tends to infiltrate through the soil in a period of days or weeks, which leads to the conclusion that NAPL present in a vadose-zone soil months or years after a spill event is by definition immobile residual. Therefore, soil samples that are used to demonstrate that soil

concentrations are below the maximum allowable criteria should emphasize soil samples collected from the zone of seasonal water table fluctuation and if the source of the hydrocarbon is known (for example, a leaking underground storage tank [UST]) the samples should be collected close to the suspected source of the NAPL. Because the API residual saturation values vary significantly depending on soil texture, the soil textures present at a site should be verified by sieve analysis and the sieve analysis samples should be collected from the zone of seasonal water table fluctuation.

2. *Monitor for the presence of oil in monitoring wells located in the NAPL- contaminated soil source area.* If mobile oil is present at a site, then the oil must be continuously connected between adjacent soils pores over a significant distance (tens of feet), and the oil must exert an oil pressure greater than the water displacement pressure of the site soils. Oil that is "continuous" between adjacent soil pores will tend to collect in monitoring wells screened through the continuous oil layer. If oil does not collect in "properly located, installed and monitored" monitoring wells, then no mobile oil is present at the site and the concerns about the increased potential for migration embodied in the "maximum allowable concentration" criteria can be considered to have been met even if measured soil concentrations exceed the API 1628 values. Note that the other environmental criteria associated with the maximum allowable concentration criteria may still have to be addressed.

   Properly installed monitoring wells must be located in the core of the NAPL-contaminated soil source area, screened through the zone of seasonal water table fluctuation, and properly developed (free-flowing and/or sediment- free). Properly monitored wells should be monitored with an oil-water interface probe and/or by visual inspection of the water in a bailer. The presence of the oil should be monitored days or weeks after well development (days in sandy soils, weeks in silty soils) and before purging the well. Additionally, monitoring for the presence of oil in the monitoring well should be conducted during a period of sustained low water, such as in the late winter or early spring (before spring breakup). Repeated measurements of the absence of oil in monitoring wells are better than one-time measurements.

3. *If oil is present in a monitoring well, then "continuous oil" is present at the site and the mobility of continuous oil at the site scale may be assessed by comparing the oil pressure to the water displacement pressure of the soil.* The thickness of oil that collects in a monitoring well and the soil texture provide a tool to assess if the oil that collects in a monitoring well has the potential to migrate downgradient into previously uncontaminated soils. Continuous oil that is not mobile at the site scale may move between adjacent contaminated soil pores but is not capable of migrating downgradient into previously uncontaminated soils. Continuous oil that is mobile at the site scale is present at sufficient pressures/thicknesses to displace water from saturated soil pores and to flow downgradient into previously uncontaminated soil pores. Differentiating sites with mobile continuous oil from sites with continuous oil that is not mobile at the site scale maybe conducted in two steps. In the first step, the thickness of the oil measured in the monitoring wells may be compared to the oil thicknesses that are necessary to overcome the water displacement pressures of the various soil textures listed by Charbeneau in API publication #7596 and presented here in Table 2. The soil texture for the site of interest would ideally be determined based on sieve and hydrometer analysis of site soils. If the oil thicknesses measured at the subject site are less

than about 50 percent of the Charbeneau thicknesses for the site soils, then it is likely that oil that is mobile at the site scale is not present and the concerns about the increased potential for migration embodied in the "maximum allowable concentration" and "no mobile free product criteria" are considered to have been met. If the oil thickness measured at the site is greater than 50 percent of the Charbeneau thickness for the site soils, then it may be necessary to collect site-specific field and laboratory data for use in the Charbeneau equation to assess the mobility of the oil on a site- specific basis. The assessment of oil mobility may include monitoring oil thicknesses, measuring the moisture-retention properties of the site soils, measuring the properties of the spilled hydrocarbon (viscosity, specific gravity, and the oil-water interfacial tensions), and measuring the oil gradient, conducting oil bail-down tests, and calculating the oil conductivity. These measurements may be used to assess if the oil that collects in a monitoring well is mobile at the site scale and will also help identify the potential further extent of oil migration and help assess if it is practicable to recover the oil. An assessment of the practicability of oil recovery is required in the current regulations.

SECTION 16

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Tables

TABLE 1
ADEC Maximum Allowable Concentrations

Reference	Associated Soil Type	Gasoline (mg/kg)	Middle Distillates/Diesel (mg/kg)	Residual Range (mg/kg)
ADEC Maximum Allowable Concentrations Listed in Table B2 of 18 AAC 75	none listed	1,400	12,500	22,000
ADEC Maximum Allowable Concentrations listed in unpublished white paper (values match API 1628)	coarse gravel	950	2,200	4,800
	Coarse Sand	2,800	6,500	15,000
	Fine Sand/Silt	7,500	17,000	39,000

TABLE 2

Example NAPL Thickness Necessary to Overcome Water Displacement Pressure for Selected Soil Textures (From Charbeneau et.al., 1999)

		NAPL Specific Gravity	
		0.775	0.85
Soil Texture	Air-Water Bubbling Pressure or Pore Entry Pressure (feet of water)	Monitoring Well LNAPL Thicknesses to Overcome Water Displacement Pressures (feet of oil)	
Sand	0.23	0.7	1.0
Loamy Sand	0.27	0.8	1.3
Sandy Loam	0.43	1.4	2.1
Loam	0.92	2.8	3.6
Sandy Clay Loam	0.56	2.3	3.0
Silt Loam	1.64	4.1	5.2
Silt	2.03	4.8	5.9
Clay Loam	1.74	4.4	5.7
Sandy Clay	1.21	3.9	4.9
Silty Clay Loam	3.28	6.1	8.2
Clay	4.10	6.6	9.5
Silty Clay	6.56	8.7	13.8

Table From Charbeneau et. al. (1999)
All Soil Textures Based on USDA/ Soil Conservation Service Soil Classifications
Soil Property Data from Carsel and Parish (1988)

TABLE 3

Changes in Oil Retention and Residual Concentration Values Referenced in Publications that Have Been Traced Back to Schwille 1970

