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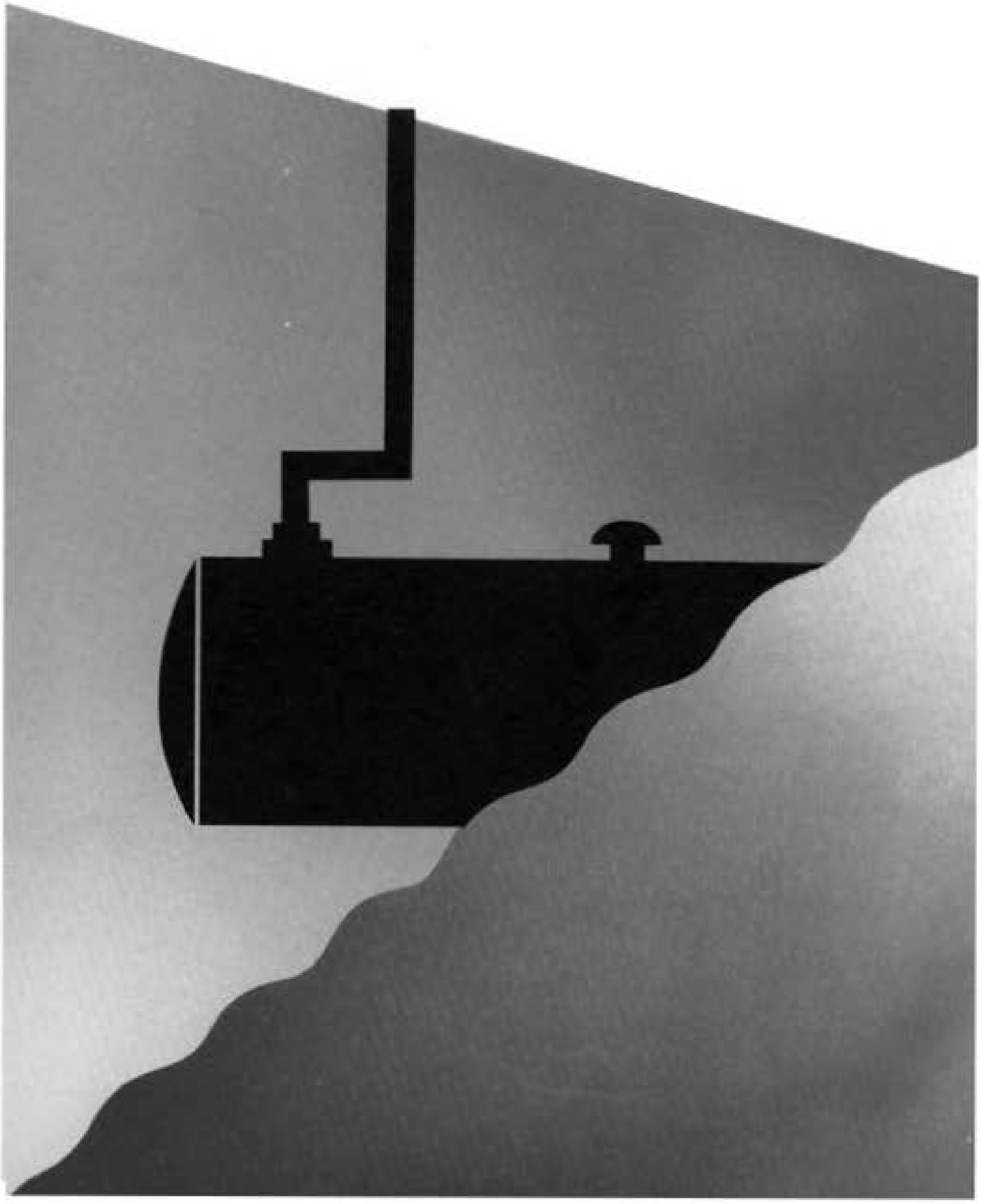
EPA

Estimating Air Emissions from Petroleum UST Cleanups



ESTIMATING AIR EMISSIONS FROM PETROLEUM UST CLEANUPS

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TABLE OF CONTENTS

Section **Page**

LIST OF FIGURES

FOREWORD

In our work to clean up contamination from leaking underground storage tanks (USTs), it is easy to become caught up in the immediate danger to our ground water supplies. While this hazard to ground water is real and must be addressed, it cannot be addressed with complete disregard to other parts of the environment. This manual is designed to address the issue of air emissions that result from petroleum UST cleanups. It will educate both those who are conducting UST corrective actions, and those who are regulating air emissions at the State and local levels. This manual will not answer the sometimes difficult policy questions that arise concerning cross-media transfer of pollutants, but it will provide the means to make more informed and responsible decisions. We hope that this manual will serve as one tool to employ in our common mission at the Environmental Protection Agency to protect human health and the environment.

We would like to thank Rebecca Zarba and Bernadette Kolb of Camp Dresser & McKee Inc. for their excellent work on this document, and the many individuals from the Federal, State and local Air and UST offices who contributed their time and thoughts to make this into a better, more useful document for everyone.

1.0 INTRODUCTION

1.1 BACKGROUND

A variety of corrective strategies may be used to remediate sites where underground storage tanks (USTs) have released gasoline into the ground. Frequently, gasoline must be removed from either the soil or ground water, and sometimes both. The corrective strategies that remove contaminants from soils include vacuum extraction, soil washing, and soil excavation. Corrective strategies that remove contaminants from water include air stripping and granular activated carbon. Some of these technologies result in the transfer of contaminants from the soil and ground water into the air. For example, air stripping towers, which are commonly used to remove volatile organic compounds (VOCs) from water, transfer a high percentage of the contaminants from the liquid phase to the vapor phase, where they may be released to the atmosphere. Likewise, two widely used technologies of soil remediation, soil excavation and vacuum extraction, involve bringing soil and/or vapors to the surface of the ground where vapors may move freely into the atmosphere.

The release of contaminants into the atmosphere may be undesirable for two reasons. First, exposure to VOCs could pose public health risks if they are released in sufficient quantities for sufficiently long periods of time (Fancy, 1987). Benzene, which commonly makes up to 2 to 4 percent of gasoline, is of particular concern because it is a known carcinogen (CDM, 1988b). Second, VOCs are ozone precursors, thus making them even more undesirable in regions that are unable to meet current ozone regulations. For these reasons, some State and local air offices have adopted standards that restrict the emissions of total VOCs and benzene at UST cleanup sites.

The air emission estimation procedures presented in this manual were developed by examining relevant literature, and through discussions with industry and regulatory contacts. Gasoline is a mixture of many hydrocarbons, the exact blend of which can vary widely due in part to differences in the original crude oil, and differences in the refining process (CDM, 1987b). A specific blend of gasoline had to be assumed in order to perform some of the emission rate calculations in this manual. This blend was used in other projects performed for the Environmental Protection Agency's (EPA) Office of Underground Storage Tanks (OUST), such as the LOCI Research Report (PEI, 1988) and the vapor phase modeling report (CDM, 1988b), and is included in Appendix A. Characteristics of other fuels such as diesel, jet fuel, and home heating oil, and their overall effect on emission rates, are also discussed in Appendix A.

Whenever possible, data from existing UST cleanup sites were used to verify that the procedures presented in this manual provide realistic estimates of emission rates. The data used was provided by regulatory and industry sources, and from published literature. In general, comparisons between the estimated and actual emission rates indicate that the procedures are adequate in providing order of magnitude estimates of emission rates.

1.2 PURPOSES OF THIS MANUAL

The purposes of this manual are:

(1) To provide State UST offices with a means of estimating air emission rates of VOCs and benzene at individual UST cleanup sites

(2) To provide general information on air emission rates that may be used to develop policies for air emissions at UST cleanup sites in a given State or locality

This manual discusses the type of information that is required and the procedure that should be followed in order to obtain an air emission rate estimate at a particular site. The type of information needed includes the cleanup technology being used, and some site specific conditions such as soil type and contaminant concentrations.

1.3 APPROACH AND ORGANIZATION

The intended users of this manual are State and local UST officials who must comply with air emission regulations at cleanup sites. A simplified approach for estimating emission rates at UST cleanup sites is presented herein. The cleanup technologies considered in this manual are soil excavation, vacuum extraction, and air stripping. Although passive venting is sometimes used to vent gasoline vapors to the atmosphere, industry officials indicate that the expected emission rates would be negligible due to low air flow rates emanating from the vents (Johnson, 1988). Soil washing is not used as frequently as excavation or vacuum extraction to remove gasoline from soils because it tends to be a more complicated and expensive technology. Despite the fact that its use is increasing, incineration also tends to be a more costly and less widely used cleanup technology. Incinerators frequently have emission control devices in place, and hence air emissions are generally not an issue. For these reasons, passive venting, soil washing, and incineration will not be discussed in this report. The contaminants considered are: (1) total VOCs from gasoline and (2) benzene.

The format of this manual has been arranged so that each corrective action technology is presented separately. Soil excavation, vacuum extraction and air stripping will be covered in Sections 2.0, 3.0, and 4.0 respectively. Each section is organized as follows:

- A brief overview of the technology and expected emission rates
- A discussion of factors that affect air emission rates and how to reduce air emission rates
- Air emission estimation procedures and graphs
- The manner in which the emission rates are expected to vary with time

A review of the equations used to calculate the emission rates is included in Appendix B.

1.4 LIMITATIONS

Limitations of this manual include the following:

(1) The emission rates calculated using the procedures provided in this manual are "ballpark" estimates. These estimates should be adequate for determining whether air emission controls or permits may be required at an UST site.

(2) The information pertaining to the change in emission rates with time is general in nature, as the actual change with time will be highly dependent upon many site specific conditions.

(3) This manual does not address the issues of emissions dispersion or the health risks that may be associated with emissions at UST cleanup sites.

2.0 SOIL EXCAVATION

2.1 OVERVIEW

Soil excavation is a widely applied corrective action technology. It involves the transfer of contaminated soil from the subsurface to the surface of the ground, where it is commonly dumped in a pile to be treated and/or disposed of at a later date.

Gasoline that has leaked from an UST frequently becomes trapped in the soil pore spaces as it moves through the unsaturated zone. For this reason, excavated soils frequently contain some liquid gasoline, the amount of which depends upon the soil type and soil moisture conditions. When liquid gasoline and air are present within the soil pores, the concentration of gasoline vapors in the pore spaces will reach an equilibrium concentration based upon the vapor pressures of the constitutive chemicals that make up the gasoline. The equilibrium concentration also represents the maximum concentration of the gasoline vapors that can exist in the pore spaces.

Before volatilization begins, the air in the pore spaces of the entire soil pile will have essentially the same equilibrium vapor concentration. The vapor concentration in the air surrounding the soil pile, however, will be negligible. This change in vapor concentration across the soil pile surface results in vapor molecules within the pile moving into the atmosphere in an effort to attain equal vapor concentrations within the pile and in the surrounding air. Thus, volatilization begins when vapor molecules move from a region having a high vapor concentration to a region having a low vapor concentration. As the gasoline vapors escape from the surface of the pile, more liquid gasoline will volatilize to the vapor phase in an effort to maintain the equilibrium concentration described above.

