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Status Report: Identification of Appropriate Standards for Corrective Action for a Release from Petroleum Underground Storage Tanks

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Status Report:
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Kentucky Water Resources Research Institute
University of Kentucky

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Research Reports

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COSTS OF CLOSURE AND REMEDIATION FOR PETROLEUM UNDERGROUND STORAGE TANKS

Glenn C. Blomquist

When closing a site with a petroleum underground storage tank (UST), the owner may encounter different situations. Consider several situations. The tank can be in good condition with no sign of a leak. The tank and surrounding area can show signs of leakage. The contamination may be localized or widespread. If the contamination is widespread it may be of negligible risk to health and the environment. If the contamination is widespread it may have degraded groundwater and pose a substantial risk through potential drinking water. The risk of exposure to concerning concentrations may be substantial. Other situations are possible. The cost of closure and remediation will depend on the situation which the owner of the UST encounters.

Different closure and remediation measures can be appropriate for different situations. For localized contamination the tank can be dug up and the soil immediately surrounding the tank can be hauled away to a landfill (yank the tank). A concrete cap can be poured over the site. For widespread contamination involving soil and groundwater remediation can be done through treatment at the UST site. Technologies such as soil vapor extraction, bioremediation, air sparging and the more traditional pumping and treatment of groundwater, see Water Science Reporter (1993). Costs are different for each closure and remediation option. Below we will consider different options and their costs systematically. First, however, we will review the estimates of the average costs of remediation.

AVERAGE REMEDIATION COSTS

The average cost of remediation for a petroleum underground storage tank which has leaked is approximately $100,000.

U.S. Environmental Protection Agency. This average cost per tank is based on information from three sources. All three point to the same average cost. The U.S. Environmental Protection Agency, Office of Underground Storage Tanks (1992) reports that clean up costs from leaky tanks vary from several thousand dollars to $1 million. EPA reports that corrective action for leaky tanks costs $28,000 to $250,000. The costs of upgrading existing, leaky tanks are from $30,000 to $100,000. EPA (1992, p. III-3) reports that the average cost of clean up for a leaky tank is $100,000 or more.

It should be recognized that this average is based on costs incurred for sites which have been remediated. The costs will vary with the extent of contamination, geological characteristics, and the clean up standards which must be met. The costs of remediation for UST sites which have not been considered can be different from the average of sites considered to date, if they differ systematically. For example, if the worst sites have been considered first, then the $100,000 average cost will be too high for future remediation. On the other hand, if the sites which are easiest to clean have been considered first, then the $100,000 average cost will be too low. We have little information about how representative the remediation experience is for projection to future remediation.

Environmental Information Ltd. (EI) EI (1992) surveyed states for information about the amounts which states reimbursed owners for remediation at contaminated sites. Reimbursement costs can be used as an estimate of remediation costs, but they may be different from actual remediation costs. States may not reimburse owners for all remediation costs incurred. States may not pay on every reimbursement claim. The states with enough remediation experience to report may not be representative of other states with different site characteristics. However, for the 16 states with sufficient comparative data, remediation costs varied from a low of $37,000 in New Hampshire to a high of $250,000 in Mississippi.

According to EI (1992, p. 25) the average remediation costs at state-reimbursed UST sites are as follows: Alabama $120,000, Alaska $155,000, Arkansas $105,000, Delaware $47,500, Georgia $210,000, Illinois $110,000, Michigan $110,000, $Mississippi $250,000, Nebraska $60,400, New Hampshire $37,000, Nevada $98,500, South Dakota $58,000, Tennessee $87,000, Utah $96,000, Vermont $54,300, and Wisconsin $57,500.

The average remediation costs at state-reimbursed UST sites is $103,500.

Groundwater Technology, Inc. The third source of information about remediation costs is a local contractor, Groundwater Technology, Inc. Andrew Gremos gave several ballpark cost estimates for different types of remediation. The cheapest alternative is for an UST site which is eventually determined to pose no threat. The most expensive alternative is for a site with widespread contamination which poses a substantial threat. The costs for these two alternatives range from $15,000 to $35,000 per site for the cheapest to $135,000 to $575,000 for the most expensive. An average cost was not given, but this cost information is consistent with the estimate of average costs of remediation of approximately $100,000 per site from EPA and Environmental Information Ltd.

COSTS FOR CLOSURE AND REMEDIATION - SCENARIOS

Simple Closure (SC). One estimate we have for cost of a simple closure (SC) is $12,500 per site from the U.S. EPA study (1992, p. C-9, Exhibit C-7). This cost must be for a straightforward closure without any indication of a leak. This estimate is roughly consistent with some ballpark, general figures which the representatives from the local engineering firms gave us at the meeting of our Kentucky Water Resources Research Institute team on March 4, 1993. They discussed costs of about $6,000 to $10,000 to dig and pull a tank if there are no problems. The estimate from Groundwater Technology, Inc. is $10,000 to $20,000.

An estimate of $12,000 for cost of a simple closure is consistent with the other information and a good estimate for our work.

Closure with Complications. If indication of a leak exists, then the cost of closure will be greater because an investigation and assessment will be done even if no remediation is necessary. Remediation will add to the costs if it is done. A decision tree with several scenarios and remediation options is shown in Figure 1. The total cost of each closure and remediation option is given at the end of each branch of the decision tree. These scenarios and rough cost estimates were given by Groundwater Technology, Inc. Three relatively low cost scenarios and one high cost scenario are described.

Local Contamination and Determination of No Threat (LN). One low cost scenario is what might be called the localized, "no threat" (LN) scenario. Leakage is suspected after examining records of purchases and sales or site monitoring. The site is investigated to determine what pollutants are present, where the ground water and surface water is in the area, and what potential receptors such as homes, wells and aquifers are present. The investigation and assessment show that the contamination is localized and poses no substantial risk. The costs are for site investigation and assessment. The cost of closure and remediation for this scenario is $15,000 to $35,000.

Widespread Contamination and Determination of No Threat (WN). Another relatively low cost scenario is widespread contamination that poses "no threat." Again the site is investigate and assessed for pollutant concentrations and potential exposure to possible receptors. If the analysis shows that the contamination poses no substantial risk the site can be closed. The costs are $20,000 to $50,000.

Localized Contamination and Remediation (DH). The other scenario which may be relatively low cost is one with localized contamination and remediation consists of digging up the soil and hauling it to a landfill. The cost of closure and remediation for this scenario is $30,000 to $100,000.

The costs depend on the quantity which must be hauled and costs of transportation and disposal. If the cost are near the low end of the range then the costs are relatively low compared to other scenarios. As the costs approach $100,000 they approach the lower end of the range of the high cost scenario which is described next.

Widespread Contamination and Remediation (WR). Two high cost options are described for this scenario. These types of remediation are appropriate if the contamination is widespread and substantial risks to health and the environment exist. The lower cost of the two remediation techniques involves air sparging. The cost of closure and remediation is about $135,000 to $295,000. The higher cost of the two involves pumping and treating. The cost of closure and remediation for pumping and treating is about $330,000 to $575,000. The lower cost and the higher cost scenarios for remediation of widespread contamination which poses a substantial risk cost substantially more than the low cost scenarios. The costs are $135,000 to $575,000.

MARGINAL COSTS OF REMEDIATION - ADDITIONAL COSTS FOR CLEANER SITES

The marginal costs of remediation are the additional costs incurred in going to progressively cleaner sites. Higher marginal costs of remediation can be worth incurring in order to avoid greater risks to health and the environment. From the costs of closure and remediation given above, the marginal costs of stricter clean up standards can be calculated. The base cost from which we start is $12,000. These closure costs must be incurred if the owner is to have a legal, clean closure.

LN: The marginal (additional) cost for the scenario of localized contamination which is eventually determined to pose no threat compared to SC is $3,000 to $23,000. It is the total cost of the LN scenario less the cost of a SC. (15-12 and 35-12).

WN: The marginal cost for the scenario of widespread contamination which is eventually determined to pose no threat compared to a SC is $8,000 to $38,000. (20-12 and 50-12).

DH: The marginal cost for the localized contamination which can be dealt with by digging and hauling compared to the SC is $18,000 to $88,000. (30-12 and 100-12). The marginal cost for DH compared to the LN with no threat is $15,000 to $65,000. (30-15 and 100-35).

We assume that the sites which are easiest to remediate would have costs at the lower bound of each remediation technique and the most difficult sites would have costs at the upper bound of each remediation technique. It follows that the range of marginal costs is from the difference between the lower bounds of the costs to the difference between the upper bounds of the costs.

WR: The marginal cost for the widespread contamination which poses a substantial risk and is remediated by sparging compared to the SC is $123,000 to $283,000. (135-12 and 295-12). The marginal cost for sparging compared to the no threat, WN scenario is $115,000 to $245,000. (135-20 and 295-50).

The marginal cost for the widespread contamination which poses a risk and is remediated by pumping and treating compared to SC is $318,000 to $563,000. (330-12 and 575-12). The marginal cost for pumping and treating compared to WN with no threat is $310,000 to $525,000. (330-20 and 575-50). The marginal cost for pumping and treating compared to sparging is $195,000 to $280,000. (330-135 and 575-295).

AGGREGATE COSTS OF UST CLOSURE AND REMEDIATION FOR KENTUCKY

The costs discussed above are costs per tank. According to Doyle Mills, head of the UST program for the Division of Waste Management for Kentucky, at our meeting held on February 2, 1993 there are about 37,000 USTs in Kentucky currently. The figure supplied to Environmental Information Ltd. (1992, p. A-38) is 38,374 of which 29,374 are registered, regulated USTs and 9,000 are estimated to be unregistered. Since the estimate from Mr. Mills is more recent than the estimate given to EI last fall, we will use the estimate of 37,000 tanks.

A Lower Bound. The change in environmental policy which calls for tank closure according to guidelines which will protect health and the environment will impose costs of closure and remediation of at least $444 million for Kentucky USTs. ($12,000)(37,000tanks)=$444 million. This estimate is a lower bound on costs since inevitably some of the existing tanks will leak and the sites will have to be remediated.

A Middle Estimate. According to Environmental Information Ltd. (1992, p. 22) about 20 percent of might be expected to leak. EPA has estimated that the rate might be 15-20% of all USTs. But, EI found that the 14 states which estimated the leak rates for the USTs in their states had an average of 22%. If we use the 20% leak rate and we use the average remediation cost of $100,000, then the aggregate costs of closure and remediation will be about $1.095 billion.

[(37)(.2)(100)+(37)(.8)(12)]. This aggregate cost is $651.2 million more than if SC were possible.

An Upper Bound. If all 20% of the tanks which leaked are found to be in environmentally sensitive locations and must have pump and treat (WR) remediation, then the aggregate costs of closure and remediation will be substantially higher. If the average cost of WR remediation is $500,000 per site, then the aggregate cost will be about $4.055 billion. [(37)(.2)(500)+(37)(.2)(12)]. This aggregate cost is $2.96 billion more than if remediation were possible at the average cost of $100,000. (4.055-1.095). This aggregate cost is $3.61 billion more than is SC were possible. (4.055-.444).

Sensitivity of Cost Estimates to the Leak Rate. These aggregate estimates depend on the leak rate. If the leak rate is higher than 20%, then our estimates are too low. For example, if the leak rate is 30%, then the middle estimate would be 1.421 billion which is higher than the $1.095 billion estimate. [(37)(.3)(100)+(37)(.7)(12)]. If the leak rate is lower than 20%, then our estimates are too high. For example, if the leak rate is only 10%, then the middle estimate would be $770 million which is lower than the $1.095 billion estimate. [(37)(.1)(100)+(37)(.9)(12)].

Impact on Small Businesses. Small vendors or single station owners are thought to own about 27,000 of the tanks according to Doyle Mills. This number is 68% of the estimated number of USTs in Kentucky. While this percentage is higher than the national estimate of 46% which EI attributes to EPA data, it may reflect the rural nature of Kentucky (Environmental Information Ltd, 1992, p. 18). Even if the number of small operators is overestimated, and it may not be since the national percentage does not account for factors specific to Kentucky, clearly a substantial share of the closure and remediation costs involve small businesses.

BENEFITS OF REDUCING RISKS

The benefits of reducing risks to human health and the environment must be weighed against the additional costs of remediation. If DH remediation costs $40,000, then it more than triples the costs over a SC. (40/12=3.3). If DH remediation costs $40,000, then WR increases the closure and remediation cost by more than a factor of 3 and perhaps as much as a factor of 14. (135/40=3.4 and 575/40=14.40).

The nature and extent of the leakage and the anthropogenic and ecological characteristics of the UST site determine the benefits of various degrees of clean up as well as the costs. Benefits may be limited for small amounts of contamination at remote sites which are not near drinking water supplies or environmentally sensitive areas such as a special wetland. Benefits can be substantial and many times greater for more extensive leaks which contaminate drinking water or damage special, sensitive ecosystems. A socially balanced policy involves a weighing of these benefits of remediation against their costs.

REFERENCES

Environmental Information LTD. The Underground Storage Tank Market: Its Current Status and Future Challenges (Minneapolis, MN (612) 831-2473, 1992).

Groundwater Technology, Inc. 805 Newtown Circle, Lexington, KY 40511, (606) 254-8223. Telephone consults with Andrew Gremos on February 25 and April 20, 1993.

National Institutes for Water. "Groundwater Remediation" Water Science Reporter 1,1 (Spring 1993)

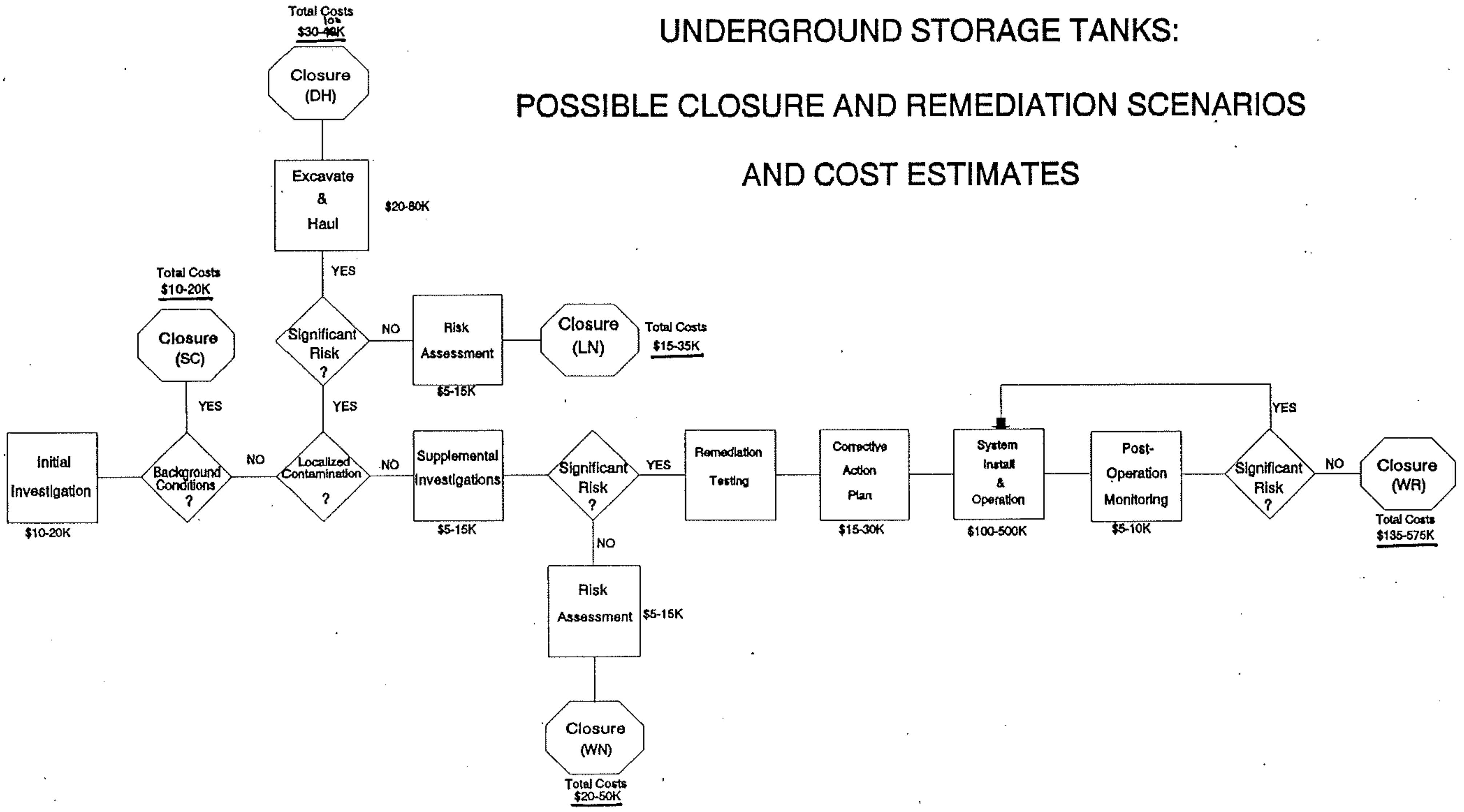
U.S. Environmental Protection Agency. Office of Underground Storage Tanks. Report to Senate Committee on Appropriations Regarding Underground Storage Tank Financial Responsibility and Related Issues (Washington, DC: GPO, April 1992).

Figure 1

UNDERGROUND STORAGE TANKS:

POSSIBLE CLOSURE AND REMEDIATION SCENARIOS

AND COST ESTIMATES



ASSESSMENT OF NUMBER AND DISTRIBUTION OF USTs

Lyle V. A. Sendlein

General Distribution

Data provided by the Division of Waste Management on the registration of USTs in Kentucky show that currently there are 37,000 tanks registered. Information provided on these registrations include the date the tank was placed in service, the location, the size of the tank and the product stored in the tank. An analysis of the data shows that the number of tanks that may be present at a single location varies from one to as many as 242. Ninety-two percent of the sites have eight or fewer tanks. Only one site, Fort Knox, has 242 tanks. The data base also shows that 63.4% of the tanks contain gasoline, 15.8% contain diesel, 6.1% contain oil, 5.3% contain kerosene, 3.7% are empty, 1.0% contain CERCLA hazardous materials, 0.3% contain jet fuel, 4.1% contain unknown materials and 0.4% contain other materials.

Figure 1 shows the frequency distribution of the number of tanks at each site. The highest frequency, 26.2% of the sites, has only one tank. Fifty-five percent of the sites have between two and four tanks. The data base shows a number with zero tanks which has not been resolved yet as to what it means.

Figure 2 shows the frequency distribution of total gallon capacity at each site. The 0-1999 gallons category accounts for 27 percent of the total gallon capacity at a site. Sixty percent of the sites account for 2,000 to 29,999 gallons. These two groups account for 87 percent of the sites.

Based on these data, approximately 87 percent of the sites can be placed into two categories, those small sites (approximately 27% of the sites based on number of tanks and total gallon capacity) that have one tank with a capacity of less than 2000 gallons, and larger sites (55% to 60% of the sites based on number of tanks and total gallon capacity respectively) that have two to four tanks with a total capacity of 30,000 gallons.

Figure 3 shows the distribution of tanks by county and Figure 4 shows the distribution of total tank capacity by county. The most number of tanks are located in Jefferson County (5291 tanks and 34.5 million gallon capacity), with Fayette (1633 tanks and 8.6 million gallon capacity) second and the adjacent counties of Boone (566 tanks and 4.2 million gallon capacity) and Kenton (732 tanks and 4.0 million gallon capacity). Ten other counties have 500 sites or more and seven of these have 3 million gallon capacity per county or more. Twenty four counties have one million gallon capacity or more and the remaining 82 counties have total gallon capacities of less than one million gallons. Within these 82 counties this roughly corresponds to 200 tanks per county or less.

This analysis allows us to understand where the greatest number of tanks occur and the associated volume of liquids stored in these locations. This will allow us to understand where the petroleum products occur with respect to the geology, potable water sources and soils. This information will be used in the development of the matrix.

TABLE 1
COUNTIES WITH HIGHEST TOTAL GALLON CAPACITY

COUNTY	TOTAL GALLONS	COUNTY	TOTAL GALLONS
JEFFERSON	34,509,444	MUHLENBERG	1,561,082
FAYETTE	8,614,617	NELSON	1,523,745
HARDIN	4,622,824	SCOTT	1,490,363
DAVIESS	4,601,656	HARLAN	1,467,583
BOONE	4,150,781	CLAY	1,465,892
WARREN	4,083,678	FLOYD	1,442,570
KENTON	4,003,568	OHIO	1,375,607
CHRISTIAN	3,728,780	UNION	1,314,625
MADISON	3,519,726	LETCHER	1,304,759
PULASKI	3,239,814	KNOTT	1,298,696
PIKE	2,963,031	BELL	1,292,176
MARSHALL	2,696,535	BOYLE	1,271,494
LAUREL	2,665,214	SHELBY	1,271,176
HOPKINS	2,512,123	GRAVES	1,271,012
BARREN	2,378,086	CLARK	1,257,714
PERRY	2,388,968	CALLOWAY	1,213,545
BOYD	2,221,096	GREENUP	1,179,415
CAMPBELL	2,137,263	LOGAN	1,172,058
FRANKLIN	2,104,894	OLDHAM	1,155,445
HENDERSON	2,010,862	GRAYSON	1,143,822
SIMPSON	1,848,578	HART	1,084,610
WHITLEY	1,765,671	CARTER	1,016,195
KNOX	1,745,053	JOHNSON	999,745
MCCRACKEN	1,602,370	TAYLOR	975,723
BULLITT	1,592,568	LAWRENCE	948,315
		MONTGOMERY	929,559
		JESSAMINE	904,905

Number of Sites and Tank Capacity Relationship To Physiographic Regions

<u>Eastern Kentucky Coal Field Province</u>

Only Pike County has 3 million gallon capacity and Boyd, Perry and Laurel Counties have between 2 and 2.7 million gallon capacity. All other counties are around one million or less.

<u>Purchase Province</u>

Marshall County has 2.7 million gallon capacity and all others are less than 1.6 million gallon capacity with the four most western counties less than 1 million gallon capacity.

<u>Western Coal Field Province</u>

Daviess County has the highest total gallon capacity with 4.6 million and Henderson and Hopkins Counties are between 2 and 2.5 million gallon capacity. Of the remaining counties, half fall between 1.1 to 1.6 million gallon capacity and the other half are below one million gallon capacity.

<u>Blue Grass Province</u>

The highest total gallon capacities are within this region. Jefferson County with it 34.5 million gallon capacity, Fayette County and surrounding counties have a total of 15.8 million gallon capacity. Kenton, Boone and Campbell Counties have a total of 10.2 million gallon capacity near Cincinnati.

<u>Mississippi Plateaus Province</u>

This province has two areas above 4 million gallon capacity (Hardin and Warren Counties) and two counties in the 3 million gallon capacity range (Christian and Pulaski Counties). Barren County has 2.4 million gallon capacity and Logan, Simpson and Hart range between 1.1 and 1.8 million gallon capacity. The remaining 20 plus counties fall below one million gallon capacity.

Figure 1. Frequency distribution of the number of tanks per site.

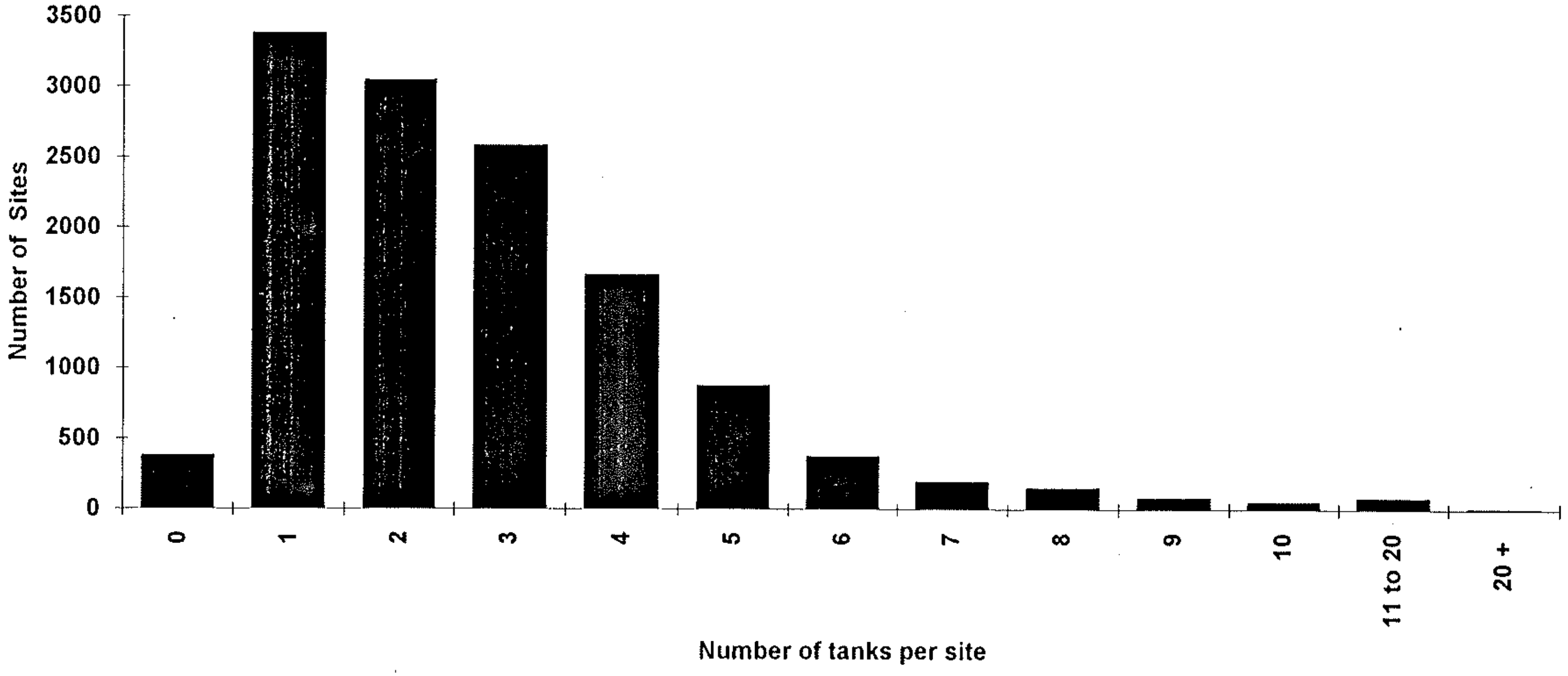
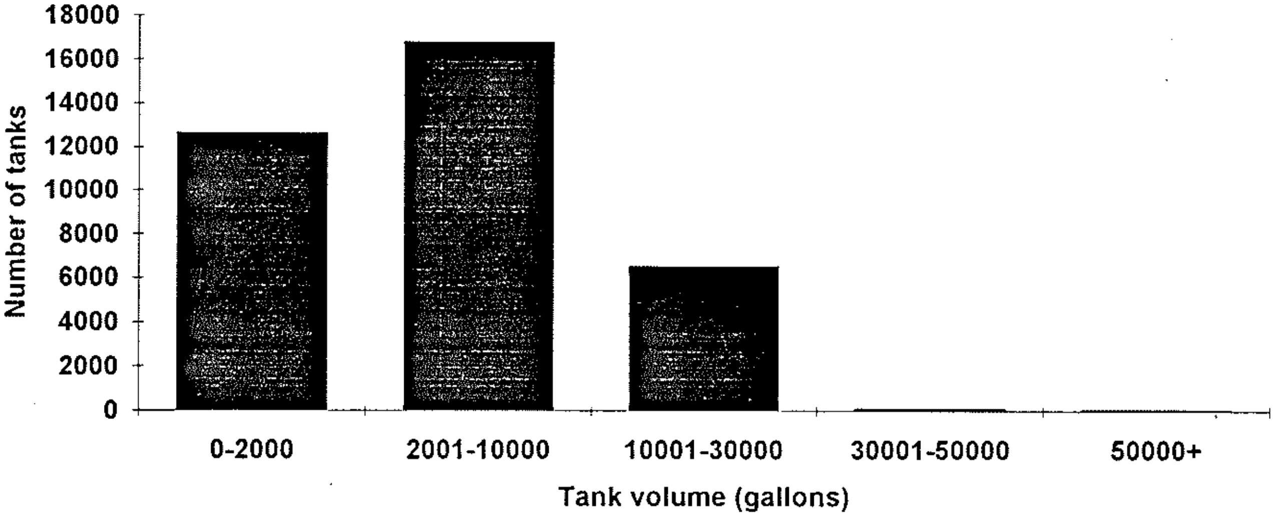


Figure 2. Frequency distribution of tank volume



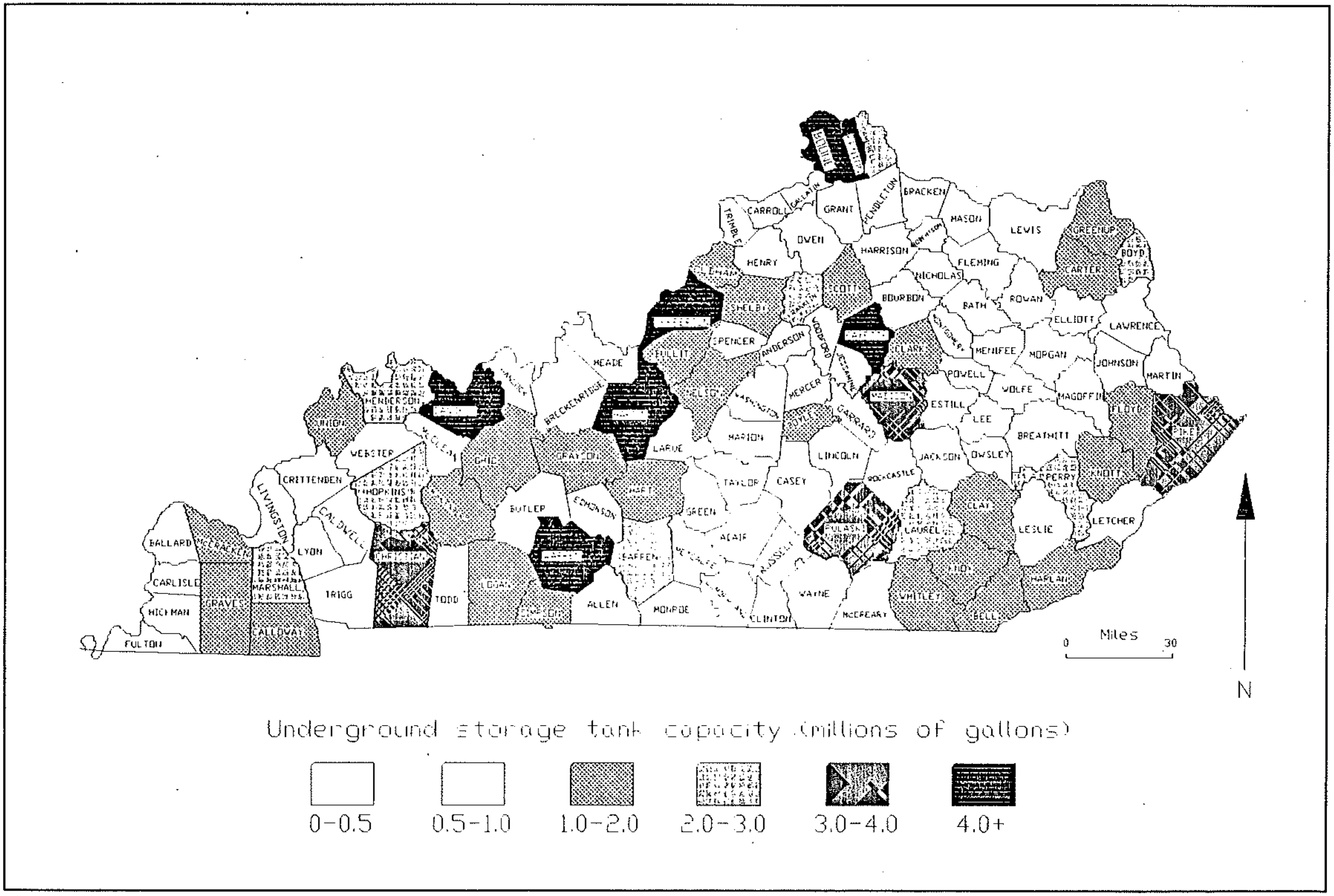


Figure 4. Distribution of underground storage capacity by county.

ANALYSIS OF POTABLE WATER SOURCES IN KENTUCKY

Lyle V. A. Sendlein

INTRODUCTION

In order to get some feeling about the source of potable water in Kentucky the literature was searched and data bases sought. Not many data points on wells were kept in easily accessible files until recently. Some data are available on USGS maps but the wells are in paper files. The recent accumulation of water well information resulting from the requirement that well drillers must file logs and other information on new wells provides some data on total well depth and depth to water. Water quality information is not available from this source. This data base was searched and produced information on 10,285 wells. A second source of recent information comes form a voluntary well survey conducted by several state agencies (the Department of Soil Conservation, College of Agriculture, Kentucky Geological Survey) and the Farm Bureau (called the Farm Bureau Study in this report). This survey did not include depth to water but did give an estimate of well depth as remembered by the well owner. The data collected from the literature and these surveys are summarized below.

SUMMARY OF LITERATURE AND DATA BASES

Whitesides Study

The study by Whitesides (1971) looked at only 106 wells in forty one counties in Kentucky. From these wells the total well depth was obtained, non-pumping water levels determined, specific capacity and well yield were measured by way of pumping tests. Depths of wells tested ranged from 21 to 1015 feet and yields ranged from less than one to several hundred gallons per minute.

Analysis of the data presented in the Whitesides report presents a general picture of the zones of rock producing potable water in 1971. The average depth of the 106 wells studied was 189 feet with an average depth to water of 59 feet.

KGS Groundwater Data Repository Data Analysis

The Kentucky Geological Survey Groundwater Data Repository searched the records and found 10285 wells with depth of well and depth to water information. An analysis of the data the depth of wells ranged from 5 feet to 1345 feet with an average depth of 143 feet. Figure 1 shows the distribution of well depth. It can be seen that is skewed toward the shallow end with the mode occurring between 60 and 100 feet with 99.7% of the wells are deeper than 20 feet, 97.1% deeper than 40 feet and 42.1% falling between 20 and 100 feet.

The depth to water ranged between 1 and 1246 with an average depth to water of 65 feet. Figure 2 shows the distribution of the depth to water is skewed toward the shallow end. Even though the mean depth is 65 feet, the mode occurs at 20 to 30 feet. Eighty four percent of the data show that the water depth is greater than 20 feet.

Figures 3 and 4 illustrate the distribution of well depth and depth to water on a state wide basis with averages for each county. Four counties did not report any wells in this data set. They are Simpson, Shelby, Henry, and Bracken.

Bienkowski Study

A study by Bienkowski (1992) of 2850 wells for the Eastern Kentucky Coal Field provides information on the depth of wells and average depth to water. She found that the average well depth was 113 feet but the median of the data was 89. The average depth to water was found to be 45 feet. Her well depth data supports the data found by Whitesides (1971) for most of the area. She did not find the very deep wells reported by Whitesides nor did she include the Whitesides data because her prime purpose was to study the water quality of the groundwater of the province.

USGS Water Atlas Study

An analysis of the Water Atlas Series of the USGS provides another picture of the potable water of Kentucky. Time did not permit analysis of all of their data but information taken from HA-32 by Brown and Lambert (1962) of the south central part of the state produced 133 well depths with an average of 84 feet and 122 depths to water with an average of 37 feet.

Farm Bureau Study

Data collected as part of a combined effort of the Kentucky Department of Soil Conservation and other agencies was conducted primarily to test the water chemistry but each participant filled out a form that provided information on the well. Water depth information was not obtained but total well depth was known by 3526 of the people surveyed.

SUMMARY TABLE

DATA SOURCE	# OF WELLS	TOTAL DEPTH (average)	DEPTH TO WATER (average)
WHITESIDES	106	189 feet	59 feet
KGS	10,285	143 feet	65 feet
BIENKOWSKI	2850	113 feet	45 feet
WATER ATLAS	133/122	84 feet	37 feet
FARM BUREAU	3526	104 feet	no data

The distribution of well depth (figure 5) data are skewed toward the shallow end where the mode falls between 80 feet to 100 feet but the calculated average depth is 104 feet. Fifty eight percent of the wells in the survey fell between 20 feet and 100 feet with 96% of the wells deeper than 20 feet and 84.9% deeper than 40 feet.

Caves In Kentucky

A compilation of data produced by Percy N. Dougherty (1985) summarized the location of caves in Kentucky. The occurrence of caves is important in understanding the occurrence of groundwater in Kentucky. Figure 6 illustrates the distribution of caves and highlights the greater abundance of caves in the Mississippian Plateaus and Blue Grass Physiographic Provinces. The concentration of caves occurs in a group of counties (Breckenridge, Meade, Hardin, Hart, Edmonson, Warren and Barren) in central Kentucky. Another concentration occurs in a string of counties in east south central part of the state (Wayne, Pulaski, Rockcastle, and Jackson).

CONCLUSIONS

One can conclude several things from the data presented here.

1. Potable groundwater is obtained from geologic units ranging in depth between 60 and 100 feet. Eighty six percent (86%) of the wells are 60 feet deep or greater.

2. The depth to water in Eighty four percent (84%) of the wells is 20 feet or greater.

3. The shallower wells and depths to water is concentrated in the Blue Grass Region.

4. The highest concentration of caves occurs in a region including Breckenridge, Meade, Hardin, Hart, Edmonson, and Warren counties and three other counties, Pulaski and adjacent Rockcastle, and an isolated Carter County.

5. The number of data points used in this analysis is large enough to be representative of the water wells present in the State.

Acknowledgement

Dan Carey and Bart Davidson of the Kentucky Geological Survey provided data from the KGS data base in a variety of formats, which were included in this report. Their assistance is greatly appreciated.

REFERENCES

Bienkowski, Lisa, 1990, Delineation and Characterization of the Aquifers of The Eastern Kentucky Coal Field, University of Kentucky Ph.D. dissertation, UK Library, pages 319.

Brown, R. F.and T. W. Lambert, 1962, Availability of Ground Water In Allen, Barren, Edmonson, Green, Hart, Logan, Metcalfe, Monroe, Simpson and Warren Counties, Kentucky, Hydrogeologic Investigations Atlas HA-32, USGS, Washington, D.C.

Dougherty, Percy N. Editor, 1985, Caves and Karst of Kentucky, KGS Special Publications 12, Series XI, Lexington, KY.

Whitesides, D. V., 1971, Yields and Specific Capacities of Bedrock Wells In Kentucky, Information Circular 21, Series X, Kentucky Geological Survey, 18 pages.

Figure 1. Frequency distribution of total well depths - KGS Database.

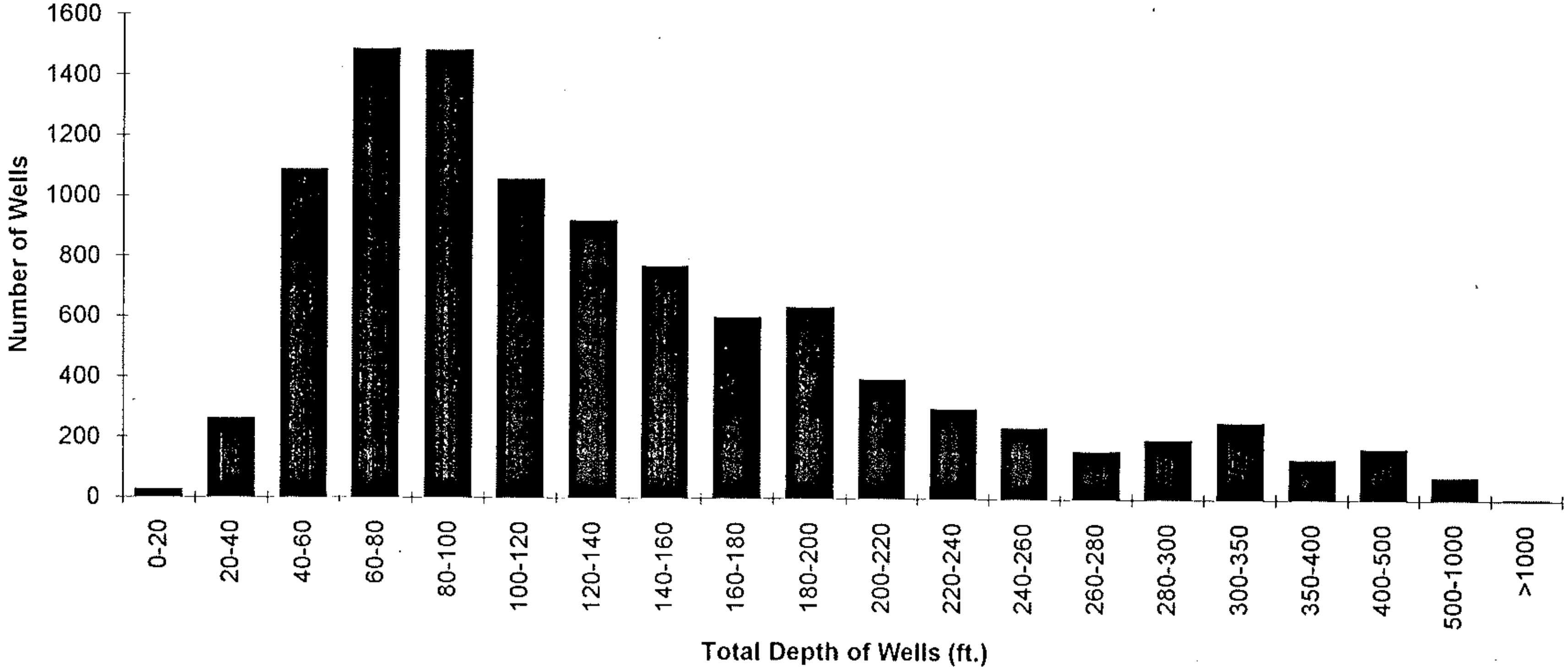
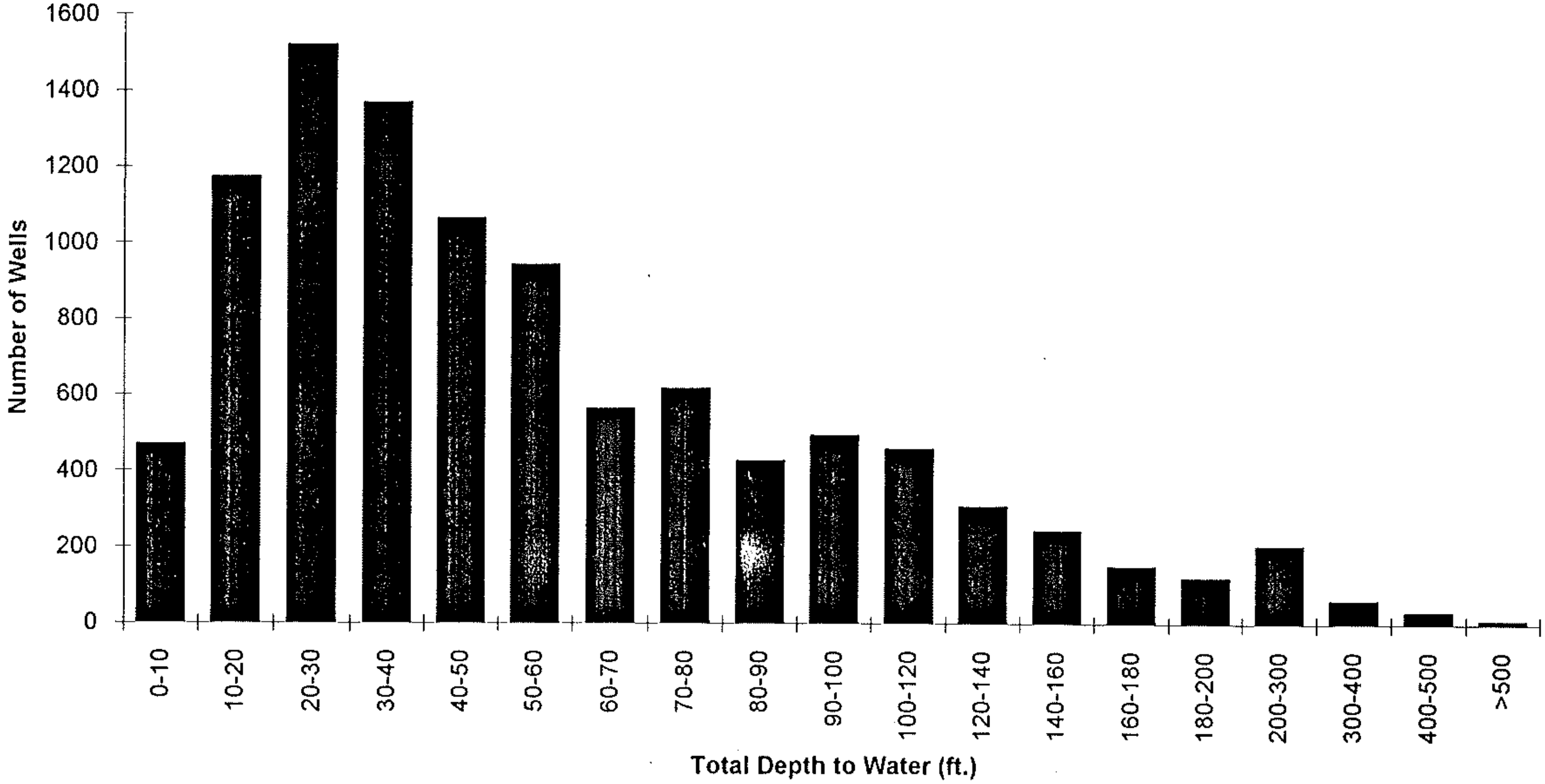


Figure 2. Frequency distribution of depth to water - KGS Database.



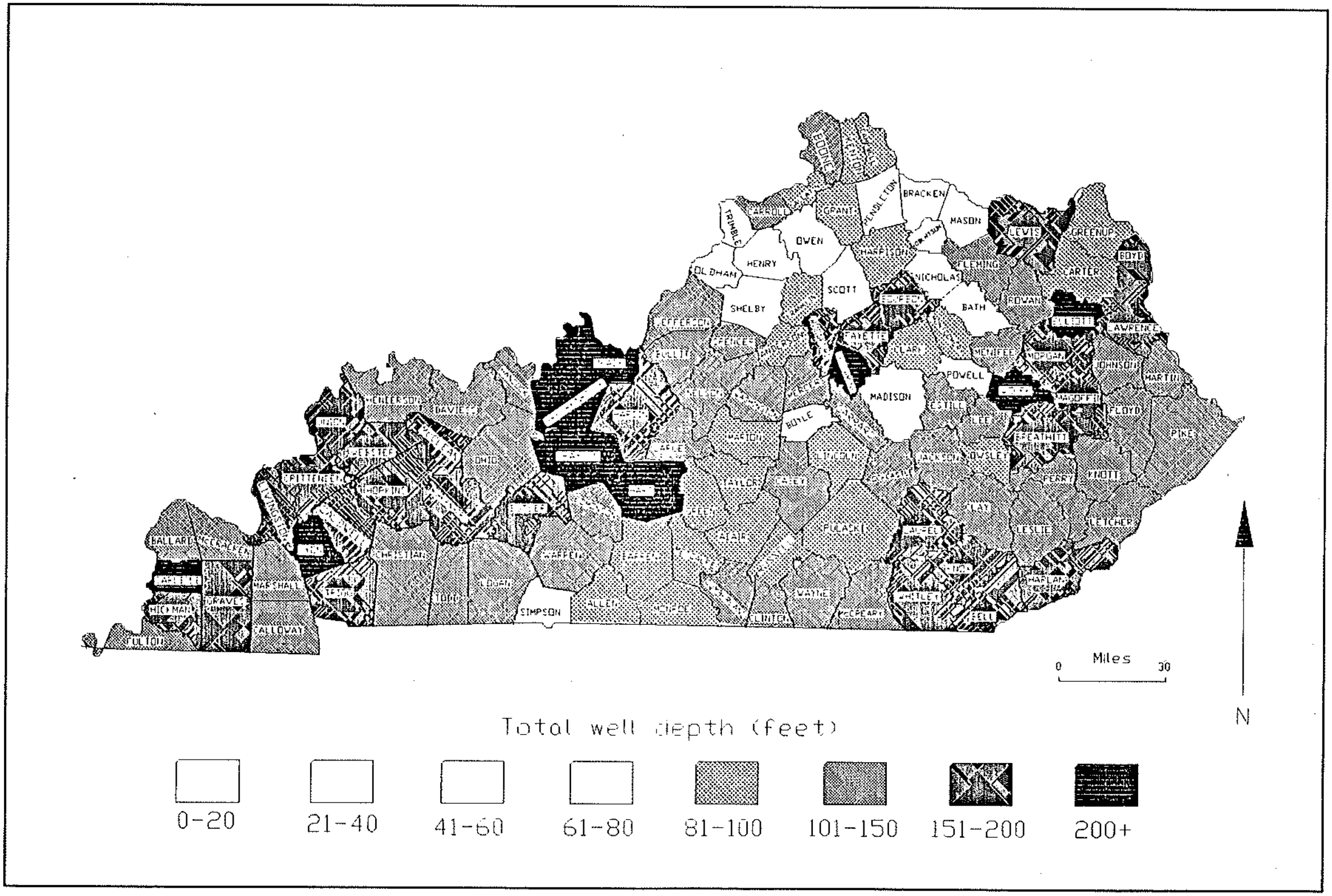


Figure 3. Distribution of total well depths by county.