German Ministry of the Interior/Schwille, 1970, Possible original source of oil retention values and oil viscosity correction factors			
Soil Description/ Texture	**Hydraulic Conductivity (cm/s)**	**Equivalent Capillary Rise (cm)**	**Oil Retention Capacity (L/m^3)**
boulders, cobble, coarse gravel	>1*10^0	<5	5
gravel, coarse sand	1*10^0 to 1*10^ -1	5 to 15	8
coarse sand, medium sand	1*10 -1 to 1*10^ -2	15 to 300	15
medium sand, fine sand	1*10^ -2 to 1*10^ -3	300 to 600	25
fine sand, more or less silty	1*10^-3 to 1*10^ -5	600 to 1000	40
Viscosity Correction Factors for Different Fuel Types (German Ministry of the Interior, 1970)	Gasoline	Kerosene & Gas Oil	Light Fuel Oil
viscosity correction factor	0.5	1	2
CONCAWE, 1974, Same values as above but presented as an oil retention constant			
Oil Retention Constant=1000 /(oil retention capacity*(1/oil viscosity factor))			
Soil Description/ Texture	**Gasoline Retention Constant (dimensionless)**	**Kerosene/ Gas Oil Retention Constant (dimensionless)**	**Light Fuel Oil Retention Constant (dimensionless)**
stone, coarse gravel	400	200	100
gravel, coarse sand	250	125	63
coarse sand, medium sand	133	67	33
medium sand, fine sand	80	40	20
fine sand, silt	50	25	13
CONCAWE, 1979, Same oil rention values as published In 1970 paper, but with viscosity factor applied			
Oil Retention Capacity= basic oil retention capacity *viscosity factor			
Soil Description/ Texture	**Gasoline Retention Capacity (L/m^3)**	**Kerosene & Gas Oil Retention Capacity (L/m^3)**	**Light Fuel Oil Retention Capacity (L/m^3)**
stone, coarse gravel	2.5	5	10
gravel, coarse sand	4	8	16
coarse sand, medium sand	7.5	15	30
medium sand, fine sand	12.5	25	50
fine sand, silt	20	40	80
API 1628, 1996, Same values as presented in 1970 paper, but presented as soil concentrations			
Residual Concentration = (oil retention capacity in L/m^3)*(viscosity correction factor)*(density of oil in kg/L)*(1000g/kg)*(1000mg/g)/((bulk density of soil in g/cm^3)*(100^3 cm^3 / m^3)/(1000g/kg))			
Soil Description/ Texture	**Gasoline Residual Concentration (mg/kg)**	**Middle Distillates Residual Concentration (mg/kg)**	**Fuel Oil Residual Concentration (mg/kg)**
coarse gravel	946	2162	4865
gravel, coarse sand (not presented in API document)	1514	3459	7784
coarse sand, medium sand	2838	6486	14595
medium sand, fine sand (not presented in API document)	4730	10811	24324
fine sand, silt	7568	17297	38919
API assumed oil density (kg/L)	0.7	0.8	0.9
API assumed soil bulk density (g/cm^3)	1.85	1.85	1.85
	(note that the published API values have been rounded off)		
The 1970 Greman Ministry of the Interior/Schwille oil retention capacity values are also used in these widely referenced publications:			
API 4682 / Charbeneau et.al, 1999	**EPA / Cohen and Mercer, 1993**		
Mercer and Cohen, 1990	**Fussell et. al., 1981**		
	API / Brost & DeVaull, 2001		

TABLE 4

Mercer & Cohen (1990) Vadose and Saturated Zone Residual Oil Concentrations

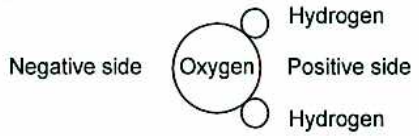
Vadose Zone Example Data From Mercer and Cohen Summary, 1990				
Soil Description/ Texture	**Lower Measured Value of Residual Concentration (mg/kg)**	**Upper Measured Value of Residual Concentration (mg/kg)**	**Oil Type**	**Reference**
coarse gravel	946	not reported	gasoline	Schwille, 1970
gravel, coarse sand	1,514	not reported	gasoline	Schwille, 1970
coarse sand, medium sand	2,838	not reported	gasoline	Schwille, 1970
medium sand, fine sand	4,730	not reported	gasoline	Schwille, 1970
fine sand, silt	7,568	not reported	gasoline	Schwille, 1970
coarse gravel	2,162	not reported	middle distillates/diesel	Schwille, 1970
gravel, coarse sand	3,459	not reported	middle distillates/diesel	Schwille, 1970
coarse sand, medium sand	6,486	not reported	middle distillates/diesel	Schwille, 1970
medium sand, fine sand	10,811	not reported	middle distillates/diesel	Schwille, 1970
fine sand, silt	17,297	not reported	middle distillates/diesel	Schwille, 1970
coarse gravel	4,865	not reported	fuel oil	Schwille, 1970
gravel, coarse sand	7,784	not reported	fuel oil	Schwille, 1970
coarse sand, medium sand	14,595	not reported	fuel oil	Schwille, 1970
medium sand, fine sand	24,324	not reported	fuel oil	Schwille, 1970
fine sand, silt	38,919	not reported	fuel oil	Schwille, 1970
coarse sand	26,002	32,936	gasoline	Hoag & Marley, 1986
medium sand	20,802	46,804	gasoline	Hoag & Marley, 1986
fine sand	32,936	104,009	gasoline	Hoag & Marley, 1986
well graded fine to coarse sand	79,741	102,276	gasoline	Hoag & Marley, 1986
glacial till	23,774	36,403	mineral oil	Pfannkuch, 1986
alluvium	37,642	not reported	mineral oil	Pfannkuch, 1986
coarse sand	23,774	not reported	paraffin oil	Convery, 1979
fine sediments	103,019	not reported	paraffin oil	Convery, 1979
Ottawa sand	21,792	39,870	paraffin oil	Convery, 1979
Saturated Zone Example Data From Mercer and Cohen Summary, 1990				
Soil Description/ Texture	**Lower Measured Value of Residual Concentration (mg/kg)**	**Upper Measured Value of Residual Concentration (mg/kg)**	**Oil Type**	**Reference**
92% sand, 5% silt, 3% clay	41,604	not reported	benzene	Lenhard & Parker
92% sand, 5% silt, 3% clay	45,071	not reported	benzl alcohol	Lenhard & Parker
92% sand, 5% silt, 3% clay	27,736	not reported	p-cymene	Lenhard & Parker
92% sand, 5% silt, 3% clay	32,936	not reported	o-xylene	Lenhard & Parker
coarse Ottawa sand	39,004	69,340	1,1,1- trichlorethene	Anderson, 1988
coarse Ottawa sand	39,004	43,337	tetrachlorethene	Anderson, 1988
medium aeolian sand	45,566	50,271	kerosene	Wilson, et al., 1990
medium aeolian sand	46,804	53,738	gasoline	Wilson, et al., 1990
medium aeolian sand	43,337	50,271	n-decane	Wilson, et al., 1990
medium aeolian sand	34,670	46,804	p-xylene	Wilson, et al., 1990
medium aeolian sand	67,606	50,271	tetrachlorethene	Wilson, et al., 1990
medium aeolian sand	43,585	64,139	soltrol	Wilson, et al., 1990
clean coarse fluvial sand	31,698	not reported	soltrol	Wilson, et al., 1990
clean medium beach sand	35,660	not reported	soltrol	Wilson, et al., 1990