The air emission estimation procedure presented in this section assumes that the extent of contamination in the soil pile is such that both liquid gasoline and air are present in the soil pores. The equilibrium concentration of the gasoline vapors can then be used to obtain the maximum emission rate that can be expected from a given soil pile. If there is no liquid gasoline in the pore spaces, the emission rate estimated using this procedure will be greater than the actual emission rate.

Total VOC and benzene emission rates from excavated soil are significantly higher than those of other types of corrective actions, but these emissions are also of the shortest duration. The maximum emission rate from soil piles occurs immediately after excavation, and can be thought of as an initial burst which rapidly declines over time. For total VOCs, the maximum emission rate for an average soil pile having an exposed surface area of 2000 ft^2 is between 50 and 200 lbs/hr, depending upon the temperature. Benzene emissions for the same soil pile would range from 0.5-2 lbs/hr, again depending upon the temperature. The air emission rate calculated using the charts in Section 2.3 represents the maximum emission rate, which occurs immediately after the soil is excavated.

2.2 FACTORS THAT AFFECT AIR EMISSION RATES FROM EXCAVATED SOIL

a) Temperature

Vapor pressure is highly dependent upon temperature, and consequently temperature greatly affects the volatilization rate (PEI, 1988). The emission rates presented in Section 2.3 have been calculated assuming temperatures of 86°F, 68°F, 50°F, and 32°F (30°C, 20°C, 10°C, and 0°C). If the temperature is warmer at a site in question, emission rates increase. Correspondingly, if the temperature at a site in question is cooler, the emission rates decrease.

b) Soil Type and Soil Moisture

Other parameters that affect the emission rate of contaminants from soil include soil type and soil moisture (PEI, 1988). The ability of contaminant vapors to move through the pore spaces depends upon how large and continuous the pore spaces are. Contaminants will take longer to move through soils having small pore spaces (such as clays) than they will in soils where the pore spaces are large and interconnected (such as gravels). Water can occupy the pore spaces of soils, and can coat the individual soil grains, thus reducing the size of the voids. Consequently, the presence of soil moisture will further inhibit the movement of contaminant vapors. Because fine-grained soils can retain more moisture than coarse soils, vapors will take longer to escape from clays than they will from soils such as sands and gravels. **The emission rates in Section 2.3 have been calculated assuming a soil having a medium grain size (such as a sand) with a porosity of 0.35 (or 35 percent), and a small amount of moisture (moisture content = 0.08).**

c) Wind

Wind plays an important role in enhancing volatilization from soil piles by mixing the contaminated air at the soil surface with the uncontaminated air above. The wind reduces the amount of the contaminant in the air surrounding the soil pile to negligible levels. As a result, the difference between the vapor concentration in the soil pore spaces and in the air is maximized. This produces a larger flux of contaminant vapors away from the soil pile (PEI, 1988). The procedure presented for estimating emission rates assumes that the wind is sufficient to mix the air above the soil pile, thus keeping the vapor concentration in the air negligible and the flux at a maximum.

d) Surface Area

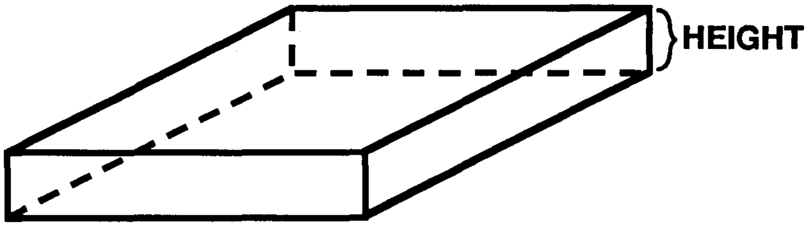
The exposed surface area of a soil pile directly affects the rate at which contaminants are emitted. Piles with greater surface area tend to emit larger amounts of VOCs and benzene than piles with lesser surface area. Piles can be managed, therefore, to decrease the rate at which contaminants are volatilized. **For example, to decrease emissions, a given volume of soil can be spread in a thick layer, as opposed to a thin layer; thus the surface area and the emission rates are reduced.**

2.3 AIR EMISSION ESTIMATION PROCEDURES

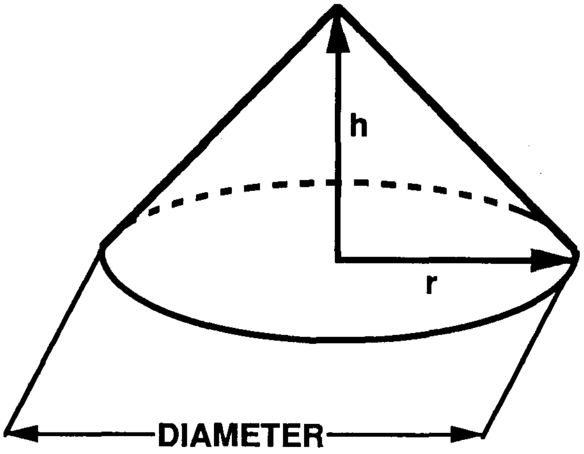
The following procedure should be followed in order to estimate an emission rate from an excavated soil pile:

(1) Determine the approximate shape of the soil pile:

a. Horizontal layer:



b. Cone:

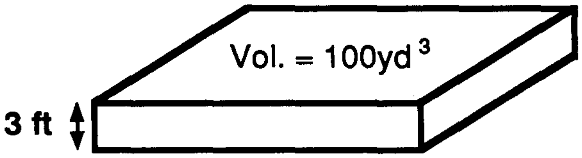


(2) Determine the surface area of the soil pile:

a. Horizontal layer:

Knowing the total volume of the soil pile (in ft^3) and the thickness of the soil layer (in ft), use the following formula to compute the surface area:

Surface area = (total volume)/thickness

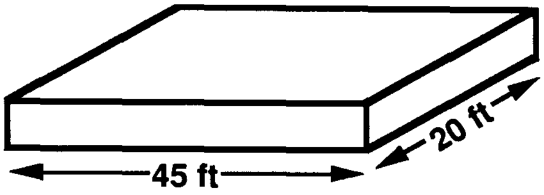


$$\text{Surface Area} = \frac{\text{Volume}}{\text{Height}} = \frac{100\ \text{yd}^3}{3\ \text{ft}} \times \frac{27\ \text{ft}^3}{1\ \text{yd}^3} = 900\ \text{ft}^2$$

or

Estimate the length and width of the soil layer (in ft), and use the following formula to compute the surface area:

Surface area = (length) x (width)



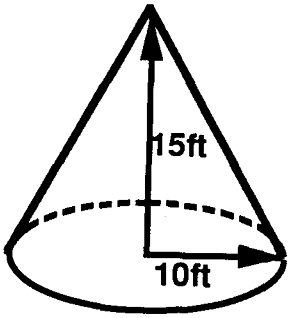
$$\text{Surface Area} = \text{Length X Width} = 45 \times 20\ \text{ft}^2 = 900\ \text{ft}^2$$

b. Cone:

Approximate or measure the diameter at the base of the pile, and the height of the pile (in ft). Then use the following formula to calculate the surface area:

Surface area = $3.142 \times r \times \sqrt{r^2 + h^2}$

where r = 0.5 x diameter

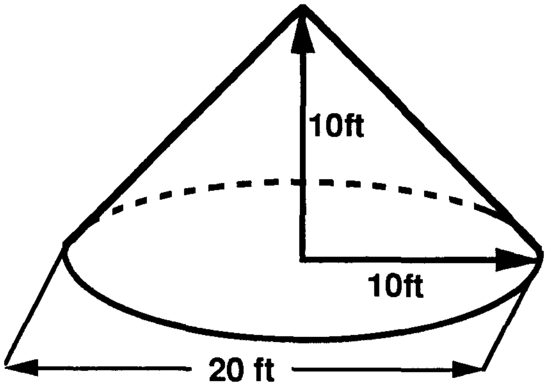


$$\text{Surface Area} = 3.142\, r \sqrt{r^2 + h^2} = 3.142\,(10)\sqrt{100+225} = 566.4\ \text{ft}^2$$

or

If the radius of the pile is approximately equal to the height of the pile, the following formula may be used to estimate the surface area:

Surface area = 1.11 x $(\text{diameter})^2$



$$\begin{aligned}\text{Surface Area} &= 1.11 \times (\text{diameter})^2 \\ &= 1.11 \times (20)^2 \\ &= 444.\ \text{ft}^2\end{aligned}$$

Appendix D has been included to assist in converting other units of length and area to feet and ft^2.

(3) Use Figures 2-1 and 2-2 to determine the expected maximum emission rate from excavated soil of gasoline VOCs and benzene, respectively. Locate the surface area of the soil pile on the x axis, and draw a vertical line up to the line on the graph. Find the line corresponding to the temperature at the site. At the intersection of these lines, draw a horizontal line over to the y axis. The emission rate can be read from the y axis at this point.

It should be noted that the emission rates presented in Figures 2-1 and 2-2 are for a soil having a medium grain size, such as a sand. Coarse soils such as gravels have emission rates which are approximately six percent greater, while fine-grained soils such as clays have emission rates that are approximately 4 percent less than the emission rates depicted in Figures 2-1 and 2-2.