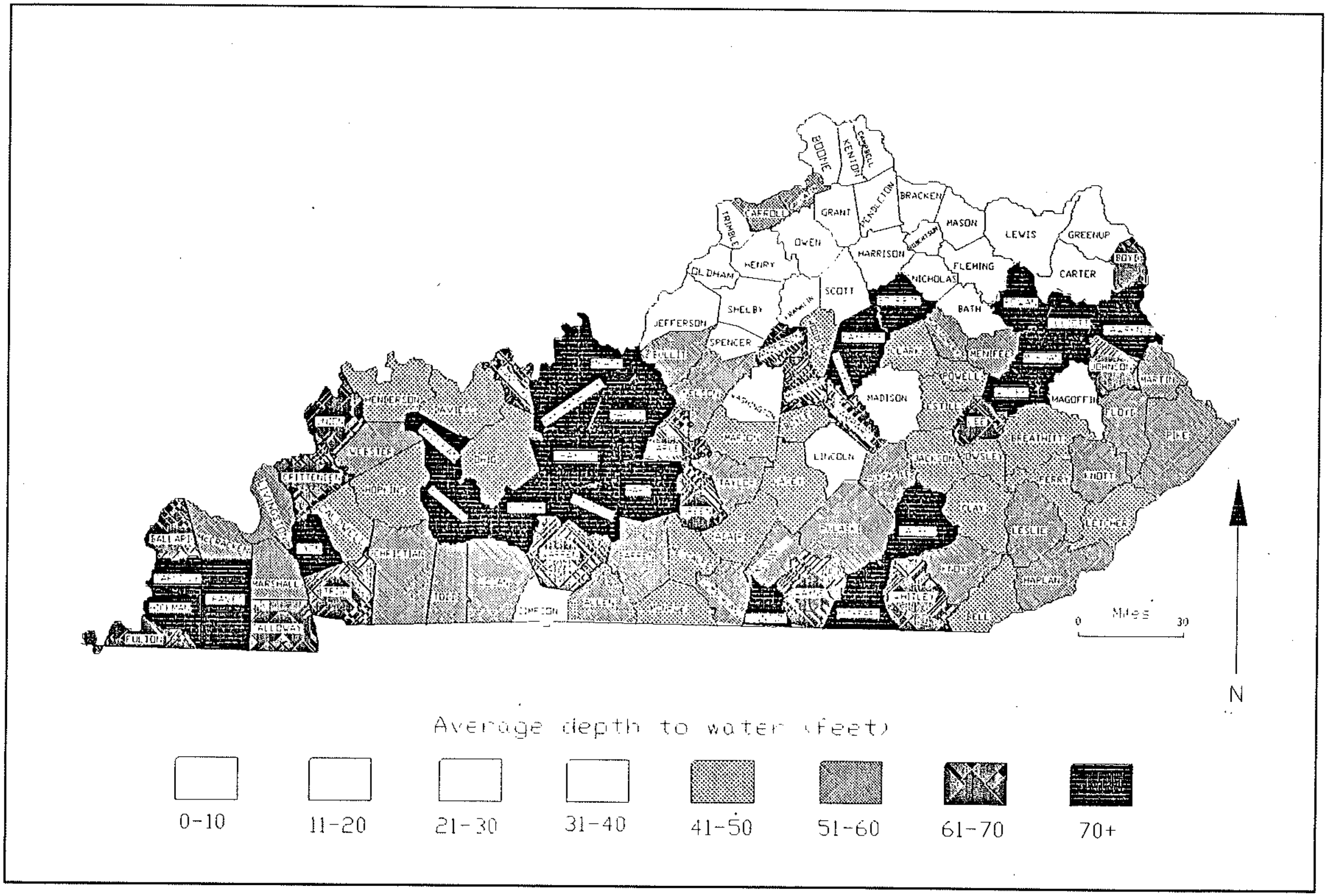
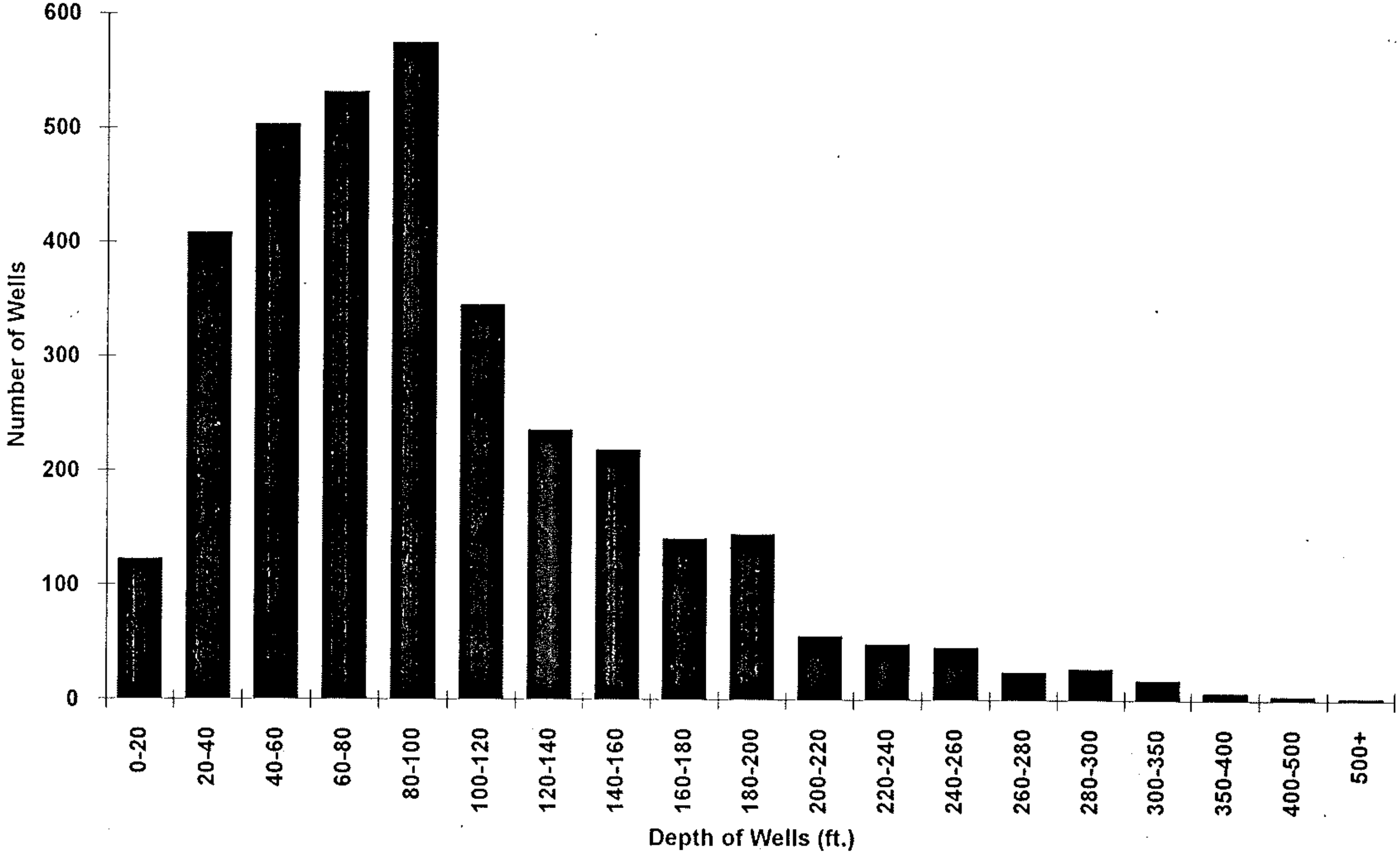


Figure 4. Distribution of depth to water in wells - by county.

Figure 5. Frequency distribution of total well depths - Farm Bureau Study.



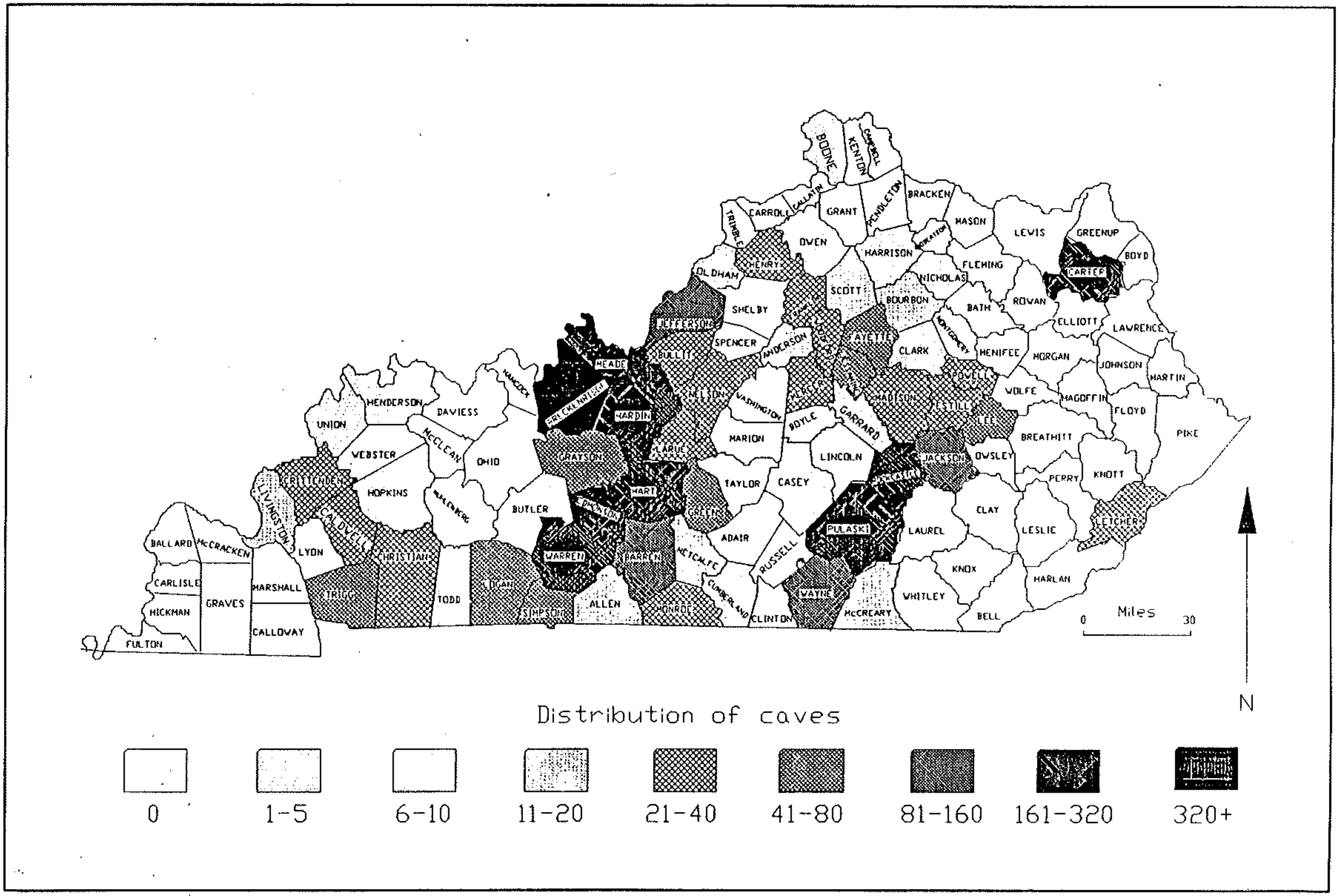


Figure 6. Distribution of caves by county.

ANALYSIS OF WELL DATA AND SOIL PARAMETERS AS RELATED TO THE STATSGO KENTUCKY GENERAL SOILS MAP

Burl I. Naugle

INTRODUCTION

In this study water well data from the Kentucky Division of Water, Kentucky Natural Resources and Environmental Protection Cabinet (KNREPC), database were related to the State General Soil Geographic Data Base (STATSGO) general soils map. Water well parameters included in the study were the depth of wells, depth to bedrock, and depth to static water level. In addition, soil parameters pertinent to modeling the flow of contaminants from underground storage tanks, average permeability and average percent organic matter, were derived for the entire soil profile and for the bottom soil layer of each mapped Kentucky soil (soil ID) and of the soils of 20 physiographic region/soil type groupings (region/type). Tables and plots showing the parameters for each soil ID and each region/type are presented. Statistical analyses were performed and documented here showing that all of the parameters were significantly different on the basis of soil id and region/type. Additional statistical analyses were performed to determine if the differences among region/types were still significant when taking into account the differences among soil IDs within the region/types.

DATA SOURCES

Kentucky STATSGO general soils data were obtained from the KNREPC in the ARC/INFO (ESRI, 1992) Geographic Information System format. Both locational (map) information and attribute (soil parameters) information were utilized to derive tabular and mapped data for individual soil IDs and for 20 physiographic regions/soil type groupings (region/type). The general soils data had been generated under a USDA Soil Conservation Service (SCS) project in 1985 (KNREPC, 1986). General soils (643 separate polygons) were mapped on 1:250,000 scale maps by KNREPC Division of Conservation and SCS employees. Soil and physical characteristics were compiled for 2137 different soil phases or sequences making up 195 different general soils categories. The percentage of each phase making up the general soil category was compiled along with other soils information for the entire soil profile of each phase. Soil parameter information for each layer of each phase (7342 phase/layer combinations) were also compiled. Entire profile means and bottom layer means of permeability and organic matter were generated for each soil ID and each region/type.

Two maps of the STATSGO data are included with this report at a scale of 1:2,000,000. The second map includes county boundaries for locational purposes only. The county boundaries had been derived from much smaller scale maps (> 1:1,000,000) than the soils data for a previous study at MARC and obviously do not align perfectly. The soil region/types included in this study are listed below along with some characteristics, physiography, and parent materials (KNREPC, 1986):

1. River alluvium: Alluvial soils formed on floodplains of large rivers.
2. Purchase loess: Soils formed in deep loess and Tertiary and Cretaceous age coastal

plain sediments in the Jackson Purchase.

3. Purchase alluvium: Alluvial soils formed on floodplains, terraces, and colluvial fans in the Jackson Purchase.
4. Western Pennyroyal: Soils formed from loess and Mississippian age limestone of the Western Pennyroyal.
5. Western Penny. alluvium: Alluvial soils of the Western Pennyroyal.
6. Western Penny. loess: Soils formed in deep loess and Tertiary and Cretaceous age coastal plain sediments of the Western Pennyroyal.
7. Western Coalfield: Soils formed from Pennsylvanian age sandstone, siltstone, and shale of the Western Coalfield.
8. Western Coalfield alluvium.
9. Western Coalfield loess.
10. Knobs: Soils formed from Lower Mississippian and Devonian age siltstone and shale of the Knobs physiographic province.
11. Knobs alluvium.
12. Eastern Pennyroyal: Soils formed from Mississippian age limestone of the Eastern Pennyroyal.
13. Eastern Pennyroyal alluvium.
14. Outer Bluegrass: Soils formed from Silurian and Ordivician age limestone and calcereous siltstone of the Outer Bluegrass.
15. Outer Bluegrass alluvium.
16. Outer Bluegrass loess.
17. Inner Bluegrass: Soils formed from Ordivician age limestone of the Inner Bluegrass.
18. Inner Bluegrass alluvium.
19. Eastern Coalfield: Soils formed from Upper Mississippian and Pennsylvanian age sandstone, siltstone, and shale of the Eastern Coalfield.
20. Eastern Coalfield alluvium.

These region/types are best seen in the large STATSGO maps. Some of the alluvial soil IDs (5) on the map had to be split in order to accomodate the region/type classification.

Kentucky water well data (13,004 records that overlaid the STATSGO map) were obtained from the Kentucky Division of Water, KNREPC. These data included the KGS Groundwater Data Repository well data discussed in Sendlein, 1993. Well parameters included latitude, longitude, depth of well, surface elevation, depth to bedrock, depth to static water level, water yield, and water yield units. Well records with depth to bedrock or static water level equal to zero were excluded from further analysis leaving 10,860 water well data records. Some of the excluded data records may have been valid, while some of the included records may have been invalid. The depth data (well depth, depth to bedrock, and depth to static water level) were all skewed to the right as shown in Sendlein, 1993. Logarithmic transformations were applied to the depth data for statistical analysis purposes in order to use standard statistical techniques which assume a Gaussian normal distribution (Zar, 1984). The resulting data were much more symmetric and appeared to reasonably approximate a normal distribution.

Only 164 of the 195 soil IDs contained valid well data. Of these, only 132 soil IDs contained more than 2 wells. Thus, some of the soil IDs do not appear in the tables that follow and some of the plots show missing data for some of the soil IDs. Three of the region/types: Western Pennyroyal alluvium, Western Pennyroyal loess, and Outer Bluegrass loess, did not have enough wells to calculate a valid mean. The Western Pennyroyal alluvium and Western

Pennyroyal loess are almost completely contained in the Land Between the Lakes (LBL), and are unlikely to be important from an underground storage tank perspective. The Outer Blugrass loess is contained in one very small STATSGO soil polygon. In addition, some of the wells (24) were located in STATSGO polygons representing water, probably the result of small scale soil mapping or misregistration.

The ARC/INFO software at the Mid-America Remote Sensing Center (MARC), Murray State University, provided the capability to analyze and map the pertinent soil parameters and well data for this underground storage tank study. The latitude and longitude associated with each well record allowed the software to associate the well data with the general soils data. The Statistical Analysis System (SAS, 1990) software on the Murray State University mainframe was used for statistical analyses.

STATISTICAL ANALYSIS

Statistical analyses were undertaken to determine if the parameter means were significantly different on the basis of soil ID and/or region/type. These analyses involved an analysis of variance (ANOVA) using the SAS GLM procedure. The GLM procedure is supposed to be capable of valid ANOVA even when the number of samples in each category are widely different as was the case here (SAS, 1990). All of the soil and well parameters (entire profile mean permeability, entire profile mean organic matter, bottom layer permeability, bottom layer organic matter, logarithmic depth of wells, logarithmic depth to bedrock, and logarithmic depth to static water level) were significantly different (alpha level much less than .05) on the basis of both soil ID and region/type classification. This does not mean, of course, that the parameters are significantly different between each and every soil ID or each region/type, but it does mean that there are at least some groups or individual categories that have significantly different parameters from other groups or individuals.

It appeared that the variation in some of the parameters due to soil ID within a region/type were larger than the differences in the means between region/types. Another statistical analysis was performed to check whether the means were different on the basis of region/type when taking into account the differences among soil IDs within region/types. A statistical technique that can be used in this case is called ANOVA with nested variables (Zar, 1984; SAS, 1990). The GLM procedure allowed the differences among region/type means to be compared with the variation due to soil ID within the region types. All of the parameters tested were still significantly different (alpha < .05) on the basis of region/type except for well depth and depth to static water level. The parameters that were still significantly different had reduced significance when compared to a straight ANOVA on region/type only. The well depth and depth to static water level were no longer significant at an alpha level of .05, but did meet a significance level of between .05 and .10. Thus the classification of well depth and depth to static water level into region/types is not a very satisfactory classification. The plots for well depth and depth to water by Kentucky soil ID should take precedence over the same plots by region/type.

DATA PRESENTATION AND DISCUSSION

Tables and maps are presented here which show the relationships of the parameters:

entire profile mean permeability, entire profile mean organic matter, bottom layer mean permeability, bottom layer mean organic matter, mean well depth, mean depth to bedrock, and mean depth to static water level by Kentucky soil ID sorted by region/type and by region/type. Tables for the well parameters contain standard deviations, minimum, maximum, and median values in addition to the means.

In many cases the separation of the soils from a physiographic region into different types of soils such as aluvium, loess, etc. results in meaningful parameter differences. However, there are sometimes larger differences in mean parameter values among soil IDs within region/types than between region/types. This is especially true for well depth and depth to static water level as discussed above.

Some of the soil layers in the STATSGO database consisted of bedrock, which did contain permeability values but did not contain organic matter data other than zero percent. This may result in some uncertainty in both the bottom layer permeability and organic matter values.

Some of the significant items from an underground storage tank perspective are:

1. The depth to bedrock is significantly larger in the Jackson Purchase (RT= 2 or 3) than in the rest of the state.
2. The average depth to bedrock in the Inner Bluegrass (RT= 17 or 18) is less than 10 feet, although these depths are not significantly different than those of much of the state.
3. Only three soil IDs that contained more than two water wells had an average depth to well water of less than 20 feet.
4. The Western Coalfield and Western Pennyroyal (RT= 4 or 7) have average depths to static water level of 128 and 93 feet (medians: 89.5 and 78 feet), respectively. The variations are so large that definitive statements cannot be made on a region/type basis. It can certainly be said, however, that most water being drawn from wells in Kentucky, especially in the Western Coalfield and the Western Pennyroyal, is coming from deep rather than surface aquifers.
5. The percent organic matter in the lowest soil layer is indeed very small. The average for the entire state is very near the 0.1 percent used in McGinley's (1993) analysis. Some of the assumptions used in the STATSGO soils database may be a little suspect, i.e. bedrock layers have no organic matter. This is somewhat compensated for, however, by the fact that the depth at which contamination would be present is below the depth of the soil profile (< 6ft) considered in the STATSGO database.
6. All of the intrinsic permeabilities of the bottom layer of soils fall within the range of those used in McGinley's (1993) analysis.

REFERENCES

ESRI (1992) ARC/INFO User's Guide. Environmental Systems Research Institute, Inc.

KNREPC (1986) Interpretive General Soils Mapping Project. National Cooperative Soil Survey Program. September 30.

McGinley, P. M. (1993) "Generic Organic Contaminant Pathway Analysis for Components of Petroleum in Soil and Groundwater".

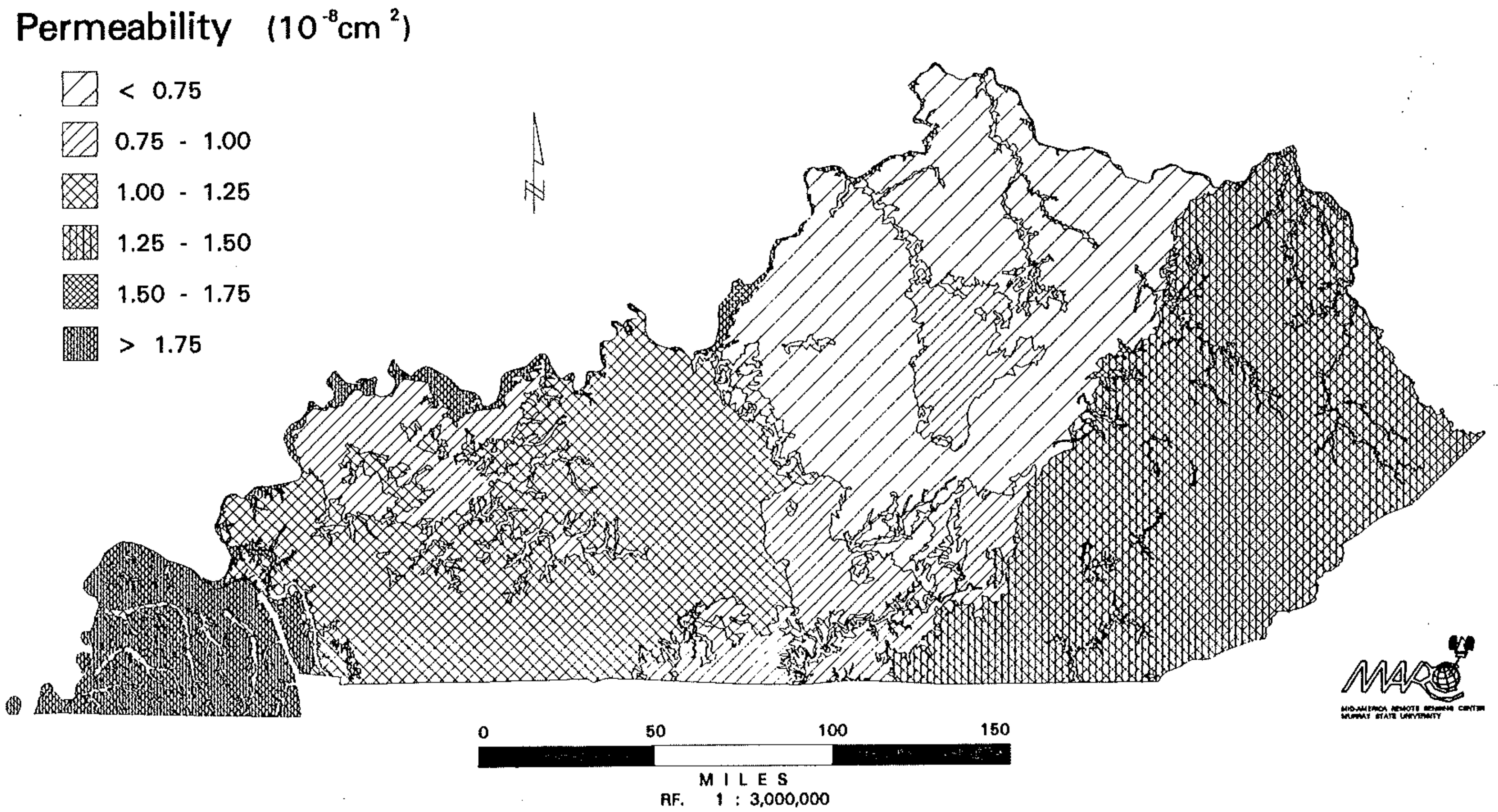
SAS (1990) SAS/STAT User's Guide. SAS Institute, Inc.

Sendlein, L.V. (1993) "Analysis of Potable Water Sources in Kentucky".

Zar, J.H. (1984) Biostatistical Analysis. Prentice-Hall. Englewood Cliffs, NJ.

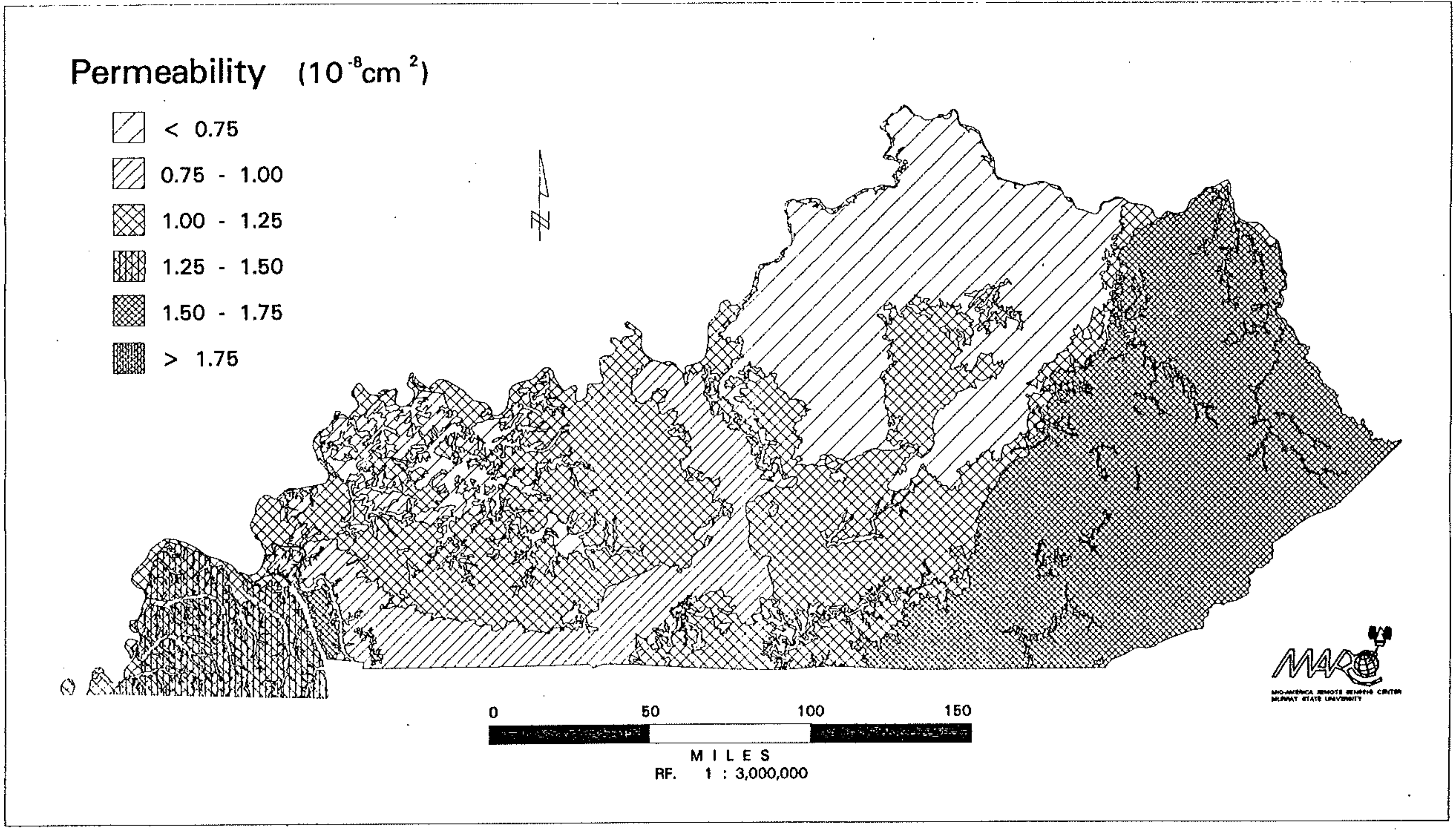
INTRINSIC PERMEABILITY: BOTTOM LAYER MEAN

By Region/Type



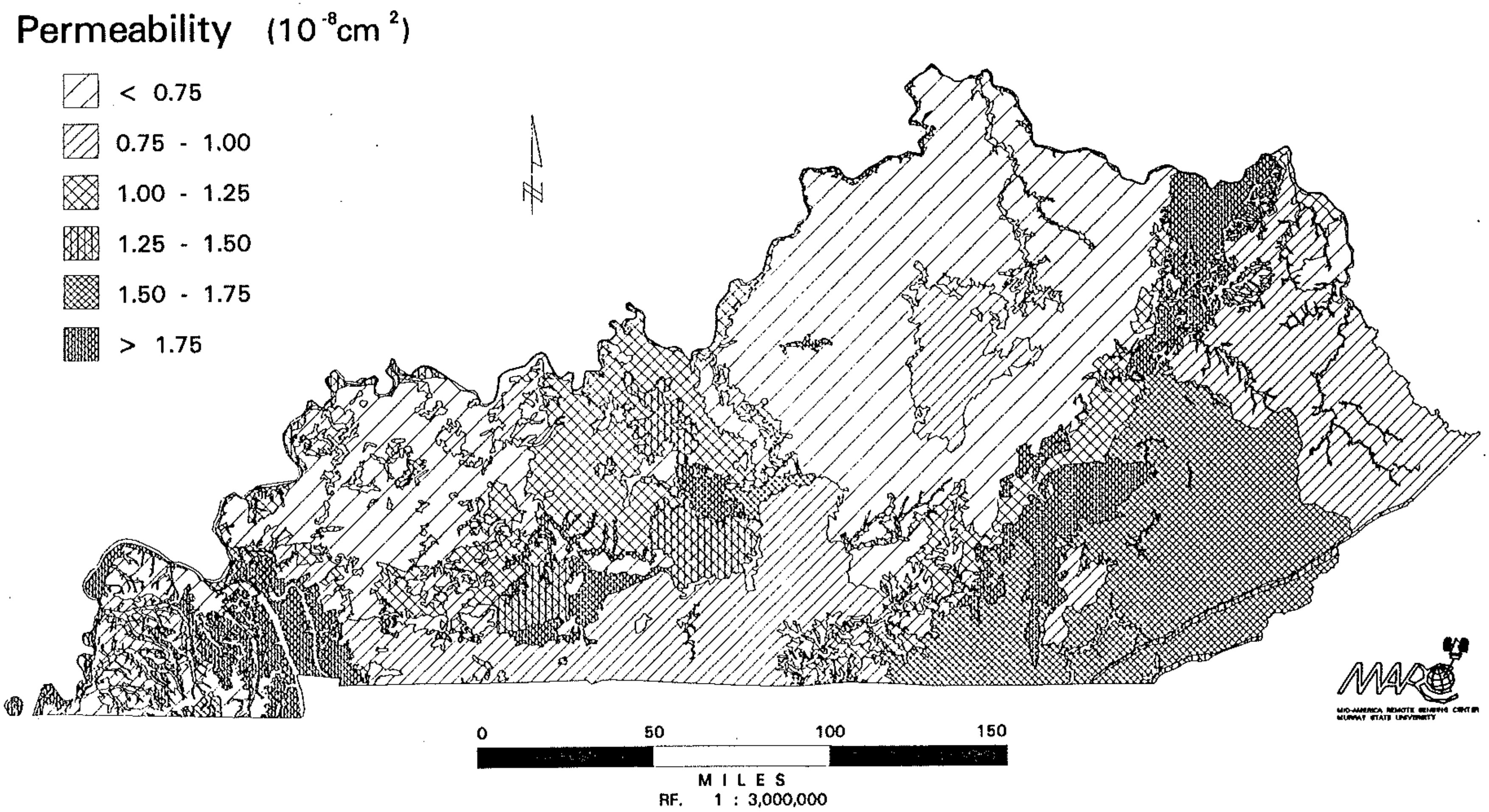
INTRINSIC PERMEABILITY: ENTIRE PROFILE MEAN

By Region/Type



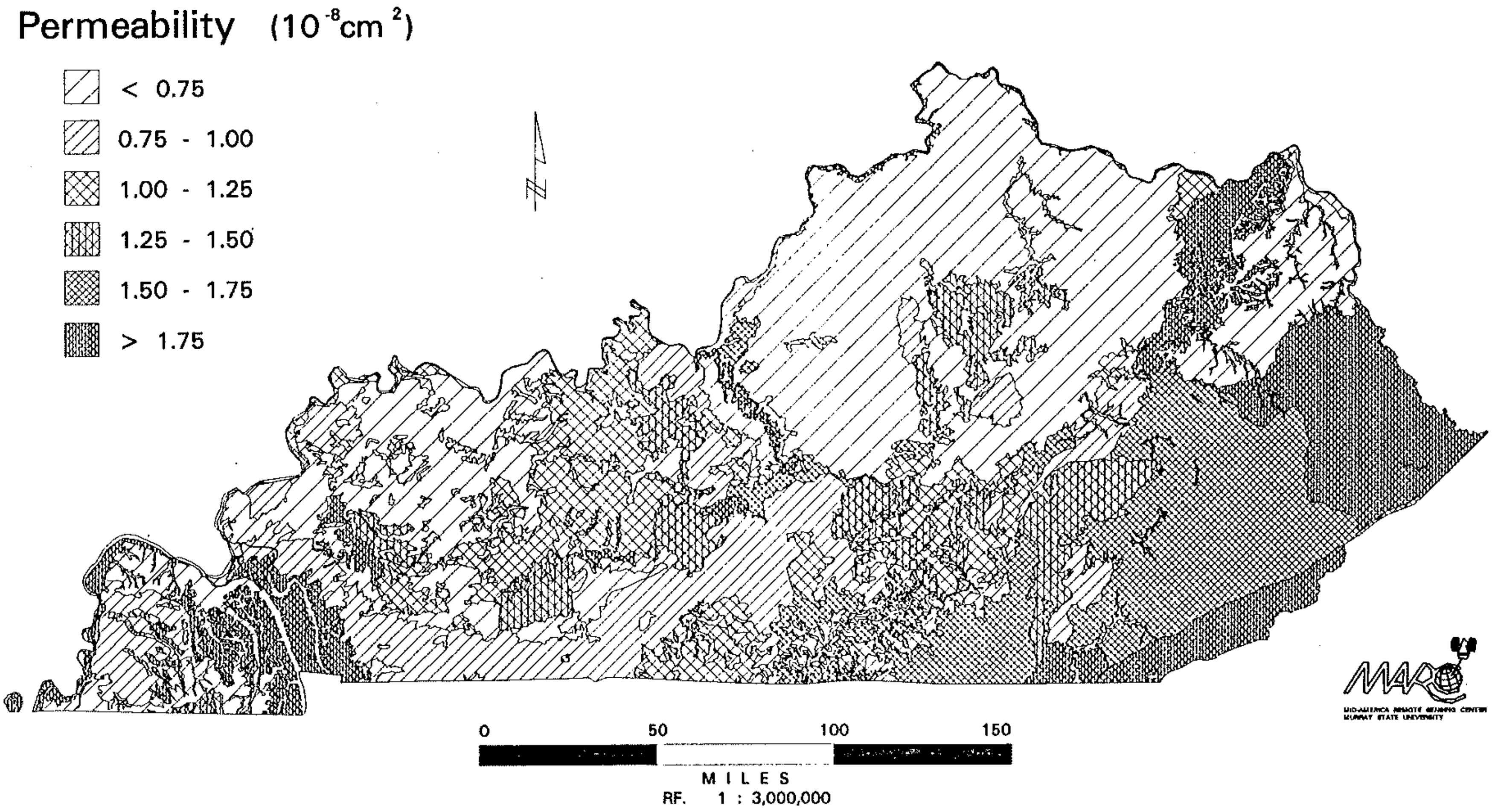
INTRINSIC PERMEABILITY: BOTTOM LAYER MEAN

By Kentucky Soil-ID



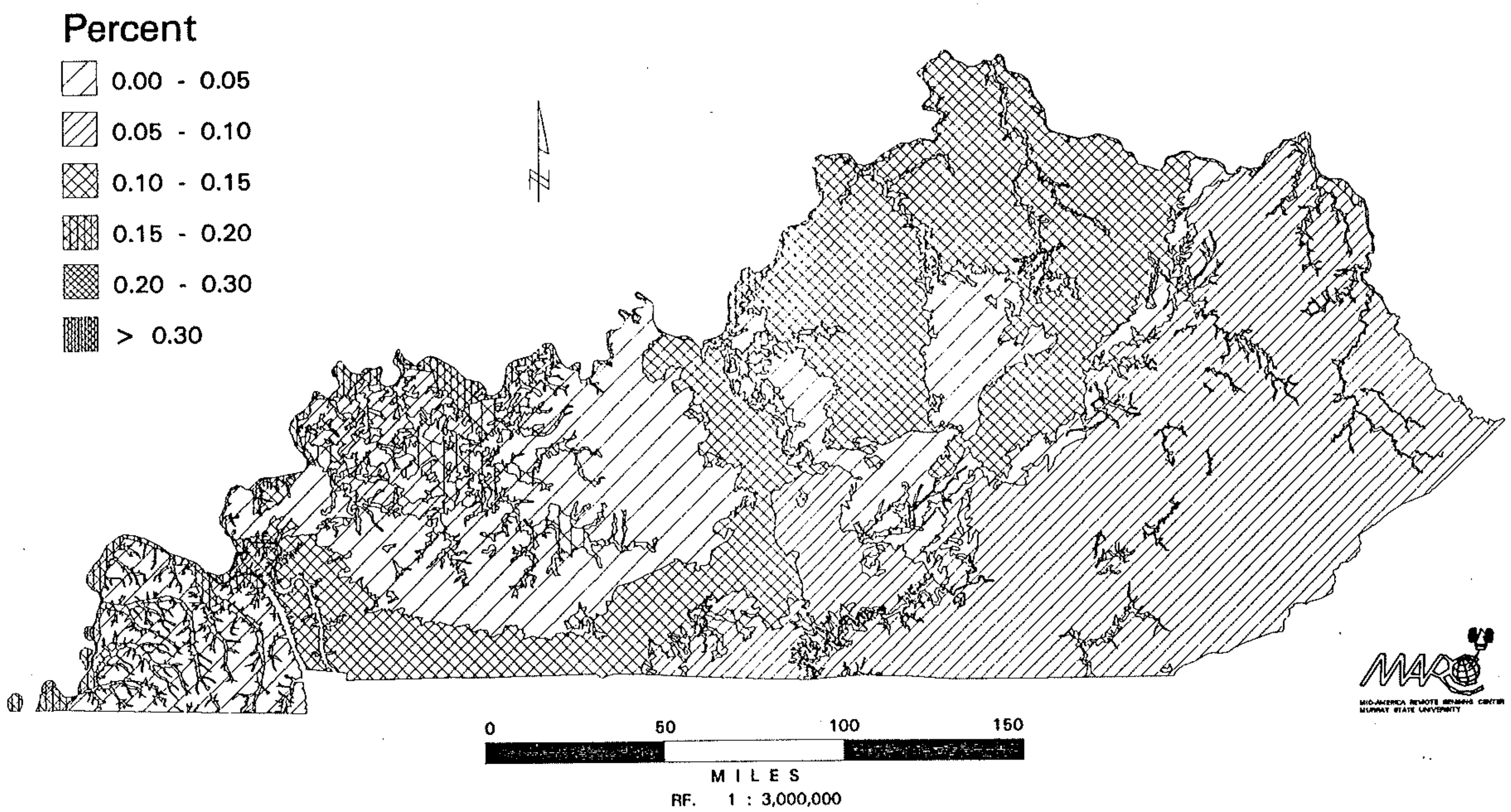
INTRINSIC PERMEABILITY: ENTIRE PROFILE MEAN