Gasoline assumed oil density (kg/L)= 0.7
Diesel assumed oil density (kg/L)= 0.8
Fuel Oil assumed oil density (kg/L)= 0.9

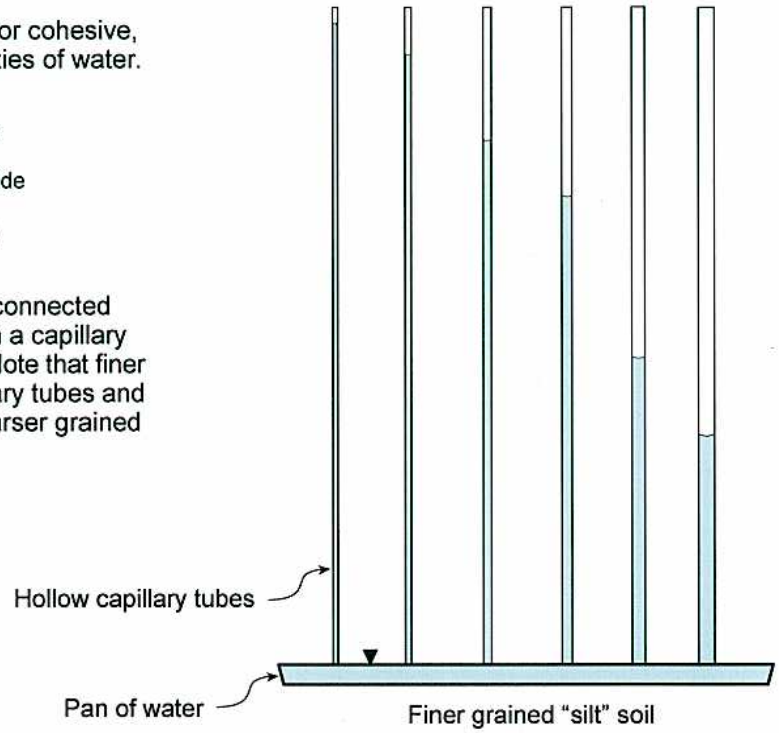
assumed soil bulk density (g/cm^3)= 1.6
porosity based on assumed bulk density= 0.396226415
Chlorinated Solvent assumed oil density (kg/L)= 1.05

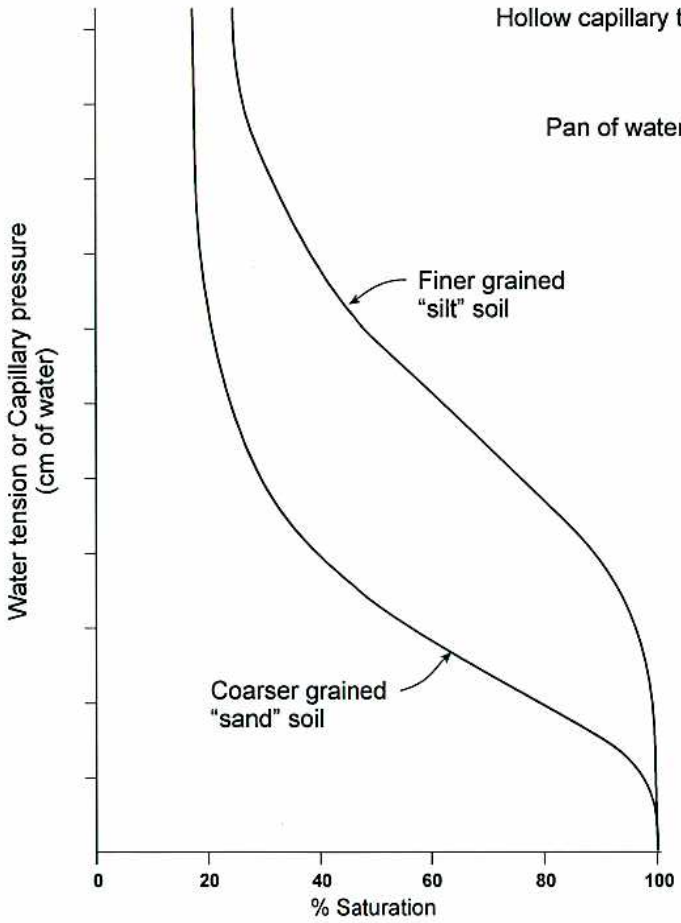
Figures

Polar water molecule is responsible for cohesive, adhesive and surface tension properties of water.

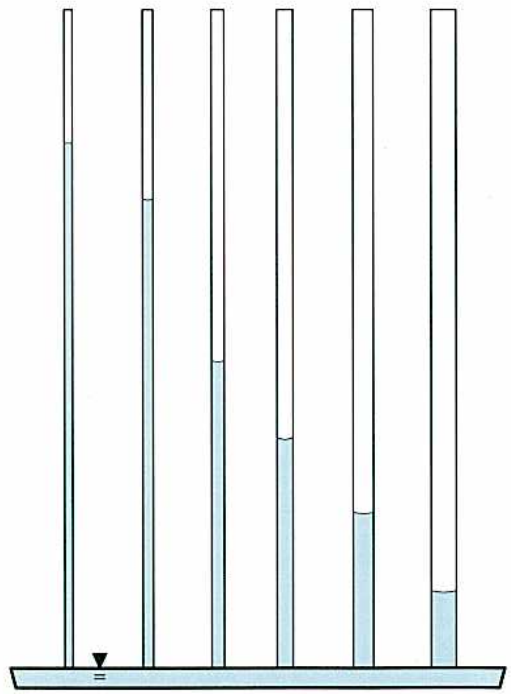


Capillary tube bundles representing connected pores of a soil. Height of water rise in a capillary tube is a function of the tube radius. Note that finer grained soil has smaller radius capillary tubes and hence holds more water than the coarser grained soil at a given water tension.