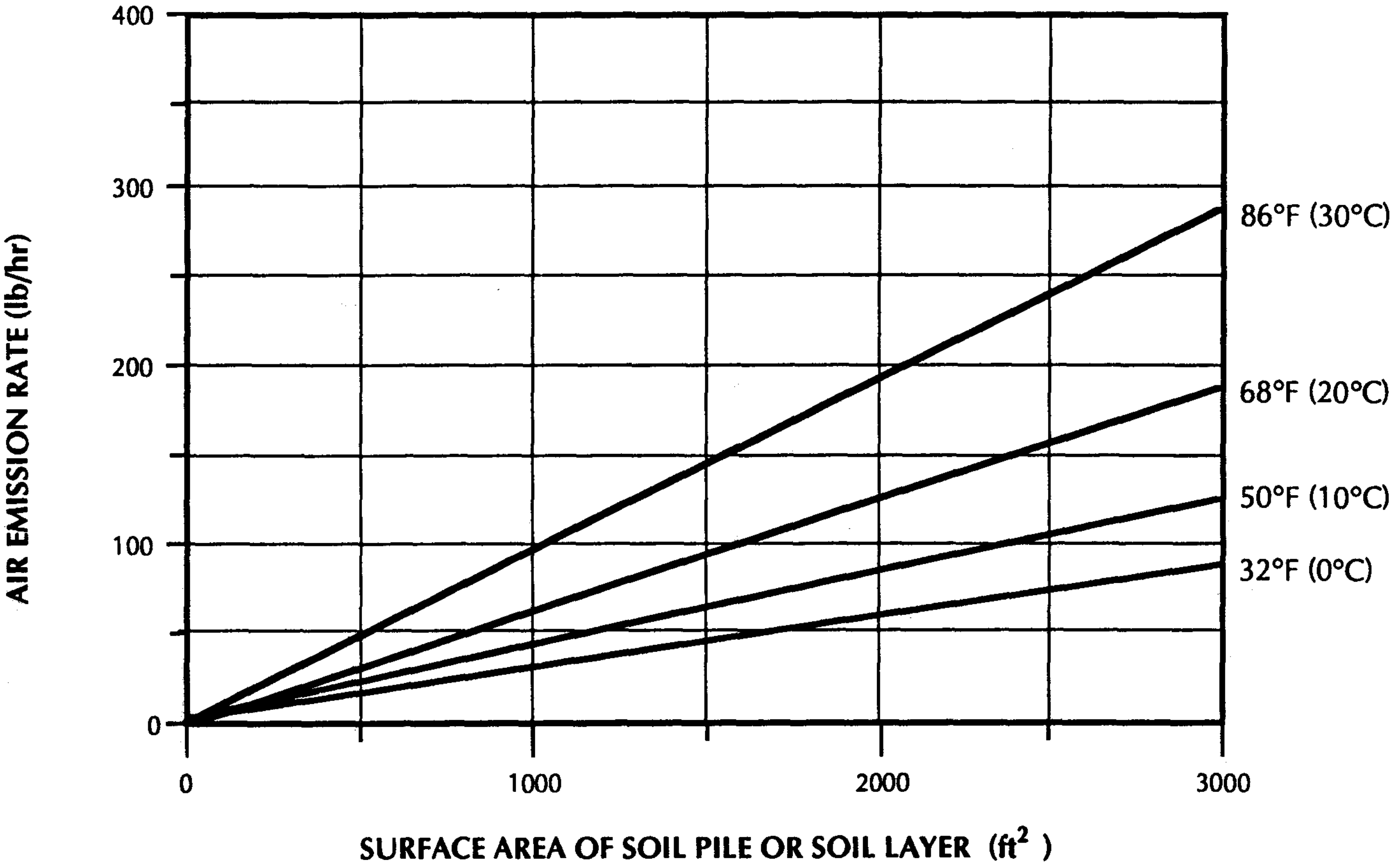


FIGURE 2 - 1
ESTIMATED SOIL EXCAVATION AIR EMISSION RATES FOR GASOLINE VOCs

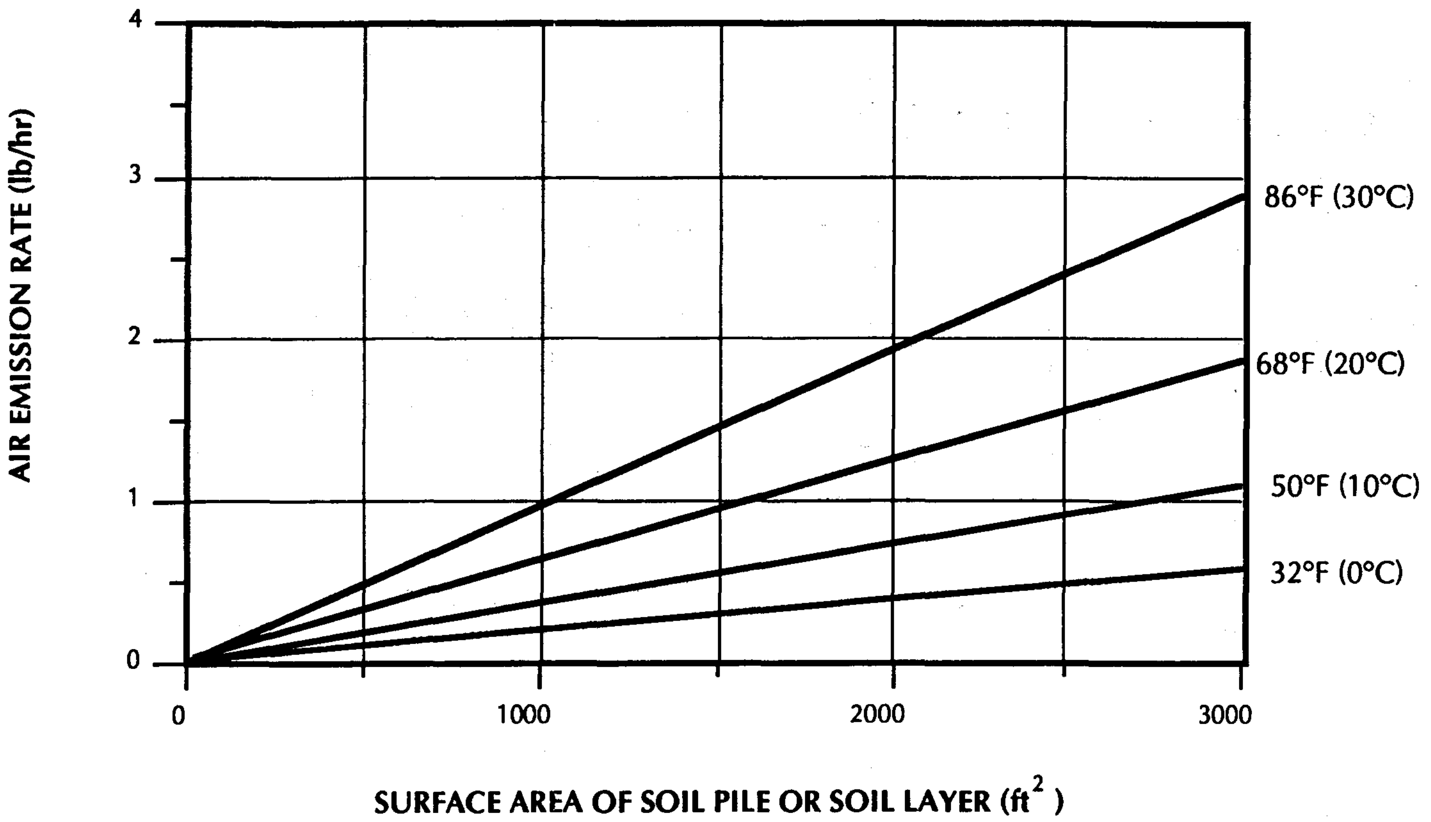


FIGURE 2 - 2
ESTIMATED SOIL EXCAVATION AIR EMISSION RATES FOR BENZENE

2.4 VARIATION OF EMISSION RATES WITH TIME

In general, emission rates for excavated soil piles can be characterized by a sharp burst of emissions followed by a rapid decline to negligible levels. The amount of time required for contaminants to volatilize from soil piles is highly variable, but tends to be on the order of a few days to weeks. The emission rate calculated using the charts in Section 2.3 represents the initial burst of emissions illustrated in Figure 2-3.

The highly volatile constituents of gasoline such as isobutane, n-butane, isopentane, and 1-pentene volatilize first, leaving behind the less volatile constituents. Because of their lower vapor pressures, the less volatile constituents will have lower concentrations in the soil pores (Johnson et al., 1988). Also, as the contaminants near the surface of the soil pile escape to the atmosphere, the vapors that are deeper in the soil pile will have to travel farther in order to reach the surface. Both of these effects contribute to the rapid decrease in emission rates with time, as shown in Figure 2-3.

Frequently, the surface of the soil pile is intentionally disturbed, perhaps through land farming or rototilling to increase volatilization. Land farming consists of removing the top several inches of soil from a horizontally distributed pile, thus exposing the more contaminated soil lower in the pile to the atmosphere. Rototilling greatly increases the size of the void spaces in the soil by physically breaking it up and loosening it. This can also expose the more contaminated portions of the soil pile to the air, thus increasing the emission rate temporarily. Figure 2-4 illustrates the effect of disturbing the soil pile upon the emission rate.