By Kentucky Soil-ID



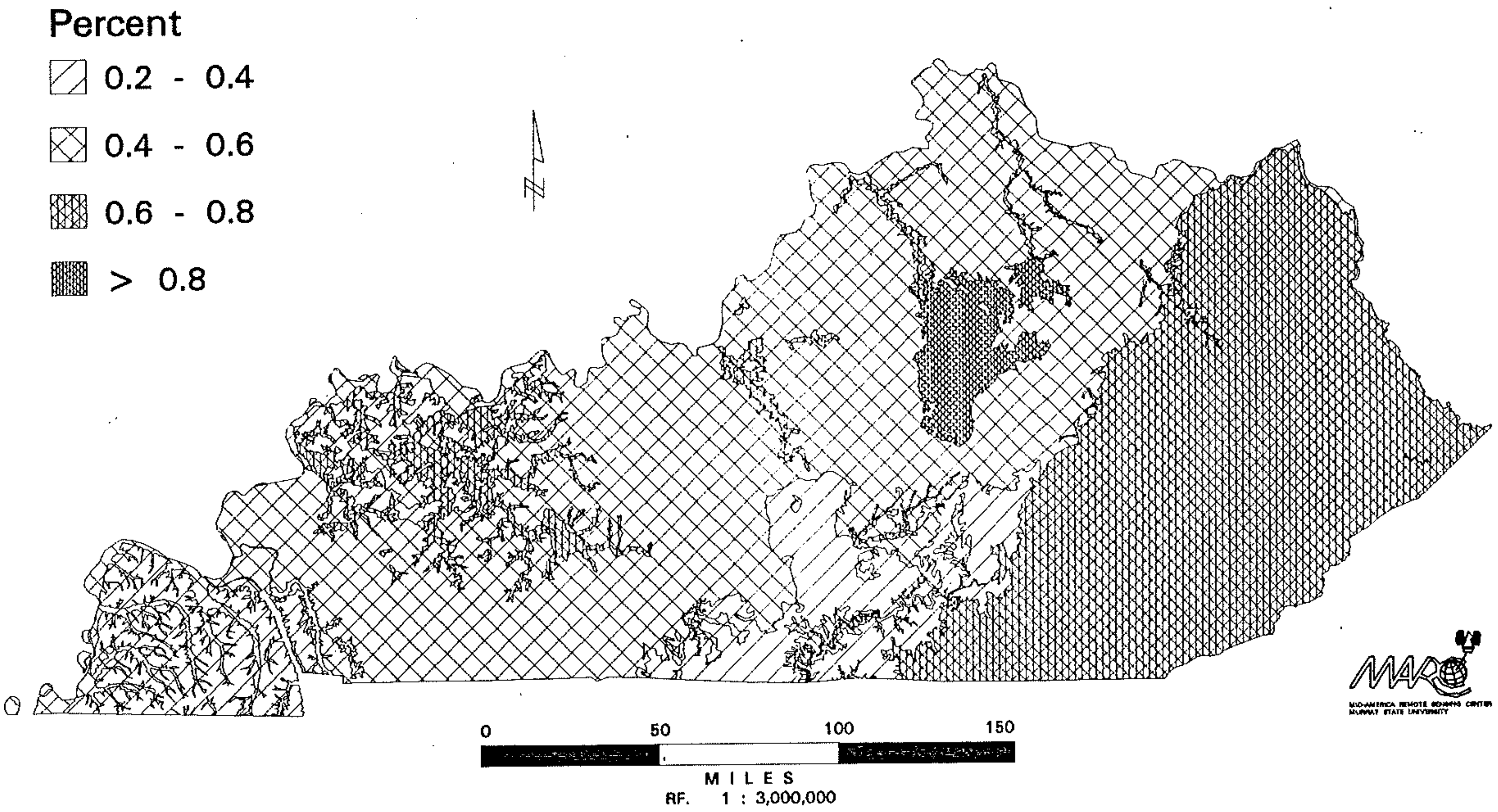
ORGANIC MATTER: BOTTOM LAYER MEAN

By Region/Type



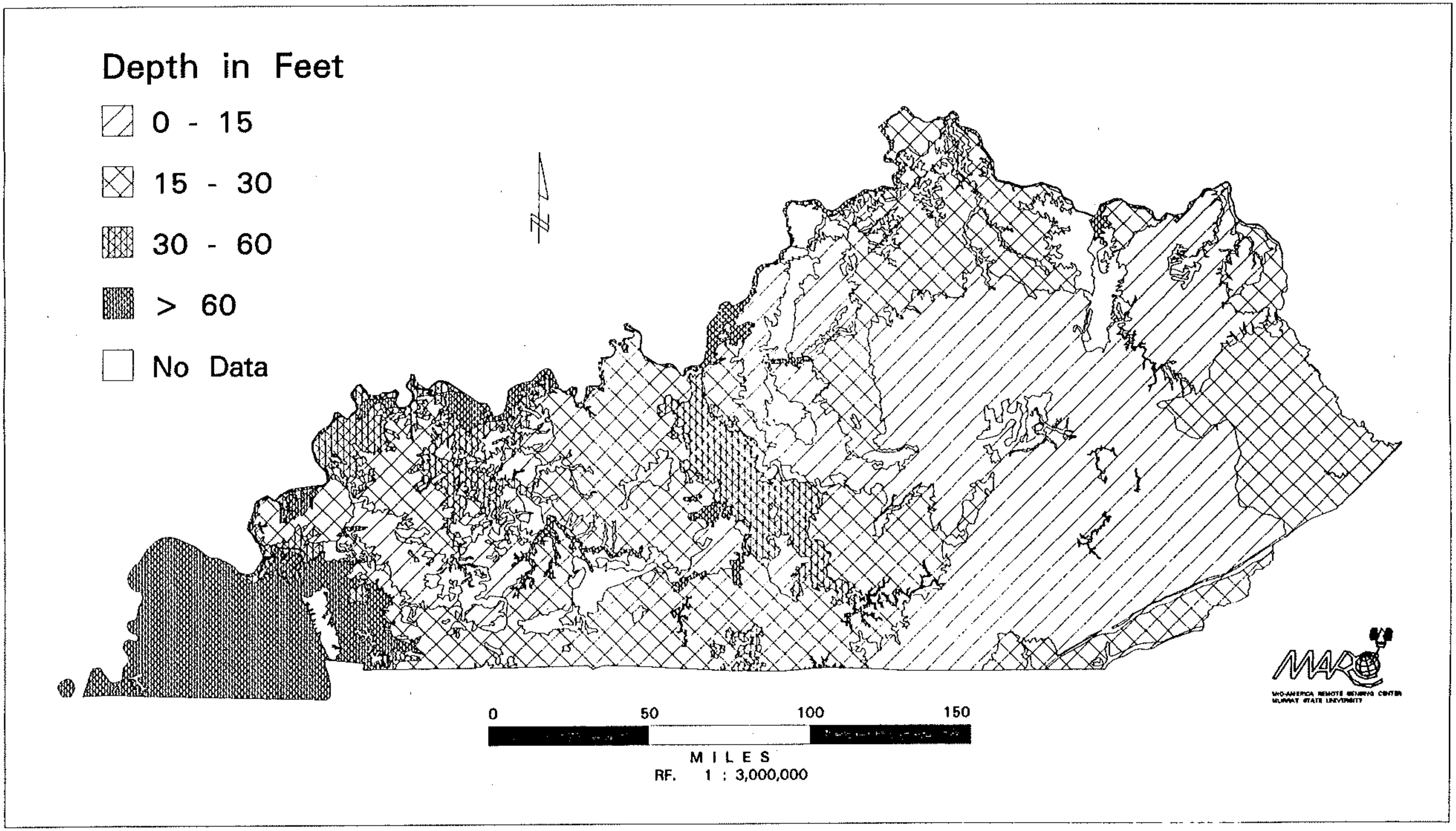
ORGANIC MATTER: ENTIRE PROFILE MEAN

By Region/Type



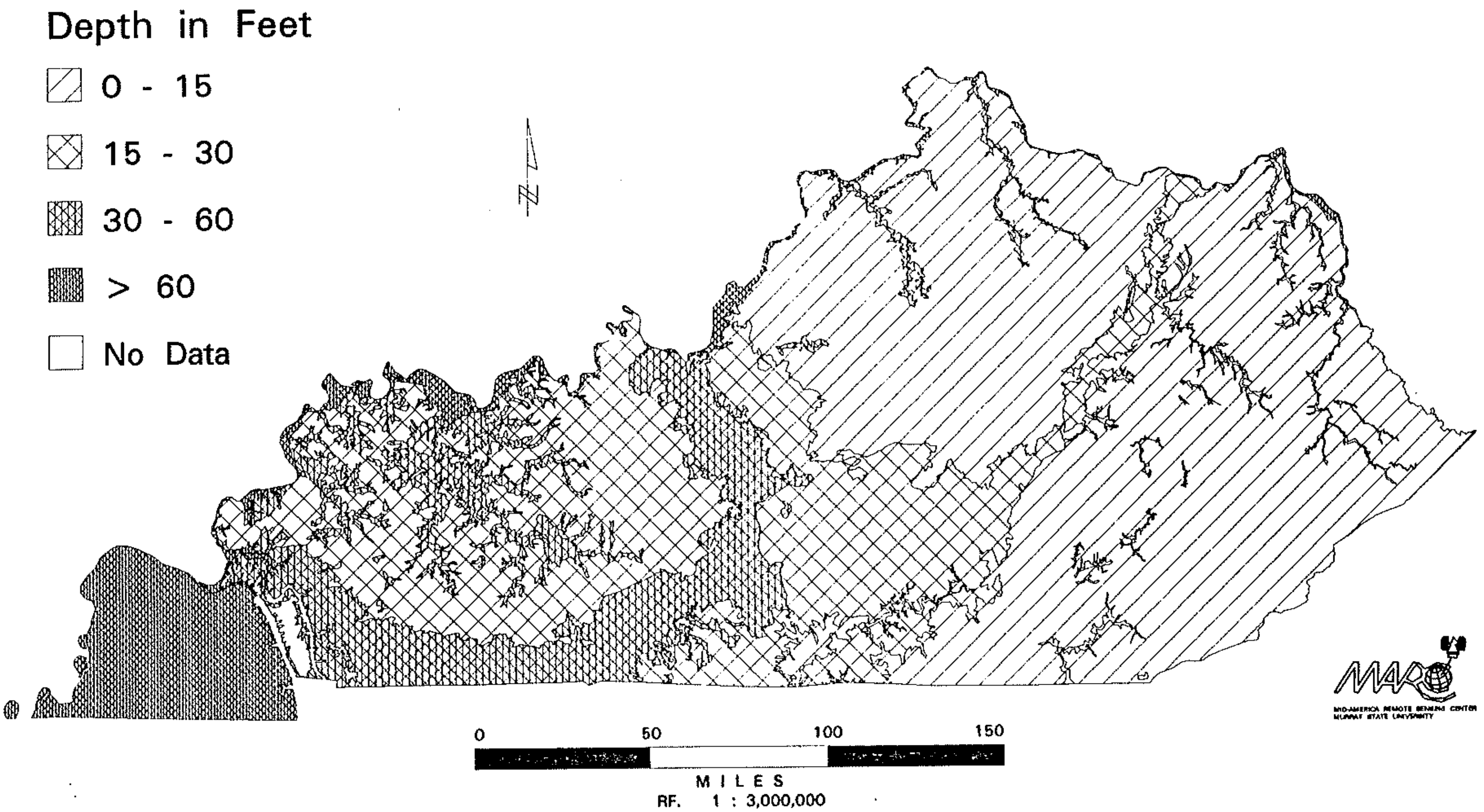
MEAN DEPTH TO BEDROCK

By Kentucky Soil-ID



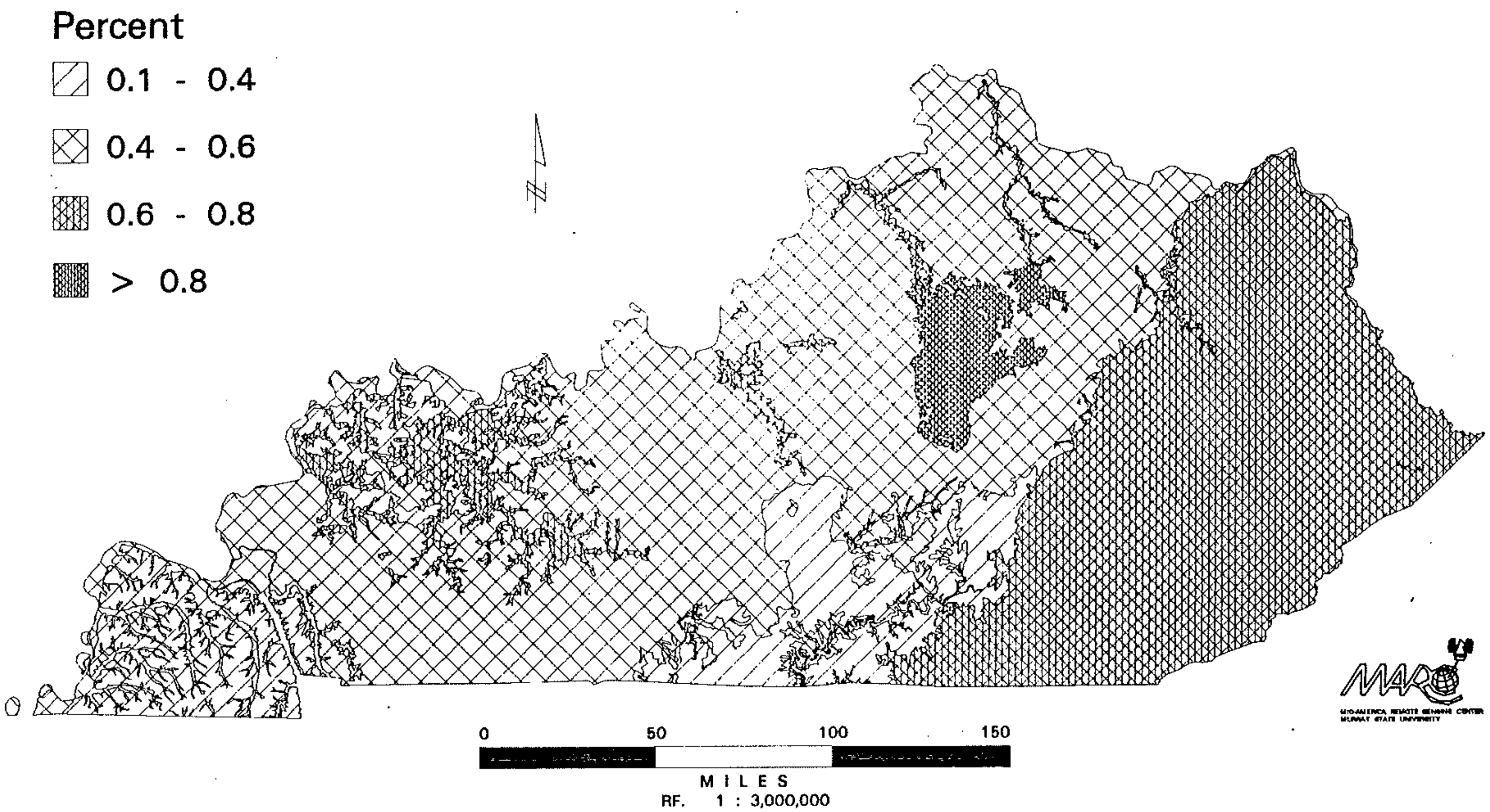
MEAN DEPTH TO BEDROCK

By Region/Type



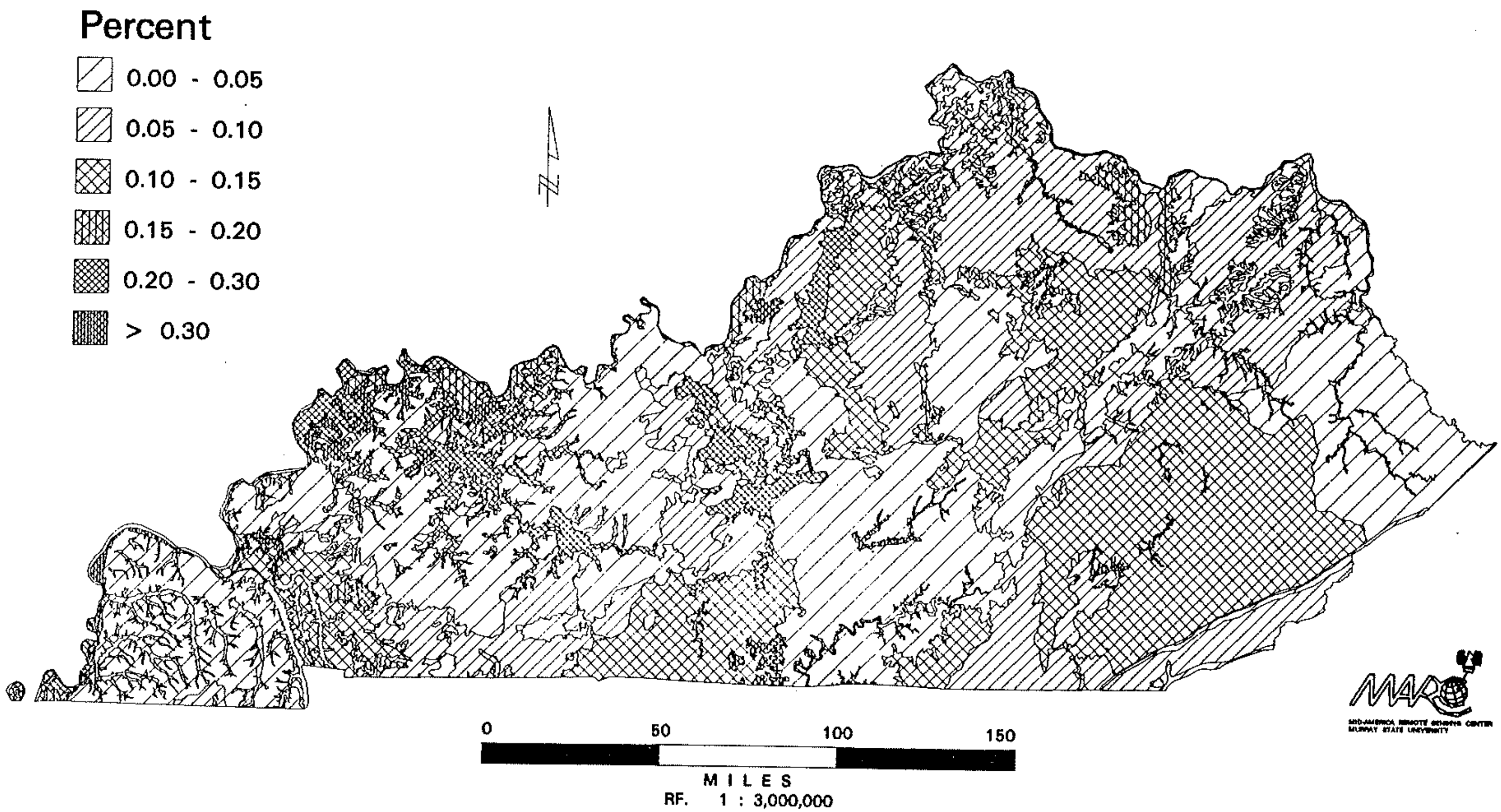
ORGANIC MATTER: ENTIRE PROFILE MEAN

By Region/Type



ORGANIC MATTER: BOTTOM LAYER MEAN

By Kentucky Soil-ID



WELL PARAMETERS BY REGION/TYPE (RT)

WELL DEPTH IN FEET

RT	FREQ	MEAN	STD	MIN	MAX	MEDIAN
0	24	111.6	60.2	45.0	280.0	102.0
1	223	104.5	67.7	29.0	467.0	90.0
2	1001	160.4	76.4	35.0	520.0	152.0
3	94	119.8	55.7	28.0	294.0	114.5
4	723	165.0	66.4	23.0	557.0	155.0
7	942	236.3	123.4	27.0	927.0	205.5
8	68	172.7	107.8	50.0	664.0	153.0
9	130	151.8	157.2	50.0	1345.0	118.5
10	299	104.3	55.8	27.0	620.0	99.0
11	24	102.2	32.5	50.0	153.0	107.0
12	679	96.2	54.0	20.0	1000.0	85.0
13	9	88.1	34.8	44.0	150.0	80.0
14	322	127.0	153.9	31.0	1276.0	90.0
15	29	81.4	21.9	40.0	128.0	81.0
17	187	161.5	155.5	40.0	1010.0	125.0
18	9	110.2	32.9	53.0	150.0	124.0
19	5777	132.8	89.2	20.0	1015.0	102.0
20	320	129.9	87.7	30.0	851.0	100.0

DEPTH TO BEDROCK IN FEET

RT	FREQ	MEAN	STD	MIN	MAX	MEDIAN
0	24	97.4	62.0	8.0	280.0	97.5
1	223	74.0	50.1	5.0	467.0	66.0
2	1001	158.8	76.3	1.0	520.0	150.0
3	94	119.8	55.7	28.0	294.0	114.5
4	723	36.9	37.2	1.0	248.0	25.0
7	942	18.6	26.0	1.0	296.0	10.0
8	68	34.8	30.7	4.0	118.0	23.5
9	130	24.7	15.1	1.0	100.0	21.5
10	299	17.2	14.2	1.0	112.0	13.0
11	24	19.5	14.8	2.0	61.0	14.5
12	679	20.5	14.8	1.0	85.0	18.0
13	9	14.4	12.4	1.0	40.0	9.0
14	322	11.9	15.7	2.0	120.0	8.0
15	29	39.3	26.7	3.0	87.0	33.0
17	187	8.3	7.1	1.0	63.0	8.0
18	9	5.6	4.0	2.0	15.0	4.0
19	5777	14.7	15.7	1.0	502.0	10.0
20	320	22.1	18.4	2.0	83.0	15.0

DEPTH TO STATIC WATER LEVEL IN FEET

RT	FREQ	MEAN	STD	MIN	MAX	MEDIAN
0	24	42.3	34.9	10.0	160.0	31.6
1	223	39.1	35.5	4.0	421.0	35.0
2	1001	78.2	37.7	3.0	240.0	80.0
3	94	43.7	32.3	3.0	125.0	38.0
4	723	92.8	58.6	5.0	511.0	78.0
7	942	127.9	108.6	2.0	545.0	89.5
8	68	43.0	29.2	7.0	150.0	39.5
9	130	55.5	86.6	1.0	700.0	37.5
10	299	48.3	42.9	5.0	545.0	40.0
11	24	30.8	13.9	6.0	50.0	32.5
12	679	54.2	32.4	2.0	245.0	45.0
13	9	39.3	23.2	17.0	90.0	35.0
14	322	52.2	109.7	2.0	1246.0	30.0
15	29	34.6	18.3	8.0	95.0	33.0
17	187	63.9	95.1	3.0	918.0	40.0
18	9	39.0	23.8	8.0	90.0	40.0
19	5777	54.9	48.2	1.0	560.0	40.0
20	320	51.1	39.5	3.0	250.0	40.0

WELL PARAMETERS BY SOIL ID SORTED BY REGION/TYPE

		WELL DEPTH IN FEET					
ID	FREQ	MEAN	STD	MIN	MAX	MEDIAN	RT
2	14	83.3	40.5	38.0	166.0	69.0	1
3	1	467.0	0.0	467.0	467.0	467.0	1
4	1	124.0	0.0	124.0	124.0	124.0	1
5	14	63.5	38.7	30.0	185.0	60.0	1
6	9	116.2	74.8	45.0	250.0	90.0	1
7	6	118.3	43.3	45.0	176.0	119.5	1
9	20	113.5	84.4	29.0	300.0	73.0	1
10	12	202.4	118.6	80.0	430.0	180.0	1
11	5	87.8	48.2	44.0	165.0	65.0	1
12	20	95.4	48.3	32.0	257.0	98.5	1
24	9	190.8	119.1	65.0	462.0	142.0	1
25	49	86.0	25.1	45.0	124.0	90.0	1
33	41	93.8	24.7	33.0	142.0	90.0	1
35	20	104.0	61.5	50.0	307.0	80.0	1
43	4	101.5	22.9	68.0	120.0	109.0	1
47	2	125.0	0.0	125.0	125.0	125.0	1
100	377	149.6	70.6	40.0	445.0	143.0	2
101	58	101.9	61.1	45.0	325.0	82.5	2
102	252	147.8	66.3	35.0	460.0	140.0	2
103	15	163.5	50.1	61.0	242.0	165.0	2
104	8	151.1	57.3	68.0	240.0	137.5	2
105	214	180.5	66.5	80.0	486.0	170.0	2
106	77	242.7	99.2	88.0	520.0	230.0	2
1	95	120.8	56.3	28.0	294.0	115.0	3
300	35	169.9	65.2	67.0	405.0	160.0	4
301	27	179.8	62.4	75.0	300.0	180.0	4
302	6	188.8	53.0	100.0	264.0	197.5	4
303	2	165.0	106.1	90.0	240.0	165.0	4
304	7	110.1	56.8	57.0	200.0	90.0	4
305	19	198.8	61.7	96.0	340.0	210.0	4
307	47	114.6	48.7	37.0	263.0	101.0	4
309	17	137.6	30.0	100.0	210.0	135.0	4
312	1	200.0	0.0	200.0	200.0	200.0	4
313	7	306.0	57.5	202.0	355.0	325.0	4
314	39	97.4	39.2	50.0	200.0	90.0	4
315	1	80.0	0.0	80.0	80.0	80.0	4
316	1	105.0	0.0	105.0	105.0	105.0	4
317	112	171.5	63.9	62.0	362.0	154.0	4
318	52	139.2	65.4	44.0	400.0	122.5	4
319	263	188.9	60.5	92.0	557.0	182.0	4
320	72	142.3	47.2	70.0	297.0	125.0	4
321	12	154.0	80.6	23.0	275.0	155.0	4
322	2	82.5	24.7	65.0	100.0	82.5	4
323	1	60.0	0.0	60.0	60.0	60.0	4
200	105	175.6	96.6	27.0	500.0	140.0	7
201	1	80.0	0.0	80.0	80.0	80.0	7
202	1	275.0	0.0	275.0	275.0	275.0	7

WELL DEPTH IN FEET

ID	FREQ	MEAN	STD	MIN	MAX	MEDIAN	RT
203	1	126.0	0.0	126.0	126.0	126.0	7
204	12	236.3	156.9	98.0	540.0	195.5	7
205	16	177.0	77.0	45.0	320.0	200.0	7
206	14	136.2	61.5	65.0	270.0	127.5	7
207	6	158.2	100.8	49.0	305.0	156.5	7
208	6	128.8	67.5	71.0	227.0	99.0	7
209	15	148.7	75.0	60.0	340.0	130.0	7
210	5	167.4	45.1	120.0	240.0	155.0	7
211	4	140.0	11.5	130.0	150.0	140.0	7
212	31	249.2	162.9	50.0	927.0	225.0	7
216	240	243.2	106.3	60.0	816.0	225.0	7
217	405	258.1	133.7	40.0	620.0	225.0	7
218	19	328.3	141.4	47.0	556.0	355.0	7
219	59	227.6	84.9	100.0	397.0	200.0	7
220	2	237.5	145.0	135.0	340.0	237.5	7
13	21	121.2	48.7	50.0	225.0	114.0	8
14	7	164.9	55.5	92.0	248.0	150.0	8
15	8	198.1	51.9	150.0	297.0	179.0	8
16	1	165.0	0.0	165.0	165.0	165.0	8
17	19	154.4	51.5	84.0	274.0	150.0	8
19	3	596.7	84.4	502.0	664.0	624.0	8
20	1	200.0	0.0	200.0	200.0	200.0	8
21	1	175.0	0.0	175.0	175.0	175.0	8
22	2	157.5	3.5	155.0	160.0	157.5	8
109	22	158.9	74.4	73.0	357.0	162.5	9
110	89	151.5	184.8	50.0	1345.0	110.0	9
111	5	146.8	54.6	88.0	201.0	150.0	9
112	14	144.2	63.9	57.0	253.0	119.5	9
500	8	178.3	181.6	80.0	620.0	108.5	10
501	174	93.2	33.8	27.0	225.0	90.0	10
502	23	100.5	38.0	45.0	180.0	85.0	10
504	62	126.1	57.7	38.0	400.0	120.0	10
505	1	150.0	0.0	150.0	150.0	150.0	10
507	13	153.3	95.2	65.0	310.0	134.0	10
508	2	97.5	3.5	95.0	100.0	97.5	10
510	3	90.0	26.5	70.0	120.0	80.0	10
512	6	57.5	18.6	35.0	85.0	57.5	10
513	2	61.0	5.7	57.0	65.0	61.0	10
514	5	69.4	21.4	37.0	90.0	75.0	10

WELL DEPTH IN FEET

ID	FREQ	MEAN	STD	MIN	MAX	MEDIAN	RT
26	8	104.0	32.3	50.0	153.0	107.0	11
29	6	129.8	11.5	115.0	150.0	130.0	11
30	9	87.9	29.9	60.0	145.0	75.0	11
56	1	50.0	0.0	50.0	50.0	50.0	11
400	55	88.8	31.9	30.0	170.0	85.0	12
401	18	92.5	25.8	55.0	133.0	87.5	12
402	78	107.0	42.7	33.0	276.0	100.0	12
404	61	92.5	38.9	34.0	228.0	96.0	12
405	12	79.3	9.5	67.0	100.0	77.5	12
406	35	67.4	16.7	40.0	100.0	70.0	12
407	7	108.6	27.2	50.0	125.0	120.0	12
408	14	80.1	25.5	50.0	145.0	77.5	12
409	33	137.1	47.9	55.0	205.0	150.0	12
410	21	111.1	34.8	59.0	220.0	100.0	12
411	291	97.3	69.1	20.0	1000.0	82.0	12
412	42	80.9	32.6	41.0	216.0	72.0	12
413	12	84.4	30.2	37.0	140.0	81.0	12
23	3	72.0	11.3	65.0	85.0	66.0	13
28	6	96.2	40.7	44.0	150.0	98.0	13
600	4	72.5	11.9	60.0	85.0	72.5	14
601	1	50.0	0.0	50.0	50.0	50.0	14
602	34	150.8	34.9	75.0	250.0	155.0	14
603	2	93.0	18.4	80.0	106.0	93.0	14
604	1	342.0	0.0	342.0	342.0	342.0	14
605	4	203.3	89.3	103.0	279.0	215.5	14
607	5	330.6	529.5	53.0	1276.0	124.0	14
608	74	179.7	236.9	45.0	1107.0	102.0	14
611	1	63.0	0.0	63.0	63.0	63.0	14
612	5	89.6	13.1	80.0	104.0	80.0	14
613	1	45.0	0.0	45.0	45.0	45.0	14

614	15	70.3	20.6	31.0	102.0	65.0	14
615	9	113.8	55.4	45.0	205.0	115.0	14
618	1	58.0	0.0	58.0	58.0	58.0	14
619	73	105.6	116.1	45.0	968.0	85.0	14
620	83	95.8	84.4	35.0	800.0	84.0	14
623	1	49.0	0.0	49.0	49.0	49.0	14
625	3	79.0	40.3	50.0	125.0	62.0	14
627	5	98.8	32.0	50.0	140.0	100.0	14
31	5	88.2	35.2	40.0	128.0	103.0	15

WELL DEPTH IN FEET

ID	FREQ	MEAN	STD	MIN	MAX	MEDIAN	RT
32	3	95.7	29.4	63.0	120.0	104.0	15
46	1	63.0	0.0	63.0	63.0	63.0	15
51	1	40.0	0.0	40.0	40.0	40.0	15
57	19	80.5	14.5	53.0	103.0	81.0	15
700	133	165.3	152.3	42.0	1010.0	145.0	17
701	54	152.0	164.0	40.0	886.0	104.5	17
44	9	110.2	32.9	53.0	150.0	124.0	18
506	133	102.3	45.0	31.0	300.0	100.0	19
800	78	134.4	76.4	33.0	400.0	117.0	19
801	1703	117.6	83.3	23.0	895.0	90.0	19
802	388	157.7	99.0	20.0	562.0	125.0	19
803	58	169.7	105.5	50.0	500.0	140.0	19
804	49	60.2	28.8	25.0	150.0	50.0	19
805	1901	118.5	66.8	35.0	653.0	100.0	19
806	42	201.9	105.9	46.0	425.0	187.5	19
807	617	176.0	120.5	34.0	1015.0	140.0	19
808	339	143.7	73.2	38.0	400.0	120.0	19
809	28	105.3	56.9	44.0	210.0	80.0	19

810	9	186.7	20.3	150.0	205.0	190.0	19
811	14	150.2	127.9	40.0	412.0	81.5	19
813	2	80.0	7.1	75.0	85.0	80.0	19
814	49	62.2	28.6	28.0	150.0	55.0	19
815	133	140.8	85.0	40.0	500.0	120.0	19
816	147	207.7	98.8	60.0	500.0	193.0	19
817	87	211.2	151.7	40.0	728.0	170.0	19
34	36	151.6	114.3	60.0	430.0	100.0	20
36	25	107.5	42.8	36.0	205.0	105.0	20
37	46	76.7	23.3	40.0	163.0	75.0	20
38	30	151.6	81.6	50.0	325.0	132.5	20
39	5	139.8	48.5	109.0	225.0	125.0	20
40	10	157.1	244.3	50.0	851.0	85.0	20
41	7	84.0	35.4	33.0	150.0	80.0	20
42	1	125.0	0.0	125.0	125.0	125.0	20
48	37	112.0	57.0	50.0	350.0	100.0	20
49	48	110.6	62.4	30.0	307.0	97.0	20
53	5	97.2	43.7	61.0	171.0	82.0	20
54	9	177.2	40.9	125.0	245.0	165.0	20
55	61	177.8	88.3	65.0	500.0	165.0	20
	24	111.6	60.2	45.0	280.0	102.0	0

WELL PARAMETERS BY SOIL ID SORTED BY REGION/TYPE

DEPTH TO BEDROCK IN FEET

ID	FREQ	MEAN	STD	MIN	MAX	MEDIAN	RT
2	14	83.3	40.5	38.0	166.0	69.0	1
3	1	467.0	0.0	467.0	467.0	467.0	1
4	1	124.0	0.0	124.0	124.0	124.0	1
5	14	63.7	38.5	33.0	185.0	60.0	1
6	9	115.1	72.6	45.0	240.0	90.0	1
7	6	118.3	43.3	45.0	176.0	119.5	1
9	20	55.5	39.9	6.0	200.0	50.0	1
10	12	40.4	32.2	6.0	91.0	27.0	1
11	5	54.0	20.4	18.0	67.0	62.0	1
12	20	78.6	35.2	18.0	136.0	89.5	1
24	9	79.0	60.2	9.0	142.0	112.0	1
25	49	79.2	31.5	10.0	124.0	78.0	1
33	41	77.4	40.2	13.0	142.0	85.0	1
35	20	26.0	18.8	5.0	63.0	20.0	1
43	4	95.5	19.3	68.0	110.0	102.0	1
47	2	32.0	0.0	32.0	32.0	32.0	1
100	377	148.5	69.1	30.0	445.0	142.0	2
101	58	102.1	61.2	45.0	325.0	82.5	2
102	252	145.7	66.7	2.0	460.0	140.0	2
103	15	163.5	50.1	61.0	242.0	165.0	2
104	8	102.8	45.3	10.0	150.0	112.0	2
105	214	179.6	67.6	1.0	486.0	170.0	2
106	77	241.6	99.6	88.0	520.0	230.0	2
1	95	118.9	56.1	28.0	294.0	114.0	3
300	35	101.2	51.2	8.0	220.0	98.0	4
301	27	66.0	28.2	20.0	130.0	60.0	4
302	6	46.0	43.9	4.0	128.0	36.0	4
303	2	5.0	0.0	5.0	5.0	5.0	4
304	7	51.6	63.6	8.0	181.0	20.0	4
305	19	90.2	41.0	30.0	152.0	100.0	4
307	47	27.3	17.4	3.0	59.0	25.0	4
309	17	28.6	12.5	15.0	52.0	25.0	4
312	1	17.0	0.0	17.0	17.0	17.0	4
313	7	11.1	17.2	3.0	50.0	4.0	4
314	39	21.9	11.1	2.0	52.0	23.0	4
315	1	40.0	0.0	40.0	40.0	40.0	4
316	1	65.0	0.0	65.0	65.0	65.0	4
317	112	33.3	38.2	1.0	178.0	20.0	4
318	52	42.8	23.3	2.0	122.0	48.0	4

DEPTH TO BEDROCK IN FEET

ID	FREQ	MEAN	STD	MIN	MAX	MEDIAN	RT
319	263	20.5	19.8	2.0	139.0	14.0	4
320	72	58.4	42.6	1.0	248.0	49.5	4
321	12	42.7	50.0	2.0	165.0	22.0	4
322	2	40.0	0.0	40.0	40.0	40.0	4
323	1	8.0	0.0	8.0	8.0	8.0	4
200	105	18.2	16.4	2.0	140.0	14.0	7
201	1	4.0	0.0	4.0	4.0	4.0	7
202	1	12.0	0.0	12.0	12.0	12.0	7
203	1	11.0	0.0	11.0	11.0	11.0	7
204	12	12.6	10.7	2.0	40.0	10.0	7
205	16	19.5	10.5	3.0	37.0	20.0	7
206	14	13.0	7.9	6.0	28.0	11.0	7
207	6	20.7	15.3	5.0	45.0	16.5	7
208	6	12.2	12.1	1.0	30.0	6.0	7
209	15	14.0	4.0	8.0	23.0	14.0	7
210	5	13.4	6.3	3.0	20.0	14.0	7
211	4	14.3	7.8	10.0	26.0	10.5	7
212	31	10.6	5.7	3.0	24.0	10.0	7
216	240	17.0	29.1	1.0	296.0	10.0	7
217	405	20.6	26.6	1.0	262.0	10.0	7
218	19	22.7	18.8	2.0	68.0	16.0	7
219	59	16.8	25.3	2.0	158.0	9.0	7
220	2	138.5	187.4	6.0	271.0	138.5	7
13	21	57.1	35.7	15.0	118.0	40.0	8
14	7	38.3	26.2	14.0	95.0	32.0	8
15	8	33.4	31.8	5.0	109.0	25.0	8
16	1	20.0	0.0	20.0	20.0	20.0	8
17	19	19.7	14.2	4.0	70.0	16.0	8
19	3	6.3	1.2	5.0	7.0	7.0	8
20	1	9.0	0.0	9.0	9.0	9.0	8
21	1	83.0	0.0	83.0	83.0	83.0	8
22	2	16.0	2.8	14.0	18.0	16.0	8
109	22	31.3	15.8	6.0	60.0	29.0	9
110	89	22.5	13.7	1.0	100.0	20.0	9
111	5	44.4	28.9	14.0	85.0	30.0	9
112	14	20.8	7.7	7.0	35.0	20.0	9
500	8	27.5	25.2	5.0	80.0	22.0	10
501	174	19.4	11.2	2.0	65.0	18.0	10
502	23	10.5	7.2	2.0	24.0	9.0	10

DEPTH TO BEDROCK IN FEET

ID	FREQ	MEAN	STD	MIN	MAX	MEDIAN	RT
504	62	9.8	10.3	1.0	70.0	8.0	10
505	1	32.0	0.0	32.0	32.0	32.0	10
507	13	27.8	36.1	5.0	112.0	12.0	10
508	2	9.0	7.1	4.0	14.0	9.0	10
510	3	9.7	3.8	7.0	14.0	8.0	10
512	6	9.0	2.7	5.0	12.0	8.5	10
513	2	31.0	26.9	12.0	50.0	31.0	10
514	5	25.0	13.9	8.0	41.0	30.0	10
26	8	22.1	12.8	6.0	43.0	22.5	11
29	6	23.2	20.4	2.0	61.0	20.0	11
30	9	15.9	13.4	6.0	50.0	12.0	11
56	1	10.0	0.0	10.0	10.0	10.0	11
400	55	24.0	15.3	4.0	70.0	20.0	12
401	18	31.1	18.9	8.0	70.0	29.0	12
402	78	22.7	17.6	1.0	80.0	18.0	12
404	61	30.0	17.9	5.0	85.0	27.0	12
405	12	21.3	10.4	9.0	40.0	18.0	12
406	35	12.9	11.5	2.0	38.0	9.0	12
407	7	7.3	4.8	2.0	15.0	8.0	12
408	14	9.4	7.3	1.0	33.0	8.0	12
409	33	9.6	8.2	1.0	30.0	8.0	12
410	21	25.1	20.1	1.0	60.0	15.0	12
411	291	19.2	12.3	1.0	80.0	18.0	12
412	42	22.8	11.1	5.0	53.0	20.0	12
413	12	13.4	10.5	3.0	31.0	12.5	12
23	3	19.0	18.2	8.0	40.0	9.0	13
28	6	12.2	9.8	1.0	30.0	11.0	13
600	4	25.5	15.9	8.0	40.0	27.0	14
601	1	19.0	0.0	19.0	19.0	19.0	14
602	34	10.1	5.0	2.0	25.0	10.0	14

603	2	7.5	3.5	5.0	10.0	7.5	14
604	1	104.0	0.0	104.0	104.0	104.0	14
605	4	9.0	3.6	5.0	12.0	9.5	14
607	5	9.2	4.1	2.0	12.0	10.0	14
608	74	9.7	12.0	3.0	86.0	7.0	14
611	1	11.0	0.0	11.0	11.0	11.0	14
612	5	24.2	11.7	15.0	38.0	17.0	14
613	1	5.0	0.0	5.0	5.0	5.0	14
614	15	6.5	4.7	2.0	21.0	5.0	14

DEPTH TO BEDROCK IN FEET

ID	FREQ	MEAN	STD	MIN	MAX	MEDIAN	RT
615	9	6.9	4.3	2.0	14.0	5.0	14
618	1	71.0	0.0	71.0	71.0	71.0	14
619	73	6.7	5.2	2.0	30.0	5.0	14
620	83	17.7	22.6	2.0	120.0	10.0	14
623	1	4.0	0.0	4.0	4.0	4.0	14
625	3	27.3	28.7	3.0	59.0	20.0	14
627	5	9.8	2.5	8.0	14.0	9.0	14
31	5	22.0	18.1	4.0	48.0	15.0	15
32	3	17.7	2.5	15.0	20.0	18.0	15
46	1	16.0	0.0	16.0	16.0	16.0	15
51	1	3.0	0.0	3.0	3.0	3.0	15
57	19	50.4	25.2	16.0	87.0	53.0	15
700	133	8.2	7.1	1.0	63.0	7.0	17
701	54	8.3	7.2	1.0	50.0	8.0	17
44	9	5.6	4.0	2.0	15.0	4.0	18
506	133	11.0	11.6	1.0	60.0	7.0	19
800	78	8.3	6.9	1.0	43.0	7.0	19
801	1703	19.2	18.6	1.0	329.0	15.0	19

802	388	14.8	27.5	2.0	502.0	10.0	19
803	58	16.4	9.9	5.0	42.0	12.0	19
804	49	10.4	8.7	2.0	60.0	8.0	19
805	1901	11.8	8.0	1.0	78.0	9.0	19
806	42	22.4	17.7	2.0	85.0	18.0	19
807	617	16.7	14.7	1.0	154.0	12.0	19
808	339	11.7	9.1	1.0	70.0	9.0	19
809	28	10.0	8.7	2.0	40.0	8.0	19
810	9	5.4	2.7	2.0	10.0	5.0	19
811	14	7.7	2.5	3.0	12.0	7.5	19
813	2	7.0	1.4	6.0	8.0	7.0	19
814	49	14.1	7.5	3.0	31.0	12.0	19
815	133	7.7	5.0	1.0	27.0	6.0	19
816	147	13.1	28.7	2.0	345.0	8.0	19
817	87	11.8	10.2	1.0	50.0	8.0	19
34	36	29.7	24.7	2.0	83.0	20.0	20
36	25	26.3	22.7	2.0	75.0	18.0	20
37	46	28.2	22.8	4.0	75.0	15.5	20
38	30	20.6	14.5	4.0	51.0	15.0	20
39	5	8.4	2.3	5.0	10.0	10.0	20
40	10	10.0	5.6	5.0	25.0	8.5	20

DEPTH TO BEDROCK IN FEET

ID	FREQ	MEAN	STD	MIN	MAX	MEDIAN	RT
41	7	10.3	3.0	8.0	15.0	9.0	20
42	1	18.0	0.0	18.0	18.0	18.0	20
48	37	24.4	16.1	5.0	75.0	21.0	20
49	48	26.9	17.9	3.0	80.0	26.5	20
53	5	20.6	24.0	4.0	60.0	6.0	20
54	9	14.8	9.5	2.0	28.0	14.0	20

55	61	12.7	6.3	2.0	30.0	12.0	20
	24	97.4	62.0	8.0	280.0	97.5	0

WELL PARAMETERS BY SOIL ID SORTED BY REGION/TYPE

DEPTH TO STATIC WATER LEVEL IN FEET

ID	FREQ	MEAN	STD	MIN	MAX	MEDIAN	RT
2	14	24.5	14.4	10.0	60.0	19.0	1
3	1	40.0	0.0	40.0	40.0	40.0	1
4	1	50.0	0.0	50.0	50.0	50.0	1
5	14	23.0	35.1	5.0	140.0	9.5	1
6	9	24.0	7.4	12.0	35.0	22.0	1
7	6	28.0	13.0	14.0	49.0	26.5	1
9	20	35.3	9.2	18.0	53.0	36.0	1
10	12	42.2	15.9	23.0	74.0	37.5	1
11	5	16.2	3.6	10.0	19.0	18.0	1
12	20	33.4	20.8	4.0	100.0	32.5	1
24	9	111.4	128.7	27.0	421.0	51.3	1
25	49	37.8	11.9	10.0	55.0	40.0	1
33	41	45.7	21.0	6.0	81.8	52.0	1
35	20	38.8	35.8	12.0	152.0	25.0	1
43	4	54.3	19.6	30.0	77.0	55.0	1
47	2	4.0	0.0	4.0	4.0	4.0	1
100	377	70.9	35.2	3.0	160.0	70.0	2
101	58	38.0	14.8	10.0	100.0	40.0	2
102	252	74.1	33.7	4.0	240.0	80.0	2
103	15	87.5	43.8	26.0	180.0	95.0	2
104	8	76.0	28.7	50.0	120.0	63.5	2
105	214	91.3	30.5	30.0	170.0	100.0	2
106	77	119.6	43.0	4.0	200.0	120.0	2
1	95	43.8	32.2	3.0	125.0	40.0	3
300	35	76.0	33.3	7.0	159.0	71.0	4
301	27	62.7	30.3	14.0	145.0	60.0	4
302	6	63.7	52.4	20.0	162.0	55.0	4
303	2	50.0	7.1	45.0	55.0	50.0	4
304	7	42.1	28.3	18.0	92.0	32.0	4

DEPTH TO STATIC WATER LEVEL IN FEET

ID	FREQ	MEAN	STD	MIN	MAX	MEDIAN	RT
305	19	64.7	23.9	15.0	120.0	60.0	4
307	47	40.3	23.4	8.0	98.0	45.0	4
309	17	63.2	16.2	26.0	82.0	60.0	4
312	1	18.0	0.0	18.0	18.0	18.0	4
313	7	114.0	43.0	60.0	190.0	100.0	4
314	39	56.0	30.7	25.0	160.0	50.0	4
315	1	50.0	0.0	50.0	50.0	50.0	4
316	1	75.0	0.0	75.0	75.0	75.0	4
317	112	93.1	60.1	5.0	285.0	70.0	4
318	52	73.5	36.5	20.0	203.0	66.0	4
319	263	130.4	60.1	30.0	511.0	122.0	4
320	72	68.4	41.9	15.0	221.0	60.0	4
321	12	86.3	61.8	6.0	180.0	71.0	4
322	2	65.0	21.2	50.0	80.0	65.0	4
323	1	10.0	0.0	10.0	10.0	10.0	4
200	105	53.0	50.7	2.0	275.0	40.0	7
201	1	21.0	0.0	21.0	21.0	21.0	7
202	1	150.0	0.0	150.0	150.0	150.0	7
203	1	66.0	0.0	66.0	66.0	66.0	7
204	12	82.3	43.6	20.0	135.0	81.0	7
205	16	45.3	23.0	14.0	77.0	40.5	7
206	14	57.6	42.4	15.0	140.0	35.0	7
207	6	71.3	111.6	5.0	298.0	34.0	7
208	6	49.8	44.6	20.0	127.0	25.5	7
209	15	48.5	54.0	18.0	230.0	30.0	7
210	5	66.8	30.6	30.0	100.0	80.0	7
211	4	68.5	45.6	20.0	130.0	62.0	7
212	31	94.2	60.5	15.0	240.0	90.0	7
216	240	130.2	77.0	8.0	390.0	110.0	7
217	405	160.1	131.9	8.0	545.0	105.0	7
218	19	209.1	124.7	40.0	456.0	170.0	7
219	59	115.9	62.6	12.0	250.0	97.0	7
220	2	143.5	143.5	42.0	245.0	143.5	7
13	21	40.6	26.3	8.0	135.0	40.0	8
14	7	48.7	40.3	10.0	135.0	39.0	8
15	8	66.8	51.4	25.0	150.0	45.0	8
16	1	30.0	0.0	30.0	30.0	30.0	8
17	19	38.2	20.7	7.0	90.0	35.0	8
19	3	44.0	3.6	40.0	47.0	45.0	8

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          DEPTH TO STATIC WATER LEVEL IN FEET
ID      FREQ    MEAN     STD     MIN     MAX   MEDIAN     RT
 20        1    14.0     0.0    14.0    14.0    14.0       8
 21        1    40.0     0.0    40.0    40.0    40.0       8
 22        2    44.5    14.8    34.0    55.0    44.5       8
109       22    55.9    37.8     8.0   135.0    32.0       9
110       89    57.2   102.0     1.0   700.0    37.0       9
111        5    38.0    14.8    20.0    54.0    43.0       9
112       14    50.4    37.8     7.0   157.0    46.5       9
500        8   107.5   178.4    23.0   545.0    43.5      10
501      174    44.3    23.2     5.0   146.0    40.0      10
502       23    52.1    34.7     7.0   140.0    45.0      10
504       62    52.7    31.6    15.0   200.0    45.0      10
505        1    70.0     0.0    70.0    70.0    70.0      10
507       13    59.0    90.9     8.0   263.0    22.0      10
508        2    40.0    28.3    20.0    60.0    40.0      10
510        3    35.0     5.0    30.0    40.0    35.0      10
512        6    35.8    22.9    10.0    70.0    40.0      10
513        2    32.5    17.7    20.0    45.0    32.5      10
514        5    16.6     6.7     6.0    24.0    17.0      10
 26        8    26.5    15.7     6.0    46.0    31.0      11
 29        6    40.5     9.9    28.0    50.0    44.5      11
 30        9    27.6    13.1     8.0    45.0    30.0      11
 56        1    35.0     0.0    35.0    35.0    35.0      11
400       55    49.2    22.5    10.0   110.0    45.0      12
401       18    43.3    24.9    20.0   105.0    37.5      12
402       78    62.8    41.2     8.0   245.0    50.0      12
404       61    55.9    35.5    17.0   200.0    45.0      12
405       12    41.8    10.7    25.0    60.0    42.0      12
406       35    32.3    11.6     5.0    54.0    30.0      12
407        7    72.4    32.1    30.0   107.0    80.0      12
408       14    30.3    13.4     7.0    50.0    30.0      12
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409	33	89.6	40.8	22.0	161.0	95.0	12
410	21	78.5	33.6	20.0	160.0	73.0	12
411	291	52.7	29.8	4.0	165.0	45.0	12
412	42	46.3	22.2	2.0	100.0	40.0	12
413	12	44.8	20.6	12.0	80.0	42.5	12
23	3	31.7	16.1	20.0	50.0	25.0	13
28	6	43.2	26.6	17.0	90.0	37.5	13
600	4	40.5	8.4	32.0	50.0	40.0	14
601	1	40.0	0.0	40.0	40.0	40.0	14

DEPTH TO STATIC WATER LEVEL IN FEET

ID	FREQ	MEAN	STD	MIN	MAX	MEDIAN	RT
602	34	57.9	28.8	22.0	120.0	53.5	14
603	2	20.0	0.0	20.0	20.0	20.0	14
604	1	300.0	0.0	300.0	300.0	300.0	14
605	4	47.0	19.9	30.0	68.0	45.0	14
607	5	297.6	531.3	25.0	1246.0	60.0	14
608	74	75.9	156.1	2.0	900.0	30.0	14
611	1	22.0	0.0	22.0	22.0	22.0	14
612	5	28.2	16.3	15.0	56.0	21.0	14
613	1	7.0	0.0	7.0	7.0	7.0	14
614	15	32.1	18.5	4.0	82.0	30.0	14
615	9	43.9	36.9	10.0	130.0	30.0	14
618	1	25.0	0.0	25.0	25.0	25.0	14
619	73	41.9	73.8	4.0	500.0	24.0	14
620	83	30.3	21.2	3.0	110.0	24.0	14
623	1	14.0	0.0	14.0	14.0	14.0	14
625	3	22.3	15.9	4.0	33.0	30.0	14
627	5	54.4	28.1	27.0	100.0	45.0	14
31	5	31.2	23.5	8.0	65.0	33.0	15

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  32      3   42.3   45.9   11.0   95.0   21.0     15
  46      1   45.0    0.0   45.0   45.0   45.0     15
  51      1   10.0    0.0   10.0   10.0   10.0     15
  57     19   35.0   10.6   21.0   56.0   35.0     15
 700    133   61.3  100.5    3.0  918.0   40.0     17
 701     54   70.3   80.9    5.0  450.0   47.5     17
  44      9   39.0   23.8    8.0   90.0   40.0     18
 506    133   63.0   32.0   11.0  170.0   65.0     19
 800     78   75.1   51.1    8.0  250.0   66.0     19
 801   1703   54.5   49.5    1.0  560.0   40.0     19
 802    388   72.2   67.9    5.0  335.0   40.5     19
 803     58   74.3   76.5    2.0  350.0   40.0     19
 804     49   19.0    9.9    8.0   60.0   17.0     19
 805   1901   48.1   36.8    2.0  300.0   40.0     19
 806     42   64.5   48.3   10.0  223.0   51.5     19
 807    617   52.1   52.0    1.0  560.0   40.0     19
 808    339   54.7   39.8    2.0  260.0   50.0     19
 809     28   50.4   35.8   12.0  155.0   41.0     19
 810      9  100.6   13.1   80.0  125.0  100.0     19
 811     14  102.7   91.7   20.0  275.0   52.5     19
 813      2   36.0    9.9   29.0   43.0   36.0     19
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         DEPTH TO STATIC WATER LEVEL IN FEET
ID      FREQ   MEAN     STD    MIN     MAX  MEDIAN    RT
814       49   25.1    13.4    5.0    60.0   21.0     19
815      133   65.5    51.5    8.0   300.0   50.0     19
816      147   90.4    57.4    8.0   320.0   70.0     19
817       87   57.9    60.2    1.0   280.0   40.0     19
 34       36   56.6    56.5   10.0   250.0   40.0     20
 36       25   49.9    21.3   13.0    90.0   50.0     20
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37	46	28.0	17.2	8.0	100.0	24.5	20
38	30	66.9	52.4	10.0	230.0	52.5	20
39	5	58.0	27.7	30.0	100.0	50.0	20
40	10	40.4	16.9	15.0	70.0	39.0	20
41	7	44.3	22.4	10.0	65.0	50.0	20
42	1	40.0	0.0	40.0	40.0	40.0	20
48	37	47.9	44.0	8.0	230.0	40.0	20
49	48	45.9	35.7	6.0	180.0	40.0	20
53	5	45.8	21.9	19.0	75.0	50.0	20
54	9	82.8	36.3	30.0	150.0	80.0	20
55	61	61.9	36.5	3.0	170.0	55.0	20
	24	42.3	34.9	10.0	160.0	31.6	0

SOIL PARAMETERS BY REGION/TYPE

RT	FREQ # SEQ.	PERMEABILITY IN/HR PROFILE	PERMEABILITY IN/HR BOTTOM	ORGANIC MATTER PERCENT PROFILE	ORGANIC MATTER PERCENT BOTTOM
1	181	1.63	2.48	0.54	0.18
2	73	1.79	2.55	0.27	0.01
3	19	1.35	1.43	0.52	0.11
4	236	1.34	1.53	0.41	0.11
5	9	1.38	1.47	0.51	0.10
6	27	3.96	6.76	0.40	0.11
7	254	1.43	1.43	0.44	0.04
8	125	1.01	1.10	0.69	0.29
9	52	1.09	1.05	0.38	0.09
10	166	1.43	0.98	0.43	0.01
11	63	0.96	1.15	0.60	0.21
12	136	1.59	1.38	0.40	0.08
13	19	1.15	1.47	0.81	0.42
14	339	0.58	0.28	0.58	0.11
15	90	1.04	1.25	0.65	0.23
16	9	0.98	0.83	0.22	0.00
17	35	1.44	1.15	0.83	0.00
18	12	1.37	1.74	0.98	0.40
19	188	2.46	1.99	0.77	0.08
20	154	2.03	2.15	0.64	0.14