Typical soil moisture retention curve showing soil water content at different water tensions



Coarser grained "sand" soil

Figure 1
Soil Moisture Curve and Capillary Tube Bundle

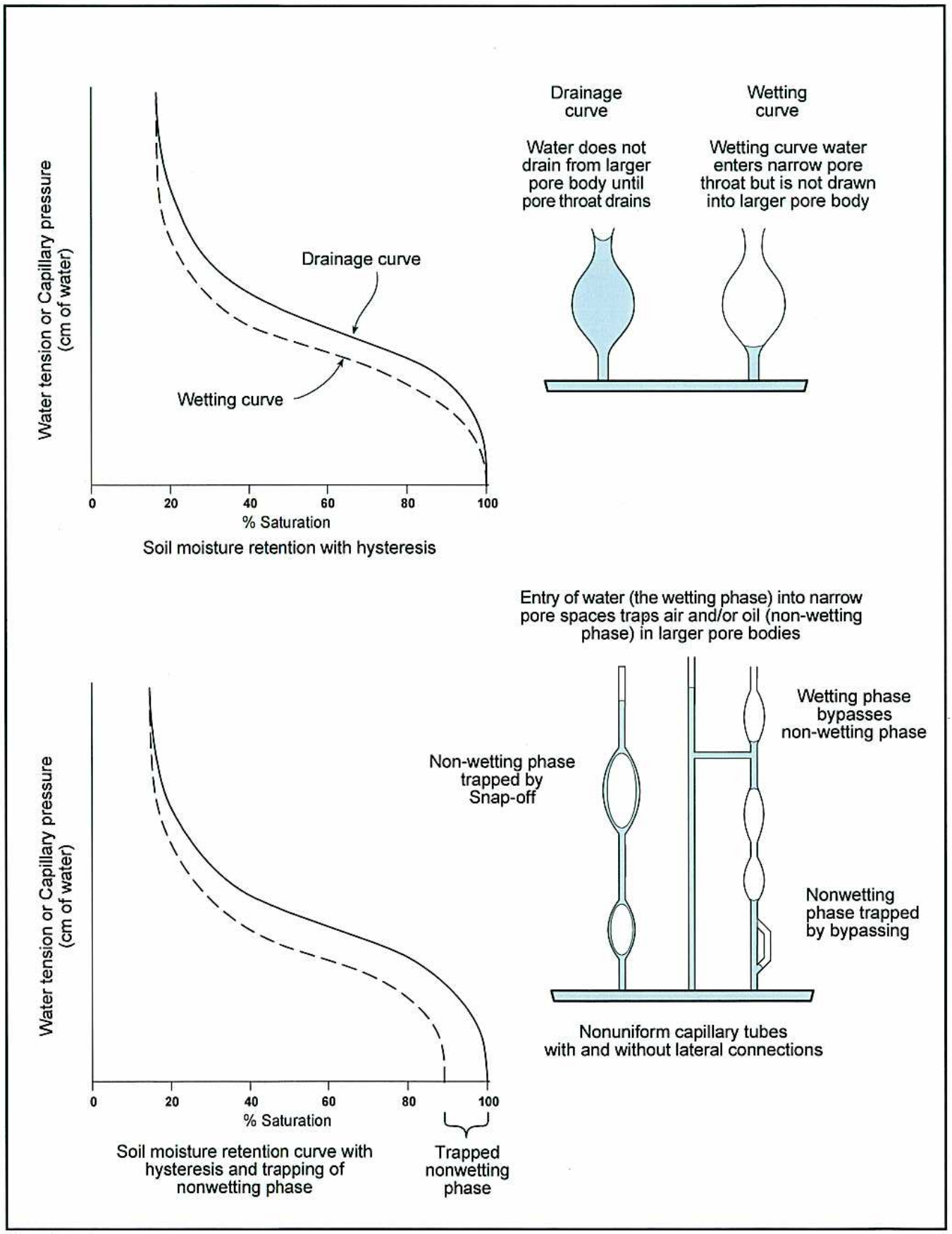


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Figure 2
Soil Moisture Curves with Hysteresis and Trapping