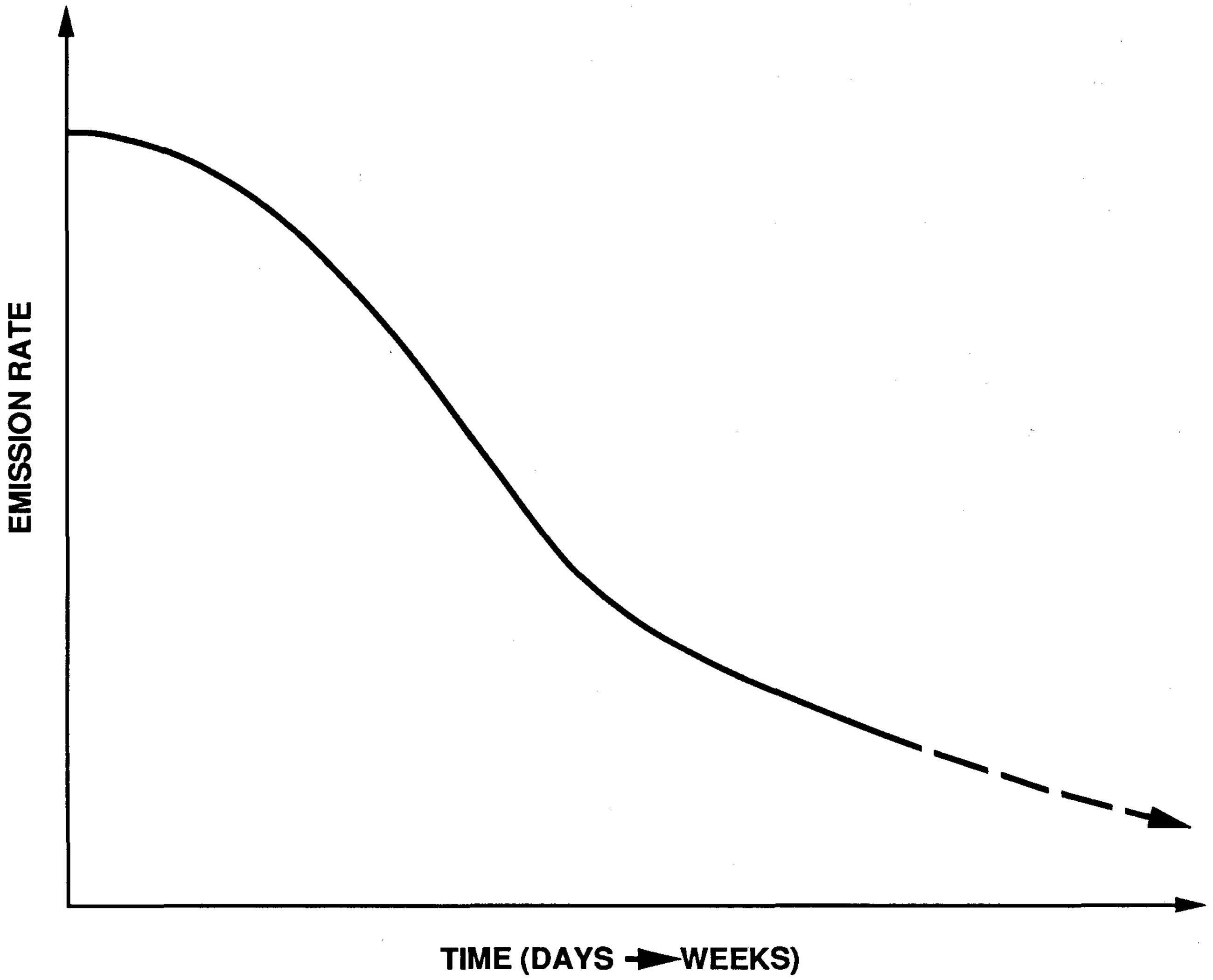


FIGURE 2-3
CHANGE IN EMISSION RATES WITH TIME
FOR AN EXCAVATED SOIL PILE

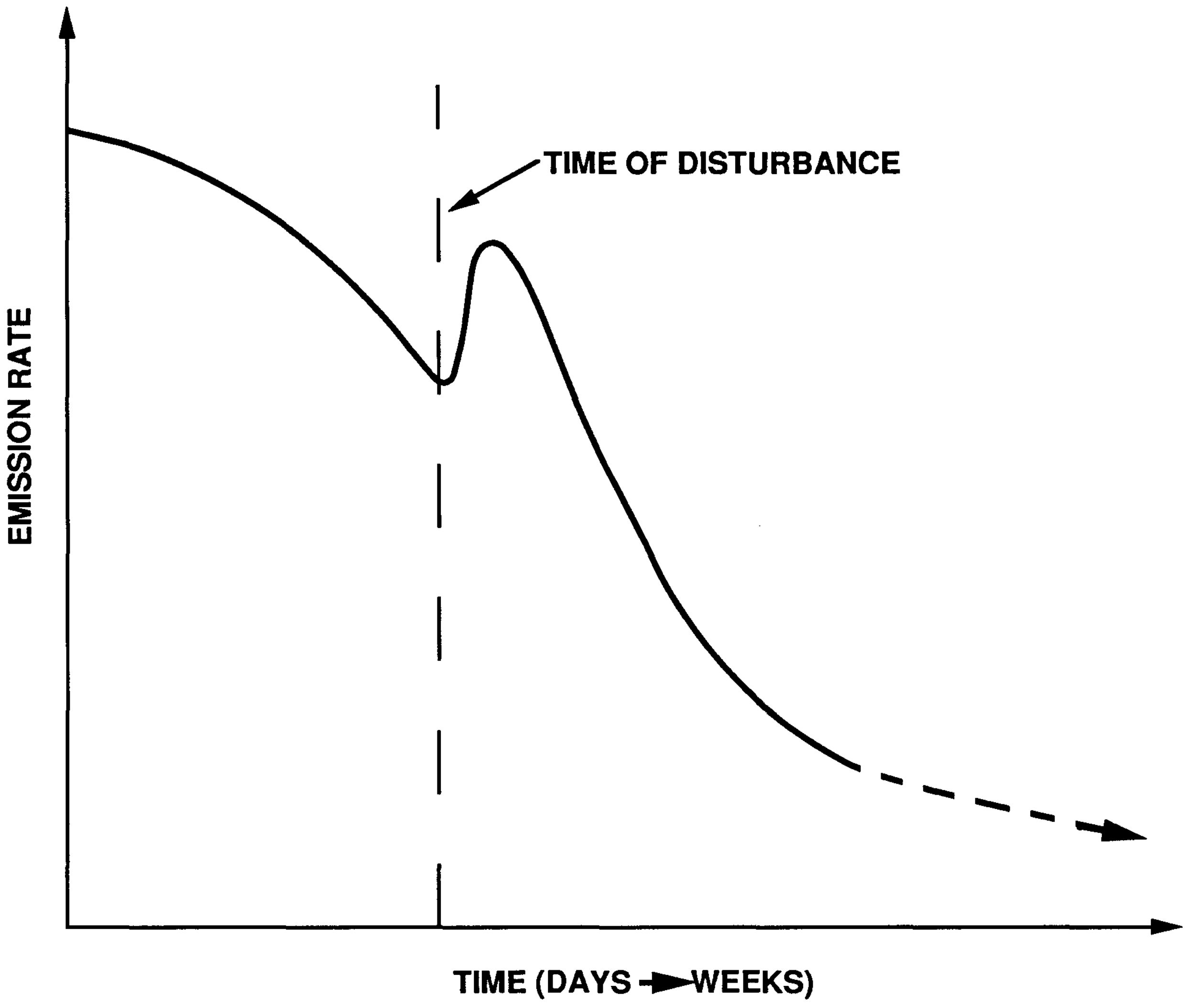


FIGURE 2-4
CHANGE IN EMISSION RATES WITH TIME FOR DISTURBED SOIL PILES

3.0 VACUUM EXTRACTION

3.1 OVERVIEW

Vacuum extraction can remove as much as 99.99 percent of contaminants from soils through the use of one or more suction wells, or a series of air injection and suction wells (CDM, 1987a). Because the soil is treated in place, vacuum extraction can be less expensive and less disruptive than excavation, and as a result, it is becoming a popular choice as a corrective action technology (CDM, 1987a).

The pressure in the ground at a suction well will be lower than the pressure some distance away from the well. This pressure difference induces the air in the soil pore space to move toward the suction well. The contaminants, which are in the vapor phase, move along with the air to the suction well. As with excavated soil piles, as the contaminant vapors are removed from the soil pores, more volatilize from the liquid phase to the vapor phase. Naturally, vacuum extraction systems will be more effective in soils which allow air to flow freely through its pore spaces.

In order to estimate air emission rates, the procedure and charts presented in Section 3.3 rely on actual soil gas contaminant concentrations (which have been measured as part of the site investigation), and the pumping rate of the vacuum extraction system. **By using measured contaminant concentrations, site specific conditions such as soil type, soil moisture, and temperature need not be considered in the emission rate determination.** These factors do affect the overall performance of a vacuum extraction system however, and they are discussed in greater detail in Section 3.2. It should be noted that many soil gas contaminant concentrations are measured as part of a typical site investigation. In order to estimate the maximum emission rate using the graphs presented in Section 3.3, the maximum soil gas concentration should be used. If an average soil gas concentration is used instead, the estimated emission rate will most likely represent the short-term average (perhaps over the first month of operation) of the actual emission rate. It should be noted that the use of an average soil gas concentration will tend to result in an air emission rate which may be significantly higher than the long term average emission rate (i.e., the emission rate over several months).

Emission rates from vacuum extraction systems are generally less than those for excavated soil, and greater than those of air strippers. Maximum emission rates tend to be under 50 lb/hr for total gasoline VOCs and under 2 lb/hr for benzene. The duration of the emissions from vacuum extraction systems is on the order of weeks to months; hence, they tend to be longer in duration than those from excavated soil piles, and less than those of air strippers. The procedure presented in Section 3.3 is commonly used by industry officials to estimate air emission rates.

3.2 FACTORS THAT AFFECT AIR EMISSIONS FROM VACUUM EXTRACTION SYSTEMS

Factors that can affect the removal rate of VOCs from contaminated soil include the soil permeability, moisture content, applied suction pressures, air flow rate, and temperature (Krishnayya, et al., 1988). The most significant of these factors are temperature and soil type and soil moisture, and they are discussed in detail below.

(a) Temperature

The contamination level within a soil can be affected by temperature due to the large effect of temperature on the vapor pressures of the contaminants. Because the procedures presented in Section 3.3 use actual contaminant concentrations to arrive at emission rates, the effect of temperature on the emission estimate is negligible as long as the variation in the soil temperature during the period of operation is not large. If the soil gas concentrations are measured during a cold season, and the operation of the vacuum extraction system runs well into the summer, the emission rate may tend to increase over expected levels.

(b) Soil Type and Soil Moisture

Typically, air under pressure can flow freely through soils having large grain sizes (such as gravels and coarse sands), while air generally cannot flow freely through fine grained soils such as clays. This relationship can be complicated by the moisture content of the soil. In general, wet soils restrict the movement of air through the pore spaces. Hence, vacuum extraction systems are more effective in dry soils.

These soil characteristics determine the ability of an extraction well to form a flow field in the soil which can encompass the contamination. The radius of influence of a single vacuum extraction well having a specific pumping rate can range from tens to hundreds of feet, depending on soil type and the depth to ground water (Terra Vac, 1987). **Therefore, within a given soil, the pumping rate can be lowered such that the radius of influence is reduced. Consequently, the well will encompass less contamination, and the emission rate can be somewhat reduced.** This may be desirable in regions where air emissions are a problem. It should be noted, however, that reducing the pumping rate can substantially reduce the volume of soil being treated, and hence can prolong the cleanup time.

3.3 AIR EMISSION ESTIMATION PROCEDURES

It should be noted that vacuum extraction systems frequently consist of more than one extraction well. In these cases, emission rates must be determined for each well, and then summed to determine the emission rate of the entire extraction system. The following procedure should be followed in order to estimate an emission rate for one vacuum extraction well:

(1) Determine the pumping rate of the well in cubic feet per minute (cfm). Appendix D has been included to assist in converting other systems of units to cfm.

(2) a. To obtain the most conservative estimate of the air emission rate, determine the maximum concentration in ppm-v (parts per million-volume) of the gasoline and/or benzene in the soil gas. This data should be obtained as part of the site investigation. The use of the maximum soil gas concentration will provide an estimate of the maximum air emission rate.

b. To obtain an air emission rate which represents more of a short term average, determine the average soil gas concentration in ppm-v of the gasoline and/or benzene. This concentration can be approximated by averaging the soil gas concentrations that were obtained as part of the site investigation.

Care must be taken to ensure that the concentration used in this procedure is the soil gas concentration as opposed to the total soil concentration. Appendix C contains information to assist in converting total soil concentrations to soil gas concentrations. A procedure for converting soil gas concentrations in units of μg/l to ppm-v is also contained in Appendix C. It should be noted that the maximum concentration of gasoline VOCs and/or benzene present in the soil pores depends upon the blend of gasoline present. Using the synthetic blend given in Appendix A, and assuming that there is liquid gasoline and air present in the soil pores, the maximum concentration of gasoline VOCs that can be present in the soil gas at 68°F is 361,000 ppm-v. The maximum concentration of benzene that can be present in the soil gas at 68°F is 3600 ppm-v.

(3) Using Figure 3-1 to estimate the emission rate of gasoline VOCs, locate the pumping rate of the well on the x axis, and the gasoline soil gas concentration on the y axis. The intersection of these two points will fall on or near a curve having a specific emission rate. This curve can be used to estimate the emission rate under the prescribed pumping rate and contamination levels. Figure 3-2 should be used to estimate benzene emission rates in the same manner.