SOIL PARAMETERS SORTED BY REGION/TYPE

SOIL ID	FREQ	PERMEABILITY IN/HR PROFILE	BOTTOM	ORGANIC MATTER PERCENT PROFILE	BOTTOM	RT
0	23	0.00	0.00	0.00	0.00	0
2	3	2.69	3.66	0.67	0.40	1
3	10	3.42	3.70	0.49	0.28	1
4	7	0.63	1.06	0.43	0.16	1
5	1	3.53	6.10	0.27	0.03	1
6	1	0.63	0.47	0.35	0.03	1
7	1	0.95	1.39	0.36	0.07	1
9	8	1.37	2.18	0.60	0.12	1
10	3	1.37	2.18	0.84	0.52	1
11	6	1.72	2.02	0.73	0.27	1
12	3	0.92	0.93	0.53	0.16	1
24	7	1.23	1.34	0.65	0.14	1
25	2	1.11	1.70	0.51	0.16	1
33	7	2.70	7.03	0.47	0.03	1
35	1	1.52	1.53	0.58	0.15	1
43	3	3.40	7.31	0.37	0.00	1
47	1	1.67	1.62	0.47	0.07	1
50	3	2.84	8.66	0.54	0.22	1
100	36	0.81	0.61	0.24	0.00	2
101	5	0.75	0.31	0.44	0.00	2
102	20	3.69	6.29	0.36	0.03	2
103	1	1.81	2.35	0.22	0.07	2
104	2	4.07	6.89	0.38	0.14	2
105	14	1.07	1.29	0.17	0.01	2
106	3	1.18	1.25	0.17	0.00	2
1	20	1.38	1.47	0.50	0.10	3
8	2	0.79	0.43	0.99	0.48	3
300	9	2.60	3.48	0.41	0.15	4
301	6	1.34	1.53	0.33	0.06	4
302	4	1.16	1.18	0.37	0.10	4
303	6	1.18	3.98	0.47	0.05	4
304	3	0.84	0.62	0.41	0.18	4

SOIL PARAMETERS SORTED BY REGION/TYPE

SOIL ID	FREQ	PERMEABILITY IN/HR PROFILE	BOTTOM	ORGANIC MATTER PERCENT PROFILE	BOTTOM	RT
305	2	1.16	1.20	0.44	0.12	4
306	3	1.29	1.48	0.43	0.00	4
307	1	1.20	1.24	0.44	0.08	4
308	3	0.69	0.47	0.27	0.00	4
309	2	1.18	1.22	0.36	0.05	4
311	1	1.10	1.04	0.36	0.03	4
312	1	0.88	0.71	0.29	0.00	4
313	1	1.32	1.88	0.34	0.00	4
314	4	1.21	1.24	0.34	0.12	4
315	1	0.83	0.63	0.35	0.02	4
316	3	1.06	0.97	0.54	0.24	4
317	3	1.26	1.61	0.62	0.27	4
318	5	0.96	0.98	0.43	0.09	4
319	1	1.28	1.72	0.40	0.03	4
320	6	1.47	1.60	0.41	0.15	4
321	1	2.35	2.35	0.50	0.30	4
322	1	1.30	1.18	0.28	0.03	4
323	1	1.14	1.74	0.42	0.12	4
324	2	1.30	1.30	0.29	0.00	4
1	2	1.38	1.47	0.50	0.10	5
107	2	4.09	7.18	0.37	0.09	6
108	3	3.87	6.48	0.41	0.13	6
200	4	1.02	0.86	0.27	0.00	7
201	6	3.68	1.27	0.36	0.00	7
202	2	1.02	2.58	0.49	0.05	7
203	3	1.03	1.35	0.41	0.00	7
204	1	3.27	0.96	0.39	0.00	7
205	4	0.96	0.69	0.36	0.06	7
206	2	1.49	1.53	0.61	0.04	7
207	2	0.64	0.46	0.17	0.02	7
208	3	1.85	0.68	0.38	0.04	7
209	4	1.00	1.01	0.30	0.06	7
210	7	1.44	1.53	0.57	0.04	7
211	2	1.19	0.70	0.30	0.00	7
212	8	1.04	0.79	0.28	0.04	7
213	8	0.68	0.53	0.18	0.03	7
214	1	0.97	0.82	0.29	0.04	7
215	1	3.54	0.65	0.45	0.00	7
216	3	1.96	1.78	0.50	0.07	7

217	4	1.43	1.44	0.54	0.03	7
218	2	0.87	0.80	0.23	0.00	7
219	1	1.05	5.16	0.45	0.02	7
220	2	3.08	3.16	0.45	0.23	7
1	1	1.38	1.47	0.50	0.10	8
10	1	1.37	2.18	0.84	0.52	8
13	6	0.97	0.76	0.76	0.37	8
14	7	1.16	0.79	1.41	0.69	8
15	2	0.56	0.58	0.56	0.24	8
16	1	0.67	0.55	0.54	0.14	8
17	26	1.11	1.10	0.75	0.29	8
18	1	0.72	0.71	0.52	0.25	8
19	4	0.77	0.83	0.45	0.19	8

SOIL PARAMETERS SORTED BY REGION/TYPE

SOIL ID	FREQ	PERMEABILITY IN/HR		ORGANIC MATTER PERCENT		RT
		PROFILE	BOTTOM	PROFILE	BOTTOM	
20	3	1.28	1.52	0.65	0.29	8
21	1	1.65	2.44	0.69	0.30	8
22	4	2.09	3.15	0.70	0.09	8
109	9	1.27	1.25	0.42	0.22	9
110	7	0.97	0.90	0.35	0.02	9
111	6	1.03	1.05	0.39	0.13	9
112	7	1.51	1.40	0.37	0.07	9
500	1	2.45	1.33	0.42	0.00	10
501	6	1.94	0.60	0.38	0.00	10
502	2	1.73	0.97	0.36	0.02	10
503	1	2.29	0.87	0.40	0.00	10
504	2	0.54	0.40	0.30	0.00	10
505	1	2.33	0.99	0.39	0.03	10
507	2	2.20	0.95	0.39	0.00	10
508	1	0.72	0.56	0.66	0.02	10
509	1	0.68	0.57	0.34	0.01	10
510	1	2.24	4.11	0.65	0.04	10
511	2	0.44	0.26	0.69	0.00	10
512	1	0.37	0.15	0.52	0.00	10
513	3	0.88	1.40	0.41	0.02	10
514	1	1.41	2.67	0.64	0.04	10
26	1	1.40	1.85	0.69	0.41	11
27	1	1.64	2.01	0.64	0.35	11
29	1	1.09	1.50	0.56	0.23	11
30	2	0.53	0.49	0.52	0.10	11
31	1	0.89	1.02	0.64	0.26	11
56	2	0.94	0.95	0.69	0.09	11

400	3	1.40	1.37	0.31	0.15	12
401	3	1.30	1.31	1.02	0.93	12
402	8	2.33	1.16	0.46	0.04	12
404	1	1.36	1.27	0.34	0.05	12
405	1	1.02	0.75	0.30	0.01	12
406	1	1.91	0.78	0.53	0.06	12
407	1	1.46	3.42	0.46	0.01	12
408	1	1.22	0.56	0.41	0.00	12
409	2	1.32	4.61	0.48	0.01	12
410	3	1.26	1.27	0.30	0.03	12
411	5	1.51	1.40	0.34	0.01	12
412	1	1.32	0.63	0.45	0.00	12
413	1	1.50	1.16	0.39	0.04	12
23	1	1.22	1.60	0.81	0.46	13
28	1	0.81	0.85	0.77	0.25	13
600	2	0.82	0.20	0.75	0.05	14
601	1	0.86	0.54	0.51	0.06	14
602	2	0.99	1.04	0.45	0.06	14
603	1	0.61	0.48	0.72	0.23	14
604	1	0.44	0.35	0.67	0.42	14
605	1	0.72	0.36	0.73	0.20	14
607	2	1.28	0.51	0.55	0.08	14
608	12	0.61	0.18	0.54	0.13	14
609	1	0.79	0.33	0.52	0.06	14
610	2	0.67	0.34	0.35	0.02	14

SOIL PARAMETERS SORTED BY REGION/TYPE

		PERMEABILITY		ORGANIC MATTER		
SOIL		IN/HR		PERCENT		
ID	FREQ	PROFILE	BOTTOM	PROFILE	BOTTOM	RT
611	2	0.55	0.18	1.33	0.08	14
612	1	0.52	0.31	0.32	0.03	14
613	2	0.85	0.55	0.34	0.14	14
614	4	0.59	0.49	0.61	0.12	14
615	3	0.78	0.16	0.72	0.15	14
616	1	0.88	0.31	0.60	0.10	14
617	1	0.44	0.17	0.99	0.04	14
618	1	0.49	0.37	1.41	0.18	14
619	2	0.75	0.28	0.62	0.15	14
620	6	0.34	0.19	0.47	0.07	14
621	1	0.67	0.14	0.70	0.20	14
622	1	0.62	0.19	0.58	0.10	14
623	1	0.55	0.48	1.21	0.19	14
624	1	0.55	0.32	0.43	0.13	14
625	1	0.62	0.41	1.20	0.10	14

626	1	0.53	0.34	0.88	0.06	14
627	2	0.75	0.25	0.73	0.15	14
628	1	0.44	0.21	1.05	0.04	14
629	1	0.72	0.59	0.73	0.10	14
21	1	1.65	2.44	0.69	0.30	15
31	1	0.89	1.02	0.64	0.26	15
32	1	1.40	1.07	0.92	0.04	15
45	1	1.20	1.14	0.61	0.10	15
46	1	1.07	1.50	0.74	0.41	15
51	1	0.97	1.08	0.65	0.14	15
57	1	0.76	1.14	0.44	0.17	15
113	1	0.98	0.83	0.22	0.00	16
700	4	1.76	1.13	0.70	0.00	17
701	2	0.96	1.19	1.05	0.00	17
702	1	1.08	0.82	0.53	0.02	17
44	1	1.37	1.74	0.98	0.39	18
506	1	2.24	2.18	0.57	0.12	19
800	1	2.40	2.27	0.66	0.07	19
801	2	3.95	1.17	0.58	0.01	19
802	10	0.86	1.23	0.73	0.08	19
803	2	0.63	0.28	0.20	0.00	19
804	4	3.25	5.48	0.60	0.01	19
805	1	2.19	2.30	0.99	0.12	19
806	2	2.42	1.72	0.97	0.07	19
807	2	3.48	2.15	1.07	0.06	19
808	5	2.16	2.09	0.91	0.14	19
809	3	1.05	1.63	0.72	0.09	19
810	3	3.01	2.26	0.34	0.00	19
811	2	3.45	2.95	0.39	0.01	19
812	4	0.49	0.23	0.40	0.01	19
813	2	0.98	1.36	0.36	0.06	19
814	1	3.20	4.57	0.57	0.06	19
815	1	1.77	2.44	0.92	0.13	19
816	1	1.15	1.09	0.56	0.07	19
817	2	4.22	2.01	0.51	0.04	19
34	2	3.86	4.14	0.56	0.08	20
36	1	3.48	3.78	0.52	0.08	20

SOIL PARAMETERS SORTED BY REGION/TYPE

		PERMEABILITY		ORGANIC MATTER		
SOIL		IN/HR		PERCENT		
ID	FREQ	PROFILE	BOTTOM	PROFILE	BOTTOM	RT
37	2	1.42	1.48	0.90	0.20	20
38	2	2.08	2.34	0.70	0.17	20
39	3	1.19	1.26	0.69	0.34	20

40	1	1.70	1.77	0.47	0.05	20
41	3	1.99	2.35	0.50	0.09	20
42	1	1.65	1.56	0.44	0.05	20
48	3	2.37	2.44	0.79	0.17	20
49	2	3.81	4.21	0.54	0.17	20
53	3	1.67	1.81	0.66	0.21	20
54	2	2.04	1.77	0.31	0.03	20
55	1	1.35	1.26	0.68	0.13	20
58	1	1.12	1.16	0.29	0.12	20

PETROLEUM PRODUCTS: CHEMICAL COMPOSITION, TOXICOLOGICAL AND ENVIRONMENTAL DATA

R. Guthrie, T Tobin, and T. Struttmann

Petroleum Products: Chemical Composition, Toxicological and Biological Data

1.0 Background

Gasoline is generally produced by distillation and catalytic treatment of naturally available petroleum. The petroleum originates from decomposition of the structurally complex chemicals present in plants and animals. The refining processes involved in gasoline production reduce the molecular size of the compounds but do little to decrease the structural variety. The catalytic reforming required to reduce engine "knock" actually increases variety by converting some of the aliphatic materials into aromatic compounds. Thus, considering its history, commercial gasoline is an extremely complex mixture of organic compounds. Literature research summarized in the California UST guidelines has produced a list of over 150 compounds, each having a distinct molecular structure. Very likely, there are many others present in trace amounts which have not been definitely identified. Diesel fuel is equally or more complex, because this material is produced by distillation at a higher temperature and consequently contains higher molecular weight compounds.

The toxicological properties of many of the compounds present in gasoline and diesel fuels have not been thoroughly studied, making risk assessment for these complex mixtures an uncertain exercise. Fortunately, the toxicological properties of compounds with related or like molecular structures are often similar, and in the absence of further testing, we will be guided by our current understanding of the toxicology of this group of compounds.

2.0 Non-ring, saturated hydrocarbons

There are over 50 non-ring, saturated hydrocarbons in the California UST list. A published analysis of different gasolines done about 25 years ago lists over 80 compounds in this class. To the best of our knowledge, no compound in this class has been identified as being either significantly toxic or carcinogenic in animals or humans. Butane and dodecane represent the high and low volatility (low and high boiling points) ends of this class. Heptane is a mid-range, relatively high-concentration member of the class of straight-chain (all carbon atoms attached sequentially) saturated hydrocarbons; and isopentane is a high-concentration member of the class of branched saturated hydrocarbons. Looking at heptane and isopentane as typical examples of this class, it is clear that neither are particularly toxic. Each requires over 14 grams per 1000 grams of body weight, taken orally, to kill 50% of a population of rats or mice. (CHEMINFO, 1993). This translates to over a pound of this material to kill a normal-sized human. It seems safe to say that it is unlikely that any person would ingest this much gasoline accidentally. Diesel fuel is composed largely of saturated hydrocarbons. The number of carbon atoms per molecule is higher in diesel fuel but the toxicological properties of these higher molecular weight saturated hydrocarbons are, very likely, similar to those of lower molecular weight homologs (members of the series).

3.0 **Ring-containing saturated hydrocarbons**

The California UST list contains 13 compounds in this class. More than double this number have been identified. (Sanders, 1968). Here again, there is no record of toxicity or carcinogenicity. As is seen in the table, cyclopentane, the most volatile member of this class detected in gasoline, shows very low toxicity in animal studies. We have also listed the two other members of this class of compounds which make the most significant contribution to the composition of gasoline, methylcyclohexane and ethylcyclohexane. Little has been determined about the physiological effects of these compounds. However, based on what is known about other members of this class of compounds, there is no reason to expect that other members of this group will be highly toxic. Based on their general inertness in chemical reactions, it may be expected that saturated hydrocarbons, including the ring-containing variety, would be relatively persistent in the natural environment. The half-lives for a prototypical member of this series, cyclohexane, are listed as 28-180 days in soil, 4 days in air, and 56-365 days in ground water (Howard, 1991).

4.0 **Unsaturated hydrocarbons**

Unsaturated hydrocarbons differ from their saturated counterparts in that, in some part of the molecular structure, two adjacent carbon atoms are doubly bonded. Because changing the position of a double bond changes the physical and chemical properties of a molecule, it is generally to be expected that several unsaturated compounds will be present corresponding to every saturated one. Thus a large number of different compounds of this sort are to be anticipated. Chemically, compounds featuring double bonds in their structures tend to be more reactive with most reagents. Although not listed in our table, a simple, prototypical member of this family of compounds, propene, has listed half-lives of 7-28 days in soil, 0.1-0.5 days in air and 14-56 days in ground water (Howard, 1991). It might also be anticipated that such compounds might be more physiologically active. Physiological data is much more scarce for unsaturated hydrocarbons. However, to the best of our knowledge, there are no available data suggesting that these are significantly more toxic than their saturated counterparts. We have listed four members of this class that represent the major contributors from this group, each present at roughly one percent by weight. Aldrich Chemical Company, which supplies these materials as pure chemicals in research quantities, states: "To the best of our knowledge, the chemical, physical and toxicological properties have not been thoroughly investigated" (Aldrich, 1993).

5.0 **Simple aromatic compounds**

For purposes of simplifying the discussion in this document, we will separate aromatic compounds containing one and two benzene rings, calling them "simple aromatic compounds" from those containing three or more benzene rings. The latter group, particularly when the benzene rings share common carbon atoms, are known as "polynuclear aromatic hydrocarbons" (PAHs). Of the former group, only benzene has been shown to represent a significant hazard to human health. Molecules of benzene contain a ring of six carbon atoms doubly bonded to each other. This simple, isolated six-carbon unit is present in eight compounds listed in our table and many other benzene-ring-containing compounds are present in gasoline. Unexpectedly, other compounds containing benzene rings with affixed saturated hydrocarbon groups have not been found to show the same hazards as benzene. Though not particularly toxic in the sense of immediate physiological response, benzene has been found to produce a significantly increased level of cancer in exposed humans. Benzene is present as a significant percentage of commercial gasolines but is present at a relatively minor level (< 10 parts per million) in diesel fuels (California LUFT Plan, 1991). Remarkably, toluene, molecules of which are almost the same as those of benzene with the exception of an attached CH_3 group on each, shows no comparable cancer risks. Animals exposed to toluene at 1,200 ppm for two years showed no increased incidence of cancer (IRIS, 1993). Other members of this series which have been studied (generally having more, or more elaborate saturated carbon chains attached) appear to resemble toluene rather than benzene in their capacity to provoke physiological response. To the best of our knowledge, no other simple aromatic compound has shown the carcinogenic characteristics of benzene.

6.0 Polynuclear aromatic compounds

When hydrocarbon molecules contain more than two aromatic rings, particularly when these rings share carbon atoms, the chemical compounds so constituted are generally referred to as polynuclear aromatic hydrocarbons. The four highest molecular weight compounds listed in our table fall in the category of PAHs. It will be noticed that only one of these has been quantitatively measured in gasoline and that at parts per million levels. In diesel fuels, which are produced from higher boiling distillates, PAHs are present at understandably higher concentrations. Even here, however, the primary constituents are simple aromatic compounds, and individual PAHs are present at levels generally less than 100 ppm. 13 PAHs are listed in the table of diesel fuel components. Some PAHs have been found to produce cancer in animals as indicated by their "B2" ratings (IRIS, 1993).

TABLE I. Physical Data for Compounds in Gasoline.

Compound	Conc. Gas.* wt. %	Mol. Wt.	Bp.	Vp.(mm)** @20-25 C	Density g/cc	Sol. $H_2$0 mg/L	Ref.
n-Butane	3.9 - 4.7	58	0	1.6e+03		6.1e+01	1,2,3,5
trans-2-Pentene	0.5 - 0.9	70	37		0.65	"insol"	1,2
1-Pentene	0.3 - 0.5	70	30	3.6e+02	0.65	1.5e+02	1,2,6
2-Methyl-2-butene	0.9 - 1.3	70	31		0.65		1,2
Cyclopentane	0.2 - 0.6	70	50	4.0e+02	0.75	"insol"	1,2,6
cis-2-Pentene	0.4 - 0.7	70	37		0.65	"insol"	1,2
Isopentane	6 - 10	72	30	6.0e+02	0.62	4.9e+01	1,2,3
Benzene	0.12 - 3.5	80	80	7.5e+01	0.87	1.8e+03	1,2,3,5,6
tert-Butyl methyl ether	6.5 - 9.6	88	55	2.3e+02	0.76	4.8e+04	1,2,7
Toluene	2.7 - 21.8	92	111	2.2e+01	0.87	5.2e+02	1,2,3,6
Methyl-cyclohexane	0.5 - 1.1	98	101	5.1e+01	0.68	1.5e+01	1,2,3
Ethylene dichloride	0.1 - 0.3	99	83	3.7e+01	1.26	8.7e+03	1,2,6
n-Heptane	0.31 - 2.0	100	98	3.5e+01		3.0e+00	1,2,4,6
Xylene	3.2 - 9.6	106	140	6.5e+00	0.87	1.3e+03	1,2,5,6,7
Ethylbenzene	0.36 - 2.9	106	136	7.1e+00	0.87	1.5e+02	1,3,5,6
Ethylcyclohexane	0.2 - 0.4	112	131	2.6e+01	0.79	"insol"	2,6
Indan	0.25 - 0.34	118	176		0.97	1.1e+02	1,2,6
Isopropylbenzene	0.01 - 0.23	120	152	1.0e+01	0.86	5.0e+01	1,2,6
1,3,5-Trimethyl-benzene	0.13 - 1.15	120	165	1.9e+00	1.62	8.6e-01	1,2,5
Naphthalene	0.1 - 0.5	128	217	5.4e-02	1.16	3.0e+01	1,2,6,7
1,4-Diethylbenzene	0.1 - 1.5	134	180	7.0e-01	0.87	1.5e+01	2,5
n-Dodecane	0.05 - 0.1	170	216	3.0e-01	0.75	"insol"	1,2,4,6
Ethylene dibromide	.0007 - .2	188	131		2.20	4.3e+03	1,2,6
Pyrene	nq	202	404	3.5e-06	1.27	1.5e-01	1,2,6
Benzo(a)anthracene	nq	228	437	2.2e-08	1.27	1.0e-03	1,2,6
Benzo(a)pyrene	.2 - 3 ppm	252	495	5.6e-09	1.35	3.8e-03	1,2,6
Benzo(g,h,i)perylene	nq	276	500	1.0e-10		2.6e-07	1,2,6

*Adapted from Appendix I, Chemical Composition of Gasoline from the California Plan.

**Denotes exponant. e.g. 2.6e+02 is 2.6 x 10^2 or 260, 3.5e-06 is 3.5 x 10^{-06} or .0000035.

nq-not quantifible
Mol.Wt.-Molecular weight
Bp.-Boiling point
Vp.-vapor pressure
Sol.-solubility in water at 20-25C

TABLE II. Physical Data for Compounds in Diesel Fuel.

Compound	Conc. Diesel % or other	Mol. Wt.	Bp	Vp.(mm)	Density g/cc	Ref.
Benzene	<10 ppm	80	80	7.5e+01	0.87	2,4
Toluene	<.3	92	11	2.2e+01	0.87	2,3,6
Ethylbenzene	<.09	106	136	7.1e+00	0.87	2,3,4,6
Xylene	<.5	106	140	6.5e+00	0.87	2,3,4,6
Isopropylbenzene	nq	120	152	1.0e+01	0.86	2
1,3,5-Trimethylbenzene	<3	120	165	1.9e+00	1.62	2,3,5,6
Naphthalene	0.2 - 3	128	217	5.4e-02	1.16	1,2,6
Biphenyl	nq	154	255	1.0e+00	0.99	1,2,6
Fluorene	300 ppm	166	298	7.1e-04	1.20	1,2,6
n-Dodecane	1 - 11	170	216	3.0e-01	0.75	1,2,6
Phenanthrene	0.2 - 0.04	178	336	9.6e-04	0.90	1,6,8
Anthracene	3 ppm	178	340	1.7e-05	1.25	1,2,6,8
Pyrene	0.5 - 80 ppm	202	404	3.5e-06	1.27	1,2,6
Fluoranthene	0.6 - 60 ppm	202	384	5.0e-06	1.25	1,2,6
Benzo(a)anthracene	0.13 ppm	228	437	2.2e-08	1.27	1,2,6,8
Chrysene	0.5 - 43 ppm	228	448	6.6e-09	1.27	2,6
Triphenylene	3 - 43 ppm	228	438	"small"	1.30	6
Benzo(b)fluoranthene	1 - 20 ppm	252		1.0e-08		1,6
Benzo(k)fluoranthene	nq	252		5.0e-07		6
Benzo(a)pyrene	0.07 ppm	252	495	5.6e-09	1.35	1,6,8
Indeno(1.2.3-c,d)pyrene	0.2 - 9 ppm	276		1.0e-10		6
Benzo(g,h,i)perylene	0.03 - 16 ppm	276	500	1.0e-10		1,6,8
Dibenzo(a,h)anthracene	nq	278	524	1.0e-10	1.28	6

TABLE III. Physical Data for Compounds from Gasoline and Diesel Fuel.

Compound	Sol. H2O mg/L	Log Kow	Henry's Law	Log Koc	Ref.
Benzene	1.8e+03	2.1	5.5e-01	2.3	3,5
Ethylene dichloride	8.7e+03				2
Ethylene dibromide	4.3e+03				2
Chrysene	"insol."	5.6	1.1e-06	5.3	2,6
Benzo(a)anthracene	1.0e-03	5.6	1.0e-06	5.3	2,6
Benzo(a)pyrene	3.8e-03	6.0	4.9e-07	6.7	2,6
Benzo(k)fluoranthene	"insol."	6.1	3.6e-05	5.7	2
Benzo(b)fluoranthene	"insol."	6.0	1.2e-05		2
Indeno(1.2.3-c,d)pyrene	6.0e-02	6.6	7.0e-08	6.2	2,6
Dibenzo(a,h)anthracene	5.0e-04	6.5	7.3e-08	6.5	6
n-Butane	6.1e+01		9.6e+01	2.7	3,5
tert-Butyl methyl ether	4.8e+04	1.3			2,12
Toluene	5.2e+02	2.8	6.7e-03	2.6	3,5,6
n-Heptane	"insol"	4.7	2.3e+02	3.6	2,5
Ethylbenzene	1.5e+02		8.0e-01	2.8	3,5
Xylene	1.3e+03	3.2			3,6
Indan	1.1e+02	3.6			
Isopropylbenzene	5.0e+01	3.7		3.7	2,6
1,3,5-Trimethylbenzene	7.3e+01		6.0e-01	2.9	5
Naphthalene	3.0e+01	2.9		3.3	6
Tetralin					
1,4-Diethylbenzene	1.5e+01		1.4e+00	3.5	5
Acenaphthylene	3.9e+00	3.7	1.5e-03	3.4	
Biphenyl	7.5e+00	3.6		3.5	6
Acenaphthene	"insol."	4.0		3.7	2
Fluorene	1.8e+00	4.1	6.4e-05	3.9	2
n-Dodecane	"insol		7.5e+02	4.9	2,5
Anthracene	"insol"	4.5	8.6e-05	4.2	2,6
Phenanthrene	1.3e+00	4.5	2.3e-04	4.1	2
Pyrene	1.5e-01	4.9	5.1e-06	4.6	2,6
Fluoranthene	2.3e-01	4.9	6.5e-06	4.6	2
Triphenylene	3.8e-02				2
Benzo(g,h,i)perylene	2.6e-07	6.5	1.4e-07	6.2	2,6

TABLE IV. Toxicological Data for Compounds from Gasoline and Diesel Fuel.*

Compound	LD50	Cancer Rating	RfD(inh) mg/m^3	RfD(orl) mg/kg/day	Uncert.	References
Benzene	930	A	8.3e-06	8.3e-07		9,10,11
		slope	2.9e-02	2.9e-02		
Ethylene dichloride	640	B2	2.6e-05	2.6e-06		9,10
Ethylene dibromide	148	B2	2.2e-04	2.5e-03		9,10
Chrysene	320	B2				6,9,11
Benzo(a)anthracene	200	B2				9,11
Benzo(a)pyrene	50	B2	1.7e-03	3.3e-04		6,9,10,11
Benzo(k)fluoranthene		B2				
Benzo(b)fluoranthene		B2				
Indeno(1.2.3-c,d)pyrene		B2				
Dibenzo(a,h)anthracene		B2				
n-Butane		D				
tert-Butyl methyl ether	3800	D				11,12
Toluene	636	D	4.0e-01	2.0e-01	300-1000	6,9,10,11
n-Heptane	15000	D				11
Ethylbenzene		D	1.0e+00	1.0e-01	300-1000	6,9,10,11
Xylene	4300	D	3.0e-01	2.0e+00	100	9,10,11
Indan		D				11
Isopropylbenzene	1400	D				6,9,10
1,3,5-Trimethylbenzene		D				
Naphthalene	533	D	4.0e-03	10000		6,9,10,11
Tetralin		D				
1,4-Diethylbenzene		D				
Acenaphthylene		D				
Biphenyl	2400	D	5.0e-02	1000		6,11
Acenaphthene		D	6.0e-02	3000		9
Fluorene	2000	D	4.0e-02	3000		6,11
n-Dodecane		D				
Anthracene	18000	D	3.0e-01	3000		6,9,11
Phenanthrene		D				
Pyrene		D	3.0e-02	3000		9,11
Fluoranthene	2000	D	4.0e-02	3000		6,9,11
Triphenylene		D				
Benzo(g,h,i)perylene		D				

TABLE V. Environmental Information on Compounds from Gasoline and Diesel Fuel.*

Compound	1/2 life soil (days)	1/2 life air (days)	1/2 life grnd water (days)
Benzene	5-16	2-21	10-800
Ethylene dichloride	100-164	12-122	100-365
Ethylene dibromide			
Chrysene	365-930	0.03-0.3	730-1905
Benzo(a)anthracene	102-680	0.05-0.2	204-1295
Benzo(a)pyrene	57-529	0.05-.1	114-1059
Benzo(k)fluoranthene	910-2025	0.05-0.5	1825-4019
Benzo(b)fluoranthene	360-540	0.05-0.5	730-1195
Indeno(1.2.3-c,d)pyrene	455-730	0.02-0.5	1150-1460
Dibenzo(a,h)anthracene	361-934	0.02-0.2	723-1879
n-Butane			
tert-Butyl methyl ether	28-180	11	56-365
Toluene	4-22	4	7-28
n-Heptane			
Ethylbenzene	3-10	4	6-228
Xylene	7-28	2	14-365
Indan			
Isopropylbenzene	2-8	4	4-16
1,3,5-Trimethylbenzene			
Naphthalene	17-48	0.01-1	1-258
Tetralin			
1,4-Diethylbenzene			
Acenaphthylene	43-60	0.05-0.1	85-120
Biphenyl	2-7	5	3-14
Acenaphthene	12-102	0.1-0.3	25-204
Fluorene	32-60	3	64-120
n-Dodecane			
Anthracene	50-410	0.02-0.1	100-910
Phenanthrene	16-200	0.1-1	32-375
Pyrene	210-1825	0.02-0.1	365-3650
Fluoranthene	140-440	0.1-1	280-830
Triphenylene			
Benzo(g,h,i)perylene	590-650	0.01-0.1	1110-1275

*Adapted from Howard 1991.

12.0 TABLE I THROUGH V - COLUMN DESCRIPTIONS

Molecular Weight
The average molecular weight of a typical gasoline (reflecting the length of the molecule) is 100. Individual constituents of gasoline/diesel have various molecular weights. The longer the molecule, the higher is its viscosity and, hence, the lower its mobility through small spaces such as soil pores.

Boiling Point
The boiling point is related to the vapor pressure. The lower the boiling point, the higher the vapor pressure.

VP - Vapor Pressure
The numbers given are the vapor pressure at 20 or 25 degrees centigrade (unless otherwise indicated). It is expressed in millimeters of mercury. Vapor pressure is related to the volatility of a substance. Vapor pressure effects evaporation time, air pollution levels and odor. The higher the vapor pressure, the higher the evaporation rate and, therefore, human inhalation potential.

Specific Gravity
Specific gravity is the ratio of the density of a compound with respect to the density of water (water = 1). Constituents of petroleum products that have a specific gravity less than 1 will float on water. The specific gravities of gasoline and diesel are .7 and .8 respectively.

Water Solubility
Water solubility is the quantity of the compound which will dissolve in a certain amount of water at a certain temperature. It is expressed as milligrams of product per liter of water. The average solubility of gasoline is 42.5 mg/L. However, benzene has a solubility of 1972 mg/L. Therefore, benzene alone would be more likely to dissolve in water and leave a contaminated area. The lower the solubility, the more likely a compound will attach to soil versus move in solution with ground water.

K_{ow} - octanol/water coefficient - Log P (oct)
The K_{ow} of Log P (oct) describes the tendency of a nonionized organic chemical to accumulate in lipid tissue and to sorb onto soil particles. K_{ow} provides a measure of the extent of chemical partitioning between water and octanol at equilibrium. The greater the K_{ow}, the more likely a chemical is to partition to octanol than to remain in water (octanol is used as a surrogate for lipids).

Henry's Law Constant (air-water partitioning)

Henry's Law combines vapor pressure, water solubility, and molecular weight to characterize a chemical's ability to evaporate from aqueous media, including moist soils. When gasoline/diesel constituents are present with both air and water, they will partition themselves between the two (i.e., some of the constituents will enter air, some will enter water). Henry's Law constant is in atmospheres per cubic meter of air per mole at a specific temperature. Values for Henry's Law can be estimated (if not know) from the ratio of vapor pressure to water solubility of a constituent. The higher the Henry's Law constant, the more likely a compound is to volatilize then to remain in the water.

K_{oc} - Organic carbon coefficient

The K_{oc} is a measure of relative sorption potential and indicates the tendency of an organic chemical to be absorbed to soil or sediment. It is a measurement of a compounds mobility in soil. It is independent of soil properties. A low K_{oc} indicates a greater potential for leaching from soil to ground water. Organic chemicals with high K_{oc} values possess greater sorption (binding potential) and, therefore, are more likely to stay near the site.

LD_{50}

Lethal dose fifty is the calculated dose which is expected to kill 50 percent of a population (of rats). It is expressed in milligrams per kilogram of body weight. The smaller the LD_{50}, the more lethal the compound. These numbers come from animal studies. Therefore, direct correspondence to humans is not always possible. For comparative, purposes a list of approximate acute LD_{50} values is presented below.

APROXIMATE ACUTE LD50'S OF
SOME REPRESENTATIVE CHEMICAL AGENTS

AGENT	LD50 (mg/kg)*
Ethyl alcohol	10,000
Sodium chloride	4,000
Ferrous sulfate	1,500
Morphine sulfate	900
Phenobarbital sodium	150
Picrotoxin	5
Strychnine sulfate	2
Nicotine	1
d-Tubocurarine	0.5
Hemicholinium-3	0.2
Tetrodotoxin	0.10
Dioxin (TCDD)	0.001
Botulinum toxin	0.00001

*LD 50 is the dosage (mg/kg body weight) causing death in 50 percent of the exposed animals.

Carcinogen Rating

The Human Health Assessment Group (HHAG) of the U.S EPA classifies chemicals into one of the following groups according to the weight of evidence from epidemiological studies and animal studies:

Group A - Human Carcinogen (sufficient evidence of carcinogenicity in humans)

Group B - Probable Human Carcinogen (B1-limited evidence of carcinogenicity in humans; B2 - sufficient evidence of carcinogenicity in animals with inadequate or lack of evidence in humans).

Group C - Possible Human Carcinogen (limited evidence of carcinogenicity in animals and inadequate or lack of human data)

Group D - Not Classifiable as to Human Carcinogenicity (inadequate or no evidence)

Group E - Evidence of Noncarcinogenicity for humans (no evidence of carcinogenicity in adequate studies)

RfD - Chronic Reference Dose

RfDs are used to evaluate the potential non-carcinogenic effects of exposures between 7 and lifetime years. Rfds are expressed in mg/kg/day. For *non-carcinogenic* chemicals, the chronic reference dose is defined as an estimate of a daily level exposure to the human population, including sensitive sub populations, not likely to cause a harmful health effect. For non-carcinogenic chemicals, the chronic reference dose is used as a benchmark for chronic toxicity and is designed to be a protective (by as much as a factor of 10) over long-term exposure to a compound. To assess the potential for non-carcinogenic effects the estimated dose is compared to the reference dose. The lower the RfD, the more toxic is the chemical.

Slope Factor

For *carcinogenic* chemicals, toxicity is quantified by estimating the compound specific potency value (also called slope factor). This is defined as the plausible upper bound (95th percentile) estimation of cancer risk probability per unit of compound over a lifetime. Slope factor X exposure amount = a risk of n in 1 million because the slope of the dose response line combined with the 1 hit theory says that one dose results in damage.

Uncertainty Factor

The uncertainty factor which is used in conjunction with a RfD reflects scientific judgement regarding the various types of data used to estimate RfD values. An uncertainty factor of 10 is usually used to account for variations in human sensitivity when extrapolating from valid human studies involving sub chronic or long term exposure of average healthy subjects. The higher the uncertainty factor, the less strong is the evidence from the existing data base.

Environmental Degradation Rates (1/2 life)

Half-lives are based upon the high and low degradation rates of the most important degradation process within a particular medium. Soil: Biodegradation was the most common degradation process in soil, with the exception of those chemicals which undergo rapid hydrolysis. Ground water: Biodegradation and hydrolysis, to a lesser extent, were the principle means of degradation.

13.0 REFERENCES FOR TABLES I-V.

1. Chemical Composition of Gasoline Appendix I and J From the California LUFT Plan.
2. Handbook of Chemistry and Physics 53rd edition. CRC press Robert Weast editor 1972.
3. Guard, James, Laughlin (1983) Characterization of Gasolines, Diesel Fuels and Their Water Soluble Fractions. Navel Biosciences Laboratory. Oakland CA.
4. USEPA Assessing UST Corrective Action Technology. EPA/600/2-91/053 Sept. 1991. A Scientific Evaluation of the Mobility and Degradability of Organic Contaminants in Subsurface Environments.
5. Tracy, James Overview of Factors Affecting Subsurface Gasoline Behavior. Planning Research Corporation Mclean VA.
6. Canadian Centre For Occupational Health and Safety, CHEMINFO (1993).
7. Potter, TL (1993) Fingerprinting Petroleum Products: Unleaded Gasoline. Contaminated Soils Lewis Publishers. p15-24.
8. Obuchi, A, Myogoro, P, Akihiko, O, (1984) Determination of PAH in Diesel Exhaust Particulate Matter and Diesel Fuel Oils. Journal of Chromotography 312: 247-259.
9. IRIS data Base 1993
10. HEAST 1991
11. Patty's Industrial Hygiene and Toxicology 1992.
12. Canadian Environmental Protection Act Priority Substances List Assessment Report No. 5. (1992).

14.0 REFERENCES

ACGIH, American Conference of Governmental Industrial Hygienists, Threshold limit values for chemical substances and physical agents and biological exposure indices, 1992-1993.

Aldrich Chemical Company, 940 West St. Paul Avenue, Milwaukee, Wisconsin, 53233. Material Safety Data Sheet, Version July 1989, product numbers 14376-6, 11126-0, 32842-1.

Barkach, J.H., Dragun, J., Mason, S.A. (1990) Soil and Ground Water Clean-up Standards as Approached By the Michigan Department of Natural Resources. The Environmental Professional 12, p 319-333.

California Luft Plan, Appendix I and J, 1991.

Canadian Environmental Protection Act. Priority Substances List Assessment Report No. 5, Methyl tertiary-butyl Ether, 1992.

Canadian Environmental Protection Act. Priority Substances List Assessment Report No. 4, Toluene, 1992.

Canadian Centre for Occupational Health and Safety, CHEMINFO (1993) CCINFO 93-1.

Guard, H. E., and James N. G., Laughlin, R. B., (1983). Characterization of gasoline, diesel fuels and their water soluble fractions, Naval Biosciences Laboratory, Oakland, CA.

Howard, Phillip H., Editor, Handbook of Environmental Degradation Rates, Lewis Publishers Inc., 1991.

Integrated Risk Information System (IRIS) Data Base, EPA, Washington, DC.

Lyman, W. J. Environmental Partitioning of Gasoline in Soil/Groundwater Compartments. Camp Dresser and McKee, Inc., Boston, MA.

MSDS from Genium's Reference Collection Genium Pub. Company, Schenectady, NY, Ethylene Dibromide, 1989.

Nash, J. H. Chemical and Physical Properties of Gasoline. CDM/Federal Programs Corporation, Edison, NJ.

Paustenback, D. S., et. al. (1991). A Proposed Approach To Regulating Contaminated Soil: Identify Safe Concentrations For Seven of The More Frequently Encountered Exposure Scenarios. Second Annual West Coast Conference On Contaminated Soils and Ground Water. March 4-7, 1991.

Sanders, W.N. and Maynard, J.B. (1968) Capillary Gas Chromatographic Method for Determining the C_3-C Hydrocarbons in Full-Range Motor Gasolines. Analytical Chemistry, 40, 527-535.

Spence, L., Salhotra, A., Claff, R., Bauman, B. (1993). An exposure/risk assessment tool for UST sites: the API decision supports framework API. API Washington, DC.

U. S. EPA, Assessing UST Corrective Action Action Technology, EPA/600/2-91/053, Sept. 1991. "A Scientific Evaluation of Mobility and Degradability of Organic Contaminants in Subsurface Environments.

U. S. EPA, Health Effects Assessment Summary Tables, FY-1991. OERR 9200.6-303(91-1).

U. S. EPA Document. Superfund Site Assessment. Chapter 6 Exposure Assessment. Chapter 7 Toxicity Assessment.

U. S. Department of Commerce, NTIS, National Technical Information Services, Polynuclear Aromatic Hydrocarbons, PB-91-181-537 (Dec. 1990)

U. S. Department of Health and Human Services PHS Agency for Toxic Substances and Disease Registry. Toxicological Profile for Benzene. (May 1989)

U. S. Department of Health and Human Services PHS Agency for Toxic Substances and Disease Registry. Toxicological Profile for Toluene. (Dec. 1989)

U. S. Department of Health and Human Services PHS Agency for Toxic Substances and Disease Registry. Toxicological Profile for Xylenes. (Dec. 1990)

HEALTH RISK ANALYSIS FOR SELECTED PETROLEUM COMPOUNDS

R. Guthrie, T Tobin, and T. Struttmann

1.0 INTRODUCTION:

(Sections 1-5 are summaries of the toxicological profiles for benzene, toluene, ethylbenze and xylenes published by the Agency for Toxic Substances and Disease Registry, U.S. Public Health Service.)

GASOLINE is not considered highly toxic. A dose of 350 gms orally is fatal to an adult, although 10 gms may be fatal to a child. The most serious danger from high concentrations of gasoline vapor is fire/explosion. High concentrations of gasoline vapor (5,000 ppm) are rapidly lethal. Prolonged exposure to lower concentrations is associated with neuropathy, possibly associated with n-hexane. Gasoline tests negative in mutagenicity assays and gasoline vapor causes tumors only in male rats. Epidemiological studies on refinery workers have shown increased incidence of cancer of the brain, stomach, skin and prostate, but death rates from cancer are lower than those of the general population due to the "healthy worker effect".

BENZENE is a component of gasoline that is a class A human carcinogen. Exposure to low levels of benzene for short periods can be associated with the development of leukemias up to 15 years later. Benzene is highly volatile and mobile in water and is used as a marker substance for gasoline contamination. Benzene is considered a critical environmental contaminant and there are strict controls on the levels permissible in air and ground water.

TOLUENE is a component of gasoline and diesel fuel of relatively low toxicity. The weight of the evidence suggests that toluene is not genotoxic and none of the available evidence suggests that toluene is carcinogenic. Toluene is sufficiently volatile such that most toluene in the environment is released directly into the air.

MIXED XYLENES, which include ortho, meta, and para-xylene and ethyl benzene are important fuel components with relatively low toxicity. Genotoxicity studies on mixed xylenes have proved consistently negative and in vivo studies in rats and humans have been negative. No definite conclusions can therefore be drawn regarding the carcinogenicity of mixed xylenes in man and animals. In soil xylenes are relatively mobile and may leach into ground water depending on soil conditions. In the environment xylenes are highly volatile and volatilization is the dominant transport system for xylenes.

MTBE (methyl-tertiary butyl-ether) is added as an octane booster to gasoline at concentrations up to 11%. MTBE is not considered toxic and is not considered a danger to the environment or to human life and health.

LEAD, in the form of tetraethyl lead was added to gasoline as an anti-knock agent until recently. Lead is a ubiquitious toxic metal in the environment and in biological systems. Lead is not destroyed by any biotic or abiotic process, and the major issue is at what point lead becomes toxic.

DIESEL FUEL is a gas oil fraction from the middle distillate of petroleum. Great variations occur between batches of diesel, depending on the source of the crude, the type of processing and the climate of the market area.

POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) are the constituents of concern in diesel fuel. Many PAHs such as benzo(a)pyrene are harmful to human health and a number of PAHs have been shown to be carcinogenic. Because of their carcinogenicity PAHs are the environmental contaminants in diesel fuel that give rise to the greatest level of concern.

2.0 **TOXICOLOGY OF GASOLINE:**

Gasolines are mixtures whose characteristics depend on the source of the crude oil, the processing techniques used and the target market. Anti-knock capability is achieved by adding small amounts of organic lead or branched chain or aromatic compounds. Gasolines consist of paraffins, cycloparaffins, aromatics and other materials. Despite substantial variability in their composition, signs and symptoms of toxicity are similar for all gasolines.

2.1 ODOR:

Gasolines have an unmistakable odor and humans can detect whole gasoline at approximately 0.1 ppm. Exposure to gasoline vapors causes nausea, drowsiness and diarrhea. Gasoline is not particularly toxic and the most acute short term threat from gasoline vapors is fire or explosion.

2.2 INGESTION:

Ingested gasoline is only moderately toxic. The fatal dose for an adult human is about 350 gms.(12 oz.), but as little as 10 gms. can be fatal to a child. Ingestion can lead to unconsciousness and coma, and death may result from asphyxia or ventricular fibrillation. Bronchitis, pneumonia and nephritis have been reported and aspiration pneumonia is a serious complication.

2.3 INHALATION:

Gasoline vapor at 300 ppm-500 ppm is an irritant to the eyes, nose and throat. Inhalation may result in symptoms like alcohol inebriation, including headache, anorexia, nausea, dizziness, flushed face, difficulty in swallowing, slurred speech, drowsiness and mental confusion. Breathing vapors at high concentrations (>5,000 ppm) can cause rapid loss of consciousness and death. In occupational settings signs and symptoms of gasoline vapor exposure include anorexia, nervousness, drowsiness, insomnia, pallor, muscle cramps and weakness. Peripheral nerves can be affected with resulting neuropathy, which may be associated with the n-hexane content. Since n-hexane is about 5% by volume, the amount in gasoline vapor is about 9 ppm, approximately 1/10th of the chronic toxicity level of about 100 ppm.

2.4 SKIN CONTACT:

Gasoline is primarily a skin irritant and prolonged exposure causes skin defatting and dermatitis. Absorption through the skin is generally insufficient to cause toxicity. Contact with the skin is not a likely cause of skin irritation. Gasoline vapors at 200 to 500 ppm are irritant to the eye.

2.5 WATER SOLUBILITY:

A significant fraction of gasoline can dissolve in water, principally as C8 aromatics. After a spill, weathering, evaporation and water solubility combine to alter the chemical composition of the remaining material.

2.6 ENVIRONMENTAL FATE:

Biodegradation is favored by aerobic conditions. Benzene has an atmospheric half-life of about two to 21 days and Ethylene Dibromide, EDB, a common additive, has a half-life in water of about five days.

2.7 MUTAGENICITY:

Unleaded gasoline has tested negative in several in vivo and in vitro mutagenicity and cytotoxicity assays.

2.8 CARCINOGENICITY:

The American Petroleum Institute American Petroleum Institute (API) 2 year study of gasoline inhalation showed microscopic tumors only in male rats. Other significant findings included a pulmonary inflammatory response, failure to gain weight and an increase in hepatocellular carcinomas in female mice.

2.9 EPIDEMIOLOGY:

Epidemiological studies on refinery workers and gasoline handlers have shown increased levels of cancer of the brain and stomach in workers in a Texas refinery. Other tumors that showed increases include leukemia and cancers of the pancreas, skin and prostate. On the other hand, at least one recent review concluded that there is no significant increase in cancer mortality in oil refinery workers. Some studies have shown a lower rate of death from all causes for refinery workers due to the "healthy worker" effect and the prohibition against smoking at refineries. A number of epidemiological studies in refineries have concentrated on the link between benzene exposure and leukemias.

3.0 **TOXICOLOGY OF BENZENE:**

Benzene is a component of gasoline and is widely used in the manufacture of plastics, detergents and pesticides. Tobacco smoke, automobile exhaust or the workplace are common sources of exposure. Occupational exposures occur in the rubber industry, oil refineries/petroleum industry and chemical plants. Acute exposure (Frank Effect Level, FEL, 1,000-10,000 ppm) causes drowsiness, dizziness and headaches. Long term exposure is associated with leukemia, blood dyscrasias and internal bleeding. The odor threshold of benzene is about 5 ppm.

3.1 GENERAL TOXICOLOGY:

Benzene must be biotransformed to be toxic, with the most sensitive organ systems being the hematopoietic and immune systems. Benzene is toxic to stem cells in the erythroid and myeloid cell lines. Exposure to benzene produces pancytopenia, followed by myelogenous leukemia in a proportion of the pancytopenia survivors. Bone marrow depression is associated with long term exposure and a sensitization phenomenon is thought to occur in certain individuals. Benzene is genotoxic in that it causes structural and numeric chromosome aberrations. However, it has rarely been shown to cause gene mutations. Benzene is not teratogenic, but exposure of the fetus in animal models is likely to result in low birth weight, delayed bone formation and bone marrow damage. Data from the human, however, is limited.

3.2 INHALATION EXPOSURE:

Benzene is very volatile and therefore the most common route of exposure is by breathing air containing benzene. About 50% of inhaled benzene is absorbed. The National Institute for Occupational Safety and Health (NIOSH) has recommended an occupational exposure limit in air of 0.1 ppm, and the Occupational Safety and Health Administration's legally enforceable limit on benzene is an average of 1.00 ppm over an 8 hour workday.

3.3 DERMAL:

No data are available for dermal lethality of benzene in humans or animals. Dermal exposure is generally from direct contact with gasoline.

3.4 INGESTION:

The EPA has set the maximum permissible level in drinking water at 5 ppb benzene.