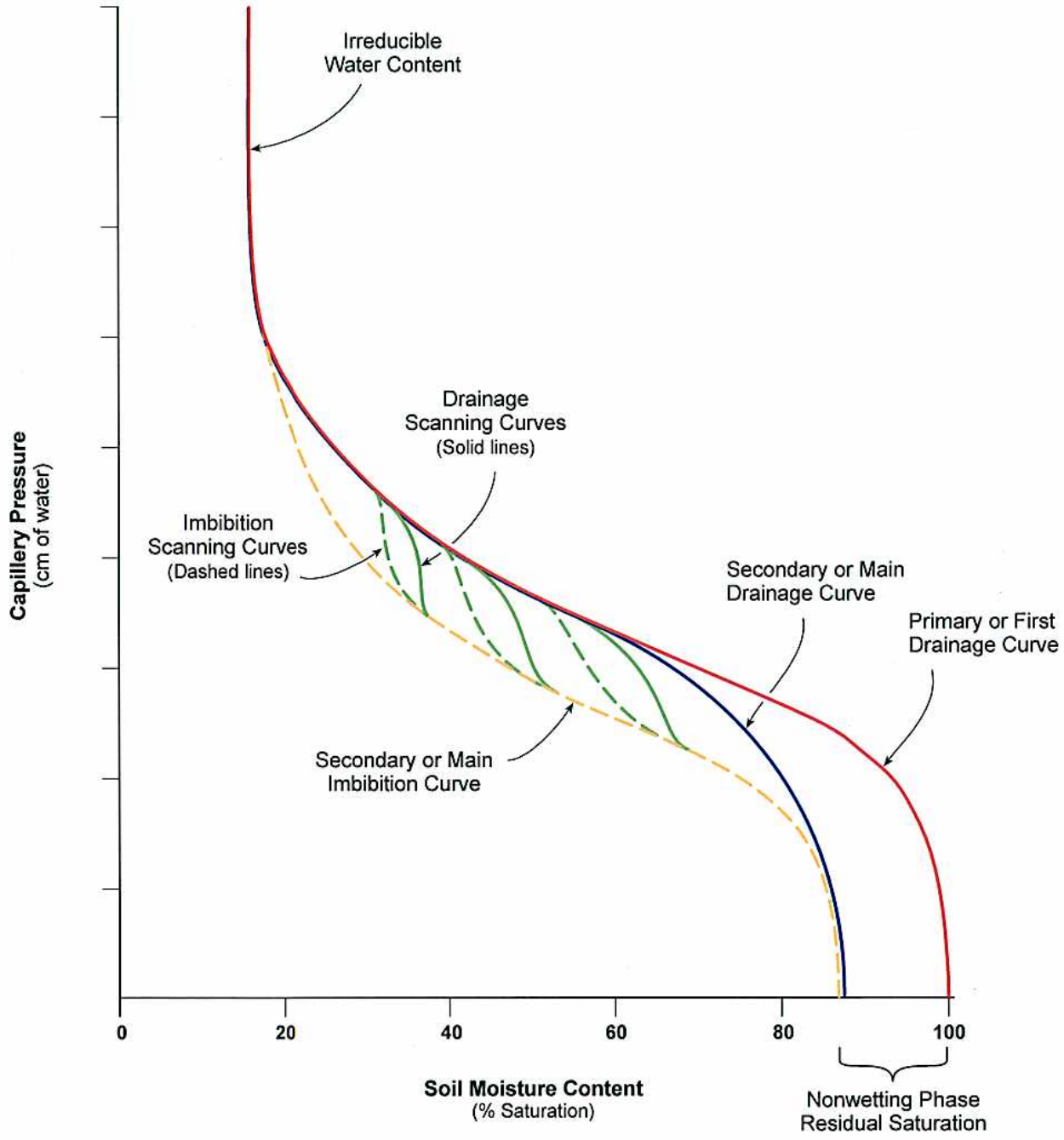

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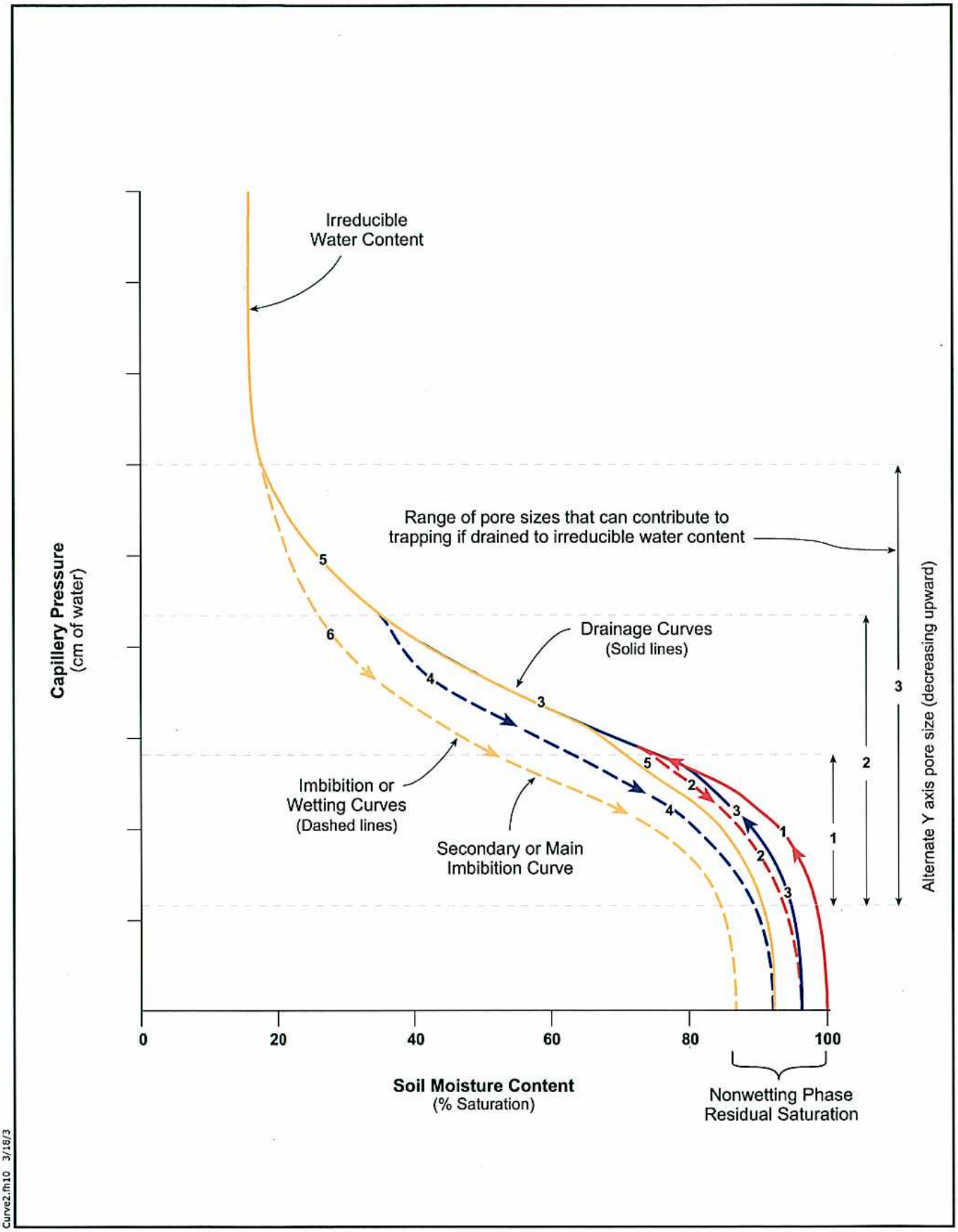
Figure 3

Example of Typical Soil Moisture Drainage and Imbibition Curves from the Literature



Curve2.fh10 3/18/3

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Figure 4

Example of Soil Moisture Drainage and Imbibition curves

Indicating that the residual saturation value measure in a soil is a function of the historical maximum oil saturation