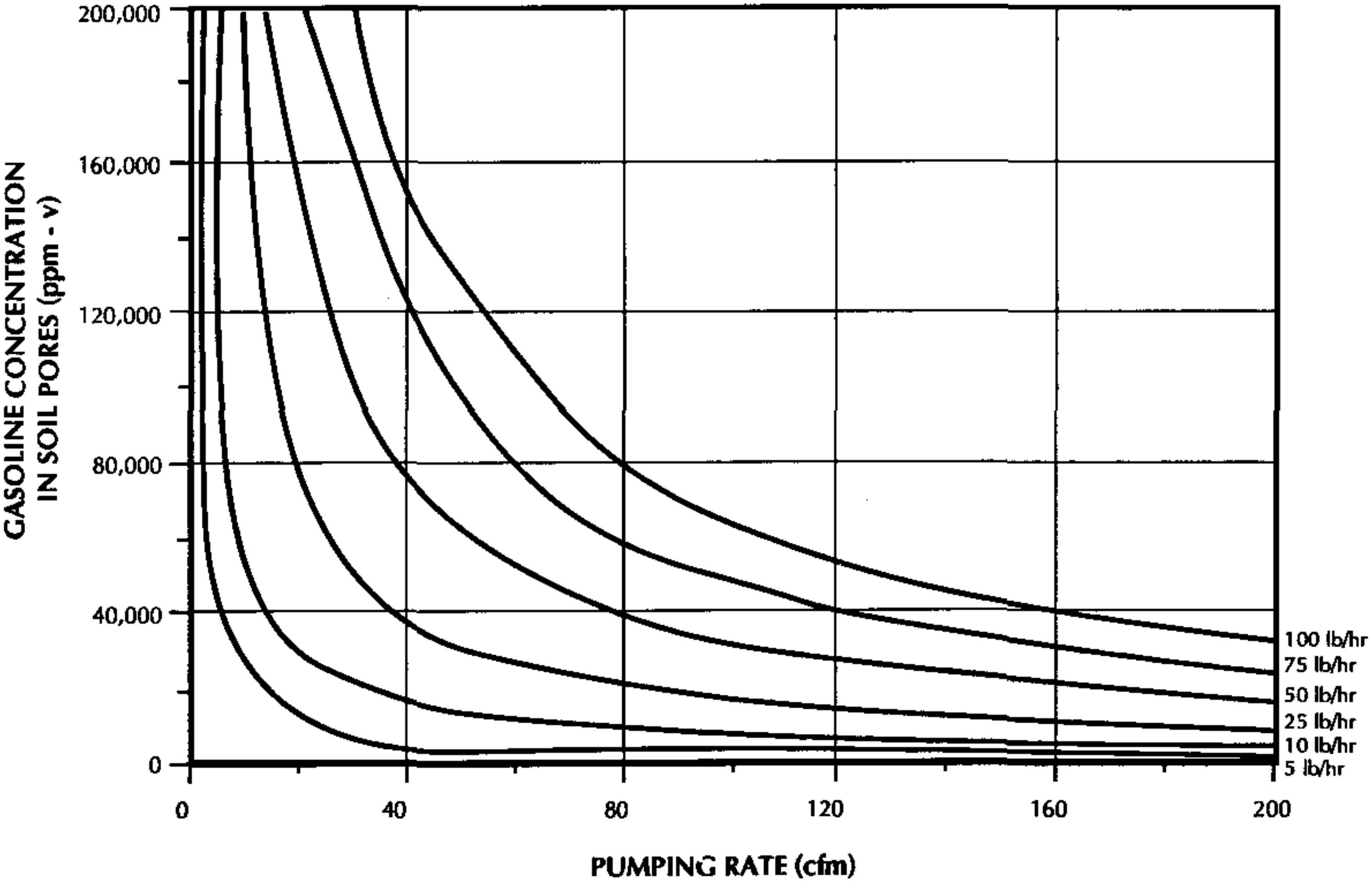


FIGURE 3 - 1
ESTIMATED VACUUM EXTRACTION AIR EMISSION RATES FOR GASOLINE VOC s

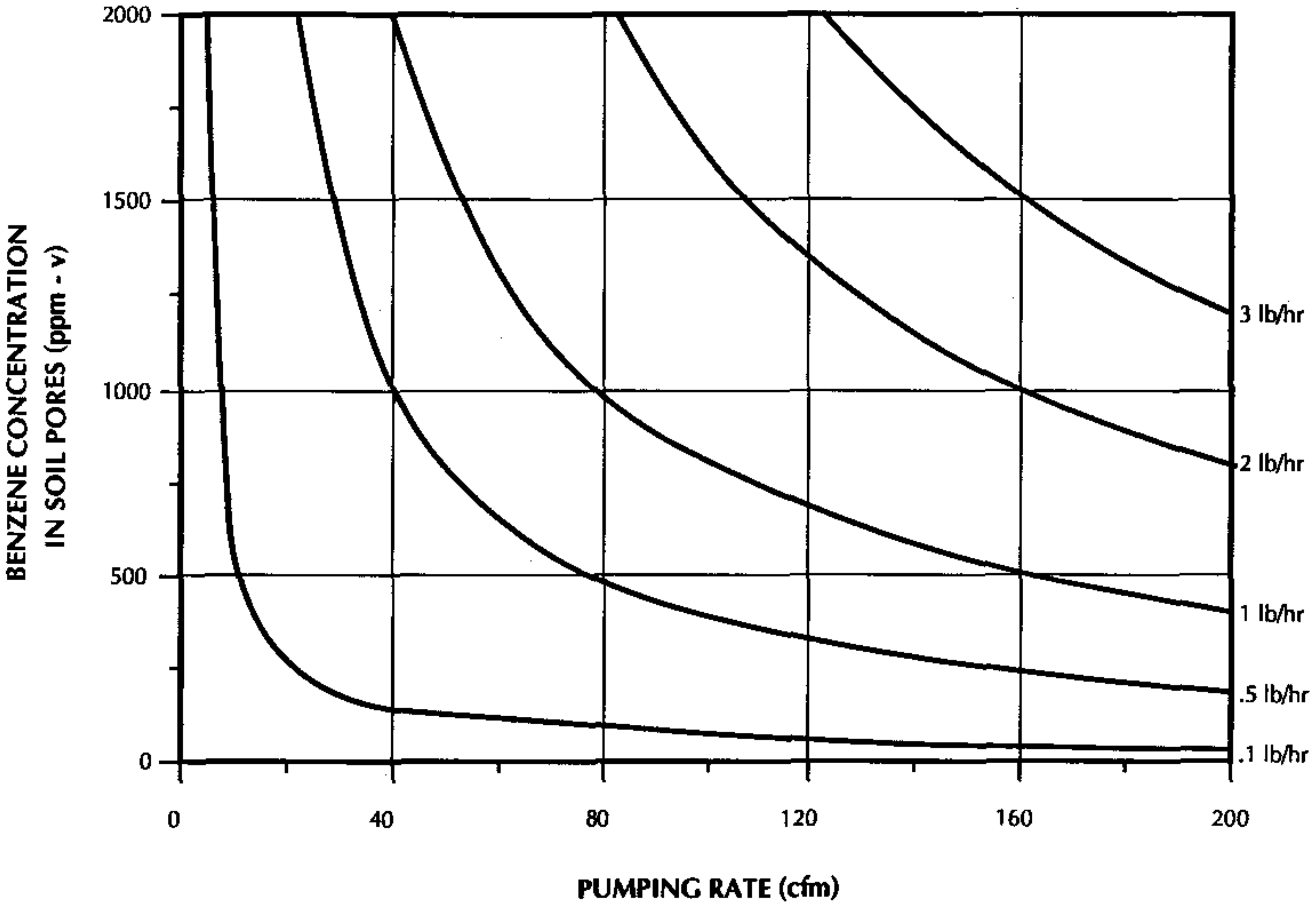


FIGURE 3 - 2
ESTIMATED VACUUM EXTRACTION AIR EMISSION RATES FOR BENZENE

3.4 VARIATION OF EMISSION RATES WITH TIME

When a vacuum extraction well begins pumping, a certain amount of time is required to establish the flow field in the soil. The soil type and moisture greatly affect the amount of time required. For example, the time required to establish a flow field in moist soil will be longer than for dry soil. Additionally, more time is required to establish a flow field in a clay soil as opposed to sand and gravel. As the flow field radiates outward from the well, the emission rate of the contaminants tends to increase, as indicated in Figure 3-3. This is because the radius of influence encompasses more contamination as it grows outward (Terra Vac, 1987).

In general, the amount of time required to reduce the VOC soil gas concentrations to negligible levels is approximately several weeks to a few months. In any soil contaminated with a mixture of VOCs, the higher vapor pressure components such as isobutane, n-butane, isopentane, and 1-pentene will volatilize first. With time, the residual in the soil will become rich in the less volatile compounds, resulting in vapor concentrations and emission rates that will decrease with time (Johnson et al., 1988). This trend is also illustrated in Figure 3-3.

After the extraction well has been pumping for some time, the air in the soil will tend to flow towards the well along preferential flow paths. The contamination will be removed from the area around these flow paths fairly quickly; however, contamination will still exist beyond the flow paths. Researchers have found that pulsing the well (turning it off and on, or systematically increasing and decreasing the pumping rate) disturbs these preferential flow paths. This encourages the air to move through more of the soil, thus removing more contamination. For pulsed systems, the highest emission rates for VOCs occur immediately after the air flow rates are changed (Rainwater, 1988). This is illustrated in Figure 3-4.