3.5 GENOTOXICITY:

Benzene, or more likely its metabolites, cause structural and numerical aberrations in chromosomes, sperm head abnormalities, inhibition of DNA and RNA synthesis and cell cycle progression. Virtually all studies with benzene that have looked for chromosomal effects were positive when the ability to metabolize benzene was present. No safe human exposure level can be determined from epidemiological data and the nature of the dose response relationship remains unclear. On this basis, no safe or threshold level for benzene can be established. Additionally, there may be a sensitive subpopulation with a metabolic idiosyncracy that is highly susceptible to benzene.

3.6 CARCINOGENICITY:

Epidemiological studies show that benzene is a human carcinogen. The risk is significant and EPA estimates a risk value of 2.6×10^{-6} for leukemia associated with a lifetime exposure of 1 ppm benzene in air. Determination of the lowest levels known to be carcinogenic in humans is difficult but one case exists in which a worker was exposed to 2 ppm for 18 months and died 15 years later at age 51.

3.7 EPIDEMIOLOGY:

For most of the US population the most likely route of exposure is inhalation.

3.8 ENVIRONMENTAL FATE:

Benzene is considered to be a highly volatile and highly mobile (K_{oc}=100) substance in water. As such, benzene released to soil can be transported through runoff to groundwater. Other factors that determine the migratory ability of benzene include soil type, amount of rainfall, depth of groundwater and extent of degradation.

3.9 DEGRADATION:

Degradation of benzene occurs through both chemical and biological means. Its most significant chemical reaction is with hydroxyl radical, which gives benzene a half-life in the atmosphere of about 5.6 days in a pristine atmosphere and 1.5 hours in a polluted atmosphere. All other atmospheric reactions are substantially slower than the reaction with hydroxyl radical. On the other hand, chemical degradation does not seem to be important in the breakdown of water borne benzene.

3.10 CHEMICAL DEGRADATION:

Benzene is biodegradable, both aerobically and anaerobically, although anaerobic degradation is slow.

3.11 POTENTIAL FOR EXPOSURE:

The presence of benzene in air has been extensively documented. Average air values are less than 5 ppb, with lowest levels running from 0.9 ppb to the highest levels (9,900 ppb) measured at a gasoline bulk loading facility. Indoor air shows higher levels of benzene than outdoor air, with smokers homes averaging 52 ppb and non-smokers homes about 30 ppb. Water levels range from 0.005 ppb in the Gulf of Mexico to 330 ppb in contaminated well water in New York.

3.12 POPULATIONS AT RISK:

Individuals occupationally exposed run the highest risk, followed by individuals living at certain chemical manufacturing sites, cigarette smokers and individuals living close to landfills. For individuals living near landfills the extent of exposure will depend on whether their drinking water becomes contaminated. Estimates of exposure figures suggest 80,000 individuals exposed to greater than 10 ppb, with 200,000 exposed to from 4.1 to 10.0 ppb as a result of living in the vicinity of chemical plants. An exposure level of 10 ppb assuming 30% systemic absorption works out at 2.8ug/kg/day for a 70kg man. This figure compares with 7.98ug/kg/day for this same man smoking 20 cigarettes/day and 2.9ug/kg/day for a man drinking well water contaminated with 100 ppb of benzene.

3.13 REGULATORY STATUS:

Benzene is a priority toxic pollutant and has been classified by the EPA as a hazardous substance. The Maximum Contaminant Level (MCL) for benzene in drinking water is 0.005mg/L or 5 ppb. It is assigned hazard ranking for specific exposure scenarios such as spills, but this is not applicable to chronic low level exposures typical at leaking storage tank sites.

4.0 TOXICOLOGY OF TOLUENE:

Toluene is a clear colorless chemical with a sweet smell. Many consumer products such as gasoline, paint, dyes and adhesives contain substantial amounts of toluene. Its major use is as a component of gasoline. Toluene rapidly evaporates/degrades in the environment and is not a widespread contaminant of drinking water. Little dose response data on human exposure to toluene is available other than acute exposure cases associated with abusive inhalation.

4.1 INHALATION TOXICOLOGY:

The only observed effect of chronically inhaled toluene is irritation of the respiratory tract, which has been observed in workers exposed to 200-800 ppm for several years. Because industrial exposure occurs in the context of complex mixtures, these studies do not establish an unequivocal relationship between toluene and mucosal irritation. The primary effect of exposure to toluene is depression of the CNS, and occupational exposure to high concentrations of toluene have led to residual or permanent CNS effects. While cardiac arrhythmia is a common cause of death in solvent abuse, toluene does not appear to be directly toxic to the cardiovascular system and it has not produced Electro Cardiographic effects in several well conducted studies.

4.2 INGESTION EXPOSURE:

Only limited data are available regarding oral exposure to toluene. No gastrointestinal effects were reported in mice or rats following oral exposure to toluene at 5mg/kg/day for 13 weeks.

4.3 DERMAL/OCULAR EFFECTS:

No studies are reported concerning dermal or ocular effects of toluene in animals. In humans, dermal contact with toluene may cause skin damage due to its defatting action. Toluene appears to be mildly irritating to skin.

4.4 GENOTOXIC EFFECTS:

The weight of the evidence suggests that toluene is not genotoxic. An increase in sister chromatid exchange has been reported in toluene exposed workers and this effect increased with years of exposure.

4.5 CANCER:

None of the available data suggest that toluene is carcinogenic. Animal bioassays have been negative. Mice and rats exposed to 1,200 ppm of toluene for two years did not have an increased incidence of cancer.

4.6 REPRODUCTIVE EFFECTS:

Women who abuse toluene give birth to offspring who show an increased risk of CNS defects including neural tube closure defects and microcephaly. Animal studies suggest that toluene is a developmental toxicant at high doses but appears to have little effect at low doses.

4.7 HUMAN EXPOSURE:

Large amounts of toluene enter the environment each year, mostly as gasoline in association with industrial and consumer use. Automobile emissions are the primary source of toluene in urban areas. Indoor air can have significantly higher concentrations of toluene resulting from household products and cigarette smoke. Toluene is rarely found in drinking water except in the vicinity of waste sites. Toluene exposures also occur in the work place, especially in the printing industry.

4.8 ENVIRONMENTAL FATE:

Toluene is sufficiently volatile such that most toluene is released directly into air. As a general rule more than 90% of the toluene in the upper layer of soil volatilize within 24 hours, and soil half times of from 1-7 days are typical. Toluene appears to be readily leached from soils with low organic content, more slowly from soils with a high organic content. Toluene is moderately lipophilic with a bioconcentration factor of about 10.7 in mussels.

5.0 **TOXICOLOGY OF MIXED XYLENE:**

Xylene is primarily a man made chemical existing in three forms, ortho, meta, and para xylene. It occurs primarily as a mixture of these forms with ethylbenzene, and this mixture is referred to as total xylene or mixed xylene. Xylenes are used in the printing, rubber and leather industries and are found in gasoline and aviation fuel. They evaporate and burn easily. Surface water generally contains less than 1 ppb of xylene, although the levels may be higher in industrial areas. Levels of xylene in drinking water vary from 0 to 750 ppb. Because xylene evaporates rapidly levels of xylene in the upper layers of soil tend to be low.

Exposure to xylene takes place via the oral and respiratory routes or through the skin. The EPA has proposed a maximum level of 0.44 ppm of xylene in drinking water. NIOSH has recommended an average limit of 100 ppm of xylene averaged over a 10 hour day/ forty hour week. NIOSH has classified exposures of 10,000 ppm of xylene in air as immediately dangerous to health.

5.1 INHALATION EXPOSURE:

Breathing paint fumes for several hours at 10,000 ppm can be fatal, with clinical signs including nausea, vomiting, cyanosis, confusion and an odor of xylene on the breath. Death from inhalation of xylene occurs from respiratory failure or ventricular fibrillation. Respiratory effects are associated with dyspnea, irritation of the nose and throat, severe lung congestion, intra-alveolar hemorrhage and pulmonary edema. Chronic occupational exposure has been associated with labored breathing and impaired pulmonary function. No cardiovascular effects were noted in humans exposed to 100 or 150 ppm xylene. Nausea and vomiting have been noted in humans exposed to high levels of xylene by inhalation. Similarly, no adverse hematological effects have been noted in rats or dogs exposed to xylene. Animal studies on the reproductive effects of xylene have shown no adverse effects on the prostate and testes or ovaries, uterus or mammary glands in the female.

5.2 GENOTOXICITY/MUTAGENICITY/CARCINOGENICITY:

Genotoxicity studies on mixed xylenes have proved consistently negative. No studies were reported concerning genotoxic effects in humans after oral exposure and similarly no data were located regarding the development of cancer in humans following oral exposure to mixed xylenes. Beyond this, the results of chronic oral administration of mixed xylenes to rats have been negative or equivocal. No definite conclusions can be drawn regarding the carcinogenicity of mixed xylenes in animals or humans.

5.3 BIOMARKERS OF EXPOSURE:

Xylene levels in the blood and its major metabolite, methylhippuric acid, are the primary biomarkers of exposure to the xylenes. Excretion of methylhippuric acid is usually complete within a day or two of exposure to xylenes. Their rapid metabolism tends to prevent bioaccumulation of xylenes.

5.4 SUSCEPTIBLE POPULATIONS:

Pregnant women, fetuses and very young children may be unusually susceptible to the effects of xylene. Additionally, people prone to epileptic seizures are at increased risk of seizures due to its excitatory CNS effects. Similarly, people with subclinical or clinical renal, hepatic or cardiac disease may be more susceptible to the effects of xylene.

5.5 ENVIRONMENTAL FATE:

Xylenes are highly volatile and volatilization is the dominant transport system for xylene. Once in the atmosphere the major transformation system is photo-oxidation by hydroxyl radicals. In soil, xylenes are relatively mobile and may leach into ground water depending on soil conditions. Bioconcentration of xylenes has been reported but is not thought to be significant. In soils and water xylenes tend to be strongly adsorbed to organic matter.

5.6 ENVIRONMENTAL LEVELS:

AIR: The largest source of xylene release into the atmosphere comes from auto emissions and as such atmospheric concentrations of xylene are related to urbanization. Xylene is also a contaminant of indoor air, where concentrations are higher than in outdoor air, indicating that contamination comes from building materials or household products.

5.7 WATER: The presence of xylenes in surface water is considered unlikely in view of its volatility. Xylene concentrations are generally less than 1 ppb unless the water is drawn close to a xylene sources. Typical concentrations range from 1-30 ppb, with occasional higher levels.

5.8 SOIL: Little data is available on xylene measurements in soil. Samples from waste disposal sites show mean concentrations of 8,388 ppm, and xylene was the second most prevalent organic chemical and has the third highest reported maximum concentration.

6.0 TOXICOLOGY OF MTBE:

Methyl-tetiary-butyl-ether (MTBE) is a colorless flammable liquid which was approved by the US EPA in 1979 for use as an octane booster in concentratios up to ll percent. MTBE is used in US gasolines to increase the oxygen content of the fuel in order to lower carbon monoxide and other hydrocarbon emissins.

MTBE is low in acute toxicity in humans via ingetion, skin absorption, and inhalation. Some effects seen at high acute exposures have included an anesthetic effect, sweating, decreased heart rate, irritation of the eye and mucous membranes, nausea, vomiting, and labored breathing. These effects disappear after cessation of exposure. Chronic exposure tudies in animals have shown similar effects, as well as decreased rate of body weight gain, and variatios in organ weights and clinical chemistry values. Some central nervous system effects have also been seen at high doses.

In animal students, it has been shwon that MTBE is absorbed rapidly in to the body and is eliminated completely (via air and in urine primarily) and rapidly, without regard to the route of exposure (Duffy, 1990). MTBE inhalation by rats results in little adverse reproductivity toxicity as shown in a 2 litter, one generation reproductivity assay in rats (Biles, 1987).

The LD_{50} oral dose for a rat is 3.8 g/Kg. The LD_{50} for percutaneous dose to a rabbit is more than 10 ml/kg. Reported LC_{50} for rats exposed 4 hours by inhalation was 85 g/m^3 (Patty, 1983).

Two lifetime cancer studies have been performed, one with mice and one with rats. In each study the animals were exposed via inhalation to 0, 400, 3000, or 8000 ppm MTBE for 6 hours per day, 5 days per week for either 18 months (mice) and 24 months (rat). Two statistically significant findings included: 1) an increase in liver tumors in mice exposed to 8000 ppm and 2) severe kidney disease in male rats exposed to 3000 and 8000 ppm. Females did not experience a significant incidence of treatment related liver tumors. It is unlikely that long term chronic exposure of humans would occur at levels anywhere like this. As well, it is known that kidney disease of this type in the male rats naturally occurs in old male rats. Therefore, this toxicity would not be directly relevant to humans.

The RfC for MTBE is set at .05mg/m^3 (IRIS, 1993). It is based on a study in which rats were exposed via inhalation to 800, 4000, and 8000 ppm for 6 hrs/day 5 days/week for 13 weeks. 800 ppm is the no adverse effect level.

7.0 TOXICOLOGY OF LEAD:

Lead is a dense bluish white metal and it is considered to be the ubiquitous toxic metal in the environment and in biological systems. There is no known biological need for lead, so the major issue is at what point it becomes toxic. The most susceptible populations are those in utero and young children, with contaminated dust a major route of exposure.

Until recently lead, in the form of tetraethyl lead, was added to gasoline as an anti-knock compound. Lead is also found incidentally in diesel fuel and it is also a component of storage batteries.

In the soil lead tends to form complexes with naturally occurring organic materials and these complexes become absorbed to clays and other mineral surfaces. At low pH values lead is less tightly bound to clays and other surfaces and as such lead is much more soluble and thus more mobile in acidic than in alkaline waters. Based on these factors lead is considered 20 to 200 times more toxic in soft than hard waters.

In aquatic environments most lead is found in bottom sediments and is therefore of primary concern to bottom dwelling organisms. The toxicity of lead is dependent on pH, organic materials, and the presence/absence of other metals. Lead may therefore be removed more readily from alkaline and neutral waters by sorption and precipitation.

Lead is not destroyed by any biotic or abiotic process, so its effective half-life is its half-life of removal. Its half-life in groundwater is estimated at 2-8 weeks, in soil 1-4 weeks and for surface water and air at about 2.3 to 9 hours. Additionally, bioaccumulation may also contribute to its removal from the environment.

Lead accumulates in animal tissues but has low potential for biomagnification through the food chain. In humans lead is found in blood and is stored in bones, kidney and the liver. Physiological and biochemical effects occur at low levels of exposure and include cognitive dysfunction in infants, reduced childhood growth, and interference with vitamin D metabolism. USEPA has recently classified lead as Group B2 probable human carcinogen (USEPA,1991). For risk analysis, oral reference doses are listed on Table I.

TABLE I: HEALTH EFFECTS ASSESSMENTS SUMMARY TABLE A: SUBCHRONIC AND CHRONIC TOXICITY OTHER THAN CARCINOGENICITY)

Update: December, 1990

	Exposure	Species		Effect of Concern	Inhalation RfC	Oral RfD	Uncertainty Factor	
Compound	Inhalation; Oral	Inhalation	Oral	Inhalation; Oral	[mg/m^3 (mg/kg/day)]	(mg/kg/day)	Inhalation	Oral
Lead alkyls: tetrabutyl, tetrawethyl, tetramethyl, tetrapropyl, triethyl, trimethyl, tripropyl, trimethyle thyl, dimethylethyl, methyltriethyl								
subchronic	NA; 0.00017 mg/kg/day by gavage for 20 weeks	NA	rat	NA; liver and neuronal damage	ND	1E-6	NA	1000
chronic	NA; 0.00017 mg/kg/day by gavage for 20 weeks	NA	rat	NA; liver and neuronal damage	ND	1E-7	NA	10,000

(EPA Health Effects Assessment Summary Tables, FY 1991, Annual, Page A-48)

8.0 TOXICOLOGY OF DIESEL FUEL:

Diesel fuel is a gas oil fraction from the middle distillate in petroleum. (Napthas for solvents being high distillates and gas oil for residual fuel oil being low distillates). Diesel is available in various grades as required by different engine types. Compositions vary in ratios of predominately aliphatic, olefinic, cycloparafinnic, and aromatic hydrocarbons, as well as appropriate additives.

Diesel fuel is used in engines that require a low viscosity and moderate volatility. The heaviest grades are used in marine and railroad engines. The characteristics of the fuel are determined by the constituents present in the crude petroleum, weather conditions, and processing technologies. Great variations between batches of the fuel exist because of the differences in the ratios of aliphatic, olefinic, cycloparaffinic, and aromatic hydrocarbons in the crude. A number of constituents are common to diesel fuel. These include benzene, ethylbenzene, toluene, xylene, napthalene, ethylcyclohexane, n-heptane, n-octane, n-nonane, decane, and other isomers. Polycyclic aromatic hydrocarbons (PAHs) are the constituents of concern in diesel and the health risks associated with exposure to PAHs are presented in the next section.

9.0 TOXICOLOGY OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs):

This material is summarized from the U.S. Department of Commerce, NTIS National Technical Information Services, Polynuclear Aromatic Hydrocarbons, PB-91, 181-537, Dec. 90 and Patty's Industrial Hygiene and Toxicology, Aromatic Hydrocarbons, 1981. Polycyclic aromatic hydrocarbons (PAHs) are a group of chemicals formed during the incomplete combustion of organic materials including coal, oil and garbage. They are stable and can last in the environment for months or years. Background levels of PAHs in drinking water are between 4-24 ppt and between 1 and 20 mg/m^3 in rural and urban air. Greatest exposure to PAHs occurs in the workplace, and also in areas where petroleum products are burned.

PAHs are released to the environment through natural and man made sources with emissions largely to the atmosphere. Natural sources include emissions from volcanos and forest fires. Man-made sources provide a much greater release volume than natural sources: the single largest source is the burning of wood in homes. Automobile and truck emissions are also major sources of PAHs. In air, PAHs are found sorbed to particulate and gases. In soil, microbial metabolism is the major process for degradation of PAHs. Although PAHs are accumulated in aquatic plants, fish, and invertebrates, many animals, including humans, are able to metabolize and eliminate these compounds.

PAHs have certain chemical and physical properties in common, such as stability, low solubility in water, and low vapor pressure. They tend to be stable in the environment and to bind in to dust particles in air and sediments in water. Over 100 different PAHs have been identified and they are generally found in nature as mixtures of two or more PAHs.

9.1 ROUTES OF ENTRY:

PAHs enter the body by all routes of exposure, distribute to fatty tissues and are readily metabolized and eliminated. Little data is available concerning absorption by different routes of exposure in humans. Inhalation exposure studies in animals show rapid clearance of benzo(a)pyrene introduced into the lungs. About 80% of a dose of chrysene administered orally to rats was eliminated in the feces. Dermal exposure studies suggest that about 20% of a dose of anthracene was eliminated in the urine and feces. The average total daily intake of PAHs by a member of the population has been estimated to be .207 ug from air, .027 ug from water and .16-1.6 ug from food.

9.2 GENOTOXICITY/CARCINOGENICITY:

Several of the PAHs including benz(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, chrysene, dibenz(a,h) anthracene, indeno(1,2,3,-cd)pyrene are genotoxic. Genotoxicity of the PAHs usually requires the presence of a mammalian metabolic activation system. PAHs have caused tumors in laboratory animals. Humans exposed for long periods to mixtures of PAHs have been shown to develop cancers. Laboratory animals fed high concentrations of benzo(a)pyrene (BaP) showed birth defects and decreased body weight but no information is available as to whether these effects occur in humans.

BaP is the smallest and therefore most easily synthesized unsubstituted polycyclic aromatic hydrocarbon that will produce tumors. BaP in contact with skin is absorbed into the metabolically active epidermis and converted to metabolities which produce the tumors. In a study by Wester et al (1991), it was found that BaP readily penetrated human skin when applied using an acetone vehicle. However significantly less BaP penetrated human skin from soil. The study concludes that BaP from soil is about 25% of that from vehicles such as acetone.

9.3 RELEVANCE TO PUBLIC HEALTH:

PAHs occur ubiquitously in the environment as a result of input from fossil fuels, tobacco smoke and industrial processes. Certain PAHs are known to be carcinogenic in humans from occupational studies. The site of tumor formation is influenced by the site of entry. Oral administration is associated with stomach tumors, dermal exposure with skin cancer and lung tumors follow inhalation exposure. PAHs tend to attack proliferating tissues such as bone marrow, lymph nodes and the intestinal epithelium. The carcinogenic members of this group markedly suppress the immune system and the degree of immunosuppression correlates with their carcinogenicity. Exposure of pregnant animals to benzo(a)pyrene produced resorbtions and malformations of fetuses. No information is available from human studies to determine the health effects of exposure to specific levels of individual PAHs, although exposure to mixtures of PAHs is known to be associated with cancer in humans.

9.4 POTENTIAL FOR HUMAN EXPOSURE:

Airborne PAHs come from residential burning of wood, automobile exhaust, incinerators, etc. Natural sources are forest fires and volcanoes. Deposition of PAHs from the air is the major source of PAHs in water, although for any given location the PAH source will vary. Similarly, PAHs in soil are considered to result from atmospheric deposition. In general, PAHs released from the atmosphere are transported and can volatilize, photodegrade, oxidize, biodegrade or bioaccumlate in plants or animals.

Low volatility PAHs are found adsorbed to particles that tend to sediment in aqueous systems. The K_{oc}'s of PAHs indicates the chemical's potential to bind to organic carbon. K_{oc}'s relate to molecular weight. The higher molecular weight PAHs have K_{oc} values in the range of 10^5 to 10^6, which indicated strong tendencies to adsorb to organic carbon. PAHs accumulate in aquatic organisms, with bioconcentration factors in the range of 100 to 2,000, with the formation and bioconcentration of genotoxic and mutagenic intermediates. However, because fish can metabolize PAHs they may be present in fish only at low levels despite high levels of environmental contamination.

In soil microbial metabolism is the major process for degradation of PAHs. Microbial degradation pathways are well known for anthracene, benzo(a)pyrene and phenanthrene, but the degradation pathways for other PAHs are largely unknown. PAH breakdown in soil is greatly affected by soil type, pH, moisture content, nutrients and the presence of other substrates that may act as co-metabolites. PAHs are ubiquitous in soil, with concentrations higher in urban than agricultural and rural soil, probably as a result of automobile emissions.

PAH concentrations in drinking water vary from about 5 ng/L in Buffalo to 600 ng/L in Pittsburgh. Higher levels are found in urban and industrial runoff, and the higher concentrations are likely to be found in sediments.

9.5 REGULATORY LEVELS FOR PAHs

NIOSH has recommended an occupational limit of 0.1mg of PAHs/m^3 for a 10 hour day/40hour work week. OSHA has established an enforceable limit of 0.2mg/m^3 of all PAHs.

10.0 TOXICOLOGY OF SELECTED DIESEL CONSTITUENTS:

The following is a list of the seven most prevalent aromatic compounds in diesel fuel (unpublished data, Ashland Oil, 1993).

Compound	PPM
Acenaphthene	120
Anthracene	48
Fluorene	144
Napthalene (weight %)	0.02
Phenathrene	520
Pyrene	40
2-Methylnapthalene (weight %)	0.44

To a lesser extent the following compounds are also present in diesel (Millner, Nye, James, 1992). Compounds with concentrations less than 1 ppm are not included here.

Compound	PPM
Benz(a)anthracene	1.2
Chrysene	2.2
Triphenylene	1.4
Benza(a)pyrene	.6

The following is a brief toxicological profile on each of these compounds.

Acenaphthene

Acenaphthene occurs in petroleum products as well as insecticides, fungicides and in the manufacturing of plastics (Clayton, 1981). Physiologic effects include irritation to the skin and mucous membranes.

Acenaphthene at 2 g/kg body weight administered orally in olive oil to 7 young rats daily for 32 days caused loss of body weight, changes in peripheral blood, and mild morphological damage to both the liver and kidney. After 32 days of treatment, the animals showed mild bronchitis and localized inflammation of the peribronchial tissues. Acenapthene administered to a mouse by gavage at 175 mg/kg/day resulted in hepatotoxic effects.

One hundred rats were exposed for 5 months to acenaphthene at a level of 12 mg/cubic meter for 4 hours a day, 6 days a week. Toxic effects on the blood, lung and glandular constituents were observed. The bronchial epithelium showed hyperplasia and metaplasia. No signs of malignancy appeared during the 8 month post-exposure observation period (USEPA, 1990). Acenapthene has not been studied extensively as a dermal toxicant.

Acenapthene has been studied as an aquatic toxicant. The 96 hour median lethal concentration (LC) for flathead minnows was 608 ug/L. The no effect level for early life stages exposures were 413 ug/L (Cairns, 1982). Acute toxicity tests were conducted for acenapthene using brown trout. The acute toxicity value was 580 ug/L. The LC for bluegill in a static bioassay was 1700 ug/L for 96 hours. The LC_{50} for flathead minnows was 1700 ug/L for 96 hours (USEPA, 1980). The half life of acenapthene in bluegill was found to be less than 1 day. Acenapthene has been shown to be non-mutagenic in salmonella typhimurium using 0.10, 100, and 250 ug/ML.

The RfD for chronic exposure is .06 mg/kg/day (EPA, 1991).

Anthracene

Anthracene is the simplest tricyclic aromatic compound. Anthracene occurs in coal tar naphtha and is used in the preparation of anthraquinone and fluorescent dyes. Anthracene asserts a phototoxic and photoallergic action on human skin (Clayton, 1981). This has been observed in workers occupied in coal tar and pitch processing. Coal tar fumes containing mainly anthracene and phenanthrene used in field roofing operations produce aerosol droplets that can be inhaled.

Anthracene is photosensitizing (Alred and Giesy 1985). It can cause acute dermatitis with symptoms of burning, itching, and edema which are more pronounced in the exposed bare skin regions. Skin damage is associated with irritation of the conjunctiva and upper airways. The acute symptoms disappear within several days after cessation of contact (ILO, 1983). Prolonged exposure gives rise to pigmentation of the bare skin regions and cornification of it's surface layers. A dose response relationship in a study by Allred and Giesy, showed that solar radiation is related to the toxic effects of anthracene in Daphnia. (Allred and Giesy, 1985).

Intragastric administration of pure anthracene does not cause animals to die after a single dose administration of the maximum possible dose of 17 g/kg. Repeated poisoning of albino rats gives rise to a decrease in hemoglobin, leukopenia and increase in residual blood nitrogen. (ILO, 1983). After subcutaneous administration of 20 mg anthracene per day of 33 weeks, five of nine animals surviving more than 17 months developed fibromas and sarcomas in the region of injection. In the rat .5 mg, when injected subcutaneously, decreased the antioxidative activity of the pancreas during the 25 days after injection. The pancreatic insular cells showed increases in the cell, nucleus and nucleolus size (Clayton, 1981).

Chronic inhalation of anthracene aerosol in concentrations of .05 and .01 mg/L is associated with a reduced gain in body weight and a decrease in hemoglobin and leukopenia in albino rats (ILO, 1983).

Anthracene at 1000 ug/ml for 20 hours produced very little effect on chinese hamster ovary cell cultures (Garrett and Lewtas, 1983). Anthracene showed no mutagenic activity in salmonella typhimurium and showed no carcinogenic activity in swiss albino mice.

A significant increase in the formation of non-neoplastic melanotic tumors was observed among first and second generation progeny of Drosophila melanogaster that had been exposed chronically as larvae to low concentrations of anthracene. In one study it was concluded that anthracene solubilized with detergents could induce autosomal dominant melanotic tumors (Corwin and Gottlieb 1978).

Acute mortality of blue gill sunfish dosed with anthracene at 12.7 ug/L and exposed to sunlight was observed during a study of anthracene fate in outdoor channel microcosms (Bowling, 1983).

Five normal adult volunteers without cutaneous disease applied 2% crude tar to the skin for 8 hour periods on 2 consecutive days. Blood extracts subjected to GC/MS yielded evidence of absorption in all 5 volunteers. Phenanthrene, *anthracene*, pyrene and fluoranthene were found in 4 of the volunteers (Storer, 1984).

The chronic oral RfD for anthracene is .3 mg/kg/day (USEPA, 1991).

Fluorene

Fluorene is highly soluble in adipose tissue and lipids (Sittig, 1981). Static toxicity tests were conducted with fluorene on daphnids, amphipods, snails, may flies, bluegill, rainbow trout, flat head minnows and green algae. Daphnids were the most sensitive organism tested with a 48 hour median effective concentration of .42 mg/L. Flat head minnows were least sensitive with no mortality at fluorene concentrations as high as 100 mg/L. In a 14 day test, fluorene exposure inhibited algae production at a threshold level of 3.0 mg/L. Daphnid reproduction was significantly reduced at fluorene levels of .125 mg/L after 14 days (Finger, 1985).

Fluorene is inactive as a tumor initiator. No increase in tumor incidence when mice were given a single dose of fluorene (USDHHS, 1990). At 125 mg/kg/day, gavage administration to a mouse resulted in a decreased red blood cell count.

No data are available in humans. There is inadequate evidence of carcinogenicity in animals. Fluorene is not classifiable as to its carcinogenicity in humans (IARC, 1987). The oral RfD is .04 mg/kg/day for chronic exposure (USEPA, 1991).

Naphthalene

Naphthalene occurs in crude oil and is isolated from cracked petroleum. In both solid and liquid, it is flammable. It is used extensively in the chemical, plastics and dye industries, as a moth repellent and air freshener. It is used in the manufacturing of insecticides, fungicides, lacquers, and varnishes, and to preserve wood (Clayton, 1981).

Naphthalene has been studied in both human and animal subjects. Poisoning from naphthalene may occur by ingestion of large doses, or skin absorption (Budavari, 1989). Naphthalene is considered to be non-sensitizing (Papciak, 1990).

Naphthalene vapors may cause eye and respiratory tract irritation, headaches, and nausea. Optic neuritis has been observed. Corneal ulcerations and cataracts have been observed from vapor exposure.

Ingestion of naphthalene can cause abdominal cramps with nausea, vomiting, diarrhea, headaches, profuse perspiration, listlessness and confusion. In severe poisoning coma can result. It causes irritation to the urinary bladder (Gosselin, 1984).

On repeated contact, naphthalene may cause erythema and dermatitis especially in hypersensitive individuals (Clayton, 1981). Naphthalene cataracts and ocular irritation from direct contact have been noted. Skin irritation results from contact. However, lesions clear spontaneously as soon as exposure is terminated. Percutaneous absorption is inadequate to produce acute systemic reactions except in newborns (Gosselin, 1984). Toxicity and death have been reported in newborn infants exposed to naphthalene vapors from clothes or blankets that had been stored in moth balls (USEPA ODW, 1990).

Oral administration of 1 g/kg/day to rabbits leads to ventricular changes within 2 weeks and the development of cataracts (Amdur, 1991).

No carcinogenic activity was observed in an in-vitro rat embryo cell with doses up to .1 g/L (USEPA ODW 1990). Naphthalene was tested for mutagenicity in the salmonella assay where it was determined to be negative (Garner, Stanton, and Martin, 1986). Very large doses (5925 mg/kg) given to rats intraperitoneally over days 1-15 of pregnancy caused structural abnormalities. Dogs administered 420 and 1530 mg/kg naphthalene in solid form in a single oral dose showed decreases of 29 and 33% respectively in blood hemoglobin concentrations (USEPA ODW 1990).

The LD_{50} oral dose for a mouse is 533 mg/kg. The LD_{50} oral dose for a rat is 1780 mg/kg. The chronic oral RfD for naphthalene is .004 mg/kg/day (USEPA 1991).

Phenanthrene

Phenanthrene has been identified as a mild allergen and human dermal photosensitizer. Limited acute and chronic animal experiments show that phenathrene is of moderate to low toxicity and when dermally applied was weakly neoplastic (Clayton, 1981).

In a study of mammary tumor induction, single oral doses of 200 mg phenanthrene dissolved in sesame oil were administered to 10 female rats 50 days old. No tumors were produced in 60 days (IARC, 1983).

A group of 40 mice were injected subcutaneously in the interscapular region with 5 mg phenanthrene. Twenty seven mice survived 4 months. No local tumors were observed. A group of 20 mice received 10 applications of .3 ml of an 18% solution of phenanthrene in acetone 3 times weekly on the back. Five of the 20 surviving animals were observed to have 12 benign tumors (IARC, 1983). Phenanthrene at 150 mg/kg dissolved in dimethyl sulfoxide given to rats produced an elevation of serum aspartate and aminotransferance 24 hours after injection

(Yoshikama, 1985). Intraperitoneal and single dose subcutaneous administration of Phenanthrene to a mouse resulted in no increase in tumor incidence (USDHHS, 1990).

There is inadequate evidence of carcinogenicity in animals. There are no human data. It is unclassifiable as to its carcinogenicity to humans (IARC, 1983). Phenanthrene was ineffective as an initiator and also was inactive as a tumor promotor (USDHHS, 1990). There is inadequate data available on phenanthrene for a quantitative risk assessment (no RfD).

Pyrene

Pyrene is a colorless solid, soluble in organic solvents (Clayton, 1981). Pyrene is also strongly photo-toxic (Kochevar, 1982).

Rats given oral doses at near the LD_{50} succumbed in 2-5 days (Clayton, 1981). The LD_{50} for rats is 2700 mg/kg (CHEMINFO,1993) Mice given 75 mg/kg/day by garage for 14 weeks had minor renal effects (USEPA, 1991). Pyrene is poorly absorbed via ingestion.

Cutaneous applications on mice for 10 days caused hyperemia, weight loss, and hemopoietic changes. Application for 30 days produced dermatitis. An application of 10 g/kg on mouse skin was of low toxicity (Clayton, 1981). Mice chronically administered 10 % pyrene solution did not develop tumors (USDHHS, 1990).

The median threshold limit for mosquito fish was .0026 mg/L/96 hours in static bioassay (Verschuerin, 1983).

Inhalation caused hepatic, pulmonary and nasogastric pathogenic changes. The number of neutrophils, leukocytes and erythrocytes decreased. There is fairly rapid absorption by inhalation and skin contact. Absorbed pyrene is broken down in the body and excreted (Clayton, 1981). Chronic exposure to pyrene is likely to result in liver, kidney and lung injury and damage to the blood system. However, no human information is available.

No information is available on the carcinogenic risk of pyrene to humans. It is not classifiable by IARC (IARC, 1983). There is no human data on reproductive toxicity and mutagenicity. However, it is considered generally non-mutagenic in short term in-vitro and in-vivo assays in bacterial cells, yeast, insects, and mammalian cells in culture (CHEMINFO, 1993). Pyrene has been shown to be inactive as an initiator (USDHHS, 1990). The oral RfD for chronic exposure is .003 mg/kg/day (USEPA; 1991).

2-Methylnapthalene

2-methylnapthalene, has not been extensively studied for its toxic properties. The LD_{100} was 5 ml/kg administered orally to a rat.

Methylnapthalene in the 1 or 2 isomer form is used as a component in slow release insecticides and mole repellent. Methylnapthalenes are not a human skin irritant or photosensitizer. Intraperitoneal injection of the 1-methyl derivative was about 4 times less lethal to rats than napthalene and the 2-methyl derivative showed no effect (Clayton, 1981).

Benz(a)anthracene

Benz(a)anthracene occurs in crude oil, coal tar, and flue dust, and as a pyrolysis in tobacco smoke and coal derived products. In comparison to anthracene, benz(a)anthracene appears more highly toxic but less so than phenanthrene by dermal or subcutaneous route (Clayton, 1981).

Studies in laboratory animals have demonstrated the ability of benz(a)anthracene to induce skin tumors following intermediate dermal exposure (USDHHS, 1990). Topically applied graded concentrations of benz(a)anthracene in toluene to the backs of mice for 50 weeks resulted in dose-related increases in tumor incidence (USDHHS, 1990). Malignant tumors were observed at dose levels of about .02% benz(a)anthracene (.15 mg/kg/day).

Experiments using crushed paraffin wax as a vehicle for bladder implantation were carried out on mice. With this technique about 2 mg benz(a)anthracene induced 17 carcinomas and 1 papilloma in the bladders of 52 mice surviving 40 or more weeks (IARC, 1983).

Single injections of 50 ug in 1% aqueous gelatine to newborn and 2 to 8 day old mice induced pulmonary adenomas and adenocarcinomas. Twenty rats received subcutaneous injections of 1.9 mg benz(a)anthracene in tricaprylin. All the rats were alive for 4 month. Nine were alive after 14.5 months (IARC, 1983).

Twenty five rats painted daily for 5 months with a saturate solution of benz(a)anthracene in acetone experienced no tumor development in 9 of the surviving rats after 18 months (IARC, 1983). Ten hamsters received bi-weekly paintings with .05% benz(a)anthracene in mineral oil for 10 weeks. Six animals were surviving at 50 weeks and the last animal died at 85 weeks. No tumors were reported (IARC, 1983). It was found that benz(a)anthracene was effective in causing chromosomal aberrations in cultured hamster cells without any exogenous metabolic activation.

Extracts of typewriter ribbons and carbon papers were mutagenic in salmonella typhimurium microsome assay. Fractionation of ribbon extracts indicated that at least 2-3 difference classes of mutagenic components are present in these extracts. One was benz(a)anthracene at 5.5 mg/sheet (Moeller, 1983).

There is sufficient evidence of carcinogenicity in animals. No human information is available as to mutagenicity, teratogenicity, or reproductive toxicity (CHEMINFO, 1993). IARC classifies benz(a)anthracene into group 2A: probably carcinogenic to humans. There is no RfD available for benz(a)anthracene (USEPA, 1991).

Chrysene

Chrysene can be isolated from crude petroleum and coal tar. It occurs in cigarette smoke and has been detected at low levels in community air (Clayton, 1981). Chrysene exerts low toxicity orally, dermally, to the eye and by inhalation.

Chrysene has elicited skin tumors following chronic (68-82 weeks) dermal exposure to mice. Dermal application of 100 mg chrysene in acetone to the shaved backs of mice resulted in both papillomas and carcinomas (Hecht, Bondinell and Huffman, 1974). The lack of dermal carcinogenicity of acetone has been well established. An average dose of 1.2 mg/kg/day is the lowest dose of chrysene that has been found to elicit malignant tumors in laboratory animals. Chrysene is on the list of chemicals potentially carcinogenic to humans published by the Human Health Assessment Group of U. S. EPA.

Chrysene has been implicated as an etiologic determinant of chemical carcinogenesis. The ability of chrysene to induce aryl hydrocarbon hydroxylase in cultured human lymphocytes has been described. A significant increase in enzyme induction occurred in the chrysene induced cultures compared with controls (Snodgrass, 1979).

Mice were painted with synthetic chrysene as a .3% concentration in benzene twice weekly. Five of 20 mice lived longer than 440 days and 1 developed a papilloma in 771 days. One epithelioma was induced among 16 mice surviving after 31 weeks of biweekly painting with .2% solution in acetone (IARC, 1973). Among 20 female mice painted 3 times weekly with 1% solution of chrysene in acetone, papillomas appeared in 9 animals and carcinomas in 8. There was an obvious shortening of the mouse life span (IARC, 1973).

One subcutaneous injection of 2 mg purified chrysene did not produce sarcomas among 50 mice observed for 45 weeks. Similarly two subcutaneous implantation of 10 mg each to 30 mice gave negative results (IARC, 1973).

Using the salmonella microsome test, no mutagenic activity was found when chrysene alone was tested. Chrysene, 450 mg/kg suspended in gum arabic was given to hamsters by oral, garage and intraperitoneal administration, the results showed no mutagenic effects (Basler, 1977).

Toxicity assessment on fetal lung cells of hamsters showed chrysene to be neither a stimulatory nor inhibitory to colony formation (Emura, 1982). The LD_{50} for a mouse by intraperitoneal injection was greater than 320 mg/kg (IARC, 1983).

There are inadequate data for quantitative risk assessment of chrysene. There are no RfDs. Chrysene is classified by the EPA as a group 2B- sufficient evidence of carcinogenicity in animals with inadequate or lack of evidence in humans.

Triphenylene

The information on triphenylene is very limited. Triphenylene almost never occurs in pure form. It is not commercially manufactured. It is present in fuels, coal tar, motor vehicle exhaust and cigarette smoke (IARC, 1983). Triphenylene dusts and fumes may cause irritation of the nose, throat, and chest, accompanied by dizziness, nausea, headache, weakness and loss of appetite. No information is available on triphenylene but these symptoms have resulted from inhalation of other PAHs such as anthracene. Vapor exposure to triphenylene and other PAHs is negligible (CHEMINFO, 1993).

There is no human or animal information on terategonicity or reproductive toxicity. Triphenylene was mutagenic in short-term assays using bacterial cells and cultured human white blood cells (IARC, 1983). Triphenylene is readily absorbed by ingestion and stored in fatty tissues where it is slowly released, broken down in the body and excreted (Bartosek, 1984).

Mice treated by skin application of .3% and .5% solutions of triphenylene in hydrocarbon solvents such as benzene or a mixture of decalin and dodecane did not have significantly increased incidence of skin tumors (IARC, 1983).

There is inadequate evidence to evaluate triphenylene as a carcinogen (IARC, 1983). There are no RfDs.

Benzo(a)pyrene BaP

BaP occurs naturally in crude oils, shale oils, and coal tours. It is also emitted with gases and fly ash from volcanos. Cigarette smoke and tar contain up to .1 percent BaP. In a 20 cubic meter area where 2 person smoked, a concentration of 9.7 to 11.1 ng/m^3 BaP were detected (Clayton, 1981). Residual energy production in coal and wood furnaces account for the greatest addition of BaP to the atmosphere. Concentrations in soil are proportional to concentrations in the atmosphere. From soil, migration into plants can occur although BaP is degradable by some soil microorganisms.

Intraparatoreal administration of single doses of 10 mg BaP produced immediate and sustained reduction in growth rate of young rats (IARC, 1983). The effects of BaP on stratification of epithelium in organ clusters of rat trachea and stratification of epithelium have been reported (Crocker, 1965)(Dirksen and Crocker, 1968). Consistent findings in rat trachea were suppression of mesenchyme, stimulation of basal-cell replication and induction of metaplasia.

A single topical application of .05 ml of 1% solution of BaP in acetone to the interscapular area of hairless mice induced an increase in the mitotic rate of epidermal cells (Elgjo, 1968). Twice weekly painting with .3% solution BaP in Benzene for 400 days produced 1 carcinoma and 10 papillomas among 10 rabbits. Results of this study have been confirmed repeatedly (IARC, 1983).

No stomach tumors were found at the end of 110 day treatment with diets containing up to 30 ppm BaP. Tumor incidence lower than 10% were observed in mice receiving 40-50 ppm for 110 days, where as mice bearing stomach tumors exceeded 70% among those given 50-250 ppm BaP for 122-197 days (IARC, 1983).

Single intragastric administration of .2 mg/mouse in polyethylene glycol produced a total of 14 tumors per mouse in the forestomach in 5 of 11 animals. Tumors appeared following single doses of .05 and .012 mg/mouse. Diet containing 250 ppm BaP fed for different periods of time produced the following incidence of tumors of forestomach. One day of feeding 0%, 2-4 days of feeding 10%, 5-7 days of feeding 30-40%, 30 days of feeding 100% (Neal and Rigdonm 1967). In subsequent experiments diet containing 250 ppm fed 140 days to mice provided leukomias and lung adenomas in addition to a stomach tumors (Neal, Rigdon, 1969).

Weekly IP injections of 2 mg BaP to 80 mice induced abdominal fibrosarcomas in 82% of 40 females and 73% of 40 males with an average latency period of 33 weeks (IARC, 1983). Single IP administration of 10 mg BaP produced 2 mammary and 2 uterine carcinomas among 10 rats within 1 year (IARC, 1983). IP administration of 100-150 mg/kg body weight to mice in mid or late pregnancy results in marked and persistent suppression of the immune system in the offspring (Urso, Gengozian, 1980).

Benzo(a)pyrene and Human Health

BaP dust and fumes may cause irritation of the nose, throat and upper respiratory system, accompanied by dizziness, nausea, headache and weakness. Very high doses may cause respiratory collapse. There is practically no exposure to the vapor of BaP and related pahs because of their extremely low vapor pressure.

BaP dust and solutions may be mildly irritating to the skin. Like other PAHs BaP is photosensitizing. BaP is mildly irritating to the eyes. Ingestion may cause irritation to the upper digestive tract.

Based on animal studies, the induction of cancer appears to be the day and point of toxicity following long term exposure to BaP. Long-term exposure may also cause injury to the liver, kidneys, blood and lymph systems.

BaP is classed B2 (probably carcinogenic to humans). The LD50 intraperitoneal administration to a mouse is 250 mg/kg. Subcutaneous LD50 rat is 50 mg/kg. Benzopyrene has shown low acute oral and dermal toxicity to animals (CHEMINFO, 1993). The oral slope factor is 7.3 mg/kg/day (IRIS, 1993).

TABLE II

EXPOSURE LIMITS FOR SELECTED PETROLEUM COMPOUNDS

AGENT	AGENCY	EXPOSURE LIMIT
Benzene	NIOSH	0.1 ppm air
Benzene	OSHA	1.0 ppm 8 hr work day air
Benzene	EPA	5 ppb drinking water
PAHs	NIOSH	0.1 mg/m^3 10hr day/40hr week
PAHs	OSHA	0.2 mg/m^3
Xylene	EPA (Proposed)	0.44 ppm drinking water
Xylene	NIOSH	100 ppm, 10hr day/40hr week

American Conference of Governmental and Industrial Hygienists
(ACGIH) Occupational Exposure Limits Based on 8 Hours/Day 40 Hour Work Week

	PPM	mg/m^3
nButane	800	1900
Ethylene Dichloride	10	40
n-Heptane	400	1640
Cyclopentane	600	1720
Methylcyclohexane	400	1610
1,3,5-Trimethylbenzene	25	123
Napthalene	10	52
Biphenyl	0.2	1.3
Fluorene	1.0	1.6

ACGIH evaluates chemical compounds for their harmful effects on humans in the work place. Maximum exposures are set based on the level of a contaminant known to produce acute effects, allowing some margin for safety of sensitive workers. The limits do not protect against long term or subclinical effects on the body such as changes in blood chemistry, liver function, or the reaction time of the central nervous system.

Threshold limit value (TLVs) refer to airborne concentrations of substances and represent conditions under which it is believed that nearly all workers may be repeatedly exposed day after day without adverse health effects.

TLVs are based on the best available information from industrial experience, from experimental human and animal studies, and, when possible, from a combination of the three. The amount and nature of the information available for establishing a TLV varies form substance to substance.

SUMMARY OF ANALYTICAL METHODS

T. Struttmann

INTRODUCTION

The selection of analytical methods for addressing problems associated with leaking underground storage tanks (LUSTS) is complicated by such variables as the nature of the matrix containing the sample and the nature of leaked material itself which may or may not be established at the time of initial detection. Moreover, even when the nature of the leaked material is established, the composition of commercial petroleum products is known to fluctuate widely (Wixtrom and Brown 1992). Gasoline can have over 1200 individual hydrocarbon compounds (Domask, 1984). Measuring for total petroleum hydrocarbons (TPH), which assesses the volatile organic compounds (VOCs), can be used for both gasoline and diesel fuel, but is not without problems. It may not fully discriminate between indigenous organic compounds and petroleum products. TPH will be addressed in section 3.0. Gasoline, with a high volatility, and diesel fuel, with a relatively low volatility, require somewhat different methods of analysis. Several chemical classes may be represented including paraffins, olefin, aromatics, hetroaromatics, and polar hydrocarbons containing oxygen, nitrogen and sulfur (Sanders and Magnard, 1968). Product from three matrices, water, soil and air, require different preparation methods. Further, the relative composition of such mixtures changes with time through volatilization, dissolution, biotic and abiotic degradation (Potter, 1993). The changes may be affected by the matrix involved.

The analytical methods chosen must be broad enough to accommodate these variables but must have selectivity and sensitivity such that target compounds can be identified. Once the target compounds are identified, quantifiable clean up levels can be established.

Analysis of gasoline components is usually restricted to detection of benzene, toluene, ethylbenzene, and xylene (BTEX) because: (1) They are readily measurable by gas chromatography, (2) they pose a serious threat to human health (benzene is a known carcinogen), (3) they have potential to move through soil and contaminate groundwater, and (4) their vapor pressures are relatively high creating fire and explosion hazards.

The BTEX fraction of gasoline typically constitutes approximately 15% of unleaded gasoline (Domask, 1984). It is important to selectively analyze for benzene. Its cancer hazard is compounded by it's relatively high water solubility and volatility. Benzene typically comprises 1-3% of gasoline.

In addition to BTEX, analysis for TPH is commonly conducted. This analysis detects aliphatic and aromatic hydrocarbons contained in fuels. Detection is reported as the sum total of all hydrocarbons in the sample, rather than as individual chemical compounds. This analysis tends to pick up the less mobile hydrocarbons at a UST site. However basing clean up levels solely on a TPH level does not allow for traditional risk assessment since it is not compound specific.

Analysis should be limited to BTEX, TPH and perhaps polynuclear aromatic hydrocarbons (PAH) except where site specific conditions warrant analysis of additional constituents.

In the case of organic lead, it must be recognized that laboratories analyze only for total lead and cannot readily distinguish between organic and inorganic lead. Because inorganic lead is indigenous to many Kentucky soils, the use of total lead analysis could lead to misleading or false readings of organic lead being reported. Using background total lead concentrations as a comparison may only give an approximation of organic lead in the soils. However, organic lead is extremely toxic and its presence and concentration should be assessed where significant leaded gasoline leaks have occurred or where an investigator feel that there may be the potential human contact in the area such as next to or in a school yard. As organic lead compounds are no longer added to commercial gasolines, this problem should only exist for older, inactive tanks.