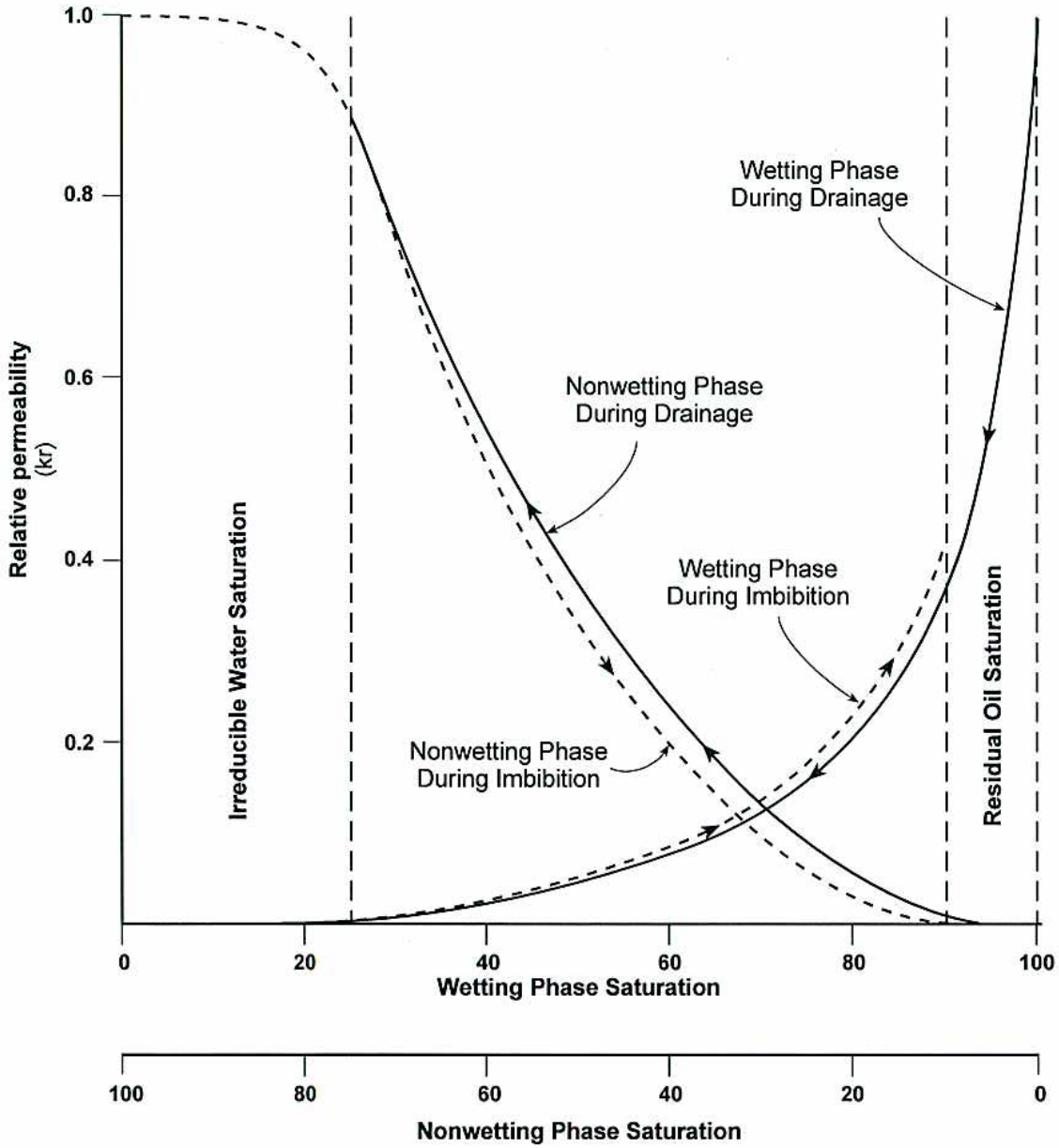

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Figure 5

Relative permeabilities for a wetting and nonwetting fluid as a function of the degree of saturation

In more detail, the relationship between LNAPL thickness in a well and the volume of LNAPL in formation is complex. Following Farr et al. (1990), Figure 3 considers a simple case in which LNAPL has migrated laterally into a uniform porous media where the watertable is stable. Panel 1 shows that LNAPL in the well extends below the LNAPL in the formation. Within this extension the pressure difference between the LNAPL in the well and the water in the formation is not large enough to push the water out of the formation (capillary pressure is less than displacement pressure). The extension of product in the well, below the elevation in the formation, increases as soils become finer and as the densities of the liquids becomes more similar.

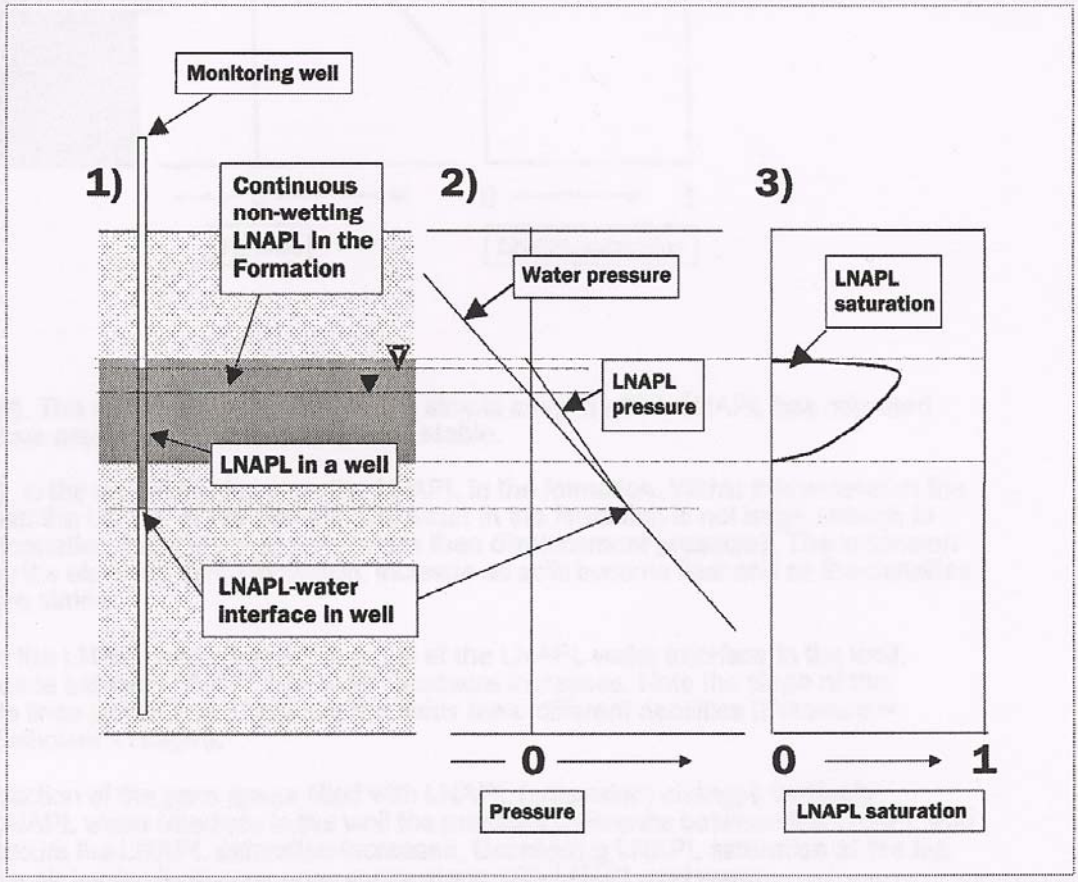
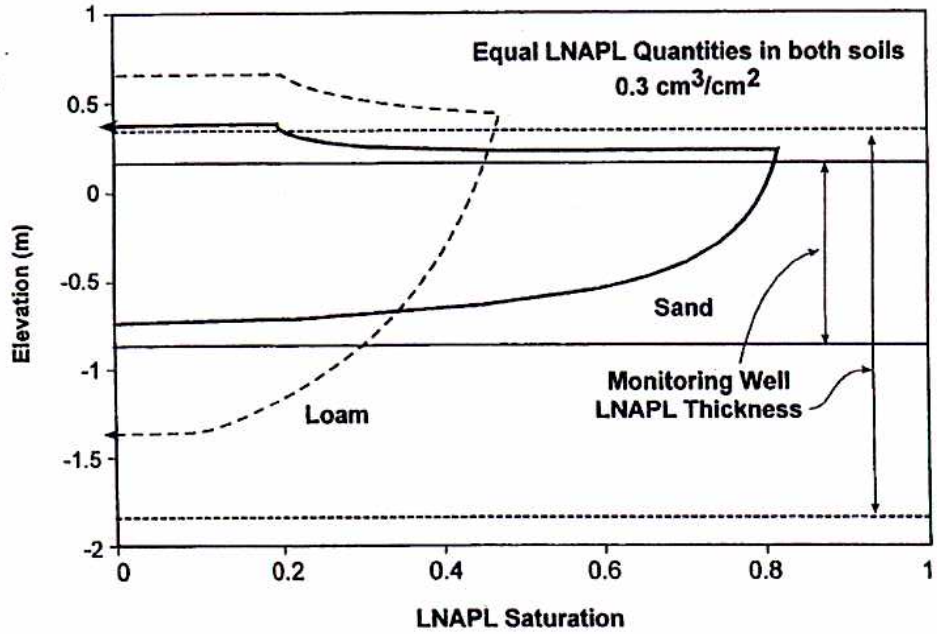