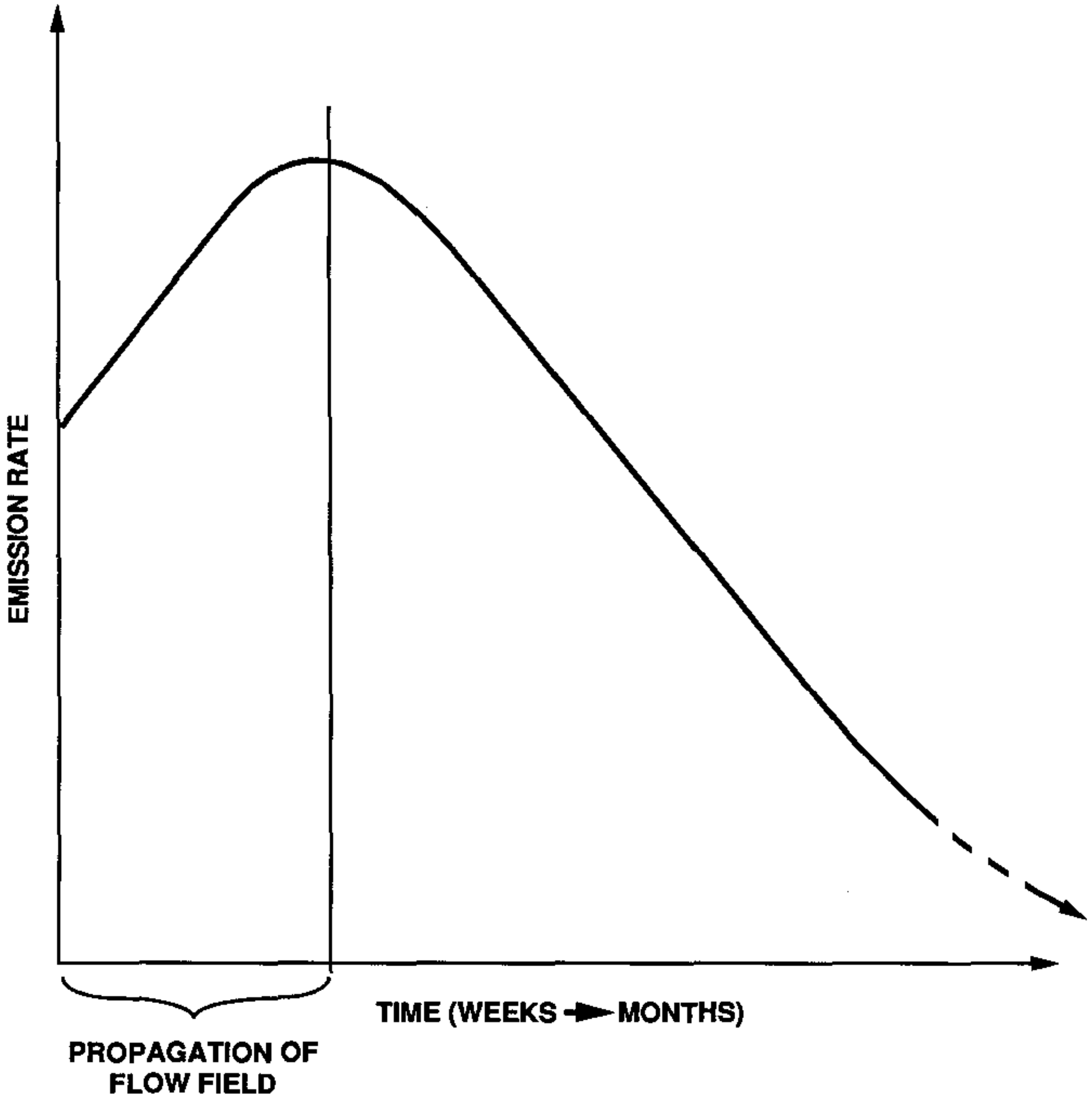


FIGURE 3-3
CHANGE IN EMISSION RATES WITH TIME FOR VACUUM EXRACTION SYSTEMS

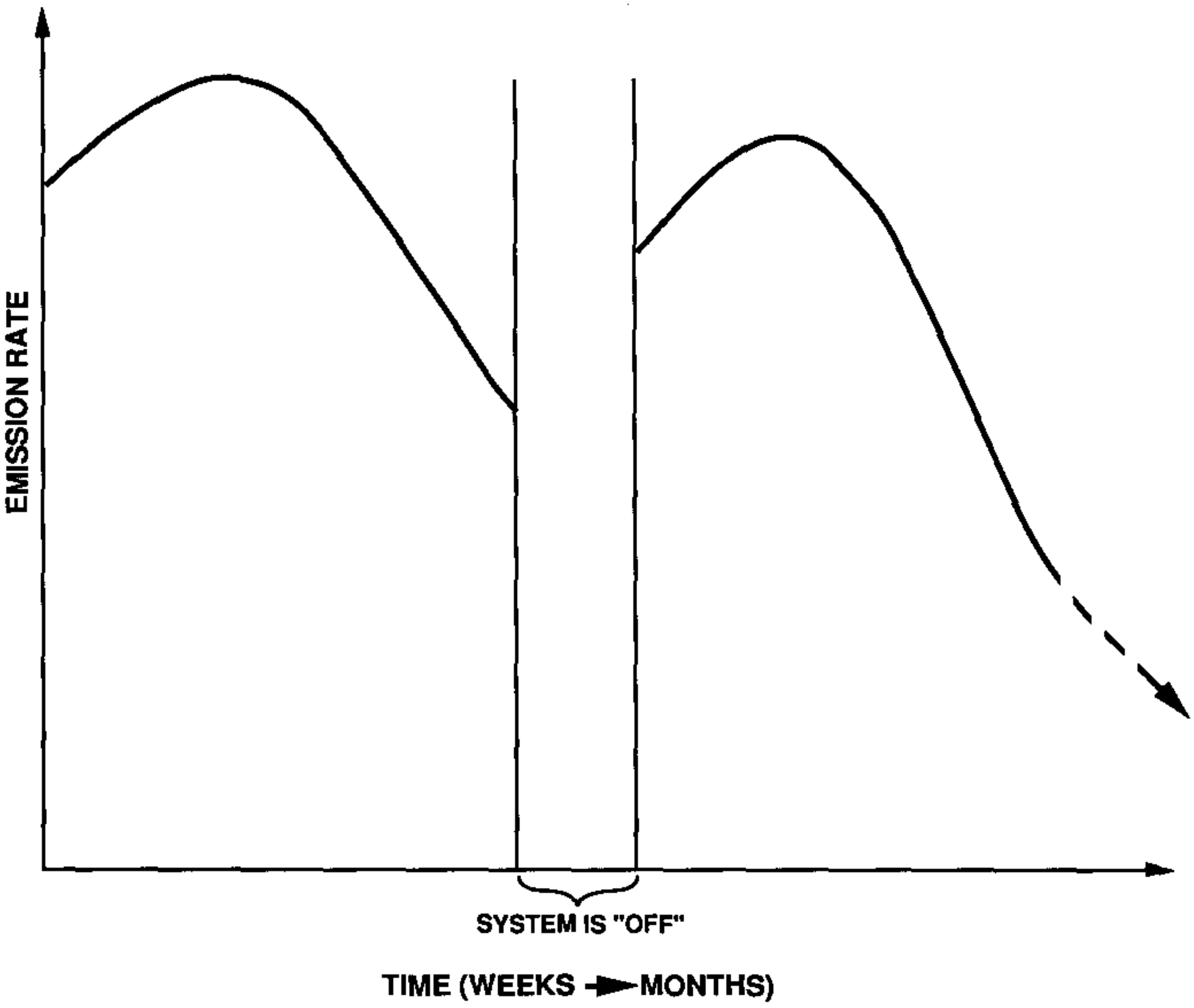


FIGURE 3-4
CHANGE IN EMISSION RATES WITH TIME
FOR PULSED VACUUM EXTRACTION SYSTEMS

4.0 AIR STRIPPING

4.1 OVERVIEW

Air stripping is widely used to remove VOCs from ground water. The removal efficiency of an air stripper depends upon the volatility of the contaminants, but is generally in the range of 99 to 99.5 percent for most VOCs found in gasoline (CDM, 1987a).

Air stripping involves pumping contaminated water from the ground and allowing it to trickle over packing material in an air stripping tower. At the same time, clean air is circulated past the packing material. When the contaminated water (which coats the packing material in a thin film) comes into contact with the clean air, the contaminants tend to volatilize from the water into the air. The contaminated air is then released into the atmosphere.

A typical site investigation will generally result in several ground water contaminant concentrations, each sampled at a different location. In order to estimate the maximum emission rate using the graphs presented in Section 4.3, the maximum ground water concentration should be used. If an average ground water concentration is used instead, the estimated emission rate will represent a long-term average of the actual emission rate (perhaps over the first six months of operation).

The procedure presented in Section 4.3 for estimating emission rates is commonly used by industry and regulatory officials. It relies on information pertaining to the design of the air stripper (such as pumping rate and removal efficiency), along with field measurements of the contaminant concentration in the ground water. The procedure was checked against examples published in the literature to ensure that realistic estimates were obtained.

Emissions from air strippers tend to be less than the emissions from excavated soil piles and vacuum extraction systems; however, they tend to be longest in duration. Air stripper emission rates depend in part upon the pumping rate and removal efficiency of the system. For systems pumping at less than 100 gpm and having removal efficiencies between 85 and 99.99 percent, VOC emissions will range from 0.5-4 lb/hr. Benzene emissions will generally be between 0.1-0.5 lb/hr.

4.2 FACTORS THAT AFFECT AIR EMISSIONS FROM AIR STRIPPERS

(a) Solubility of Contaminants

The solubility of the contaminants largely determines the concentration of the contaminant in the ground water. The solubility of many of the compounds typically found in gasoline can increase tremendously in the presence of additives. It should be noted that the synthetic gasoline described in Appendix A contains no additives.

(b) Removal Efficiency

The removal efficiency is largely determined by the design of an air stripper, and to a lesser extent, the volatility of the compound being removed. Typically, air strippers can remove more than 99 percent of the volatiles found in gasoline. Three removal efficiencies (85, 95 and 99.99 percent) are used in Section 4.3 to represent the entire range of removal efficiencies that might be encountered under operating conditions.

(c) Pumping Rate

The pumping rate of the ground water extraction well and the contaminant concentration determine the pollutant loading to the air stripping system. The pollutant loading and the removal efficiency then determine the emission rate from the system. Reducing the pumping rate can lower the pollutant loading to a system, and hence reduce the emission rate as well. It should be noted, however, that reducing the pumping rate in an effort to lower emissions can significantly increase the time and cost of cleanup.

4.3 AIR EMISSION ESTIMATION PROCEDURES

The following procedure should be used to estimate an emission rate for an air stripping system:

(1) Determine the pumping rate of the well in gallons per minute (gpm). Appendix D contains the information required to convert other systems of units to gpm.

(2) Determine the maximum concentration (in mg/l) of the gasoline and/or benzene in the ground water. These should be available from the site investigation.

The maximum concentration of gasoline or benzene that can be measured in the water is limited by the solubility of the compounds. The solubility of gasoline in water is determined by the specific blend of hydrocarbons. The concentration of benzene in water is affected by its percent composition in gasoline. Using the blend given in Appendix A, the maximum concentrations that can be measured in the ground water are 131 mg/l for gasoline and 65 mg/l for benzene.

(3) Determine the removal efficiency of the air stripping system. The removal efficiency is largely determined by the air-water ratio and packing height of the air stripping tower (Radian, 1987).

(4) Select the figure corresponding to the removal efficiency of the air stripper and the contaminant being considered. Three graphs corresponding to removal efficiencies of 99.99, 95, and 85 percent have been provided for both gasoline and benzene, as follows:

Figure 4-1: Gasoline, removal efficiency: 99.99%
Figure 4-2: Benzene, removal efficiency: 99.99%
Figure 4-3: Gasoline, removal efficiency: 95%
Figure 4-4: Benzene, removal efficiency: 95%
Figure 4-5: Gasoline, removal efficiency: 85%
Figure 4-6: Benzene, removal efficiency: 85%