This summary is divided into four sections. The first involves a description of field screening equipment. The second is a review of commonly used EPA methods of analysis (Oliver and Kostecki, 1992). The third is a review of the TPH method as a decision tool. Finally test method recommendations for Kentucky LUST sites are described.

1.0 Field Screening

When gathering site information, field screening of samples should be conducted. Field sampling may be done using one of four types of equipment described in section 1.2.

When sampling is performed, the sample locations should follow those outlined in *Underground Storage Tank System(s) Closure Outline For Collection of Samples and Laboratory Analysis For Underground Storage Tank Systems in Kentucky* printed by the Natural Resources and Environmental Protection Cabinet Division of Waste Management Underground Storage Tank Branch. However, variations from this procedure may be appropriate in certain cases.

Field sampling does not take the place of laboratory analysis. In the field the sample should be divided into two parts. One part should be sent to a laboratory for analysis consistent with EPA SW 846 guidelines found in *Test Methods For Evaluating Solid Wastes: Physical/Chemical Methods*, the other is analyzed in the field. EPA methods will be described in section 2.0.

1.1 Purpose of Field Screening

The purpose of field screening is to characterize the site in order to 1) provide immediate entry to the decision tree for closure and 2) suggest immediate measures to simplify remediation strategy. Conventional site assessment procedures include installing monitoring wells. The information can be used to locate optimal drilling sites for taking soil and ground water samples, to monitor the effectiveness of remediation, to conduct broad area investigations and, to the extent possible, assess immediate contamination risk.

Real time field sampling procedures are used as either a quick indicator of contamination or to quantify the magnitude of contamination on the spot. Site remediation and cleanup can begin sooner, curtailing a spreading plume, which ultimately reduces site remediation costs. Decisions can be made and cleanup initiated if accurate field screening is employed early in the process.

In some cases, lab analysis costs can be reduced. An on-site soil gas method allows the survey of an area covering 15-20 monitoring wells for less than the cost of drilling one well. (Rapaport, 1991). Early site characterization can save money in determining clean up strategies (Taylor, 1993).

An adequate soil sampling and analysis plan should include the parameters to be analyzed, number of samples and locations, sample type (either grab or composite), a quality assurance/quality control plan and custody procedures. These are outlined in the Kentucky document "Underground Storage Tank System(s) Closure Outline for Collection of Samples and Laboratory Analysis For Underground Storage Tank Systems in Kentucky."

1.2 Field Instruments

The instruments described below are portable (battery operated). Vapor is drawn through a probe, analyzed and the response is read from a scale or digital readout. The instruments can be used to check vapor in ambient air or by placing the probe close to contaminated soil to detect vapor coming directly from soil. For simplicity and expediency of operation, virtually all portable field units are designed to analyze samples at ambient temperatures.

Soil suspected of being contaminated is placed in a jar to about 1/3 capacity. The jar is sealed, heated in the sun or oven, and after 15 minutes the head space is analyzed with a PID, FID, or combustible gas indicator. This method is not highly precise. However, it does offer a qualitative approach that may be used as an indicator of volatiles in soil. It is therefore a valuable tool to initially quantify and develop a site characterization.

1.2.1 Portable Photoionization Detector (PID):

This device uses an ultraviolet light source to activate compounds for analysis. It is especially sensitive to aromatics such as benzene, toluene, and xylene and is less sensitive to non-aromatic hydrocarbons. Aromatics are present in gasoline at approximately 28% by volume (Wixtrom and Brown, 1992). The unit's lamp ionizes the sample which is drawn into the instrument via an internal pump. The ionized sample produces an ion current, which is proportional to the concentration and is measured with an ammeter in electron volts. The PID is not sensitive to any compound such as methane or ethane with an ionization potential greater than the photon energy from the light source. However, the light source can be changed to expand the range of analysis. Mixed vapors may cause erroneous readings when oxygen or other electron capturing materials pass through the detector. This phenomenon is known as quenching (Senum, 1981). This instrument is useful as a general field survey tool.

1.2.2 Portable Flame Ionization Detector (FID):

This is an organic vapor analyzer (OVA) which uses a hydrogen flame detector instead of ultraviolet light to detect flammable gasses. The instrument measures organic vapor concentration by producing a response to an unknown sample. Results are then related to a gas of known composition with which the instrument has previously been calibrated. During normal survey mode operation, a continuous sample is drawn into a probe and transmitted to the detector chamber by an internal pump. The sample stream is metered and passed through particle filters before reaching the detector chamber. Inside the detection chamber, the sample is exposed to a hydrogen flame which ionizes organic compounds. An electric field drives the ions to a collecting electrode. As the positive ions are collected, a current corresponding to the collection rate is generated. This current is amplified and displayed on a dial. (Foxboro, 1985) The unit can operate as a limited field unit or as a gas chromatograph if the unit is equipped with a chromatographic column with which to separate individual analytes. Gas chromatography (GC) is covered in section 1.4. The OVA can be calibrated in a lab for various gasses. In the field survey mode, the FID reflects the total concentration of vapors present (TPH). As the detector, in essence, burns the sample, all flammable compounds will produce a response. When connected to a chart recorder, (GC mode) individual analytes can be quantified.

1.2.3 Colorimetric Indicator Tube

Specially made glass tubes filled with a reagent material will react quickly with a gas vapor. They are pre-calibrated for easy reading in parts per million (ppm) or percentage concentration. A fixed volume of air is drawn into the tube through a small bellows. If the vapor reacts with the reagent material, a readily observable color change occurs in the tube. The length of the color change in the tube corresponds to the contaminant concentration. This is a semi-quantitative measurement. They are simple to operate and of moderate cost. Storage of tubes prior to use is critical. Refrigeration is required. Colorimetric tubes have very limited use in UST field screening, but they could be used by back hoe operators to roughly gauge the level of contaminant present.

1.2.4 Combustible Gas Indicator (explosion meter)

The purpose of this instrument is to alert workers in the area of a potential explosive atmosphere. This unit detects gas vapor in air and indicates whether the atmosphere contains a flammable level of gas vapor. This instrument is not likely to be of value unless concentrations of explosive gas exceed 100 ppm. Also, combustion indicators do not provide accurate measurements under deficient oxygen conditions. (e.g. confined spaces). As a safety tool, a combustible gas indicator may be useful at an UST site.

1.3 Field Screening to Characterize a Site

Field screening with an FID enhances the decision making process. Three dimensional data are obtained by sampling at discrete depths to profile contaminant distribution vertically across the site. By using narrow diameter sampling points, such as a 3/4" diameter steel sampling rod driven with a hammer drill, samples are taken at discrete depths and recorded. Using field screening in this way, if removal by excavation is an option, by knowing the amount of impacted soil within 10-20%, cost saving remediation strategies can be recommended. Field screening using this sampling methodology and an FID can accurately characterize a subsurface condition.

Field screening is limited by the care and experience of personnel carrying out the tests. Calibration of analytical equipment prior to operation at each site is crucial. Careless handling can lead to cross contamination in which materials sampled in prior analyses are retained in the equipment or sampling bottles giving erroneous results. It is useful to carry out blank analyses on samples known to be free of hydrocarbons prior to analysis of new samples.

1.3.1 Cone Penetrometer Testing (CPT)

To further characterize a site for subsequent risk management, a slightly more expensive technology is available which has proven effective in some locations. The cone penetrometer method is based on pushing small diameter probes directly into the soil subsurface without drilling a bore hole. A high capacity, truck mounted, 20 ton hydraulic ram is used to push probes to desired depths. Standardized methods have been developed for this technology (ASTM 1988). Using this method, no cutting or contaminated drilling fluids are generated that could affect samples.

The electronic cone penetrometer test consists of measuring the soil resistance to penetration (Campanella 1990). CPT soil resistance are readily interpreted to identify aquifers and aquitards (Strutynsky AI, Sainey TJ, 1990). The cone pentetrometer is capable of determining variations in soil media physical properties, both saturated and unsaturated media. With a piezometric pressure transducer direct measurement of continuous hydrogeologic parameters, including water tables, and estimation of horizontal permeabilities can be assessed. Soil electrical conductivity can also be continuously logged during the ramming. All measurements are displayed, recorded and interpreted in real time using on-board computerized data acquisition systems. This data which enables direct identification of potential contaminant migration pathways and barriers is used to guide subsequent groundwater sampling activities for plume identification. The CPT rig can also be used to deploy ground water sampling probes to delineate the extent of a contaminated plume.

A second devise, a hydropunch is of similar value and is capable of collecting in-situ pore water samples (Chiang CY, Loos KR, Kloop RA, Beltz MC,).

These two technologies, CPT and hydropunch, can be used to identify and define subsequent exploration points or monitoring well locations (Wallace RT, Marrale M, Sims JT, 1992). However, they may have limited use in Kentucky because of the underlying geology (Edge RW, Cordry K, 1989).

1.4 Gas Chromatography (GC)

GC provides a method for analyzing fuel hydrocarbons in solids, soil, and water. Two GC detectors are used for identification of motor fuel components:

1) PID: commonly used for detection of BTEX and other aromatic hydrocarbons
2) FID: this method will detect any volatile petroleum hydrocarbons in either gasoline or diesel fuel. It can be used to determine total petroleum hydrocarbons (TPH).

These detection methods are identical to those discussed for direct read PID and FID units with the exception that operating temperatures are controlled in GC analysis and mixtures of chemicals can be separated and the components identified individually. The precision and accuracy are known, therefore these procedures are both qualitative and quantitative in nature. Analysis by GC usually requires sample preparation (extraction from the soil or water) and transport to a laboratory. Detection limits for fuel products is in the low parts per billion (ppb) range for water and ppm range for soil.

Using GC it is sometimes possible to estimate the length of time hydrocarbons have been in the subsurface strata as well as identify the potential sources of the contamination (Senn and Johnson 1987).

2.0 EPA Methods

Methods are outlined in "Methods For Chemical Analysis of Water and Wastes" (EPA 600/4-79-020), "Test Methods For Evaluating Solid Waste: Physical/Chemical Methods" (EPA SW-846) or "Test Methods For Organic Chemical Analysis of Municipal and Industrial Waste Water" (EPA 600/4-82-057).
Following is a brief description of the most commonly used methods at UST sites.

For gasoline the majority of states use the 8020 or 602 method for BTEX analysis. Methods such as 8020 are used for analysis of wastes such as contaminated soil or ground water. The 600 series methods are used for analysis of waste water discharge permitting process. For diesel fuel, clean up levels are either set for specific PAH target analytes such as benzo(a)pyrene or for total hydrocarbon content by TPH (Oliver and Kostecti, 1992).

Because a constituent's analytical detection limit in soil is dependent upon the characteristics of the matrix, it's value varies. However, minimum detection limits (MDL) have been established by laboratories. Using SW-846 methods, MDL is defined as the minimum concentration of a substance that can be measured and reported with a 99% confidence that the value is above zero. Therefore the MDL is the analytical detection limit. MDL is a function of method and concentration of the analytes. The closer the detected concentration is to the MDL, the less accurate the result is due to matrix interferences with quantifying small concentrations. The practical quantitation limit (PQL) is the lowest concentration of a substance that can be consistently quantified.

2.1 Sample Preparation

Some samples require preparation before analysis can be done. Two methods are briefly described below.

2.1.1 Method 5030 (Purge and Trap Method)

Method 5030 describes sample preparation and extraction for analysis of volatile organics by a purge trap procedure. The gas chromatographic procedures are found in methods 8020, 8260, and 8021. It is used for most VOC's that have boiling points below 200 degrees Celsius and are insoluble or slightly soluble in water. The method is limited to compounds that elute as sharp peaks from a GC column packed with graphitized carbon lightly coated with a carbowax. Such compounds include low molecular-weight halogenated hydrocarbons, aromatics, ketones, ethers, and sulfides.

2.1.2 Method 3510 (Separatory Funnel Liquid-Liquid Extraction) and Method 3520 (Continuous Liquid-Liquid Extraction)

Both 3510 and 3520 are procedures for isolating organic compounds from aqueous samples. The method is applicable to the isolation and concentration of water insoluble and slightly water soluble organics in preparation for a variety of chromatographic procedures.

2.2 Method 418.1 Total Petroleum Hydrocarbons by Infrared Spectroscopy

Method 418.1 is not a part of SW-846. The procedure for 418.1 includes extraction from the matrix (water or soil), and subsequent analysis using an infrared spectrometer. The result can not distinguish between different types of organic molecules, rather the spectroscope analyzes one particular band that is associated with most organic substances in the sample.

Thus the TPH analysis using method 418.1 detects several classes of organic compounds including components of diesel fuels, PCBs, bacteria, fungi, esters, ketones, amines, and a variety of other organic compounds without distinguishing them from one another. The true concentration of petroleum distillates may be lower then the reported TPH value.

Method 418.1 should not be used as a measure for clean up standards. It *can* be used effectively as a screening tool to characterize a site. More detailed analysis for specific compounds is necessary to assess risk and establish subsequent clean up levels. The cost of this test is about $26.00. (Personal Communication 21 June) A further review of TPH is in section 3.0.

2.3 Method 602 Purgeable Aromatics-Waste Water

Method 602 is not a part of SW-846. It was developed for use at waste water discharge points to evaluate contaminants.

Method 602 is used to determine purgeable aromatics. It is not used as often as 8020. The following compounds can be quantified using this method:

Benzene
Chlorobenzene
Dichlorobenzenes
Ethylbenzene
Toluene

Xylenes can also be detected using this method provided the analyst calibrates for them. However, xylenes are not specified as target analytes in the official method. Benzene, toluene, and ethyl benzene have detection limits of .2 mg/L using this method. This purge and trap method was developed primarily for waste water from municipal and industrial sources. By bubbling an inert gas through the water sample, the aromatics are transferred from aqueous phase to vapor phase. The vapors are trapped on a medium, heated, back flushed with the inert gas and then entered onto the chromatographic column. A photoionization detector (PID) gas chromatograph is used. The cost of this method is low.

Interferences from impure purge gas, sample contamination from diffusion of volatiles through the septum seal or the apparatus and carry over contamination where high level samples and low level samples are sequentially analyzed can cause inaccurate results. However, when quality control/quality assurance procedures are followed, this method will produce useful results.

2.4 Method 8240 Gas Chromatography/Mass Spectrometry For Volatile Organics

Method 8240 is used to determine volatile organic compounds in a variety of solid waste matrices. This method is applicable to nearly all types of samples regardless of water content, including groundwater, and soil.

Method 8240 can be used to quantify most volatile organic compounds that have boiling points below 200 degrees Celsius and that are insoluble or slightly soluble in water. The method incorporates method 5030 as a preparation step to analysis by GC/MS.

Method 8240 quantifies an extensive list of compounds including BTEX and over 70 other volatile organics. Because of it's breadth, the method is employed when prior use of a tank is unknown. When employed by an experienced analyst, this method can often identify components of a complex mixture even when standard compounds are unavailable for comparison.

The quantitation limit of method 8240 for an individual compound is approximately 5 mg/kg for soil and 5 mg/L for ground water. This method can be used as a first screening tool in the case the tank prior use cannot be determined from historical records. The costs for this method are somewhat higher than those associated with 8020, mainly because the instrumentation is more costly. However, the cost of GC/MS instrumentation has been decreasing and a good bench top instrument can now be obtained for under $60,000. A comparably equipped GC with FID or PID detection costs under $20,000 (1993 prices). Operator training required to make maximal use of a GC/MS is somewhat greater than for a GC and probably requires college-level training in chemistry to accommodate non-routine analytical situations. However, the information obtainable from the GC/MS technique is orders of magnitude more definitive than that from GC alone although FID or PID detectors are somewhat more convenient for quantitation. It seems likely that analysis by GC/MS followed by quantitation using FID-detected GC will eventually become the standard methodology for dealing with UST problems.

2.5 Method 8100 FID for Polynuclear Aromatic Hydrocarbons

Method 8100 is used to determine concentration of certain polynuclear aromatic hydrocarbons (PAH). This method uses an FID and chromatographic separations to identify compounds. Because the FID is not a selective detector, other hydrocarbons may interfere with PAH quantitation (Potter, 1993). The following compounds have been detected by this method:

<u>Compound</u>

Acenaphthene
Chrysene
Dibenz(a,h)anthracene
Dibenzo(a,h)pyrene
Fluorene

Indeno (1,2,3-cd) pyrene
Naphthalene
Pyrene
Phenanthrene
Acenaphthylene
Anthracene
Benzo(a)anthracene
Benzo(a)pyrene
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(g,h,i)perylene

This method however cannot distinguish between 4 pairs of compounds: anthracene and phenanthrene; chrysene and benzo(a)anthracene; benzo(b)fluoranthene and benzo(k)fluoranthene; dibenzo(a,h)anthracene and indeno (1,2,3-c,d)pyrene. If quantitative distinctions between these are necessary at a site, method 8310 should be used. Method 8310 uses a high performance liquid chromatographic technique to detect ppb of these specific PAHs. The cost of method 8100 is about $200.00 per analysis (Personal Communication 21 June).

2.6 Method 8020 and 8021 Volatile Organic Compounds in Water By Purge and Trap Capillary Column Gas Chromatography With Photoionization and Electrolytic Conductivity Detectors In Series

Method 8020 is used to determine the concentration of various aromatic organic compounds. The following compounds may be determined by this method: Benzene, ethyl benzene, toluene, and xylenes. Detection limits in mg/L using a purge and trap method (Method 5030) are 0.2, 0.4, 0.2, and 0.2 respectively.

Method 8020 is a photo-ionization detection (PID) gas chromatograph technique. Samples can be analyzed using direct injection in limited applications or by the purge and trap method. Ground water and soils are usually prepared using method 5030. Calibration of the equipment must follow procedures outlined in method 8000. The method is inexpensive compared to 8240. Method 8021, an updated version of 8020, is broad yet sensitive enough to detect 1 ug/kg in soil and 1 ug/L in water. More than 45 analytes can be quantified.

2.7 Method 8015 Gas Chromatography-Flame Ionization

Method 8015 is used to determine the concentration of various non-halogenated volatile organic compounds. This method has been modified to some extent and is now used in Arkansas, Colorado, Delaware and a few other states as a monitor for clean up levels (Oliver and Kostecki, 1992). There is no nationally recognized, documented "modified 8015" method. Detection limits for gasoline and diesel are 0.5 mg/L in water and 10.0 mg/kg in soil using the California modified 8015 method. Specific calibration standards using known concentrations of gasoline and diesel are necessary.

2.10 Method 8270 GC/MS For Semivolatile Organics: Capillary Column Technique

Method 8270 is used to determine the concentration of semi volatile organic compounds in extracts prepared from all types of solid or liquid matrices. PAHs, chlorinated hydrocarbons, pesticides, and numerous others can be quantified using this method. This is an extensive test capable of identifying in excess of 130 compounds. The cost is relatively high, however, see comments above in section 2.4.

2.11 Method 8310 Polynuclear Aromatic Hydrocarbons

Method 8310 is used to determine the concentration of specific PAHs. It is similar to method 8100 but is much more sensitive to PAHs. Method 8100 detection limits are at the ppb range where 8310 limits are at the ppt range.
The method is used to specifically detect:

Acenaphthene
Acenaphthylene
Anthracene
Benzo(a)anthracene
Benzo(a)pyrene
Benzo(b)fluoranthene
Benzo(g,h,i)perylene
Benzo(k)fluoranthene
Chrysene
Dibenzo(a,h)anthracene
Fluoranthene
Fluorene
Indeno(1,2,3-c,d)pyrene
Naphthalene
Phenanthrene
Pyrene

3.0 TPH

The least specific and most general analytical approach to petroleum detection is the total petroleum hydrocarbon (TPH) measurement. TPH analysis is comparatively low cost. However, interferences, extraction methods and inaccurate standards may lead to false readings. EPA method 418.1 involves extraction of hydrocarbon residues from the media using an organic solvent, trichlorotrifluoroethane (EPA 600/4-82-057). After extraction, the solvent is treated with silica gel and analyzed using an IR spectrometer. The total hydrocarbon concentration is assessed relative to detector response to a known mixture. The standard mixture is the petroleum product reference mixture.

3.1 Advantages

The advantages of this test are that instrument costs are modest and extensive technical training of analysts is not required. Measurement precision (reproducibility) is good.

3.2 Disadvantages

Measurement accuracy may vary depending on the products involved and extent of post release chemical changes (weathering). Three disadvantages of this method are interference, nonrepresentative extraction, and inadequate standard availability.

3.2.1 Interferences

All compounds containing an aliphatic carbon to hydrogen bond will produce positive results.

Therefore this TPH method does not measure petroleum distillates exclusively. Almost all organic compounds contain at least one aliphatic carbon/hydrogen bond. Some compounds, such as alcohols, ketones, esters, and organic acids are not present in petroleum products but could be produced by the biodegradation of petroleum products in soil. Bacteria, spores, plant material and their metabolic products can produce positive TPH results. Even with the extraction, silica gel absorption procedure, small amounts of these compounds could show up.

3.2.2 Extraction Methods/Sample Preparation

A significant portion of the more volatile compounds (BTEX) in gasoline may be lost in the solvent concentration step (Potter 1993, EPA 418.1) Therefore TPH is a poor method for analyzing the carcinogenic compounds found in petroleum products because it is not compound specific. It does not measure the polynuclear aromatic carcinogens except in aggregate. Also, constituents of the heavy distillates (diesels) are poorly soluble in trichlorotrifluoromethane. One study has indicated false positive TPH results when the test is performed on clay ar limestone soils. Without the silica gel clean up. TPH tests will measure vegetable or animal hydrocarbons (organic acids, fats) which can bias results to the high side. Use of silica gel clean up may remove complex aromatic compounds and other hydrocarbons which can bias results to the low side (Walters, 1991).

3.2.3 Standard Selection

The reference materials used in TPH analysis may or may not provide an adequate calibration. If the analytes and reference materials have the same characteristics, then accuracy can be expected. However, when the original product has varying composition or if it contains material of unknown chemical structure, selecting a reference that is exactly like the sample is problematic. Artificially weathering a standard introduces another variable and potential for error in results.

Using method 418.1 to quantify contamination at a site is suspect. Interpretation of results from 418.1 is uncertain. Because the data from 418.1 are not compound specific, they are of little value for risk analysis.

4.0 TABLE OF RECOMMENDED ANALYTICAL METHODS

Analytical Group	Constituent	Analytical Method For Soil Samples	Analytical Method For Water Samples
1.GASOLINE (Motor Gasoline, Aviation Gasoline, and Gasohol)	Benzene	EPA Method 8021	EPA Method 8021
	Toluene	EPA Method 8021	EPA Method 8021
	Ethylbenzene	EPA Method 8021	EPA Method 8021
	Total Xylenes	EPA Method 8021	EPA Method 8021
	Total Petroleum Hydrocarbons(TPH)	N.A.	
2.MIDDLE DISTILLATES (Kerosene,Diesel Fuel, Jet Fuel, and Light Oils)	Benzene	EPA Method 8021	EPA Method 8021
	Toluene	EPA Method 8021	EPA Method 8021
	Ethylbenzene	EPA Method 8021	EPA Method 8021
	Total Xylenes	EPA Method 8021	EPA Method 8021
	PAH'S	EPA Method 8100	EPA Method 8021
	TPH'S	N.A.	
3.USED OIL AND UNKNOWNS	Volatile Organic Compounds	EPA Method 8240	EPA Method 8021
	TPH	N.A.	

Method 8021 for BTEX detection should be used for soil and water samples. Method 8021-Volatile Organic Compounds By Purge and Trap Capillary Column Gas Chromatography With Photoionization and Electrolytic Conductivity Detectors in Series, has both selectivity and sensitivity which make it the most useful method for UST investigations. This method should be used for suspected gasoline leaks. Backup using 8270 or 8240 would also be desirable to confirm identity particularly with samples of unknown history.

Weathering effects product composition. Upon release of a petroleum product into the environment, certain fractions are lost via volatilization, dissolution/leaching or biodegradation. More persistent fractions are left behind as weathered product. Therefore, the residue differs from the original relative concentrations of compounds. To address this, method 8021 quantities the trimethylbenzenes. Trimethylbenzene, with a relatively high molecular weight, low vapor pressure and high K_{oc} will tend to stay at the site. See table 1. Although it represents only a small percentage of the original mixture, it's physical and chemical characteristics make it a persistent compound. The age of the product in the soil can be estimated by looking at the relative quantities of BTEX and trimethylbenzene.

Table 1

	mol.weight	vapor pressure	K_{oc}	Original concentration weight %
Benzene	78.11	75.2	190	.1-3.5
Toluene	92.14	21.8	380	2.7-21.8
1,3,5-Trimethyl benzene	120.2	1.73	940	.1-1.5

Because the product from a leaking underground storage tank is usually not fresh, this inexpensive GC method is recommended. The technique is sensitive and sufficiently specific to meet the needs of risk analysis and remediation technologies. See Appendix 1. Minimum detection limits are between .009 to .05 ug/L. Where any doubt exists about the chemical identity of components, a GC/MS method should be used as back up.

Diesel Fuel- Method 8100:

Method 8100 was originally developed for RCRA sites. Specific PAH compounds identified using this method include:

Acenaphthene
Chrysene
Dibenzo(a,h)anthracene
Dibenzo(a,h)pyrene
Fluorene
Indeno(1,2,3-c,d)pyrene
Naphthalene
Pyrene
Phenanthrene
Acenaphthylene
Anthracene
Benzo(a)anthracene
Benzo(a)pyrene
Benzo(b)fluoranthene
Benzo(k)fluoranthene

Benzo(g,h,i)perylene
(SW-846)

The concentration of PAH's in No.2 fuel oil (diesel) are:

	ppm
Phenanthrene	429
2-Methylphenanthrene	7677
1-Methyl phenanthrene	173
Fluoranthene	37
Pyrene	41
Benzo(a)anthracene	1.2
Chrysene	2.2
Triphenylene	1.4
Benzo(a)pyrene	0.6
Benzo(e)pyrene	0.1

(Millner 1992)

These constituents are present in diesel fuel in relatively low concentrations. This limits the reliability of this method for confirming a history of contamination with diesel fuel. Thus 8100 cannot be regarded as an ideal method. However, at this time it is the only widely accepted method. It would be desirable to back up 8100 with GC/MS identification before data are used for risk assessment.

A method to measure diesel contamination has been adopted by Tennessee. This method is designed to measure the concentration of diesel range organics in water and soil. This corresponds to an alkane range of C_{10}-C_{24}. The method is based on solvent extraction and comparison with a standard using a GC procedure. This method should be more reliable for confirming the presence of diesel fuel, but does not directly assess the concentration of PAHs and is thus of limited value for risk assessment purposes. Where reliable identification and quantification of PAHs is required, data obtained using this method should be backed up by method 8310 or a GC/MS procedure.

Method 8100 Extended:

The difficulties of finding a specific and sensitive method have been well documented. The Kentucky EPA, Division of Waste Management (DWM) has addressed this problem with the "8100 Extended" method. The DMW has decided to accept supplemental data from an "8100 extended" version of the SW-846 PAH/PNA method. This method is both site specific and product specific. It can accurately identify waste oil, heating oils and others. The method uses a GC/MS to fully identify and quantify products.

There is no certification available for this extended analysis at this time. Labs that perform this test are required to supply a product-site specific QA/QC package with test results for evaluation by the DWM.

When standards of applicability are established, method 8100 extended should be used when diesel or other long chain hydrocarbons are suspected at a site.

REFERENCES

ASTM, 1988. Standard Method For Deep, Quasi-static, Cone and Friction-cone Penetration Tests of Soil. Designation D3441-86, Vol. 4.08. Soil and Rock, Building Stones: Geotextiles, pg. 409-414.

Campanella, RG. (1990). The Seismic Piezocone Penetration Test: A Practical Site Investigation Tool. Seminar Presentation at University of Washington. Seattle, Washington.

Chaing CY, Loos KR, Kloop RA, Beltz MC. A Real-time Determination of an Aquifer by Penetration Testing. Shell development Co and Terra Technologies. Houston, Texas.

Domask, WG (1984) Introduction to Petroleum Hydrocarbons Chemistry and Composition in Relation to Petroleum-Derived Fuels and Solvents. Renal Effects of Petroleum Hydrocarbons. Princeton Scientific Princeton NJ.

Edge RW, Cordry K. (1989). The Hydropunch: An In-Situ Sampling Tool For Collecting Groundwater From Unconsolidated Sediments. Groundwater Monitoring Review. Dublin, Ohio.

Foxboro Model OVA128 Century Organic Vapor Analyzer Instruction Manual December 1985.

Millner GC, Nye AC, James RC (1992) Human Health Based Soil Clean up Guidelines for Diesel Fuel No.2. Contaminated Soils p.165-216. Lewis Publishers.

Personal Communication, 21 June 1993, Tim Barrett Commonwealth Technologies.

Potter TL (1993) Analysis of Petroleum Contaminated Soil and Water: An Overview. Principles and Practices For Contaminated Soils p.1-24 Lewis Publishers

Rapaport, D (1991) Using Soil/Gas Surveys for VOC's Environmental Protection Sept 1991.

Senn RB, Johnson SJ (1987) Interpretation of Gas Chromatographic Data in Subsurface Hydrocarbon investigations. Groundwater Management Review 1987 p. 58-63.

Senum GI, (1981) Quenching or Enhancement of the Response of the Photoionization Detector. Journal of Chromatography, 205. 413-418.

Sanders WN Maynard, JB (1968) Capillary Gas Chromatographic Method for Determining the C3-C Hydrocarbons in Full-Range Motor Gasolines. Analytical Chemistry 40. No.3 527-535.

Strutynsky AI, Sainey TJ. (1990). Use of Piezometric (One Penetration Testing and Penetrometer Groundwater Sampling for Volatile Organic Contaminant Plume Detection. Proceedings of Petroleum Hydrocarbons and Organic Chemicals in Groundwater: Prevention, Detection, and Restoration. Water Well Journal Publishing Co. Dublin, Ohio.

Taylor, M (April 1993). Taking Aim at Site Cleanup: Accurate Site Characterizations Will Get You Where You Need to be Fast, Reliably and Cost Effectively. LUST Line: A Report on Federal and State Programs to Control Leaking Underground Storage Tanks.

Oliver T, Kostecki P (1992) State by State Summary of Cleanup Standards, Soils December 1992.

USEPA 1986. Test methods for evaluating solid waste: physical/chemical methods. SW-846. Third edition, Office of Solid Waste and Emergency Response. US EPA. Washington, DC.

USEPA 1982. Test Methods For Organic Chemical Analysis of Municipal and Industrial Waste Water. EPA 600/4-82-057. US EPA Environmental Monitoring and Support Laboratory. Cincinnati, Ohio.

USEPA 1983. Methods For Chemical Analysis of Water and Wastes. US EPA 600/4-79-020, Revised March 1993. US EPA Environmental Monitoring Laboratory, Cincinnati, Ohio.

USEPA Health Effects Assessment Summary Tables FY-1991 Annual. OERR 9200.6-303(91-1) January 1991.

Wallace RT, Marrale M, Sims JT. (1992). Innovative Applications of Direct Push/hammer Systems To Enhance Site Characterization.

Wixtrom RN, Brown SL (1992) Individual and Population Exposures to Gasoline, Journal of Exposure Analysis and Environmental Epidemiology 2. 1 23-78.

TABLE 1.
CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC COMPOUNDS ON PHOTOIONIZATION DETECTION (PID) AND HALL ELECTROLYTIC CONDUCTIVITY DETECTOR (HECD) DETECTORS

Analyte	PID Ret. Time,[a] minute	HECD Ret. Time, minute	PID MDL, ug/L	HECD MDL ug/L
Dichlorodifluoromethane	-[b]	8.47		.05
Chloromethane	-	9.47		.03
Vinyl Chloride	9.88	9.93	0.02	.04
Bromomethane	-	11.95		1.1
Chloroethane	-	12.37		0.1
Trichlorofluoromethane	-	13.49		0.03
1,1-Dichloroethene	16.14	16.18	ND[c]	0.07
Methylene Chloride	-	18.39		0.02
trans-1,2-Dichloroethene	19.30	19.33	0.05	0.06
1,1-Dichloroethane	-	20.99		0.07
2,2-Dichloropropane	-	22.88		0.05
cis-1,2-Dichloroethane	23.11	23.14	0.02	0.01
Chloroform	-	23.64		0.02
Bromochloromethane	-	24.16		0.01
1,1,1-Trichloroethane	-	24.77		0.03
1,1-Dichloropropene	25.21	25.24	0.02	0.02
Carbon Tetrachloride	-	25.47		0.01
Benzene	26.10	-	0.009	
1,2-Dichloroethane	-	26.27		0.03
Trichloroethene	27.99	28.02	0.02	0.01
1,2-Dichloropropane	-	28.66		0.006
Bromodichloromethane	-	29.43		0.02
Dibromomethane	-	29.59		2.2
Toluene	31.95	-	0.01	
1,1,2-Trichloroethane	-	33.21		ND
Tetrachloroethene	33.88	33.90	0.05	0.04
1,3-Dichloropropane	-	34.00		0.03
Dibromochloromethane	-	34.73		0.03
1,2-Dibromoethane	-	35.34		0.8
Chlorobenzene	36.56	36.59	0.003	0.01
Ethyl benzene	36.72	-	0.005	
1,1,1,2-Tetrachloroethane	-	36.80		0.005
m-Xylene	36.98	-	0.01	
p-Xylene	36.98	-	0.01	
o-Xylene	38.39	-	0.02	
Styrene	38.57	-	0.01	
Isopropyl benzene	39.58	-	0.05	
Bromoform	-	39.75		1.6
1,1,2,2-Tetrachloroethane	-	40.35		0.01
1,2,3-Trichloropropane	-	40.81		0.4

* From EPA Method 8021

TABLE 1.
(Continued)

Analyte	PID Ret. Time,[a] minutes	HECD Ret. Time, minutes	PID MDL, ug/L	HECD MDL ug/L
n-Propyl benzene	40.87	-	0.004	
Bromobenzene	40.99	41.03	0.006	0.03
1,3,5-Trimethyl benzene	41.41	-	0.004	
2-Chlorotoluene	41.41	41.45	ND	0.01
4-Chlorotoluene	41.60	41.63	0.02	0.01
tert-Butyl benzene	42.92	-	0.06	
1,2,4-Trimethylbenzene	42.71	-	0.05	
sec-Butylbenzene	43.31	-	0.02	
p-Isopropyltoluene	43.81	-	0.01	
1,3-Dichlorobenzene	44.08	44.11	0.02	0.02
1,4-Dichlorobenzene	44.43	44.47	0.007	0.01
n-Butylbenzene	45.20	-	0.02	
1,2-Dichlorobenzene	45.71	45.74	0.05	0.02
1,2-Dibromo-3-Chloropropane		48.57		3.0
1,2,4-Trichlorobenzene	51.43	51.46	0.02	0.03
Hexachlorobutadiene	51.92	51.96	0.06	0.02
Naphthalene	52.38	-	0.06	
1,2,3-Trichlorobenzene	53.34	53.37	ND	0.03
Internal Standards				
Fluorobenzene	26.84	-		
2-Bromo-1-chloropropane	-	33.08		

[a] Retention times determined on 60 m x 0.75 mm i.d. VOCOL capillary column. Program: Hold at 10°C for 8 minutes, then program at 4°C/min to 180°C, and hold until all expected compounds have eluted.

[b] Dash (-) indicates detector does not respond.

[c] ND = Not determined.

TABLE 2.
SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR VOLATILE ORGANIC COMPOUNDS IN WATER[d]

Analyte	Photoionization Detector		Hall Electrolytic Conductivity Detector	
	Recovery,[a] %	Standard Deviation of Recovery	Recovery,[a] %	Standard Deviation of Recovery
Benzene	99	1.2	-[b]	-
Bromobenzene	99	1.7	97	2.7
Bromochloromethane	-	-	96	3.0
Bromodichloromethane	-	-	97	2.9
Bromoform	-	-	106	5.5
Bromomethane	-	-	97	3.7
n-Butylbenzene	100	4.4	-	-
sec-Butylbenzene	97	2.6	-	-
tert-Butylbenzene	98	2.3	-	-
Carbon tetrachloride	-	-	92	3.3
Chlorobenzene	100	1.0	103	3.7
Chloroethane	-	-	96	3.8
Chloroform	-	-	98	2.5
Chloromethane	-	-	96	8.9
2-Chlorotoluene	ND[c]	ND	97	2.6
4-Chlorotoluene	101	1.0	97	3.1
1,2-Dibromo-3-chloropropane	-	-	86	9.9
Dibromochloromethane	-	-	102	3.3
1,2-Dibromoethane	-	-	97	2.7
Dibromomethane	-	-	109	7.4
1,2-Dichlorobenzene	102	2.1	100	1.5
1,3-Dichlorobenzene	104	1.7	106	4.3
1,4-Dichlorobenzene	103	2.2	98	2.3
Dichlorodifluoromethane	-	-	89	5.9
1,1-Dichloroethane	-	-	100	5.7
1,2-Dichloroethane	-	-	100	3.8
1,1-Dichloroethene	100	2.4	103	2.9
cis-1,2 Dichloroethene	ND	ND	105	3.5
trans-1,2-Dichloroethene	93	3.7	99	3.7
1,2-Dichloropropane	-	-	103	3.8
1,3-Dichloropropane	-	-	100	3.4
2,2-Dichloropropane	-	-	105	3.6
1,1-Dichloropropene	103	3.6	103	3.4
Ethylbenzene	101	1.4	-	-
Hexachlorobutadiene	99	9.5	98	8.3
Isopropylbenzene	98	0.9	-	-
p-Isopropyltoluene	98	2.4	-	-

TABLE 2.
(Continued)

	Photoionization Detector		Hall Electrolytic Conductivity Detector	
Analyte	Recovery,[a] %	Standard Deviation of Recovery	Recovery,[a] %	Standard Deviation of Recovery
Methylene chloride	-	-	97	2.8
Naphthalene	102	6.3	-	-
n-Propylbenzene	103	2.0	-	-
Styrene	104	1.4	-	-
1,1,1,2-Tetrachloroethane	-	-	99	2.3
1,1,2,2-Tetrachloroethane	-	-	99	6.8
Tetrachloroethene	101	1.8	97	2.4
Toluene	99	0.8	-	-
1,2,3-Trichlorobenzene	106	1.9	98	3.1
1,2,4-Trichlorobenzene	104	2.2	102	2.1
1,1,1-Trichloroethane	-	-	104	3.4
1,1,2-Trichloroethane	-	-	109	6.2
Trichloroethene	100	0.78	96	3.5
Trichlorofluoromethane	-	-	96	3.4
1,2,3-Trichloropropane	-	-	99	2.3
1,2,4-Trimethylbenzene	99	1.2	-	-
1,3,5-Trimethylbenzene	101	1.4	-	-
Vinyl chloride	109	5.4	95	5.6
o-Xylene	99	0.8	-	
m-Xylene	100	1.4	-	-
p-Xylene	99	0.9	-	-

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[a] Recoveries and standard deviations were determined from seven samples and spiked at 10 ug/L of each analyte. Recoveries were determined by internal standard method. Internal standards were: Fluorobenzene for PID, 2-Bromo-1-chloropropate for HECD.

[b] Detector does not respond.

[c] ND = Not determined.

[d] This method was tested in a single laboratory using water spiked at 10 ug/L (see reference 8).

TABLE 3.
DETERMINATION OF PRACTICAL QUANTITATION LIMITS (PQL) FOR VARIOUS MATRICES[a]

Matrix	Factor[b]
Ground water	10
Low-level soil	10
Water miscible liquid waste	500
High-level soil and sludge	1250
Non-water miscible waste	1250

[a] Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achievable.

[b] PQL = [Method detection limit (Table 1)] x [Factor (Table 3)]. For non-aqueous samples, the factor is on a wet-weight basis.

SOIL VOLUME CALCULATIONS FOR UST INSTALLATIONS

Lyle Sendlein, James Dinger, Ralph Huffsey

Introduction

The volume of soil removed during a cleanup operation will vary for the size of the operation. A preliminary study of the tank registration data indicates that the sites can be divided into at least two groups, those smaller than 3000 gal capacity and those larger than 3000 gal capacity. According to the 1991 Annual Underground Storage Tank Survey 34% of the tanks fall below 1999 gal and the remaining 66% fall in the group above 2000 gal.

An analysis was conducted of Tank Closure Reports included in applications to the Petroleum Environmental Assurance Fund files. One hundred thirty-one files were selected out of approximately 400 files. Of these 131 files, 55 contained closure reports.

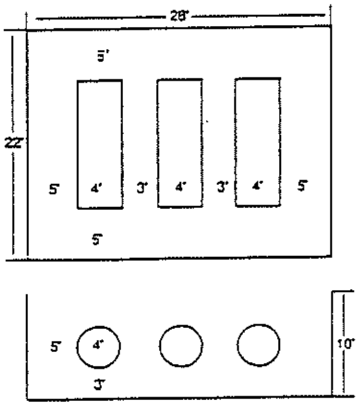
A plot of the volume of cubic yards removed vs. tank capacity, Figure 1, shows a clustering of the data between 300 to 3000 gal with an average of 1550 gal at 120 cubic yards soil removed, and 19,199 gal capacity with 1100 cubic yards soil removed. The data and the short report is included in the Appendix.

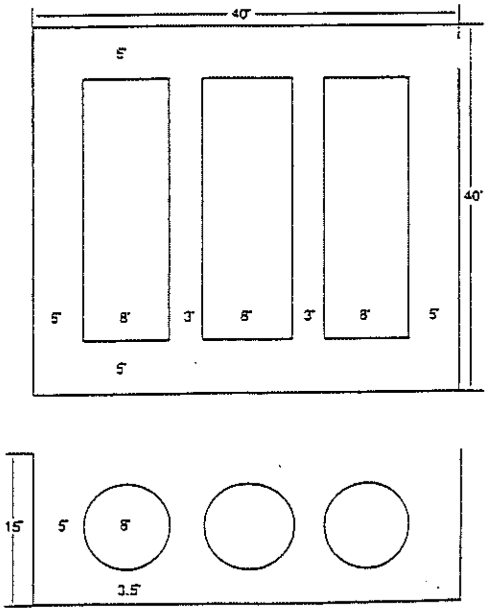
An independent analysis was made to arrive at the volume of soil impacted by leaking tanks based on information obtained from contractors who place and remove tanks. Information provided by them allowed the following assumptions to be made:

Three tanks will be required for each location

Two sizes of tanks with the following dimensions will be assumed
1,000 gal tanks (12′ x 4′ dia.)
10,000 gal tanks (27′ x′ 8′ dia.)

Tank pit configurations and dimensions are shown below:





Computations For one 1,000 GAL Tank Installation

The computations are based on the dimensions provided above.

Total pit volume = 2200 ft^3 (82 yds)
Tank volume = 150 ft^3 (6 yds)
Pit soil volume = 2050 ft^3 (76 yds)

Computations For Three 1,000 GAL Tank Installation

The computations are based on the dimensions provided above.

Total pit volume = 6160 ft^3 (228 cubic yards, yds)
Tank volume = 400 ft^3 (15 yds)
Pit soil volume = 5700 ft^3 (211 yds)

The total potential soil volume that could be contaminated within the excavated pit is 211 yds. If one assumes that additional soil would have to be removed because of contamination, the following represents the amounts required for each foot taken from the sides and bottom of the pit.

one foot = 1800 ft^3 (67 yds) + 211 yds = 278 yds (7506 ft^3)
two feet = 1992 ft^3 (74 yds) + 278 yds = 352 yds (9504 ft^3)
five feet = 2568 ft^3 (95 yds) + 521 yds = 616 yds (16632 ft^3

Computations For Three 10,000 GAL Tank Installation

The computations are based on the dimensions provided above.

Total pit volume = 24000 ft^3 (889 yds)
Tank volume = 4000 ft^3 (148 yds)
Pit soil volume = 20000 ft^3 (741 yds)

The total potential soil volume that could be contaminated within the excavated pit is 741 yds. If one assumes that additional soil would have to be removed because of contamination, the following represents the amounts required for each foot taken from the sides and bottom of the pit.

one foot = 4300 ft^3 (159 yds) + 741 yds = 900 yds (24300 ft^3)
two feet = 4600 ft^3 (170 yds) + 900 yds = 1070 yds (28890 ft^3)
three feet = 4900 ft^3 (182 yds) + 1070 yds = 1252 yds (33804 ft^3)
four feet = 5200 ft^3 (193 yds) + 1252 yds = 1445 yds (39015 ft^3)
five feet = 5500 ft^3 (204 yds) + 1445 yds = 1649 yds (44523 ft^3)

Summary

For the small sites that utilize 1000 gal tanks 161 cubic meters (211 yds) of pit soil would have to be removed and if the soil is contaminated for a zone of five feet around the sides and bottom a total of pit soil plus this contaminated soil would be 471 cubic meters (616 yds).

Information generated from the search of files on actual soil removal indicates that 120 yds of soil is the average with a range between 10 yds and 300 yds. Two hundred and eleven (211 yds) is a conservative figure.

For the larger stations that utilize 10,000 gal tanks 567 cubic meters (741 yds) of pit soil would have to be removed and if the soil is contaminated for a zone of two feet around the sides and bottom, a total pit soil plus this contaminated soil volume would be 1070 yds.

Information generated from the search of files on actual soil removal for large sites indicates that 1100 yds of soil is the average with a range between 200 yds and 3330 yds. The 741 yds generated by the construction data is a little below the average generated by the actual removal analysis. This probably indicates that on average, two (2) more feet has to be removed to reach the 1ppm standard for removal.

From these data we have assumed the following surface areas and pit depths for the models to be developed later.

Small Station-one tank	76 yds	Surface Area	220 ft^2
Small Station-three tanks	211 yds	Surface Area	616 ft^2
Large Station-three tanks	616 yds	Surface Area	1600 ft^2

As shown above in the figures for each site the depth of pit is assumed to be 10 feet for small stations and 15 feet for large stations.

References

Annual Underground Storage Tank Survey For 1991, Division of Waste Management, Natural Resources and Environmental Protection Cabinet, Frankfort, KY,

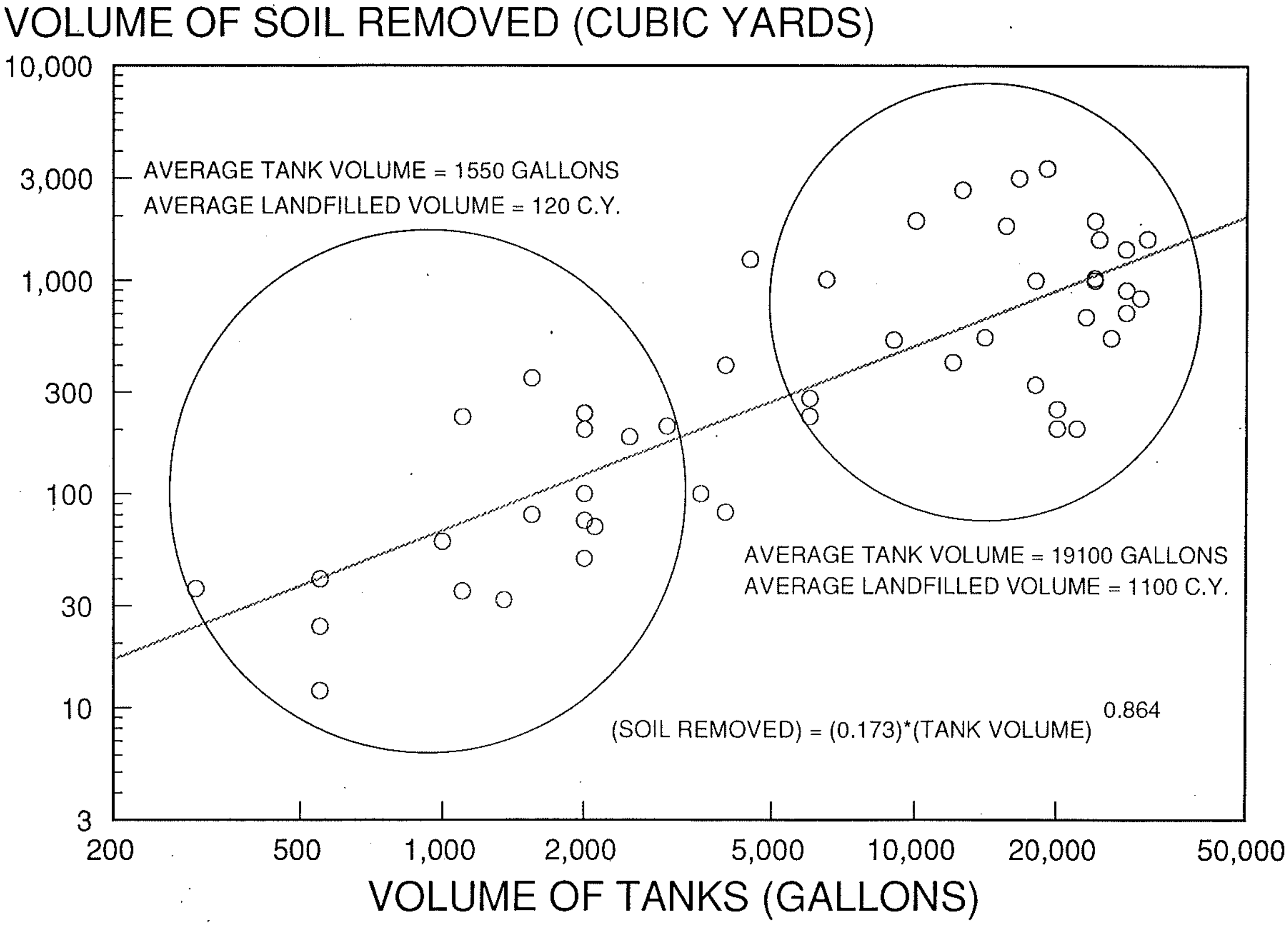

VOLUME OF SOIL REMOVED (CUBIC YARDS)
10,000
3,000
1,000
300
100
30
10
3
200
500
1,000
2,000
5,000
10,000
20,000
50,000
VOLUME OF TANKS (GALLONS)
AVERAGE TANK VOLUME = 1550 GALLONS
AVERAGE LANDFILLED VOLUME = 120 C.Y.
AVERAGE TANK VOLUME = 19100 GALLONS
AVERAGE LANDFILLED VOLUME = 1100 C.Y.
(SOIL REMOVED) = (0.173)*(TANK VOLUME) 0.864

FIGURE 1

APPENDIX

June 23, 1993

TO: Lyle Sendlein

FROM: Stephen Bassett

SUBJECT: Underground Storage Tank Excavation

Our survey included 131 contaminated underground storage tank sites chosen at random. To date, 55 of these sites have been accepted for closure. Of the 55 sites surveyed, 50 sites landfilled the contaminated soil and 5 left the soil on site. 8 sites reported their contaminated soil volume in tons. A conversion to cubic yards was made by assuming an average soil unit weight of 110 pounds per cubic foot. A list of the sites surveyed is enclosed.