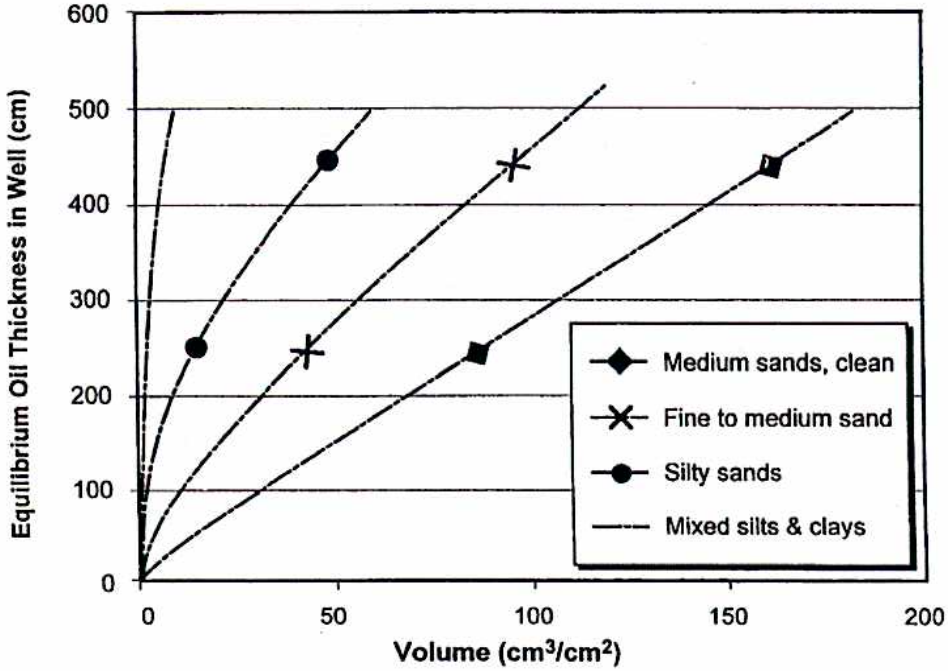
Figure 3 – Idealized conceptualization of LNAPL in a well and adjacent formation

Panel 2 shows pressure in the LNAPL and water to be equal at the LNAPL water interface in the well. Above this point the difference between LNAPL and water pressure increases. Note the slope of the LNAPL and water pressure lines are different because the fluids have different densities (Pressure = Fluid Density x Gravitational Coefficient x Height). As shown in Panel 3 the fraction of the pore space filled with LNAPL (saturation) changes vertically. Moving upward from the LNAPL water interface in the well the pressure difference between the LNAPL and water increases. As this occurs the LNAPL saturation increases. Decreasing LNAPL saturation at the top reflects the condition where air begins to occupy pore space along with LNAPL and water.

Figure 6
Distribution of Oil Indicated by
Presence of Oil in a Monitoring Well
From: API Soil and Groundwater Research Bulletin 18, 2003



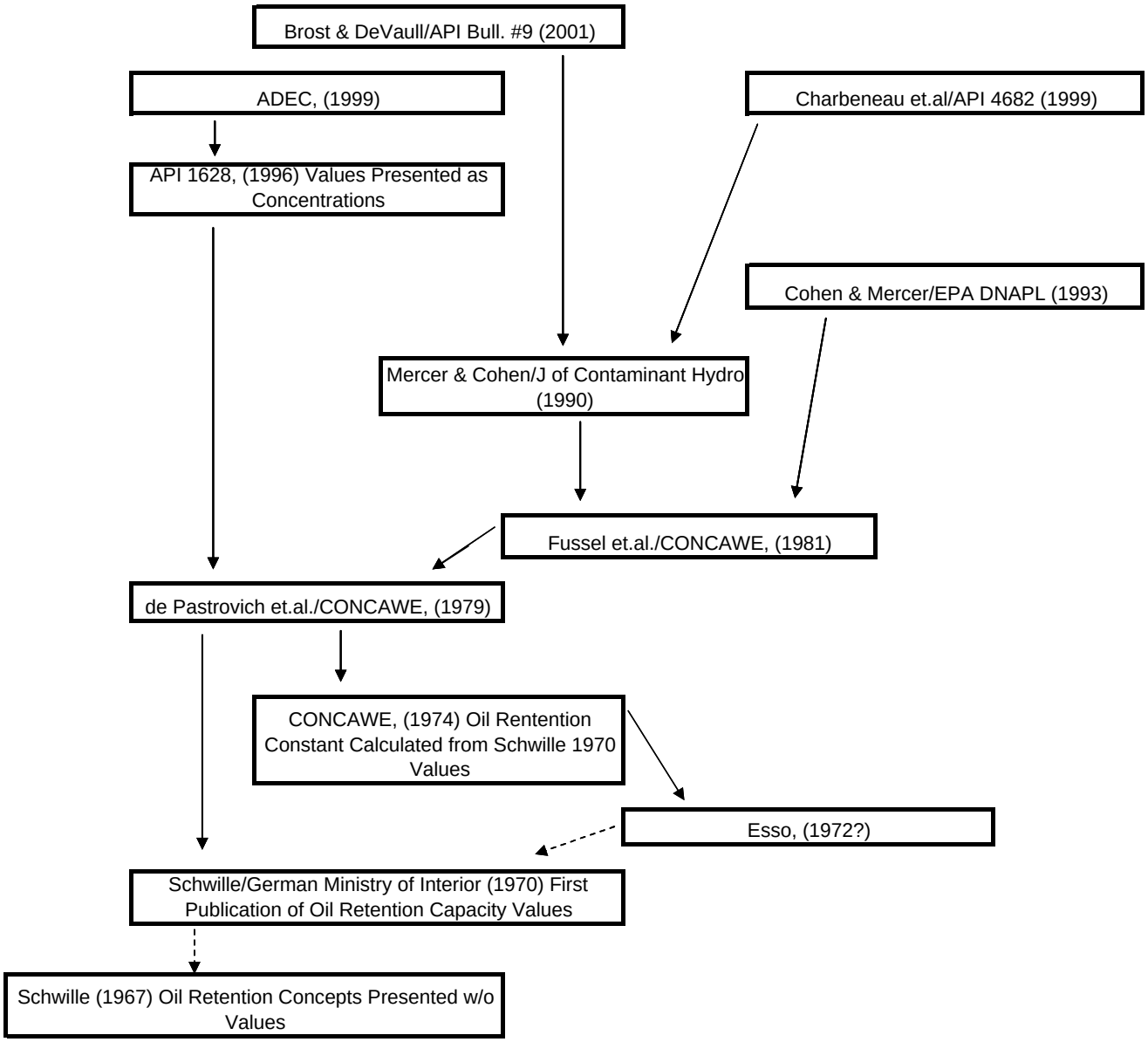
Vertical Saturation Distribution of LNAPL (35° API Fuel in a Sand and Loam Soil where both Profiles have the same LNAPL Quantity). From: API/Charbeneau et.al.(1999)



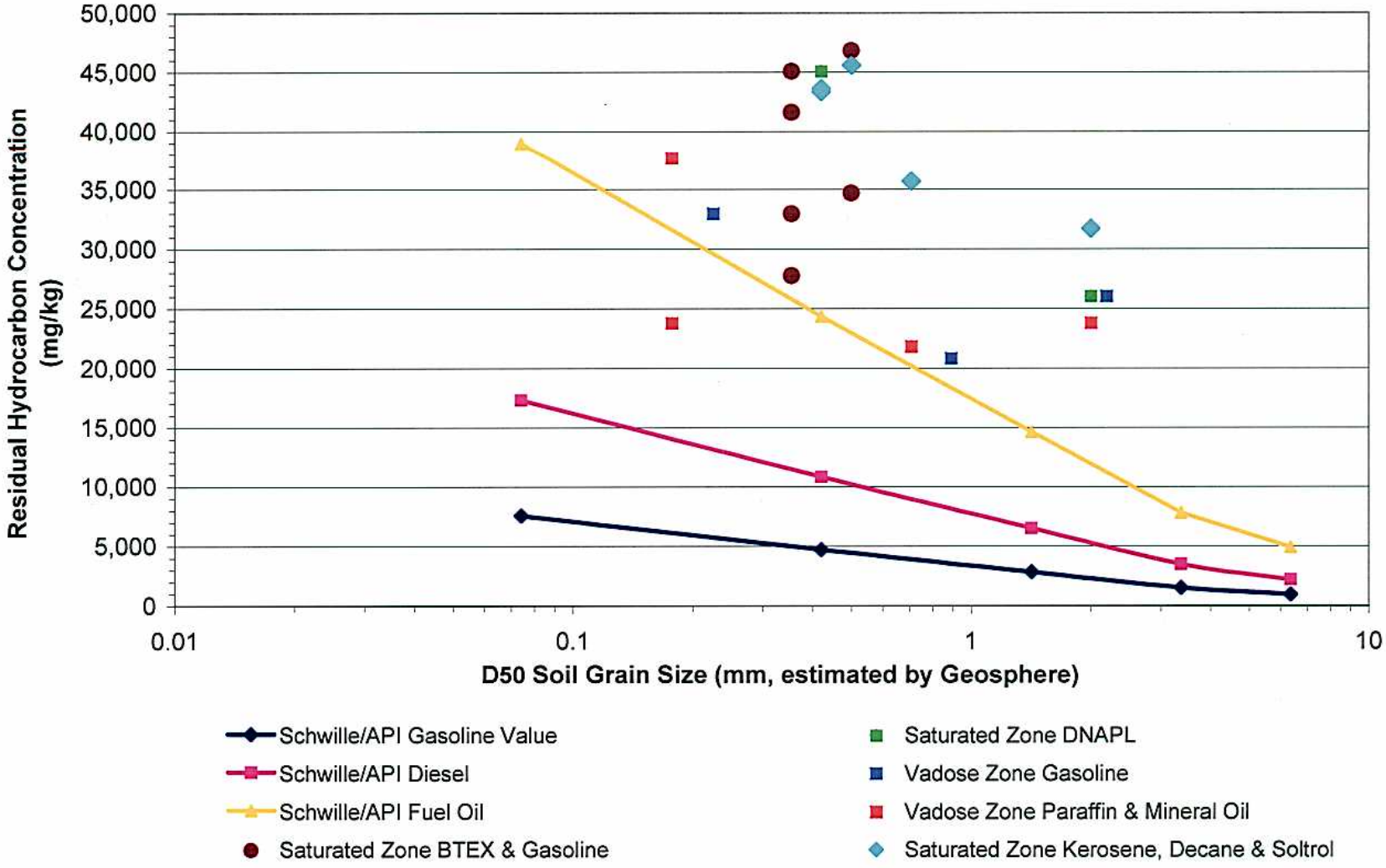
LNAPL Volume as a function of Oil Thickness in a well (assumes vertical equilibrium). From: API/Hantley & Beckett (2001)

Figure 7
Example Relationships between Mobile Oil Volume per Unit Area and Oil Thickness in Monitoring Well Soils with Differing Textures

Figure 8 Residual Saturation Literature Values Traced to German Ministry of the Interior (Schwille, 1970)



The residual saturation concentrations referenced by the ADEC and in several other published articles maybe traced to a 1970 publication by the German Ministy of the Interior. Note that the oil retention values listed in the 1970 paper maybe based on professional judgement and not a tabulation of field or laboratory data.

FIGURE 9

Mercer & Cohen (1990) Residual Oil Concentrations as a Function of Soil Grain Size