The enclosed graph reveals a relationship between the volume of the soil taken to the landfill and the total volume of tanks removed. A regression analysis was performed on the 50 sites which landfilled their contaminated soil. The following relationship was derived:

$$\text{soil landfilled} = 0.173 * (\text{tank volume})^{0.864}$$

The sites were then classified as either small or large sites. The small sites were those sites composed of tank volumes in the range of 300 gallons to 3000 gallons. The average tank size for these sites was 1550 gallons and the average soil excavated was 120 cubic yards. The large sites were classified as those sites which had tanks in excess of 6000 gallons. The average tank volume for the large sites was 19100 gallons and the average soil excavated was 1100 cubic yards.

UNDERGROUND STORAGE TANK SOIL DISPOSAL DATA

COMPANY NAME	SOIL REMOVED	# OF TANKS (GALLONS)	DISPOSAL SITE	COUNTY
A&B TRUCK SERVICE	3330 C.Y.	10000 GAS 6000 GAS 3000 GAS	WASTE MANAGEMENT OUTER LOOP LANDFILL	JEFFERSON
CASTLEMAN OIL CO.	100 C.Y.	1000 DIESEL 500 WASTE OIL 500 KEROSENE	GRAVES CO. LANDFILL	GRAVES
ASHLAND BRANDED MARKETING, INC. (ABMI)	12 C.Y.	550 USED OIL	BFI WASTE SYSTEMS	FAYETTE
ABMI	75 C.Y.	2000 GAS	BFI-LAUBSCHER MEADOWS; EVANSVILLE	HENDERSON
ABMI	40 C.Y.	550 USED OIL	BFI, BENSON VALLEY LANDFILL, FRANKFORT	HENDERSON
ABMI	1800 C.Y.	3000 GAS 6000 GAS 6000 GAS 550 WASTE OIL	OUTER LOOP LANDFILL LOUISVILLE, KY	JEFFERSON
ABMI	208 C.Y.	1000 GAS 2000 GAS	OUTER LOOP LANDFILL LOUISVILLE, KY	HART
CERTIFIED OIL STATION	1000 C.Y.	8000 GAS 8000 GAS 8000 GAS	BFI WASTE SYSTEMS FRANKFORT, KY	ROWAN
JAMES W. ANDERSON	354.13 TONS	1000 GAS 1000 GAS	STATEWIDE ENVIRONMENTAL SERVICES, INC.	GREEN
ADVANCE TRANSPORTATION COMPANY	1900 C.Y.	2000 GAS 8000 DIESEL	GRAVES COUNTY LANDFILL	MCCRACKEN
VAN METERS STANDARD SERVICE	1008 C.Y.	2000 GAS 2000 GAS 1000 GAS 500 GAS 500 GAS 250 USED OIL 250 USED OIL	SOUTHERN SANITATION LANDFILL RUSSELVILLE, KY	
CEDAR GROVE GENERAL STORE	32 C.Y.	250 KEROSENE 550 GAS 550 GAS	OUTER LOOP LANDFILL	BULLITT
WD DUCKWALL	200 C.Y.	1000 DIESEL 1000 GAS	BFI LANDFILL FRANKFORT, KY	JEFFERSON
LEVINSON STEEL CO.	60 C.Y.	1000 GAS	BFI LANDFILL FRANKFORT, KY	MUHLENBERG

COMPANY NAME	SOIL REMOVED	# OF TANKS (GALLONS)	DISPOSAL SITE	COUNTY
MR. OTHO JEFFERSON	35 C.Y.	550 USED OIL 550 DIESEL	BFI LANDFILL FRANKFORT, KY	BRACKEN
HAGER CONSTRUCTION CO	240 C.Y.	1000 GAS 1000 DIESEL	BFI LANDFILL FRANKFORT, KY	JESSAMINE
CLYDE BURTON	70 C.Y.	560 GAS 1000 GAS 550 GAS	BFI LANDFILL FRANKFORT, KY	BOYLE
ABMI 341-002	3000 C.Y.	4000 GAS 4000 GAS 4000 GAS 4000 DIESEL 550 UNUSED OIL	BFI LANDFILL FRANKFORT, KY	SCOTT
ASHLAND SS 025-070	350 C.Y.	550 GAS 1000 GAS	BFI LANDFILL FRANKFORT, KY	MEADE
DARLING & CO	50 C.Y.	1000 DIESEL 1000 DIESEL	BFI LANDFILL FRANKFORT, KY	GARRARD
J.R. ASHERY 211-231	100 C.Y.	550 GAS 1000 GAS 2000 GAS	BFI LANDFILL FRANKFORT, KY	BOYLE
CHARLES WRECKER SERVICE	80 C.Y.	1000 GAS 550 GAS	BFI LANDFILL FRANKFORT, KY	JEFFERSON
YELLOW FREIGHT	250 C.Y.	10000 GAS 10000 GAS	CITY RECYCLING SERVICES, HOPKINSVILLE	CHRISTIAN
LOG CABIN	1000 C.Y.	8000 GAS 10000 GAS	RIVER CITY REFUSE, HICKMAN	LIVINGSTON
FAIRLANE CARRYOUT #2	414 C.Y.	4000 GAS 4000 GAS 4000 GAS	BAVARIAN LANDFILL	CAMPBELL
KENNETH SINCLAIR GROCERY	0 C.Y.	560 GAS 560 GAS 1000 GAS	EXCAVATED AND PUT ON PLASTIC AT SITE	ADAIR
SHORTSTOP FOOD MART	540 C.Y.	8000 GAS 6000 GAS	OUTER LOOP LANDFILL LOUISVILLE	JEFFERSON
CORNER GARAGE PHILLIPS 66	1250 C.Y.	2000 GAS 2000 GAS 500 KEROSENE	GRAVES COUNTY LANDFILL	MARSHALL
STEWARDS CAR RENUE (AMOCO)	300 TONS	8000 GAS 6000 GAS 6000 GAS	GREEN EARTH TECH, PIKEVILLE	WHITLEY
STEWART MECHANICAL ENTERPRISES	526 C.Y.	4000 GAS 5000 GAS	OUTER LOOP LANDFILL	JEFFERSON

COMPANY NAME	SOIL REMOVED	# OF TANKS (GALLONS)	DISPOSAL SITE	COUNTY
RICH OIL #7206	300 TONS	4000 GAS 4000 GAS 4000 GAS 4000 GAS 4000 GAS 2000 OIL	BFI LANDFILL FRANKFORT, KY	BOYD
FORMER MOBIL TRUCK PLAZA	1555 C.Y.	10000 GAS 10000 DIESEL 4000 GAS 550 USED OIL	BFI LANDFILL FRANKFORT, KY	MADISON
SUPERAMERICA	900 C.Y.	4000 GAS 4000 GAS 4000 GAS 4000 GAS 12000 GAS	OUTER LOOP LANDFILL	JEFFERSON
FACILITY RE 264	36 C.Y.	300 USED OIL	BFI LANDFILL FRANKFORT, KY	JEFFERSON
SWIFTY SERVICE STATION	800 TONS	6000 GAS 10000 GAS 10000 GAS	BAVARIAN LANDFILL WALTON, KY	KENTON
TAYLOR COUNTY HIGH SCHOOL	7 LOADS DUMP TRUCK	5000 #2 FUEL	BROWNING FERRIS INDUSTRIES	TAYLOR
PT-3 GAS INC	411.57 TONS	3 PIPES	WASTE MGT. BLUE RIDGE IRVING, KY	MADISON
DIRECT #085-15	1000 TONS	6000 GAS 7000 GAS 10000 GAS	BEING HELD AT DON BELL TAYLOR FARM; AWAITING DISPOSAL APPROVAL	
THONI OIL MAGIC BENZOL GAS STATION	1897 C.Y.	4600 GAS 4600 GAS 4600 GAS 10000 GAS 200 WASTE OIL	MORGANTOWN/DOZIT COMPANY LANDFILL	MCCRACKEN
THONI OIL MAGIC BENZOL GAS STATION	1393 C.Y.	8300 GAS 6000 GAS 6000 GAS 4600 GAS	BUTLER COUNTY LANDFILL	WARREN
THONI OIL MAGIC BENZOL GAS STATION	708 C.Y.	10000 GAS 6000 GAS 6000 GAS 6000 GAS	BUTLER COUNTY LANDFILL	WARREN
VERSAILLES WATER PLANT	341.3 TONS	550 GAS 550 GAS	BFI LANDFILL FRANKFORT, KY	WOODFORD
PHILLIPS 66 SERVICE STATION	2635 C.Y.	4000 GAS 4000 GAS 4000 GAS 550 USED OIL	SOUTHERN SANITATION LANDFILL RUSSELVILLE, KY	TRIGG

COMPANY NAME	SOIL REMOVED	# OF TANKS (GALLONS)	DISPOSAL SITE	COUNTY
DAYS INN MOTEL	1026 C.Y.	8000 GAS 8000 GAS 8000 GAS	OUTER LOOP LANDFILL	HARDIN
WEBSTER SERVICE STATION	280 C.Y.	4000 GAS 2000 GAS	STOCKPILED ON SITE WILL GO TO BFI IN FRANKFORT	HENRY
NON SUCH GROCERY	SOIL ON SITE	1000 GAS 550 GAS	SOIL ON SITE	WOODFORD
WESTVACO CORP	343 TONS	3000 DIESEL 3000 GAS	LWD, INCORPORATED CALVERT CITY	BALLARD
BILL WHITE SUNOLO	324 C.Y.	6000 GAS 4000 GAS 4000 GAS 4000 GAS	OUTER LOOP LANDFILL	JEFFERSON
WRIGHTS GROCERY	NOT AVAILABLE	1000 GAS 1000 GAS 2000 GAS 550 DIESEL	PLACED BACK IN EXCAVATION	FRANKLIN
SEVEN/ELEVEN	24 C.Y.	550 WASTE OIL	VALLEY VIEW LANDFILL	OLDHAM
RUBY'S BOAT DOCK	185 C.Y.	500 GAS 1000 GAS 1000 GAS	BAVARIAN LANDFILL	GRANT
SUPERAMERICA	828 C.Y.	10000 GAS 10000 GAS 10000 GAS	BAVARIAN LANDFILL	CAMPBELL
RHODES SUPPLY	1560 C.Y.	500 DIESEL 500 DIESEL 10000 GAS 10000 GAS 10000 GAS	GRAVES COUNTY LANDFILL	GRAVES
REED CRUSHED STONE	400 C.Y.	2000 2000	LOUISVILLE OUTER LOOP LANDFILL	LIVINGSTON
PURHAM GROCERY	82 C.Y.	2000 GAS 2000 GAS	PULASKI LANDFILL	LINCOLN

GENERIC ORGANIC CONTAMINANT PATHWAY ANALYSIS FOR COMPONENTS OF PETROLEUM IN SOIL AND GROUNDWATER

P.M. McGinely

CONTENTS

TABLES

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I. INTRODUCTION

Generic soil standards are levels of contaminants protective of human health and the environment for sites which may share only several general characteristics. When such standards are employed, only limited information about site characteristics may be incorporated. Consequently, generic standards must accomodate uncertainty in many site conditions. Important aspects of establishing generic soil standards are the processes which occur during the transport of organic compounds in soil and groundwater. Processes occurring along this pathway may determine whether contaminants will contact a receptor and, if so, at what level that contact occurs. Aspects of the pathway which are important in establishing generic standards are 1) the site characteristics which control contaminant release; and, 2) the concentrations of contaminants which can be expected to derive from different levels of soil contamination.

Although models are available which predict the anticipated effects of different processes on the fate and transport of contaminants for well-defined conditions, these processes may be linked in ways which defy generic description. As a result, application of such models to sites which are defined by only several conditions cannot be expected to describe all related situations; however, simple models of contaminant migration which use general, limiting assumptions may be useful to determine the sensitivity of contaminant fate to the different processes and to quantify the outer bounds of contaminant concentrations deriving from contaminated soil. A review of the literature and analysis of pertinent assumptions was used to develop several generic migration pathway models which are applied generically to soil contamination after underground storage tank (UST) removal.

Two aspects of contaminant behavior in natural systems will be examined in this pathway analysis: 1) contaminant chemistry; and 2) contaminant transport. Contaminant chemistry will be examined within the context of the equilibrium partitioning of individual organic compounds. It will only briefly address the rates at which contaminants redistribute between the phases in a natural system because partitioning processes are expected to be relatively rapid compared to the time-frame for transport. The analysis presented will be limited to low concentrations of contaminants. This constrains the analysis to UST situations where contaminated soil is the only reservoir of contaminants. Both vapor phase diffusion of contaminants and the migration of contaminants through unsaturated and saturated media will be examined. The absence of well-defined boundary conditions for generic standards constrains the models to straightforward mathematical descriptions of contaminant behavior. The result does not constitute a mathematical description of a particular natural system, but rather, a general model of contaminant fate.

II. EQUILIBRIUM PARTITIONING OF ORGANIC CONTAMINANTS

Organic contaminant molecules can distribute between the different phases present in a natural system. For example, a fraction of the total contaminant may be directly associated with, or sorbed by, a solid phase, another fraction may be dissolved in the water phase, and a fraction may also be present in the air phase. Although not examined in this analysis, at very high concentrations (e.g., when a petroleum product phase is also present), a portion of the contaminant may also be present within the petroleum product.

Equilibrium distribution of contaminants between soil, water, and air can be described using partition relationships. These relationships quantify concentrations in two different phases. In turn, once determined, partition relationships can be combined with phase characterization in a different system to predict the equilibrium distribution of contaminants.

At the relatively low concentrations of organic contaminants examined here, the vapor phase concentration of an organic contaminant can be related to the solution phase concentration of a contaminant using the Henry's constant:

$$H=\frac{P_a}{C_w} \qquad (1)$$

where P_a is the partial pressure of the contaminant in the air phase and C_w is the concentration in the water phase. The Henry's constant, H, in Equation 1 is independent of the concentrations in both phases, or is a linear partition. It is often useful to express the partitioning between phases as a ratio of concentrations (mass per unit volume of the phase). If the vapor concentration of the contaminant is ideal, the ratio can be expressed:

$$K_H=\frac{C_{air}}{C_w}=\frac{H}{RT} \qquad (2)$$

The Henry's constants for several compounds are shown in Table 1.

The partition of the contaminant between soil and water is also observed to be linear. This seems to be a good approximation at low concentrations, e.g. half-solubility, of contaminant (Chiou et al., 1983), although certain types of geological materials can have nonlinear partition relationships (Weber et al., 1992). The quantity of contaminant which actually resides on the soil can then be expressed as a function of the concentration in the solution using:
where:

$$C_s = K_D C_w \qquad (3)$$

C_s = concentration of contaminant in soil expressed as mass of contaminant per unit mass of dry soil (e.g., mg/kg)
C_w : concentration of contaminant in solution (e.g., mg/l)
K_D : linear distribution coefficient (units depend on those selected for C_s and C_w, e.g., l/kg)

Experimental measurements of contaminant distribution between soil and water has shown that the distribution coefficient (K_D) can be related to the organic matter content of the soil (higher organic matter soils have larger K_D) and properties of the contaminant (less water-soluble organic contaminants have larger K_D). Using the organic carbon content of the soil as a measure of the organic matter content, leads to a carbon-normalized distribution coefficient has been empirically determined for many organic contaminants:

$$K_{OC} = \frac{K_D}{f_{OC}} \qquad (4)$$

where:

f_{OC} : the mass fraction of the dry soil which is organic carbon, typical values for soil range from 0.05 down to 0.001 (representing 5% down to 0.1% organic carbon by weight)
K_{OC} : the organic carbon-normalized distribution coefficient. This has the same dimensions as K_D, but is often listed without dimensions. In that case, it is most likely in l/kg or equivalently, cm^3/gm.

K_D can then be calculated using a K_{OC} obtained from literature compilations values and the f_{OC} of the soil. Table 2 shows typical K_{OC} values for benzene, ethylbenzene, toluene, and a xylene (BTEX). Including the K_{OC} and f_{OC}, Equation 3 can be rewritten:

$$C_s = f_{OC} K_{OC} C_w \qquad (5)$$

The concentration of contaminant on the soil is related to properties of the soil (f_{OC}), the compound (K_{OC}), and the solution (C_w).

The presence of a pure organic (e.g., benzene) in the system is an additional phase where the contaminant may reside. Distribution of the contaminant between a pure phase and an adjacent aqueous or vapor phase is described by the solubility of the compound or the vapor pressure, respectively. In the presence of mixed organic phases (e.g., gasoline), the concentrations in air and water adjacent will not be those of the pure organic compounds, but will be most likely be lower (Lyman et al., 1991). To estimate the concentrations in the aqueous or air phases at equilibrium, the solubility or vapor pressure can be scaled by the mole fraction of the contaminant in the organic phase. Concentrations in water can be increased by large quantities of water-soluble organic compounds such as methanol in the gasoline because they dissolve the aqueous phase and increase the solubility of the compound (Poulsen et al., 1992). The focus of this analysis will be low concentrations of petroleum components in water and air, pure and mixed phase relationships of these compounds will not be considered further.

Contaminant partitioning relationships are important in contaminant migration because the extent to which a contaminant is associated with stationary phases (e.g., the soil solid phase), will reduce the migration within a moving phase (e.g., soil water or groundwater). Partition relationships also provide insight into the distribution of contaminants in reported soil concentrations. For example, in soil analysis which reports a total mass of contaminant per unit of dry soil, the total concentration of a contaminant (mass of contaminant per mass of dry soil), C_T, can be related to the concentrations in the different phases by:

$$C_T\rho_b=\theta_w C_w+\theta_a C_a+\rho_b C_s \qquad (6)$$

Where C_T represents the total concentration of contaminant in the soil sample (contaminant in the air, water and sorbed onto solid phase of the soil) expressed per unit mass of dry soil, Θ_a is the air-filled porosity, and Θ_w is the water filled porosity, p_b is the dry bulk density or the mass of dry soil per unit of the total volume of soil/water/air. Both porosities are defined as the fractions of the total soil volume which is air or fluid-filled.

Similarly, total concentrations can be converted to a common concentration using linear partition relationships. The total soil concentration, C_T, relates to the concentration in the fluid phase, C_W, through:

$$C_T\rho_b=\theta_w C_w+\theta_a K_H C_w+\rho_b K_{OC} f_{OC} C_w \qquad (7)$$

The extent to which partitioning of contaminants leads to variations in the concentrations in different phases is shown in Table 3 for benzene at a unit level of contamination (1 mg benzene/kilogram soil). When the quantity of organic carbon in the soil is 2%, which might be typical for a surface soil, most of the benzene exists sorbed by the soil; however, if the concentration of organic carbon is 0.1%, which might be typical for a subsoil, less than half the benzene is actually sorbed by the soil. This is an important relationship because the soil sorbed form of the contaminant is likely to be stationary, and greater soil f_{OC} will lead to slower migration of contaminant. In the migration pathway analysis below, a conservative f_{OC} of 0.001 is always assumed because this represents the greatest potential for contaminant migration.

Equation 6 (or variations thereof) can be used to establish total soil concentrations which represent equilibrium with required solution concentrations. For instance, if a maximum benzene concentration in the water is assumed to be 0.005 mg/l, and $\Theta_w = 0.4$, $\Theta_a=0$ (saturated) and the soil f_{OC} is 0.001, then the total soil concentration (C_T) which could be present in a saturated soil would be 0.0017 mg benzene/kg soil. If the soil organic carbon is greater, a larger percentage of the C_T remains in the solid phase and total soil concentrations could be increased. For a f_{OC} of 0.01, the acceptable soil concentration would be 0.005 mg/kg. Examples of the impact of soil f_{OC} and MCL for different BTEX compounds are shown in Table 4. These results do not include any additional mechanisms for concentration reduction which might be expected to occur during transport to receptors, but provide a baseline for comparing protective C_T which are obtained through generic migration pathways.

III. SURFACE VOLATILIZATION PATHWAY ANALYSIS

Introduction

Where unsaturated soil exists between the contaminated soil and the groundwater or soil surface, the contaminants may migrate upward, downward, or laterally in soil air. This migration results from diffusion in soil air, and transport within moving soil air. Diffusion is a process where contaminant concentrations change in response to gradients in contaminant concentration. Contaminants migrate in the direction of decreasing concentration. For petroleum components which contaminate a soil below the surface, movement of the contaminants to the soil surface will occur when lower concentrations of contaminant are present at the surface. For the case where soil air is also in motion (e.g., soil vacuum extraction or in response to variations in barometric pressure), the contaminant migration in the vapor phase will also reflect the moving air phase. In the analysis here, only contaminant migration in static soil air systems will be considered and contaminants will be assumed to move vertically to the surface.

Volatilization Modeling

Three methods of analysis will be used to estimate contaminant volatilization to the surface: 1) a uniform release of contaminant out of the soil over a time period (e.g., 17 months); 2) a steady-state diffusion from a zone of contamination to the soil surface; and, 3) an unsaturated zone contaminant transport model, SESOIL.

The three methods were applied to the large UST site which was described by Sendlein et al. (1993). This site has a surface area of 1.2 x 10^6 cm^2 and a depth of 4.5 meters. A unit level of contamination, C_T, of 1 mg benzene/kg soil is used in all models, but the results can be linearly scaled for any concentration in the soil. Several different distributions of contaminated soil will be examined: in one, the entire depth of soil (4.5 meters or approximately fifteen feet) which would fill the pit will be assumed to be contaminated, in another, the upper 1.5 meters of soil will initially be clean, and in the third, 3.0 meters of clean soil will overlay the lower 1.5 meters of contaminated soil. Because the soil is assumed to contain 1 mg/kg of benzene, the total mass of benzene will be reduced as the depth of contaminated soil is reduced. The model UST volatilization situation is shown in Figure 1.

Volatilization Method I: Uniform Release of Contaminant

The total quantity of benzene in the contaminated soil if the entire depth is contaminated is: Then if the benzene leaves the soil uniformly over a 17 month period of time, the quantity of benzene

$$Total\ Benzene = (540m^3)(\frac{1600\ kg\ soil}{m^3})(\frac{1\ mg\ benzene}{kg\ soil}) = 8.64x10^5\ mg\ benzene$$

which leaves the soil each day is:

$$Benzene\ Volatilized = \frac{8.64x10^5\ mg\ benzene}{(17\ months)(\frac{30.4\ days}{month})} = \frac{1671\ mg\ benzene}{day}$$

If the contaminated zone is only 3.0 meter deep, but is buried below 1.5 meter of clean soil, this model predicts a volatilization of benzene which is reduced only by the reduction in benzene mass (take 2/3 of the value above) and cannot reduce the rate of benzene movement into the atmosphere due to the burial depth. The results of the model are summarized in Table 5.

Volatilization Method II: Steady-State Diffusion Model

Another model for benzene volatilization assumes the transport of benzene to occur by diffusion through the gas-filled pores of the soil. In a steady-state analysis of this model, a fixed concentration of benzene in soil air is assumed at some depth in the soil and at the surface. These assumptions are likely conservative because they do not allow for a reduction in the concentration of contaminant as the diffusion process continues. This conservative approach has value in validating the outer boundary for anticipated diffusion, and might be appropriate where the nature of the source (i.e., depth of contaminated zone) is unknown.

The gas concentration can be computed from the total soil concentration using the methods described in the previous section (Equation 8) and the concentration at the surface will be considered zero (representing rapid distribution into the atmosphere). The rate of contaminant volatilization from a site of area A can be expressed:

$$Benzene\ Volatilization = \frac{(A)(D_e)(C_a)}{L}$$

where D_e is the effective diffusion coefficient adjusted for soil conditions, C_a is the gas concentration of the contaminant at depth, L. D_e can be computed using a diffusion coefficient in air, D, which is adjusted for the tortuosity of the soil and for equilibrium partition into the soil solids and soil water. The following relationship can be used to approximate these effects :
where the first term after D reflects the retardation of contaminant by distribution into soil water and sorption onto soil, and the second term is an adjustment for the porosity and tortuosity of the media (Millington and Quirk, 1961).

$$D_e = D\left(\frac{1}{1+\frac{\rho_b K_D}{\theta_a K_H}+\frac{\theta_w}{\theta_a K_H}}\right)\left(\frac{\theta_a^{3.33}}{(\theta_a+\theta_w)^2}\right)$$

As an example, consider the diffusion of benzene from a 1 mg/kg soil concentration with Θ_w = 0.1 and Θ_a = 0.3, and p_b = 1.6 gm/cm^3 and f_{OC} = 0.001. Assuming the gas phase diffusion coefficient of benzene, D, is 0.09 cm^2/s at 25 degree C (Lyman et al., 1991), but after adjustment for retardation and tortuosity in the media the D_e is 0.0022 cm^2/s. This reduction in diffusion coefficient indicates the extent to which the diffusion through the soil is hindered over that in air. The calculated fluxes of benzene for the two buried soil conditions and the large site are shown in Table 5.

The steady-state model uses fixed conditions both at depth (unit concentration in soil) and at the surface (zero concentration at the very top of the soil where it is assumed in equilibrium with an infinite quantity of air). As such, this description leads to a linearly varying concentration of benzene throughout the soil profile and a constant flux of benzene out of the soil. The average concentration of benzene in the soil at different depths can be obtained through linear interpolation. These values are shown in Table 5 as the average concentration of benzene near the surface. Of course, if there are conditions at the surface of the soil which reduce the diffusion of volatile contaminants, such as a compacted layer of soil of very low permeability or of higher organic carbon content, then the profile of contaminant concentration may not be linear from the zone of contamination to the surface, and higher total concentrations of contaminant could be found below the lower permeability or higher sorbing zones. This analysis also does not consider the enhanced volatilization by fluctuations in atmospheric pressure (Wagenet et al., 1989).

Volatilization Model III: SESOIL Model

An alternative method for estimating the volatilization of benzene from the soil surface is the model SESOIL. SESOIL is a one-dimensional model for the transfer of contaminant between different layers in the system. Moisture routing in the model is accommodated with a water budget analysis and local weather conditions input by the user. The three different test cases were examined for diffusion to the surface and two soils. The benzene volatilization over the first year is shown in Figure 2 for a sandy soil. The maximum benzene volatilization for all three cases is predicted to occur within several months. A similar simulation for a finer grained soil (silt) lead to a delayed migration of benzene to the surface and a lower maximum volatilization. The maximum monthly quantity of benzene volatilized was converted to an average daily rate and compared to the other two simulation methods in Table 5.

The accuracy of SESOIL for predicting volatilization of contaminants from the subsurface has not been explicitly tested. Recent modeling with SESOIL in Oregon, reduced the predicted volatilization through an adjustable factor in the model (Anderson, 1992). The simulations described here did not reduce the volatilization when examining the vapor phase transport pathway. Movement of contaminant downward through the soil profile is also permitted in the SESOIL simulations. In the case of a relatively volatile contaminant such as benzene, SESOIL predicts the majority of the contaminant will volatilize quickly and over that time, only a small fraction actually moves downward through the profile. In the later sections of this report which examine the groundwater pathway, SESOIL simulations which do not include or reduce the volatilization will be used.

The same SESOIL simulations were also used to estimate the concentration of benzene in upper soils resulting from the burial of contaminated soil. In Table 5, the concentrations of benzene at the surface which are predicted using the different models are shown. Comparison of those soil concentrations to that calculated using the conservative steady-state analysis demonstrates that the SESOIL maximums are less, although of the same range as that predicted using a steady-state analysis. This is anticipated, because SESOIL reduces the concentration in the soil with time as the benzene is depleted through volatilization. The model system examined in these models assumed that the organic carbon content of the soil was a constant 0.001% throughout. Although increased concentrations of organic carbon would be expected to reduce the rate of volatilization because the contaminant would be more strongly sorbed by the soil, increased organic carbon in the surface soil would also be expected to increase the concentration of contaminant at the surface because a greater percentage might be sorbed by the soil.

IV. GROUND WATER PATHWAY ANALYSIS

Introduction

Water which moves through contaminated soils can acquire contaminants and move them through the soil profile. In a relatively humid climate, such as that in Kentucky, these compounds may eventually enter a saturated zone. Once in the saturated zone, these contaminants can move with migrating water, although the rate at which they are transported will depend on the velocity of flow and the extent to which the contaminants are sorbed by the solid phases in the groundwater.

Many models are available to predict the time rate of contaminant leaching from through soils and the migration of contaminants in saturated subsurface zones, but to develop a generic pathway analysis, the various components of the process will be examined independently to permit a sensitivity analysis for the assumptions of each step. Components of the path will be combined to provide factors which can be used to scale soil concentrations to determine model predicted groundwater concentrations at various distances from the UST. An overview of the overall groundwater pathway analysis is presented in Figure 3.

The segments of the pathway will be used to develop concentration adjustments which convert soil concentrations to water concentrations. The groundwater concentration at the receptor will be the product of different steps in the process:

$$C_r = C_T f_u f_v f_h f_t$$

where the groundwater concentration of the contaminant at the point of receptor contact, C_r, is the product of C_T, the total soil concentration, and the adjustments for unsaturated soil transfer, (f_u), vertical mixing in the saturated zone, (f_v), horizontal transport and degradation in the saturated zone, (f_h), and transverse mixing and reaction, (f_t). Contaminant reaction at any point during this migration can reduce the total quantity of contaminant. The reactions included in the generic pathway are volatilization, sorption by solids, and biodegradation. Volatilization will be permitted only in the unsaturated zone. Sorption will be included in both the unsaturated and the saturated zone using the linear partition relationships described above. Biodegradation will be included using reaction kinetics. Determining the relationship between site variables and the reactions which may reduce contaminant concentration is important to determining generic soil standards.

Many of the organic contaminants frequently associated with UST can be biologically degraded. The absence of benzene in a recent California ground water quality survey was attributed to biodegradation (Hadley and Armstrong, 1991). Unfortunately, the rate and extent of biodegradation reflects a host of factors, including: concentration, biomass concentration, temperature, pH, and availability of inorganic nutrients and electron acceptors, and microbial adaptation, all of which cannot be easily included in generic models.

The biodegradation of organic contaminants will be included in this analysis using simple rate laws to describe a time rate of change in contaminant concentration. One such rate law which has found application in the description of biological degradation is the first-order:

$$\frac{dC}{dt}=-kC$$

where C is the concentration of the pollutant and k is the first order rate constant. The rate constant for biodegradation will relate to the quantity of microorganisms and concentration of other reactants which are necessary. The time to halve the concentration is often referred to as the half-life, $t_{1/2}$. In a first-order kinetics, the half-life can be related to the rate constant independently of the initial concentration of the contaminant:

$$t_{\frac{1}{2}}=\frac{0.693}{k}$$

Consequently, reference to a contaminant half-life fixes the rate constant for biodegradation. First-order or half-life representations of biodegradation rates can be included in most models of contaminant transport, but they may not always be the most appropriate description of the process. In those cases where the first-order rate expression is not a useful description of the rate, the half-life is, in general, not independent of concentration.

The biological degradation of benzene demonstrates the difficulty in the generic application of rate laws to this natural process. Benzene can be biologically degraded under aerobic (oxygen present) conditions and a field study which examined the degradation of benzene in a shallow alluvial aquifer in Mississippi (Boggs et al., 1993) found benzene disappearance which followed a first order rate law, with a half-life of 69-87 days. In the absence of oxygen (anaerobic), benzene biodegradation may be much slower (Hutchins et al., 1991; Barker et al., 1987). Barboro et al (1992) report that benzene did not degrade after 300 days within a leachate plume where oxygen was not detected. The aerobic decomposition of organic compounds consumes oxygen, and because the relatively low solubility of oxygen limits concentrations in the groundwater to less than 10 ppm, degradation of large quantities of benzene and other organic compounds may lead to oxygen depletion and limit the biodegradation rate. Under those conditions, the first-order rate law may no longer be appropriate. Tucker and Zavala (1992), for example, used a zero-order rate law when oxygen-limitation might slow the biodegradation of BTEX.

The generic fate and transport pathway analysis presented here will use a first-order rate law for pollutant biodegradation. In many cases, this may be an appropriate description, and in all cases it is useful because the results can be scaled independent of initial concentrations. To discount potential error in its application, three different biodegradation rates will be examined: 1) no biodegradation; 2) a half-life of 100 days (corresponding to field-observed benzene disappearance); and 3) a half-life of 700 days (reported for the anaerobic disappearance of benzene).

Unsaturated Zone Modeling

Contact of infiltrating soil water with contaminated soil will lead to a downward migration of the contaminant through the soil profile. In this portion of the pathway, the contaminant will be assumed to only travel downward in moving fluid and equilibrium partitioning will be used to characterize the concentration of the contaminant in the fluid phase. Two methods of analysis will be employed to calculate water concentrations which have contacted contaminated soil: 1) equilibrium with infiltrating moisture; and 2) the model SESOIL. Both methods can be used to compute a scaling factor, C_u, which can be used to adjust the total soil concentration of a contaminant to the soil water concentration at entry to the saturated zone.

Unsaturated Zone Model I: Equilibrium with Infiltrating Moisture

If infiltrating moisture is assumed to be in equilibrium with the contaminated soil, concentrations of contaminants in the water can be computed using the equilibrium partitioning described earlier. This is likely to be a conservative concentration because it neglects other potential mechanisms for loss of the contaminant in the unsaturated zone. The rate at which the contaminant passes through the unsaturated zone can be estimated with knowledge of the rate of flow. Although these rates are complex and site-specific, a simple analysis can use maximum monthly precipitation and assume it provides a steady flow in the saturated zone. This neglects evapotranspiration and other factors which act to reduce the quantity of precipitation which becomes infiltration.

Calculation of the soil percolate concentration can be done using the relationships such as Equation 7. For the unit contamination level of 1 mg benzene per kg of soil, the concentration of benzene in the liquid associated with the soil will vary with the bulk density of the soil, porosity, and the water content. Assuming the same soil as examined earlier ($f_{OC} = 0.001$, $\Theta_a = 0.3$, $\Theta_w = 0.1$, dry bulk density = 1.6 gm/cm_3), the concentration of benzene in the soil water will be 5.35 mg/l. This value can be scaled linearly for other soil concentrations. If a central Kentucky climate is assumed, then approximately 11 cm of precipitation might be assumed for a peak month. For the large UST site examined earlier, the quantity of benzene which would enter the saturated zone in this model can be calculated:

$$Benzene\ Entering\ Saturated\ Zone = (\frac{5.35ug}{cm^3})(11cm)(1.2x10^6cm^2) = \frac{7.06x10^7\ ug}{month}.$$

Higher soil f_{OC} will reduce the fraction of the benzene in the soil which is in the soil percolate, and reduce the quantity of benzene moving through the profile. This calculation, although simple, provides a baseline for comparing other models.

Unsaturated Zone Model II: SESOIL

SESOIL is a soil compartment model which can provide estimates of pollutant movement in the soil (Hetrick et al., 1989). Several states (California, Oregon, Wisconsin) have employed SESOIL for examining contaminant migration in soils (State of California, 1989; Anderson, 1992; Science Technology Management, Inc, 1993). The model combines a moisture balance with chemical-specific information on volatilization and soil sorption (using linear partitioning) and degradation reactions. Validation of the SESOIL model for petroleum compounds was not found in the literature. In the present analysis, the model was used primarily to determine what the concentration of contaminant would be in the soil moisture at the base of the unsaturated zone.

Application of SESOIL in a humid climate results in an input of contaminant which varies during the year. Normal monthly precipitation and temperature for Lexington, KY were based on the mean for 1935-1970 (NOAA, 1988). Table 6 shows those values and the other climate information which was input. In the SESOIL model, most of the information is used to calculate the evaporation. Both program estimated values and a no evaporation condition were compared. Contaminant properties included the K_{OC}, K_H, air diffusion coefficient, and first-order biodegradation rate constants. Only fluid-phase biodegradation was used in the SESOIL model. Soil porosity, organic carbon content, intrinsic permeability and pore disconnectedness were the parameters required to describe the soil. The purpose of this application of SESOIL was a screening of the sensitivity of contaminant concentration to different depths and types of soil. A recent application of the model in Wisconsin (Science Technology Management Inc., 1993) demonstrated the sensitivity of soil concentrations to soil permeability and biodegradation rate. These were the focus parameters in this analysis, and what were viewed as conservative values for the other parameters were employed. Soil organic carbon content was set to 0.1%, porosity was 0.4, soil bulk density was 1.6 gm/cm3, soil pore disconnectedness was 4.5. The pore disconnectedness index is a one parameter fit to the hydraulic conductivity moisture content relationship in the soil. Model calibration may be required to accurately determine this parameter, but a likely range is from 3.7 to 10 (Watson and Brown, 1985). Lower values correspond to uniform sands and higher values to structured clays. With respect to determining the maximum concentration at the base of a soil profile, lower values appear to more conservative (lead to slightly greater concentrations) and a value of 4.5 was used for most of the simulations. Soil intrinsic permeability from 10^{-10} cm^2 to 10^{-7} cm^2 was used. 10^{-7} cm^2 will be referred to as "sand", 10^{-9} cm^2 as "silt", and 10^{-10} cm^2 as "clay".

As shown in the previous section, contaminant volatilization can lead to a reduction in the quantity of contaminant in the soil, and subsequently will have an effect on contamination in the groundwater pathway. It is difficult to examine both of these routes of exposure simultaneously, yet remain conservative. In analysis of downward migration, upward volatilization of the contaminant was only partially permitted. This conservative use of the model was suggested by several users (Anderson, 1992; Nold, 1993). A reduced volatilization index (VOLF in the SESOIL model) of 0.2 was used. In contrast, the upward migration of contaminants through volatilization which was used to predict surface concentrations employed the SESOIL model with full volatilization (VOLF = 1.0).

Examples of SESOIL model results are shown in Figure 4 as a comparison of the quantity of benzene leaving the soil profile for two different soil types and different rates of biodegradation. It is apparent that the sandy soil would lead to benzene movement out of a 6 meter zone of soil earlier than the silty soil, as expected. When first-order biodegradation is included, a reduction in the quantity of benzene which enters the groundwater is observed. A 700 day half-life leads to only a modest effect on the anticipated benzene flux in both soils, but a half-life of 100 days substantially reduces the mass flux, particularly in the silt soil for which the contaminant residence time within the unsaturated zone is much longer. The maximum mass fluxes of benzene for these simulations are summarized in Table 7. Comparison of these values to the equilibrium soil percolate model demonstrates that some reduction in monthly loading over the maximum value might be anticipated, but without mechanisms for benzene disappearance, such as biodegradation and volatilization, only minor reductions are predicted.

SESOIL simulations are shown in Figure 5 as concentrations of benzene in the moisture which leaves the unsaturated zone for two different depths of contaminated soil and a 6 meter thickness of uncontaminated soil. Increasing the depth of the contaminated soil does not have a significant effect on the maximum concentration in the soil percolate, an effect which is expected since equilibrium partitioning is used to predict these concentrations, but it does increase the time over which higher concentrations are present in the soil percolate.

SESOIL results for benzene and a variety of different unsaturated zone leaching simulations are shown in Table 8 as the maximum concentrations in the moisture which enters the saturated zone. As was shown in Figure 5, the maximum benzene concentrations occur early in the time over which contaminant movement is expected. Several trends are apparent in the results presented in Table 8. The depth to groundwater has only a minor effect on the maximum concentration in the absence of volatilization, but it can significantly reduce the maximum concentration when biodegradation is included. Increasing the initial contaminant concentration in the soil has an almost proportional affect on the concentration predicted for concentrations leaving the unsaturated zone. This is a useful result (although expected for linear partitioning and first-order kinetics) in that it permits the results to be scaled for any initial concentration by adjusting those values obtained for a unit level of initial concentration (1 mg/kg). The effect of soil type on the maximum concentration depends on the mechanisms for contaminant reduction which are also included. If only volatilization is included, the more impermeable silt leads to soil percolate concentrations which are similar to the sand. But if biodegradation is included, the greater residence time in the silt leads to a much lower concentration than is predicted for the sand.

The results from using SESOIL to model the transport of toluene, ethylbenzene and xylene are shown in Tables 9, 10 and 11, respectively.

The results shown in Tables 8-11 will be used as the first adjustment to the total soil concentration in the generic groundwater pathway. Multiplying soil concentrations by the values in Tables 8 can be used to predict the maximum concentration of benzene at the entrance of soil water into the saturated zone. To summarize the magnitude of this adjustment, Figure 6 shows the maximum concentrations in soil percolate for 1 ppm soil concentration for three different soils. For shallow soils typical of those found in Kentucky, the permeability of the soil does not impact the maximum concentration at a 700 day half-life as much as the soil depth. This reflects a tradeoff between volatility and degradation. More permeable soils permit less degradation because the contaminant moves more quickly, but they also have greater loss to the surface through volatilization. In contrast, shorter half-lives make the reduction in concentration much more sensitive to the soil permeability.

Using the maximum concentration for the soil percolate and a 700 day half-life in the SESOIL model reduces the sensitivity of climate on the results. For example, in the benzene and toluene results (Tables 8 and 9), SESOIL simulations in the absence of evapotranspiration (No ET) leads to maximum concentrations of toluene which are only slightly higher than those with evapotranspiration. This result is expected because any climatic conditions which increase infiltration, will lead to a faster movement of contaminant and less time for degradation processes.

Saturated Zone Modeling

In the generic ground water pathway, the introduction and transport of contaminant in ground water acts to further reduce concentrations due to dilution and perhaps biodegradation. In natural systems, these reactions take place through three-dimensional plume development. In this model, three different aspects of the pathway will be used for obtaining pathway contaminant concentrations in the saturated zone beneath UST sites. Vertical mixing will be approximated using balance approach (EPA, 1989) and groundwater transport will use both a one dimensional, steady-state, analytical solution and a multiplier for mixing in a second dimension.

Vertical Mixing

Vertical mixing in the saturated zone will take place as part of a 3-dimensional mixing, the extent of which relates to properties of the aquifer and flow conditions. The vertical component of this process will be estimated by assuming that a fraction of the water in the saturated zone completely mixes with incoming water from the unsaturated zone. Although is not a rigorous depiction of the processes which occur at the interface between the unsaturated and saturated zones, it does permit the potential dilution to be quantified in a very simple way.

The flow rate of flow in the saturated zone (the velocity of flow times the area of impact) and the flow rate of water into the groundwater from the unsaturated zone are combined to provide a total quantity of flow in the saturated zone. The quantity of contaminant which enters that zone by movement through the unsaturated soil is then distributed equally to the total flow. As the quantity of groundwater flow is increased, the dilution is increased. Factors which contribute to a greater degree of concentration reduction include increasing the depth of the saturated mixing zone and increasing groundwater velocity. In field situations, the quantity of precipitation which actually moves into the saturated zone will vary depending on the run-off, soil type and evapotranspiration. The quantity will vary with location and climate. In the generic pathway model, an annual rainfall of 120 cm was assumed and considered to entirely move into the saturated zone (average 0.33 cm/day). Site dimensions were assumed to be those of the large site described by Sendlein et al. (1993). The vertical dilution adjustment to the concentration, f_v, is shown in Table 12 for different conditions.

The product of soil percolate concentration and soil moisture flow rate represents the mass of contaminant entering the saturated zone. An alternative to the simple analysis presented here, models such as SESOIL can also be used to calculate a rate of mass input into the saturated zone from the unsaturated column. Comparing these two methods for 6 meter of sandy soil beneath the UST pit where benzene degrades with a half-life of 700 days leads to the following mass flux calculation for benzene:

which may be compared to the SESOIL predicted monthly maximum of 4.6×10^6. These values are comparable, yet represent only the maximum input of benzene into the saturated zone. In the generic

$$(0.54\frac{mg}{\ell})(1000\frac{\mu g}{mg})(1000\frac{\ell}{cm^3})(0.33\frac{cm}{day})(30.4\frac{day}{month})(1.2x10^6 cm^2) = 6.5x10^6\frac{\mu g}{month}$$

groundwater path analysis, these values will represent the continuous monthly discharge of contaminant to the saturated zone. This is a conservative assumption with respect to the one meter contaminated zone, yet provide a conservative evaluation for buried contaminant which is greater than 1 meter deep.

Horizontal Transport Away from Source

The transport of contaminants in the saturated zone can also be modeled with expressions describing the concentration at a horizontal distance as a function of hydraulic conditions within the subsurface and a first-order reaction rate. Two directions of transport are included in the 2-dimensional advective/dispersive equation:

$$\frac{\partial C}{\partial t}=D_x\frac{\partial^2 C}{\partial x^2}+D_y\frac{\partial^2 C}{\partial y^2}-v_x\frac{\partial C}{\partial x}-kC$$

in which the transport is characterized by three parameters, the velocity in the longitudinal direction, v_x, and coefficients of hydrodynamic dispersion in both the longitudinal, D_x, and transverse, D_y, directions. The reaction is assumed to occur for the solution and the sorbed phases of the contaminant, and reflects the application of field derived half-life. The velocity term in Equation 17 is the apparent contaminant velocity which reflects the hydraulic gradient, properties of the medium, and is reduced when the contaminant is sorbed by solid phases. The contaminant velocity can be related to the groundwater flow velocity in a saturated system using:

$$v_x=\frac{v_{gw}}{R}$$

where v_{gw} is the flow velocity of the groundwater and R, the retardation factor which reflects partitioning to the soil is calculated using:

$$R=1+\frac{\rho_b}{\theta_w}K_{oc}f_{oc}$$

Dispersion reflects the molecular and physical spreading the contaminant plume in the saturated zone. The dispersion will be related to the velocity of the contaminant:

$$D_x=\alpha_x v_x$$

$$D_y=\alpha_y v_x$$

where the dispersivities, α_x and α_y, have dimensions of length and here units of meters will be employed.

In site-specific analysis, parameters which reflect the local conditions can be employed, but in analyzing a generic pathway, all potential variations in aquifer properties cannot be included. Conservative values for dispersivity and other parameters will be used in this analysis.

One-Dimensional Transport

Approximate solutions to the advective/dispersive equation can be developed by combining solutions for both longitudinal (x) and transverse (y) directions (Domenico and Schwartz, 1990). If flow and mixing are assumed to take place in only the longitudinal direction, the transport can be modeled with the apparent velocity, dispersivity, and reaction rate constant. If the concentration of the contaminant is known at the source, the extent to which distance will reduce that concentration relies on either mixing with the other water in the saturated zone or biodegradation. For a generic site which has an unknown depth of contaminated soil, a steady-state solution to the equation will be employed where the only mechanism for concentration reduction is reaction of the contaminant in the flow. For a constant initial concentration, the concentration at any distance from the source can be obtained using an analytical solution expressed as an adjustment to the initial (vertical mixing zone) concentration: (Domenico and Schwartz, 1992):

$$f_h=\exp[(\frac{x}{2\alpha_x})(1-\sqrt{1+\frac{4k\alpha_x}{v}})]$$

where x is the distance from the source of constant concentration, and k is the first-order rate coefficient for the disappearance of the contaminant.

In a steady-state, one-dimensional model with biodegradation, increasing the dispersivity will increase the concentration of contaminant at a particular distance from the source. Dispersivities of 10 and 100 m were selected to provide a conservative estimation of the extent to which contaminants would disperse in near-surface saturated zones (Domenico and Schwartz, 1990). Tables 13 and 14 indicate the extent to which one-dimensional flow with biodegradation will reduce initial concentrations for a dispersivity of 100 m. These values can be used to adjust the concentration obtained after vertical mixing to obtain concentrations at different receptor distances. It is apparent from the results that biodegradation can have a significant impact on the concentrations of a contaminant which would be expected at a receptor for low velocities of groundwater flow.

One-dimensional transport is a conservative method to describe the movement of contaminants in porous media. The flow of contaminants will also likely disperse in other directions away from the source of contamination. It is possible that the movement of contaminants may take place along the same horizontal plane (transverse) and in the vertical direction as it is transported.

Two-Dimensional Transport

Dispersion transverse to the flow direction can increase the transport time in the system and increase the time available for biodegradation. In a steady-state case, the consideration of a second dimension acts to dilute the contaminant in the flow. Mixing only in a horizontal plane along the direction of flow but not in the vertical direction can be approximated as a multiplier to the one-dimensional solution above (Domenico and Schwartz, 1990). That multiplier:

$$f_t = erf\,\left(\frac{Y}{4\sqrt{(\alpha_y x)}}\right)$$

uses the dimension of the site in the transverse direction, Y, and the error function, erf. In contrast to the one-dimensional solution, the addition of dispersion in another direction requires that the dimension of the facility be known in that direction. The size of the site was computed using the typical UST facilities of Sendlein et al. (1993). For the large UST site, Y was taken to be 12.2 meter. The extent to which transverse mixing reduces the concentration in this pathway model are shown in Table 15. This level of transverse dispersion provides reductions in contaminant concentrations which range from a 90% reduction at 1000 meters to minor changes near-site.

Groundwater Summary

The generic ground water pathway analysis as developed here provides a framework from which to estimate the sensitivity of contaminant concentrations to site variables, and to quantify a maximum groundwater impact at distances from UST for different site conditions. Within each component of the pathway analysis, uncertainty in conditions surrounding the generic site are handled through both conservative parameter estimation and model selection. These are summarized in Table 16.

This simple model permits the sensitivity of concentration reductions which occur during the transformation of contaminated soil to groundwater concentrations at receptors to be examined. In many natural systems, there will exist tradeoffs between greater dilution in fast flowing systems, yet less time for reaction in those same systems. As an example, total concentration multipliers for several assumed conditions are shown for benzene contaminated soil to groundwater concentrations at a distance of 100 meters for different saturated flow velocities are shown graphically in Figure 7. At high flow velocities, greater dilution leads to concentration reductions, and at low flow velocities, greater time for reaction leads to reductions.

As described earlier, the model presented in this analysis must be viewed as a screening-level tool to compare the sensitivity of BTEX concentration reductions during transport away from contaminated soil. It is apparent that soil type and biodegradation can play a significant role in changing the concentration. Current research indicates that site specific conditions may alter the degradation rate coefficients. Unfortunately, predicting the extent to which individual site characteristics can be used to adjust rate coefficients is not possible at this time. Further research on the anticipated values and conditions will be valuable in refining estimates of contaminant biodegradation for generic standards determination.

V. SUMMARY

The generic migration pathway analysis presented was designed to examine the sensitivity of contaminant fate and transport to ranges of model parameters, and to provide estimates of maximum contaminant concentrations at various distances from contaminated soil under different assumptions. The analysis combines models for different segments of a generic pathway where conservative adjustment factors can be developed independent of other segments of the path. The methodology is a screening-level tool and is not designed to be used in the site-specific analysis where additional information on the source of contamination and the local conditions is available.

The results demonstrate that contaminant concentrations can be very sensitive to the processes which occur during the migration of contaminants. Because the rates of these processes may be site specific it is difficult to assign values to many of the parameters required to describe them. The parameter estimates used at the different steps in the analysis are based on the results of a literature investigation and, as such, have not been validated with information from underground storage tanks in Kentucky. Although the results do demonstrate the importance of contaminant reactions such as volatilization and degradation, they must still be validated with field data for different conditions.

VI. REFERENCES

Alvarez, P.J.J. and T.M. Vogel (1991) "Substrate interactions of benzene, toluene, and para-xylene during microbial degradation by pure cultures and mixed culture aquifer slurries", *Applied and Environmental Microbiology* 57:2981-2985.

Anderson, M.R. (1992) "Development of generic soil cleanup levels based on analysis of the leachate pathway" Oregon Department of Environmental Quality.

Barbaro, J.R., J.F. Barker, L.A. Lemon, C.I. Mayfield (1992) "Biotransformation of BTEX under anaerobic, denitrifying conditions: Field and laboratory observations" *Journal of Contaminant Hydrology*, 11: 245-272.

Barker, J.F. et al. (1987) "Natural attenuation of aromatic hydrocarbons in a shallow sand aquifer. *Ground Water Monitoring Review* Winter 1987: 64-71.

Boggs, J.M, L.M. Beard, W.R. Waldrop (1993) "Transport of tritium and four organic compounds during a natural gradient experiment (MADE-2)" Final Report, TR-101998 Research Project 2485-05, Electric Power Research Institute.

Chiou C.T., P.E. Porter, D.W. Schmedding (1983) "Partition equilibria of nonionic organic compounds between soil and water" *ES&T* 17:227-231..

Domenico, P.A. (1987) An analytical model for multidimensional transport of a decaying contaminant species. *J. Hydrol.* 91:49-58.

Domenico, P.A. and F.W. Schwartz (1990) Physical and Chemical Hydrogeology, John Wiley and Sons, NY.

EPA (1989) Determining soil response action levels based on potential contaminant migration to ground water: A compendium of examples. EPA/540/2-89/057.

Hadley, P.W. and R. Armstrong (1991) Where's the Benzene, *Ground Water* 29:35-40.

Hetrick, D.M. et al. (1989) Qualitative validation of pollutant transport components of an unsaturated soil zone model (SESOIL), ORNL/TM-10672, Oak Ridge National Laboratory.

Hutchins, et al., Biodegradation of Aromatic Hydrocarbons by Aquifer Microorganisms under Denitrifying Conditions, *ES&T* 25:68-76.

Lyman, W.J., P.J. Reidy, and B. Levy. (1991) "Assessing UST corrective action technology", EPA/600/2-91/053.

Major, D.W., C.I. Mayfield, J.F. Barker (1988) Biotransformation of benzene by denitrification in aquifer sand. *Groundwater*, 26:8-14.

Millington, R.J. and J.M. Quirk (1961) "Permeability of porous solids" *Transactions of the Faraday Society*, 57:1200-1207.

Nold, A. (1993) Personal communication with USEPA.

Poulsen, M. Lemon, L., and J.F. Barker, (1992) Dissolution of monoaromatic hydrocarbons into groundwater from gasoline-oxygenate mixtures, *ES&T* 26:2483-2489.

Schwarzenbach and Westall (1981) Transport of nonpolar organic compounds from surface water to groundwater: laboratory sorption studies. *ES&T* 15:1360-1367.

Science Technology Management, Inc. (1993) "Groundwater Contamination Susceptiblity Evaluation, SESOIL Modeling" Prepared for Wisconsin Department of Natural Resources, Emergency and Remedial Response Section, Madison, WI 53707.

Sendlein L., J. Dinger, R. Huffsey (1993) "Soil volume calculations for UST installations".

State of California, (1989) Leaking Underground Fuel Tank Manual. Leaking Underground Fuel Tank Task Force, State Water Resources Control Board, Sacramento CA.

Tucker, W.A. and P.J. Zavala (1992) A Practical Model for Evaluating Passive Bioremediation of Groundwater, Proceedings of the 1992 Petroleum Hydrocarbon Conference, Houston Texas, NGWWA.

Wagenet, R.J., J.L. Hutson, J.W. Biggar, (1989) "Simulating the fate of a volatile pesticide in unsaturated soil: A case study with DBCP", *J. Environ. Qual.* 18:78-84.

Watson, D.B. and S.M. Brown (1985) "Testing and Evaluation of the SESOIL Model" Environmental Research Laboratory, Athens, GA.

Weber, W.J. Jr., P.M. McGinley, L.E. Katz (1992) "A distributed reactivity model for sorption by soils and sediments. 1. Conceptual basis and equilibrium assessments", *ES&T* 26:1955-1962.

Table 1. Henry's Constants for BTEX Compounds*

Compound	H (m^3-atm/mole)	K_H (dimensionless)
Benzene	0.0055	0.22
Toluene	0.00668	0.27
Ethylbenzene	0.00343	0.14
o-Xylene	0.00527	0.21

* Temperature 25 degree C

Table 2. Soil Organic Matter Partitioning Coefficients (KOC) for BTEX Compounds

Compound	K_{OC} (cm^3/g)
Benzene	83
Toluene	270
Ethylbenzene	575
o-Xylene	302

Table 3. Concentrations (Percent of Total) of Benzene in Soil, Water and Air at a Unit Level of Soil Contamination (1 mg benzene/kg soil)*

Soil f_{OC}	Soil Concentration (mg/kg)	Water Concentration (mg/l)	Air Concentration (mg/l)
0.001	0.71 (44%)	5.35 (33%)	1.18 (22%)
0.005	1.28 (80%)	1.93 (12%)	0.42 (8%)
0.02	1.51 (95%)	0.57 (3.5%)	0.12 (2.4%)

* $\Theta_w = 0.1$; $\Theta_a = 0.3$, bulk density = 1.6 gm/cm^3; $K_{OC} = 83$ cm^3/g

Table 4. MCL-Based Total Soil Concentrations.

Compound	MCL (mg/l)	K_{OC} (liter/kg)	C_T (mg/kg) f_{OC}= 0.001	C_T (mg/kg) f_{OC}= 0.005	C_T (mg/kg) fOC= 0.02
Benzene	0.005	83	0.0017	0.0033	0.0096
Toluene	1.00	270	0.52	1.6	5.65
Ethylbenzene	0.70	575	0.58	2.19	8.23
Xylene	10	302	5.52	17.6	56.5

Table 5. Benzene Volatilization and Soil Concentrations for Unit Level of Contamination (1 mg/kg)*

	All 4.5 m Contaminated	Upper 1.5 m Clean Soil	Upper 3.0 m Clean Soil
Volatilization Rate (Maximum Month as Daily Average)			
Maximum Volatilized SESOIL SAND	1069 mg/day	740 mg/day	329 mg/day
Maximum Volatilized SESOIL SILT	521 mg/day	166 mg/day	49 mg/day
Steady-State Model Volatilization		1858 mg/day	929 mg/day
Uniformly Distributed Volatilization (17 month)	1671 mg/day	1114 mg/day	557 mg/day
Soil Concentrations (C_T) from Buried Benzene			
Maximum Concentration Upper 30 cm Steady-State SAND	1.0 mg/kg	0.1 mg/kg	0.05 mg/kg
Maximum Concentration Second 30 cm Steady-State SAND	1.0 mg/kg	0.3 mg/kg	0.15 mg/kg
Maximum Concentration Upper 30 cm SESOIL SAND	1.0 mg/kg	0.053 mg/kg	0.030 mg/kg
Maximum Concentration Second 30 cm SESOIL SAND	1.0 mg/kg	0.11 mg/kg	0.06 mg/kg
Maximum Concentration Upper 30 cm SESOIL SILT	1.0 mg/kg	0.030 mg/kg	0.0095 mg/kg

* Large Site: 540 m^3 total volume, porosity = 0.40 Lexington Climate Note: Multiply by soil mg/kg for other soil concentration, organic carbon content=0.1%, pore disconnectedness=4.5

Table 6. SESOIL climatological input

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YEAR - 1     MONTHLY INPUT PARAMETERS
========     =======================

-- CLIMATIC INPUT PARAMETERS --

                          OCT       NOV       DEC       JAN       FEB       MAR

TEMP. (DEG C)            14.200     7.100     2.300     0.900     1.700     6.600
CLOUD CVR (FRAC.)         0.490     0.650     0.720     0.730     0.690     0.700
REL. HUM.(FRAC.)          0.760     0.760     0.760     0.750     0.740     0.710
ALBEDO (-)                0.200     0.200     0.200     0.200     0.200     0.200
EVAPOT. (CM/DAY)          0.000     0.000     0.000     0.000     0.000     0.000

PRECIP. (CM)              5.900     8.200     9.200    10.600     8.200    11.500
M.TIME RAIN(DAYS)         0.200     0.200     0.200     0.200     0.200     0.200
M. STORM NO. (-)          8.000    11.000    12.000    13.000    11.000    13.000
M. SEASON (DAYS)         30.400    30.400    30.400    30.400    30.400    30.400


                          APR       MAY       JUN       JUL       AUG       SEP

TEMP. (DEG C)            12.300    17.800    22.600    24.500    23.800    20.600
CLOUD CVR (FRAC.)         0.670     0.620     0.580     0.570     0.520     0.520
REL. HUM.(FRAC.)          0.690     0.750     0.790     0.820     0.820     0.820
ALBEDO (-)                0.200     0.200     0.200     0.200     0.200     0.200
EVAPOT. (CM/DAY)          0.000     0.000     0.000     0.000     0.000     0.000

PRECIP. (CM)              9.400     9.800    10.700    11.300     8.700     7.100
M.TIME RAIN(DAYS)         0.200     0.200     0.200     0.200     0.200     0.200
M. STORM NO. (-)         13.000    12.000    11.000    11.000     9.000     8.000
M. SEASON (DAYS)         30.400    30.400    30.400    30.400    30.400    30.400
```

Table 7. SESOIL Predicted Maximum Monthly Benzene Loadings to Saturated Zone (µg/month)

Condition	Sandy Soil	Silty Soil
1 ppm 1 meter contaminated 20 feet to saturated	2.3×10^7	1.1×10^7
1 ppm 1 meter contaminated 20 feet to saturated half-life of 700 days	1.9×10^7	3.4×10^6
1 ppm 1 meter contaminated 20 feet to saturated half-life of 100 days	5.5×10^6	2.5×10^3

* Large Site (1.2×10^6 cm^2)

Note: These can be scaled for other areal dimensions.

Table 8. SESOIL Maximum Benzene Concentrations at Entry to the Saturated Zone (mg/l)

Contaminated Soil(1) C_T / Depth	Depth(2) (m)	$t_{1/2}$ (days)	Volat (3)	Maximum Conc (mg/l)		
				Sand(No ET)	Silt	Clay
1 mg/kg / 1 meter	1	∞	Yes	1.51	2.05	
	1	700	Yes	1.44	1.55	1.88
	1	100	Yes	1.10	0.31	0.060
	3	∞	No	3.96	3.42	
	3	∞	Yes	0.91	1.86	
	3	700	No	3.55	1.80	
	3	700	Yes	0.81	1.00	1.19
	3	100	No	1.83	0.063	
	3	100	Yes	0.44	0.037	$5.0\text{x}10^{-4}$
	6	∞	No	2.74	2.27	
	6	∞	Yes	0.65	1.43	
	6	700	No	2.26	0.55	
	6	700	Yes	0.54	0.50	0.35
	6	100	No	0.71	0.0023	
	6	100	Yes	0.18	0.0016	$4.18\text{x}10^{-7}$
	9	∞	No	2.13	1.65	
	9	∞	Yes	0.53	1.14	
	9	700	Yes	0.40	0.361	0.115
	9	100	Yes	0.08	$1.45\text{x}10^{-3}$	$1.0\text{x}10^{-10}$
	13	700	Yes	0.327(.38)	0.225	0.047
	13	100	Yes	0.033	$1.3\text{x}10^{-4}$	
	19	700	Yes	0.214	0.112	
	19	100	Yes	$8.39\text{x}10^{-3}$	$3.44\text{x}10^{-6}$	
10 mg/kg / 1 meter	6	∞	No	27.4	22.7	

Notes: (1): Contaminated soil zone buried 4.5 meter; (2): Distance from contaminated soil to saturated zone; (3): Whether or not contaminant volatility is included in the model (see text)

Table 9. SESOIL Maximum Toluene Concentrations at Entry to the Saturated Zone (mg/l)

Contaminated Soil⁽¹⁾ C_T / Depth	Depth (2) (m)	$t_{1/2}$ (days)	Volat (3)	Maximum Conc (mg/l)		
				Sand (no ET)	Silt	Clay
1 mg/kg / 1 meter	1	700	Yes	0.769	1.152	1.191
	1	100	Yes	0.625	0.662	0.029
	3	700	Yes	0.379 (0.434)	0.48	0.638
	3	100	Yes	0.194	0.035	$2.00\text{x}10^{-4}$
	6	700	Yes	0.229 (0.302)	0.27	0.213
	6	100	Yes	0.072	0.0047	$2.71\text{x}10^{-7}$
	9	700	Yes	0.172 (0.229)	0.176	0.071
	9	100	Yes	0.032	7.33×10^{-4}	
	12	700	Yes	0.138	0.119	0.0258 (13m)
	12	100	Yes	0.015	1.39×10^{-4}	
	19	700	Yes	0.095	0.0525	
	19	100	Yes	3.29×10^{-3}	2.01×10^{-6}	

Notes: (1): Contaminated soil zone assumed buried beneath 4.5 meter initially clean soil

(2): Distance from contaminated soil to saturated zone

(3): Whether or not contaminant volatility is included in the model (see text)

Table 10. SESOIL Maximum Ethylbenzene Concentrations at Entry to the Saturated Zone (mg/l)

Contaminated Soil(1) C_T / Depth	Depth (2) (m)	$t_{1/2}$ (days)	Volat. (3)	Maximum Conc (mg/l)		
				Sand	Silt	Clay
1 mg/kg / 1 meter	1	700	Yes	0.489	0.647	0.838
	1	100	Yes	0.364	0.1762	0.0177
	3	700	Yes	0.317	0.366	0.496
	3	100	Yes	0.164	0.026	1.43×10^{-4}
	6	700	Yes	0.224	0.209	0.107
	6	100	Yes	0.069	3.93×10^{-3}	1.31×10^{-7}
	9	700	Yes	0.171	0.138	0.048
	9	100	Yes	0.032	6.885×10^{-4}	
	12	700	Yes	0.135	0.094	0.018 (13m)
	12	100	Yes	0.015	1.137×10^{-4}	
	19	700	Yes	0.087	0.039	
	19	100	Yes	0.0033	1.22×10^{-6}	

Notes: (1): Contaminated soil zone assumed buried beneath 4.5 meter initially clean soil

(2): Distance from contaminated soil to saturated zone

(3): Whether or not contaminant volatility is included in the model (see text)

Table 12. Adjustments to Account for Mixing Below the Large Site*

Depth of Mixing Zone (meter)	10 m/d	1 m/d	0.1 m/d	0.01 m/d	0.001 m/d
0.1	0.091	0.501	0.909	0.990	0.999
0.5	0.020	0.167	0.667	0.953	0.995
1.0	0.010	0.091	0.501	0.909	0.989
5.0	0.002	0.018	0.155	0.647	0.948
10.0	0.001	0.009	0.084	0.478	0.901

*Assumes large site length, 10 cm/month infiltration, saturated zone porosity=0.4.

Table 13. Attenuation Adjustments for One-Dimensional Transport

Degradation Half-Life of 700 Days.

Distance (meters)	Saturated Flow Velocity (meter/day)				
	10	1	0.1	0.01	0.001
10	0.99	0.99	0.93	0.73	$1.9\text{x}10^{-6}$
100	0.99	0.89	0.47	0.042	0
300	0.96	0.70	0.10	$7.7\text{x}10^{-5}$	0
1000	0.88	0.31	$5\text{x}10^{-5}$	$2\text{x}10^{-14}$	0

f_{OC}=0.001; K_{OC}=83; Longitudinal Dispersivity=100 m; bulk density=1.6 g/cm^3; porosity=0.4.

Degradation Half-Life of 100 Days

Distance (meters)	Saturated Flow Velocity (meter/day)				
	10	1	0.1	0.01	0.001
10	0.99	0.94	0.77	0.40	$1.9\text{x}10^{-40}$
100	0.92	0.56	0.08	$1.1\text{x}10^{-4}$	0
300	0.77	0.17	$4.4\text{x}10^{-4}$	$1.3\text{x}10^{-12}$	0
1000	0.43	0.03	$6.3\text{x}10^{-12}$	$2.5\text{x}10^{-40}$	0

f_{OC}=0.001; K_{OC}=83; Longitudinal Dispersivity=100 m; bulk density=1.6 g/cm^3; porosity=0.4.

Table 14. BTEX Adjustment Factors for One-Dimensional Transport with Degradation

Half-life (day)	Compound	1-D Adjustment Factor*	
		100 Meter	300 Meter
700	Benzene	0.472	0.105
	Toluene	0.361	0.047
	Ethylbenzene	0.253	0.016
	Xylene	0.346	0.041
100	Benzene	0.076	4.4×10^{-4}
	Toluene	0.036	4.6×10^{-5}
	Ethylbenzene	0.013	2.4×10^{-6}
	Xylene	0.032	3.3×10^{-5}

* Flow velocity = 0.1 m/d, KOC = 83, 270, 575, and 302 cm^3/g, respectively. Dispersivity = 100 m

Table 15. Dilution Adjustments to 1-Dimensional Results to Account for Transverse Dispersion Away from the Large Site

Distance (meters)	Transverse Dispersivity (meter)		
	100	10	1
10	0.108	0.334	0.827
100	0.034	0.108	0.334
300	0.020	0.063	0.197
1000	0.001	0.003	0.108

f_{OC}=0.001; K_{OC}=83; bulk density=1.6 g/cm^3; porosity=0.4; 12.2 meter site width.

Table 16. Assumptions used to Accommodate Uncertainty in the Generic Groundwater Pathway Migration Calculations.

Uncertain Condition	Effect on Groundwater Concentrations	GW Pathway Model Assumptions
Depth of Contamination	For contaminated zone of less than 2 meters model results indicate that concentrations leaving unsaturated zone drop rapidly; however, uncertainty in contaminant depth leads to an unknown time over which the contaminant will enter the saturated zone at a certain concentration (equilibrium partitioning leads to only a minor effect of contamination depth on maximum concentration).	Steady-state solution to advective/dispersive equation for a constant source Maximum concentration leaching from contaminated zone used in calculations
Fraction of Contaminant which Volatilizes	Volatilization of contaminant to the surface will reduce the quantity and concentration of contaminant in the soil.	Volatilization is assumed to be 20% of maximum (VOLF = 0.2) when examining the groundwater pathway, and 100% when examining upward migration.
Magnitude of Longitudinal Dispersion in Saturated Zone	Mixing in the direction of flow will lead to faster movement of contaminant away from site. For steady-state condition with biodegradation, dispersion increases the concentration at any distance from site.	Relatively large values of longitudinal dispersion employed. Longitudinal dispersion lengths of 10 and 100 meters.
Extent of Vertical Mixing in Saturated Zone	Once contaminant enters the saturated zone it will form a three-dimensional plume. The extent to which it mixes in the vertical might significantly reduce the concentration at distances from the source. The extent of vertical dispersion will depend on the depth of the saturated zone	No vertical dispersion is assumed other than a mixing zone at the entrance to the saturated zone.
Extent of Transverse Mixing	Generic boundaries are undefined in the transverse direction.	Steady-state solution to 2-D transport employed

Magnitude of Transverse Mixing in Saturated Zone	Dispersion leads to apparent reduction in maximum concentration due to dilution in the groundwater. Local conditions will determine the extent to which this occurs.	Relatively low values of transverse dispersion assumed. Dispersion length of 0.1 or 1 meter.
Magnitude of Vertical Mixing in Saturated Zone	Variations in permeability in the vertical may slow mixing. In general, it appears that vertical mixing is less pronounced than horizontal (both forward and lateral to flow).	No vertical dispersion other than a shallow mixing zone depth is used.
Sorption in Saturated Zone	Sorption slows the movement of contaminant relative to that predicted using groundwater velocity. It is related to organic carbon content of the media for most organic compounds of interest.	Use fOC = 0.001. This is 0.1% organic carbon content. Below this level, other contributors to sorption lead to an apparent leveling off of sorption (Schwarzenbach and Westall, 1981).
Biodegradation	Most petroleum constituents can be biologically degraded to less hazardous compounds. There is uncertainty in both the best rate law for these reactions and the rate constants which can be applied.	Groundwater migration pathways are computed using several different rate constants for biodegradation. First order rate laws are employed because the concentrations are relatively low.

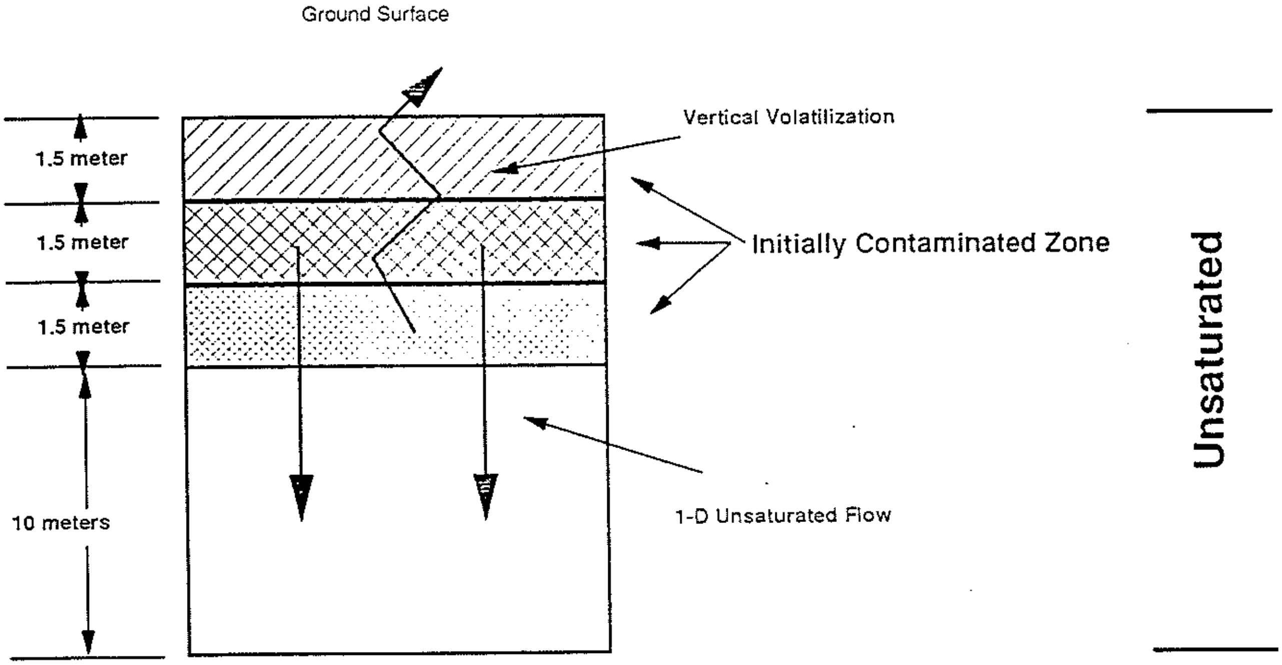

Figure 1. Model UST for modeling the volatilization of organic compounds.

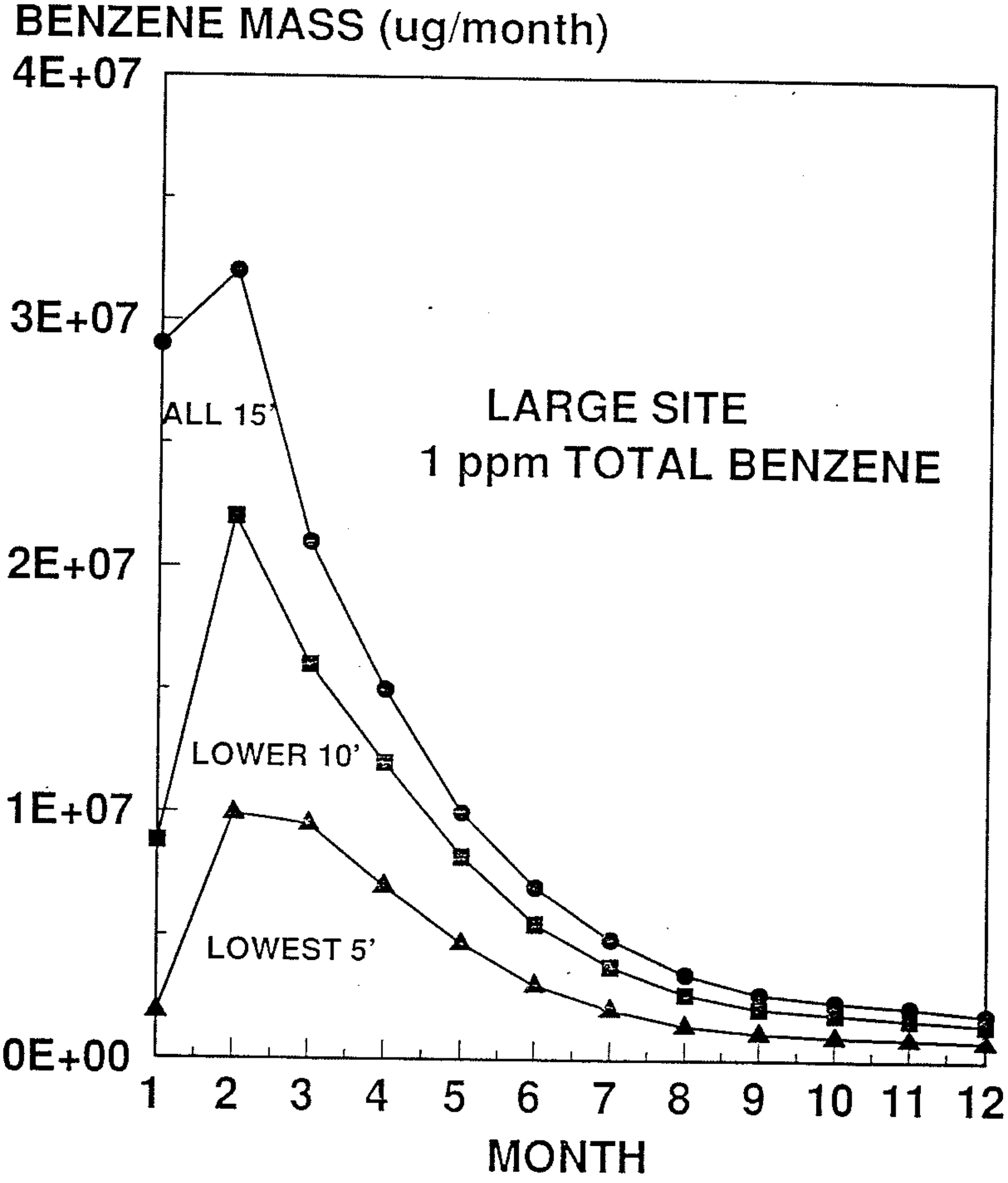

Figure 2. Benzene volatilization from 1 mg/kg contaminated soil predicted with SESOIL under three different burial conditions. Upper curve (ALL 15') represents contaminated soil up to the soil surface, middle curve (LOWER 10') represents 6 meters of contaminated soil buried 1.5 meter deep, and lowest curve (LOWEST 5') represents 1.5 meters of contaminated soil buried 6 meters.

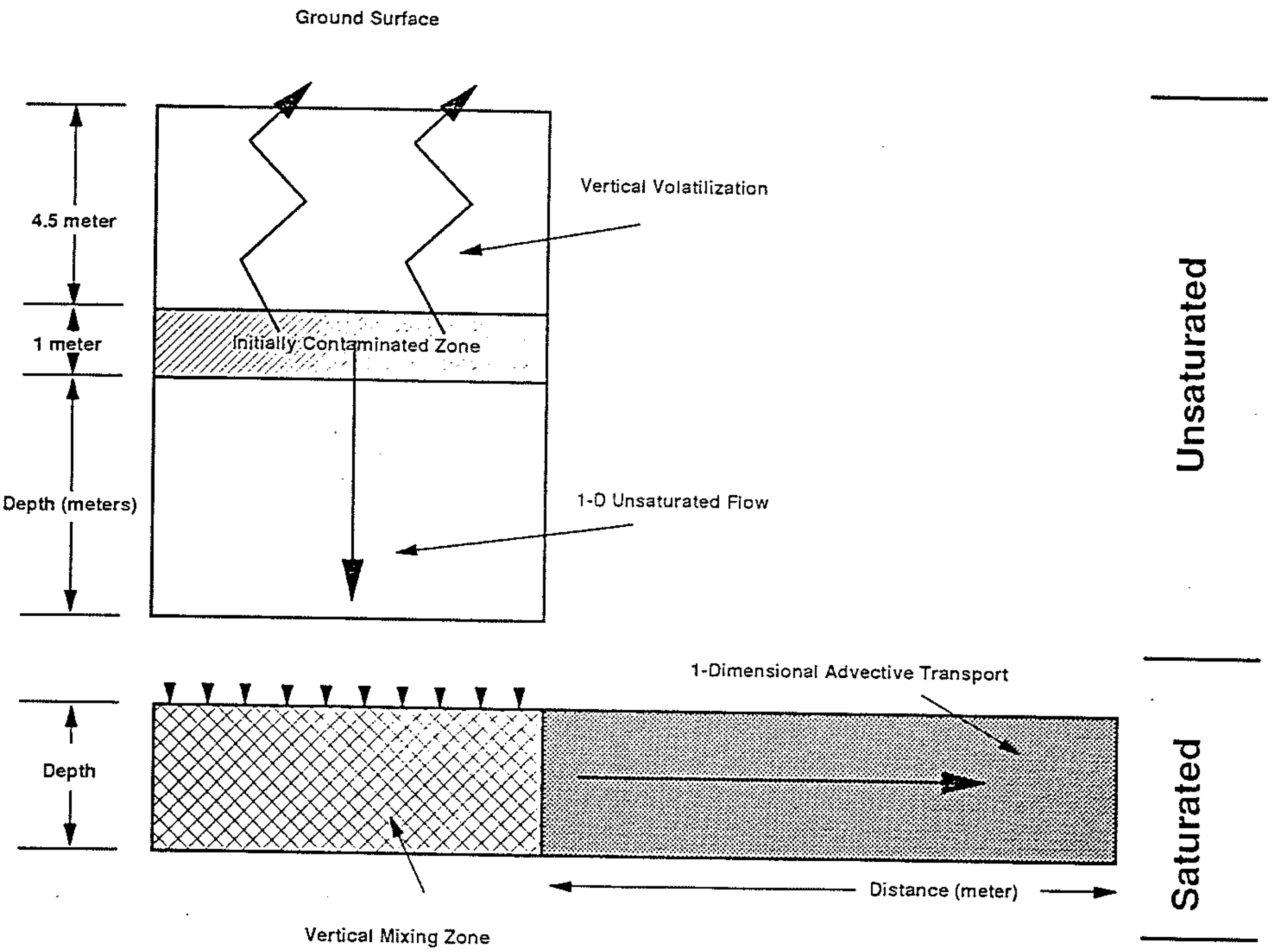

Figure 3. Groundwater pathway analysis model system.

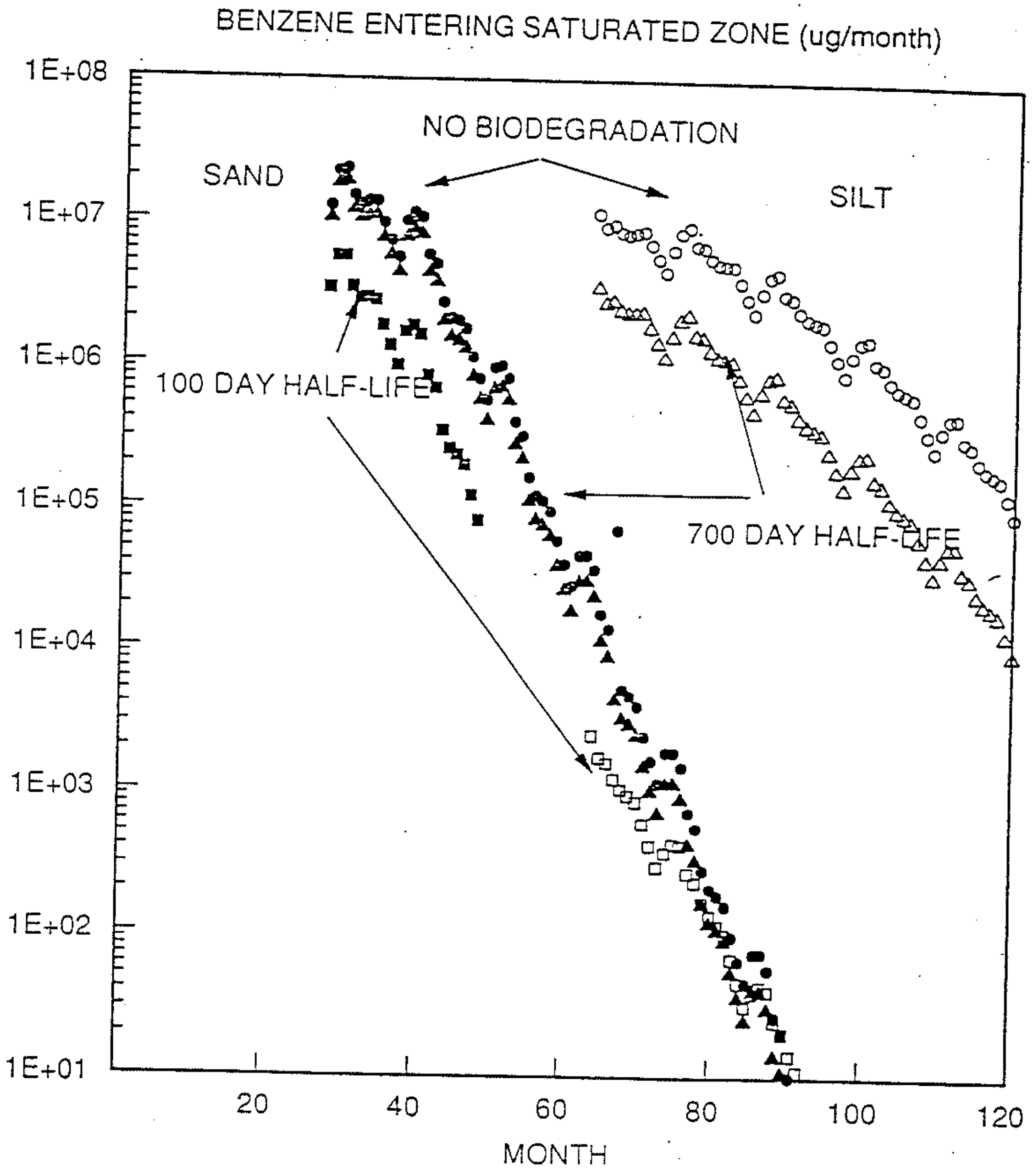

Figure 4. Benzene mass releases from the unsaturated zone for both sand and silt with different biodegradation half-lives (no volatilization and initial concentration 1 mg/kg).

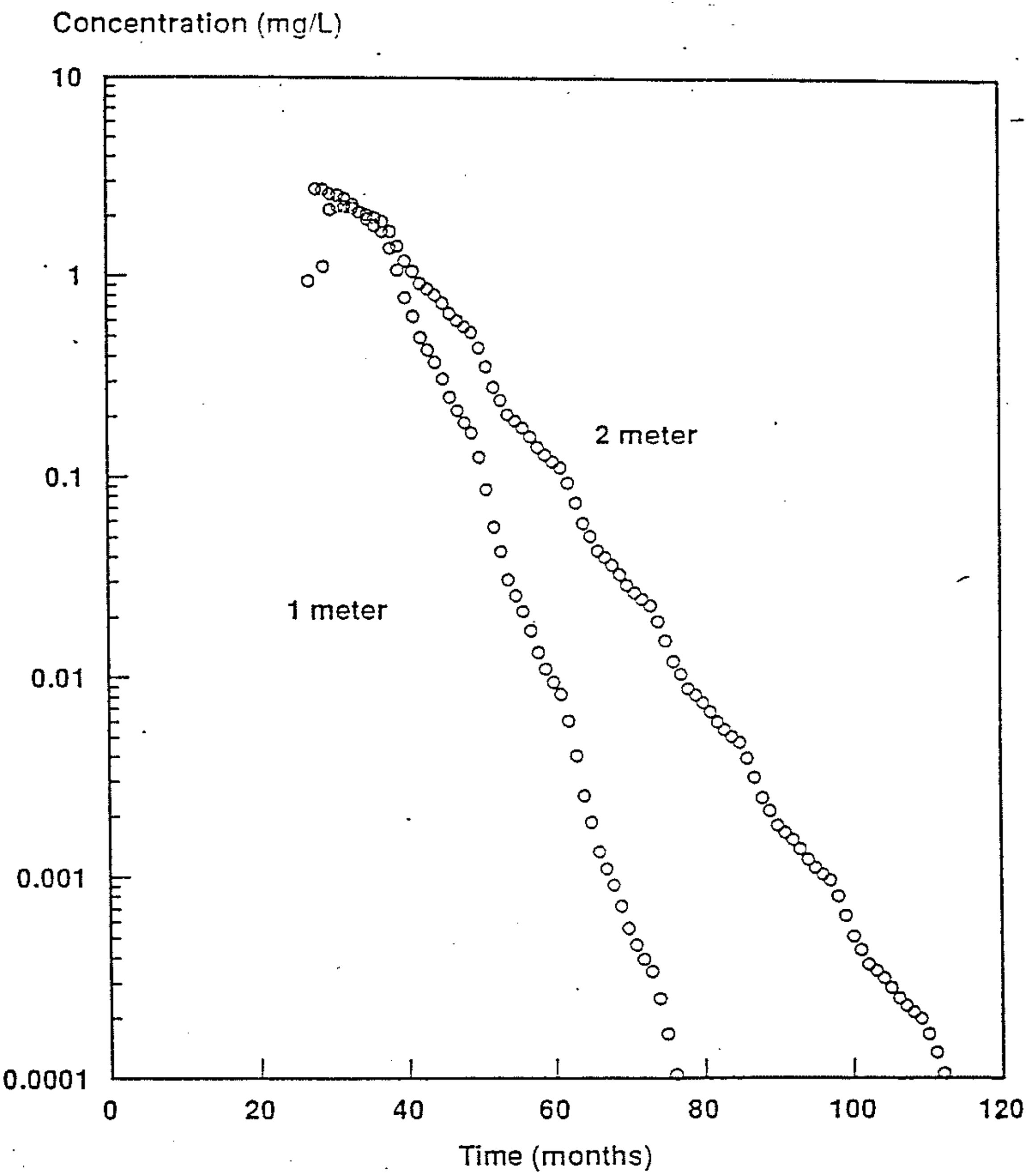

Figure 5. Concentration of benzene in soil moisture predicted by SESOIL after passage through 6 meters of unsaturated soil at two different initial depths of contaminated soil (no volatilization and initial concentration of 1 mg/kg).

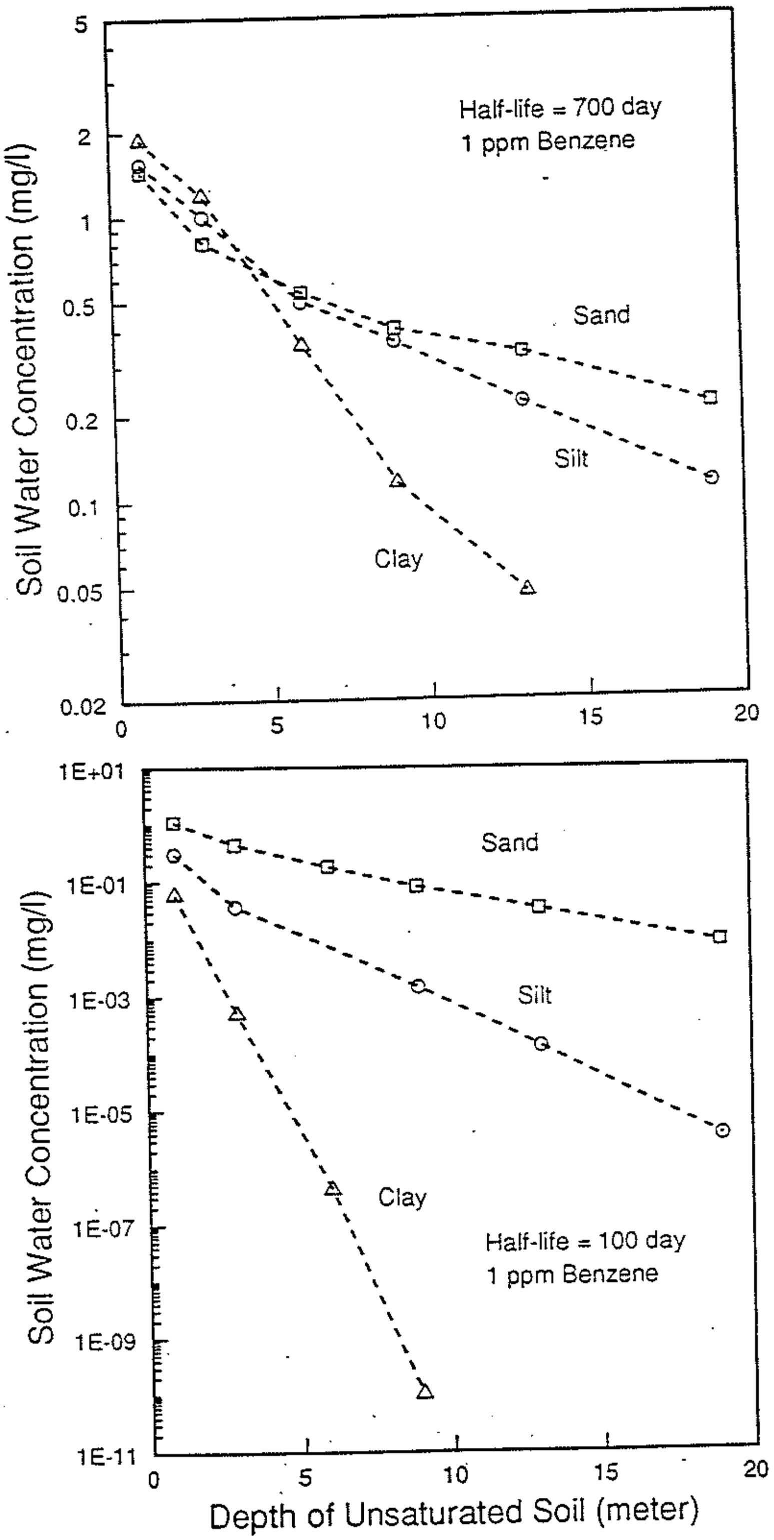

Figure 6. Maximum concentrations in soil moisture at the base of the unsaturated zone for different soil types, degradation half-lives, and soil depths for an initial soil concentration of 1 mg/kg and volatilization.

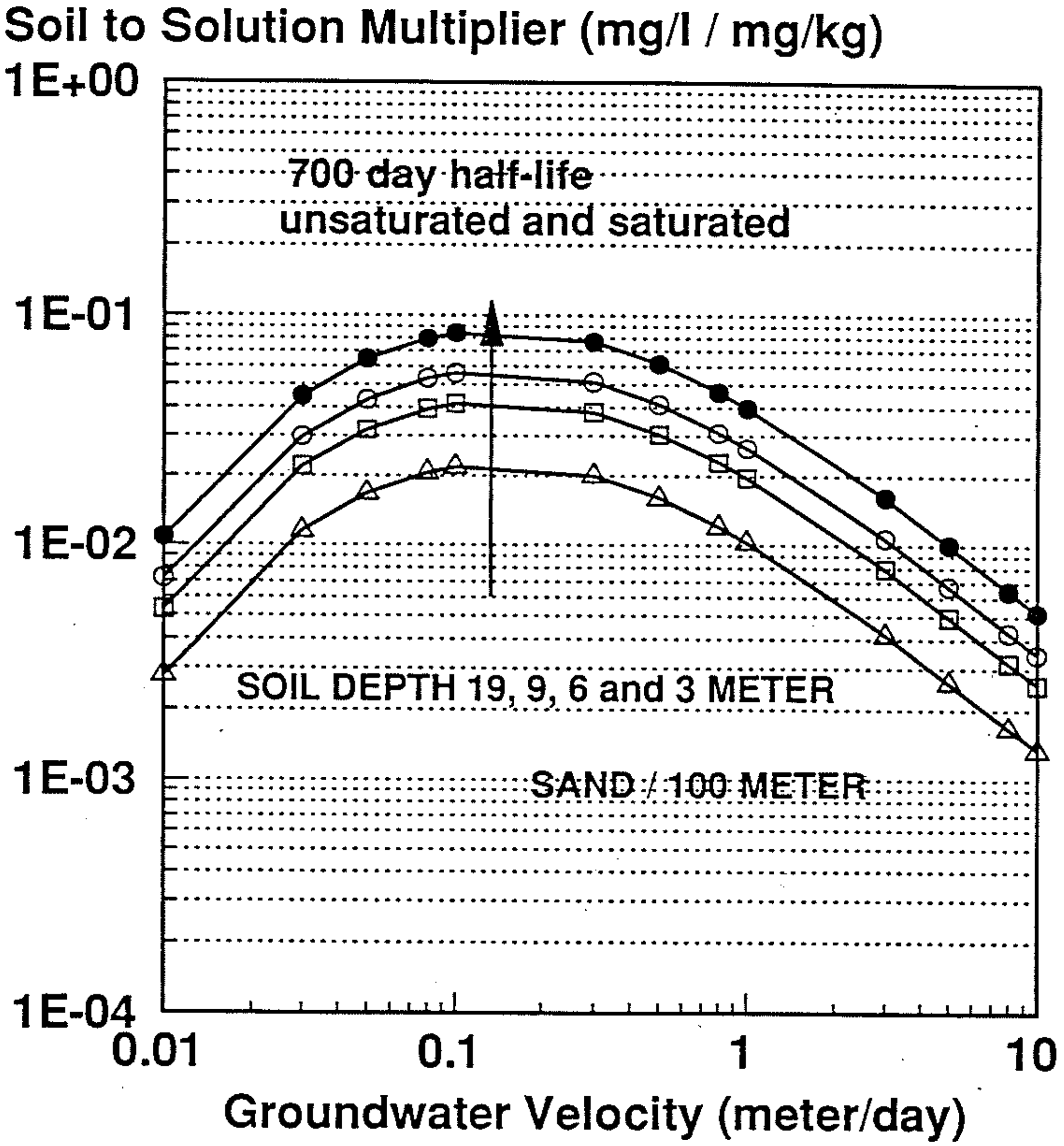

Figure 7. Groundwater pathway example showing the effect of saturated zone flow velocity and soil depth on the total concentration multiplier for distance of 100 meters from 1 mg/kg benzene contaminated soil (with unsaturated soil volatilization, 0.5 meter mixing zone, 1 meter transverse dispersivity).