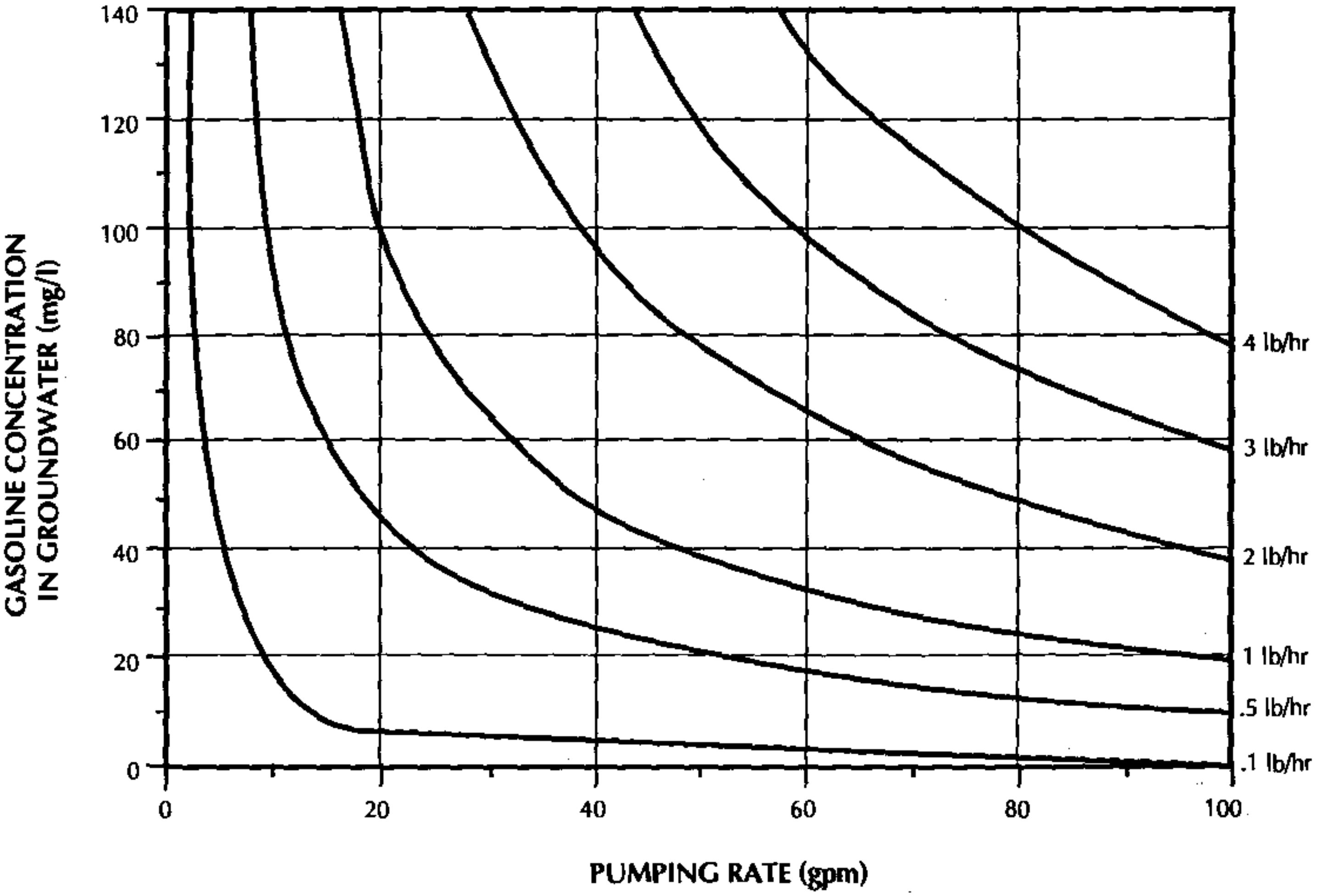


FIGURE 4 - 1
ESTIMATED AIR STRIPPER EMISSION RATES FOR GASOLINE VOCs
REMOVAL EFFICIENCY = 99.99 %

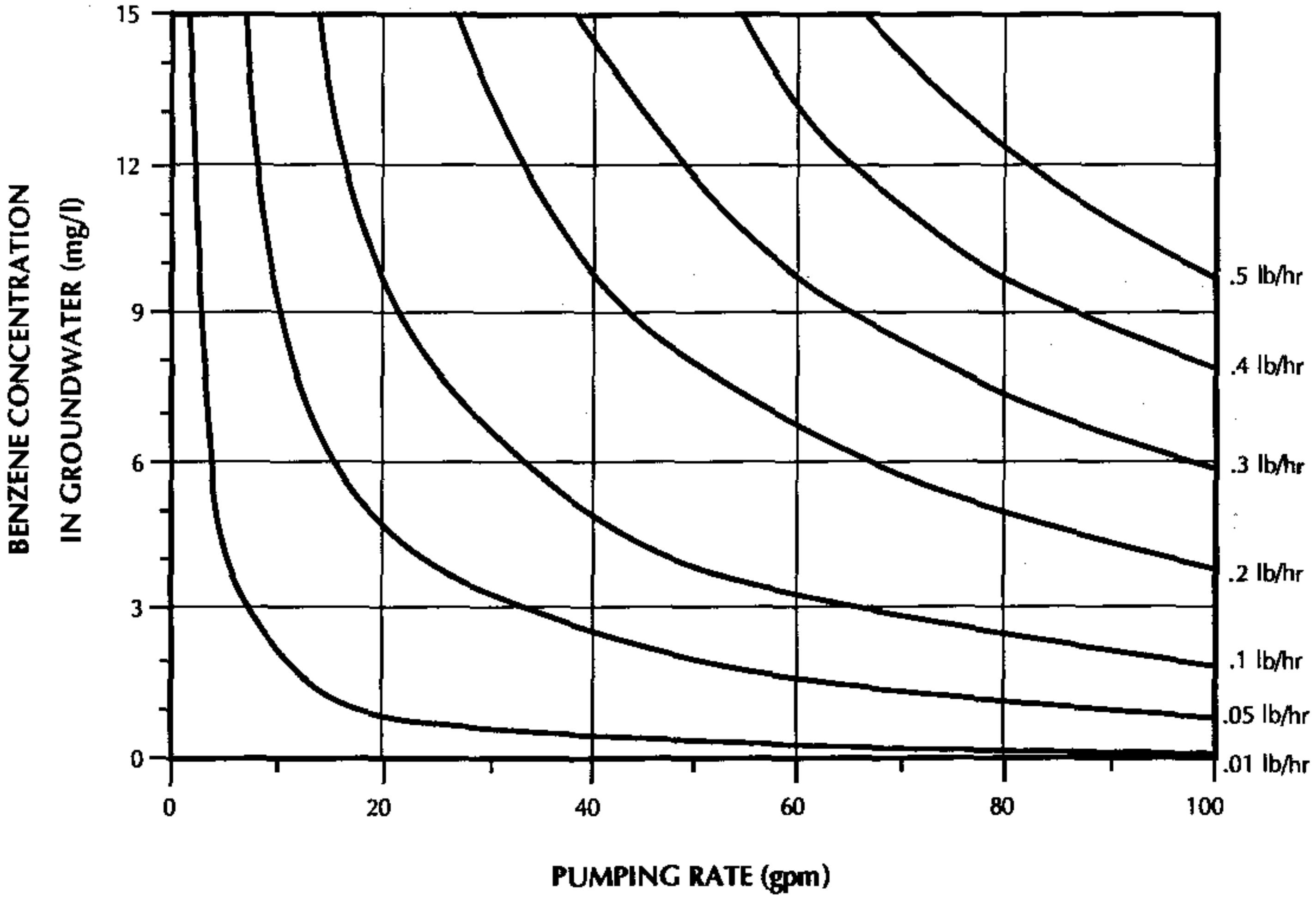


FIGURE 4 - 2
ESTIMATED AIR STRIPPER EMISSION RATES FOR BENZENE
REMOVAL EFFICIENCY = 99.99 %

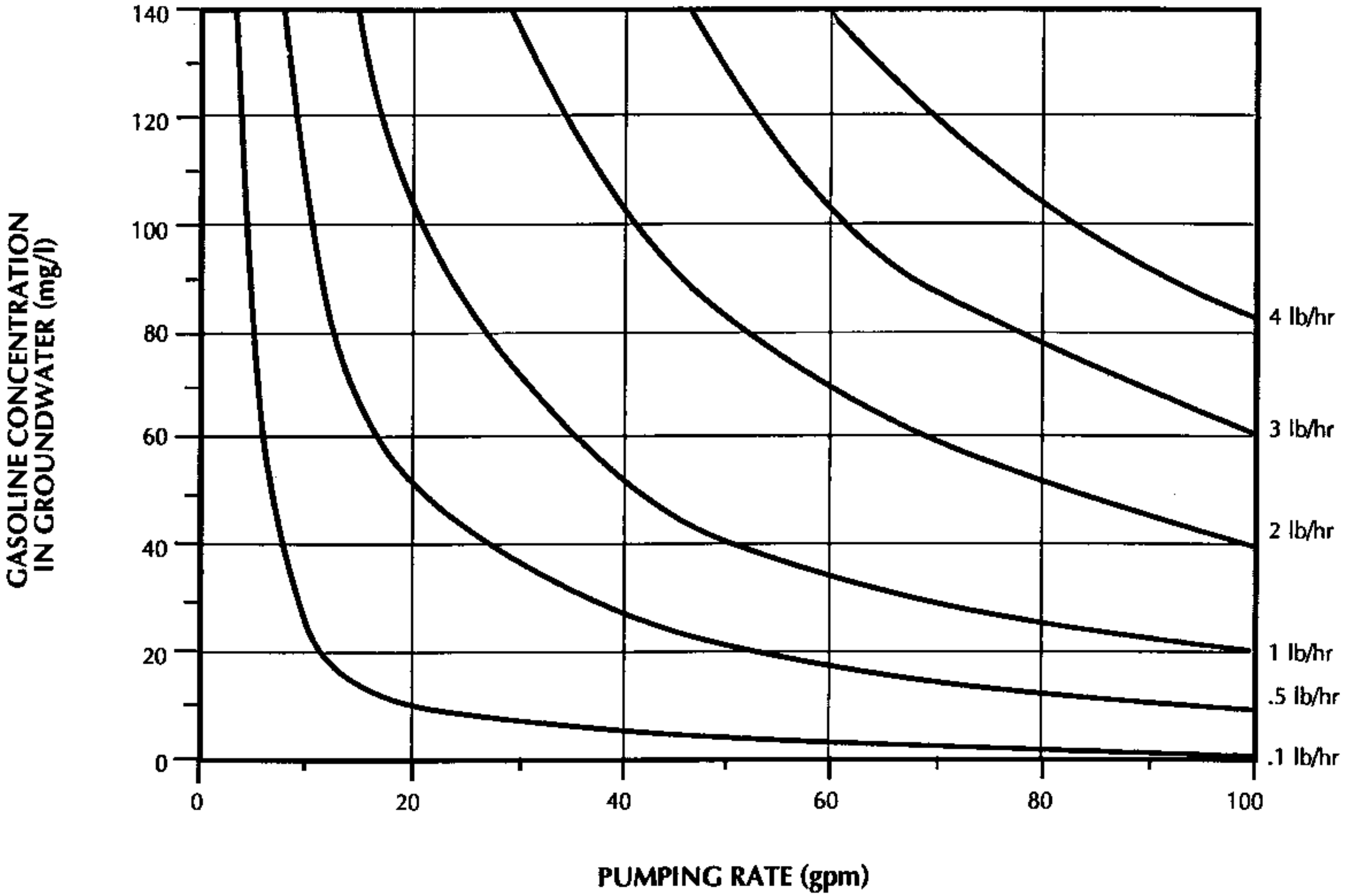


FIGURE 4 - 3
ESTIMATED AIR STRIPPER EMISSION RATES FOR GASOLINE VOCs
REMOVAL EFFICIENCY = 95.00 %

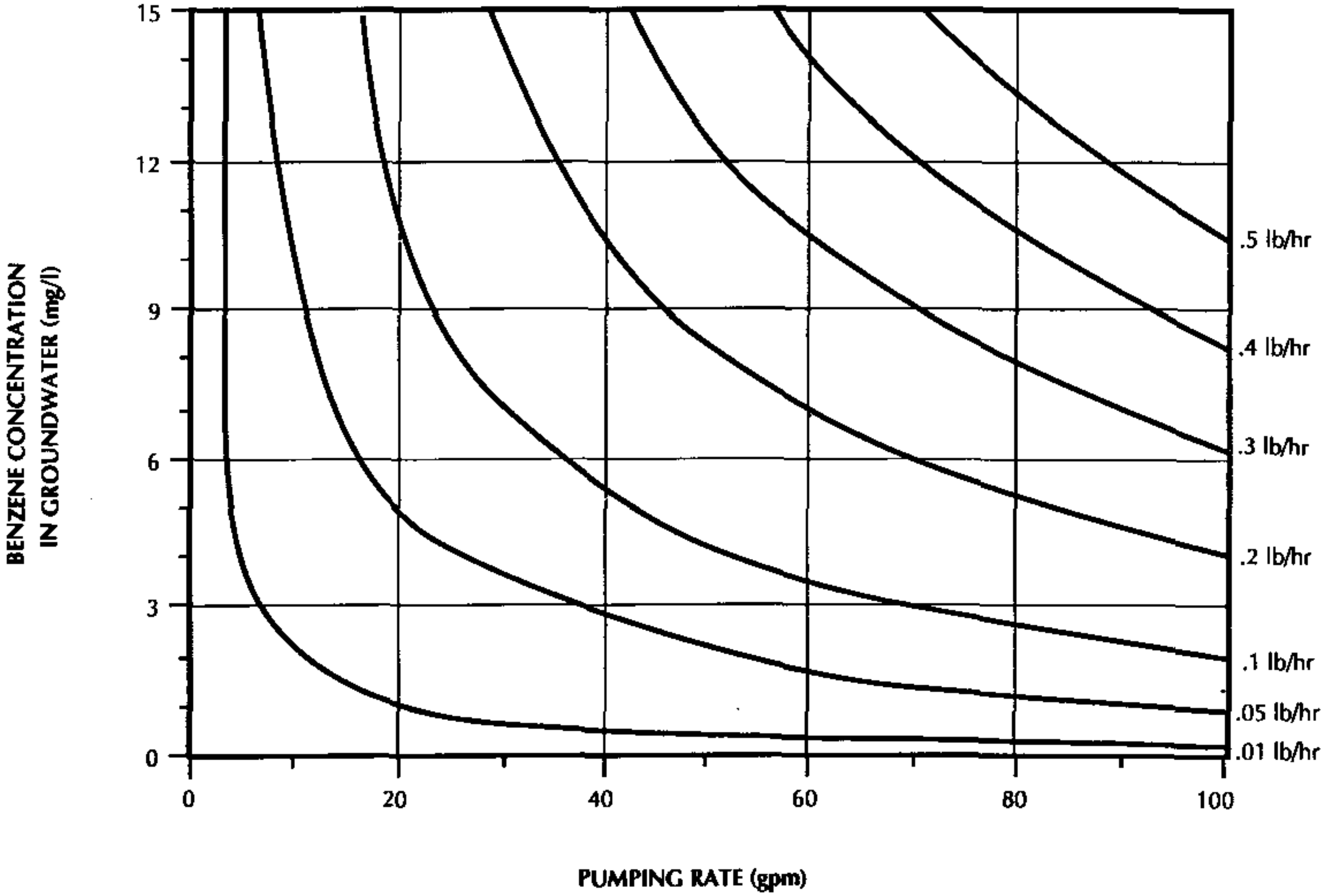


FIGURE 4 - 4
ESTIMATED AIR STRIPPER EMISSION RATES FOR BENZENE
REMOVAL EFFICIENCY = 95.00 %

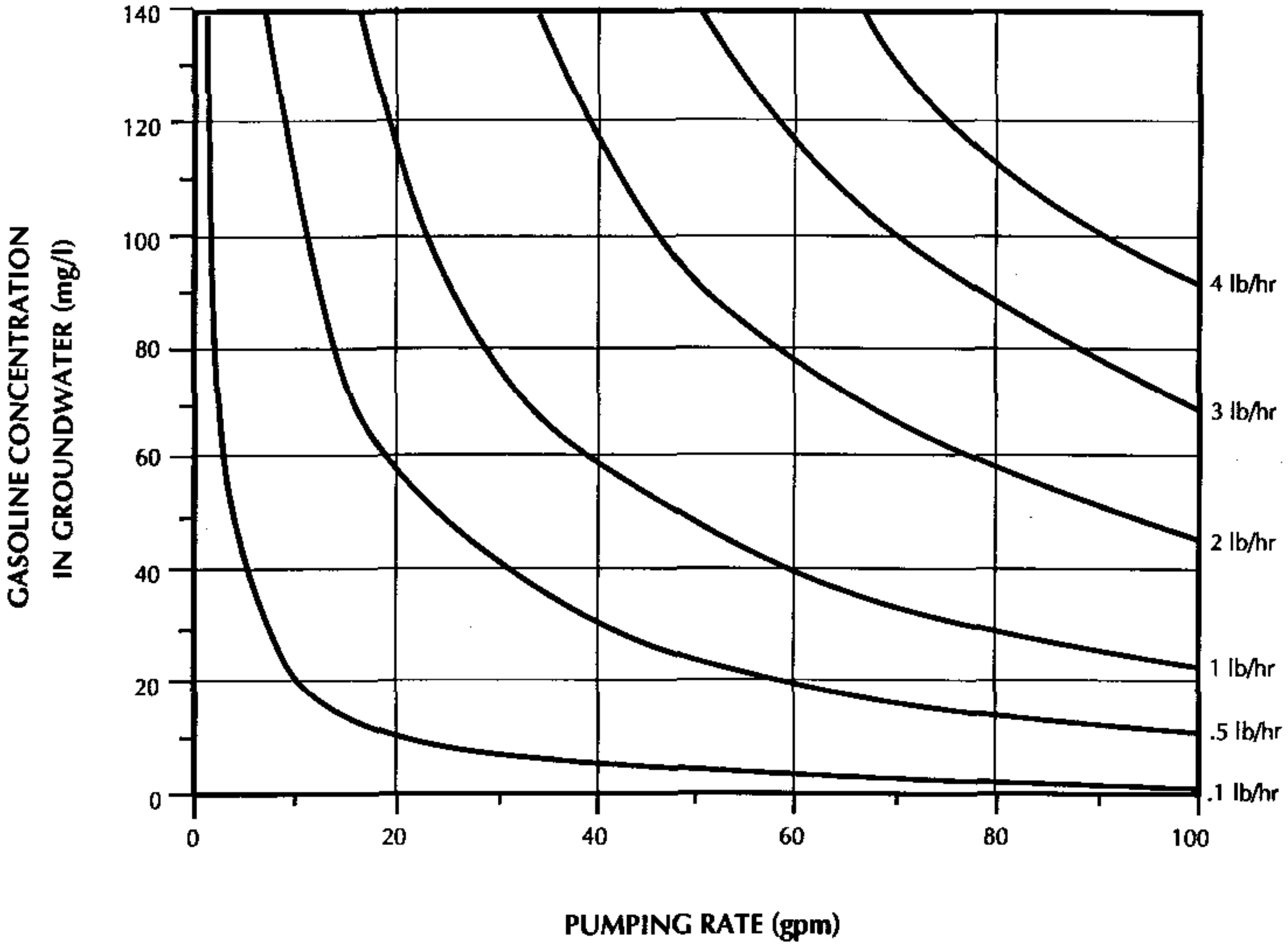


FIGURE 4 - 5
ESTIMATED AIR STRIPPER EMISSION RATES FOR GASOLINE VOCs
REMOVAL EFFICIENCY =85.00 %

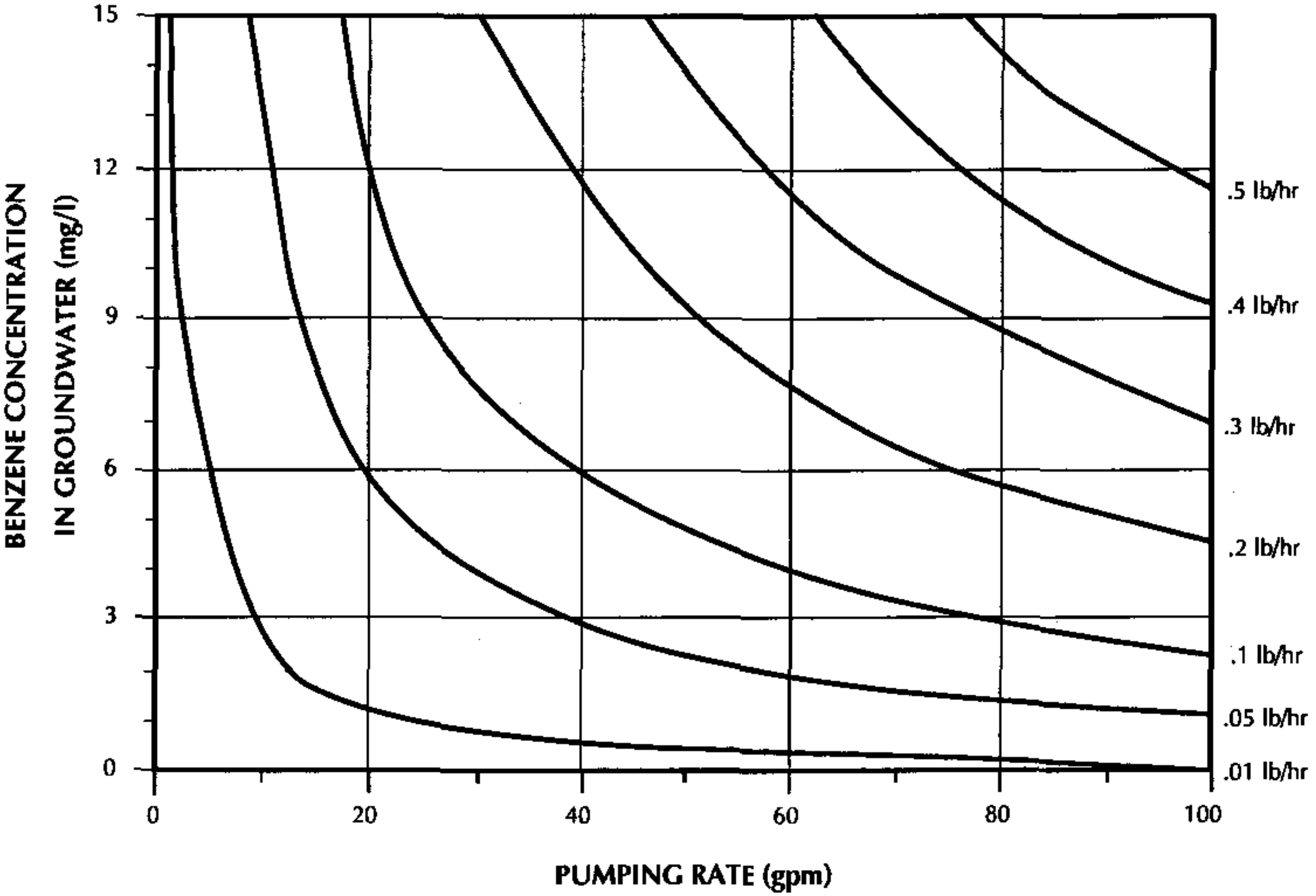


FIGURE 4 - 6
ESTIMATED AIR STRIPPER EMISSION RATES FOR BENZENE
REMOVAL EFFICIENCY = 85.00 %

Select the figure most closely corresponding to the removal efficiency of the air stripper and the contaminant being considered.

(5) Using the figure selected, locate the pumping rate of the well on the x axis, and the concentration of the contaminant in the water on the y axis. The intersection of these two points will fall on or near a curve having a specific emission rate. This curve can be used to estimate the emission rate under the prescribed pumping rate and contamination levels.

(6) If the pumping rate of the air stripper is greater than 100 gpm, equation B-12 in Appendix B can be used to calculate the air emission rate.

4.4 VARIATION OF EMISSION RATES WITH TIME

At a given site, contaminant concentrations can vary from one pumping well location to another. At a given location of pumping well, the concentration of the contaminant also can vary considerably with time, which corresponds to variations in the emission rate from the air stripping tower.

For these reasons, the exact variation of emission rate with time is extremely difficult to predict; however, the overall trend is that indicated by Figure 4-7. In general, the amount of time required to remove volatile compounds adequately from ground water is measured in years. The variation in emission rate with time is characterized by a somewhat rapid decrease during the first few months, followed by a leveling off period (Radian, 1987).

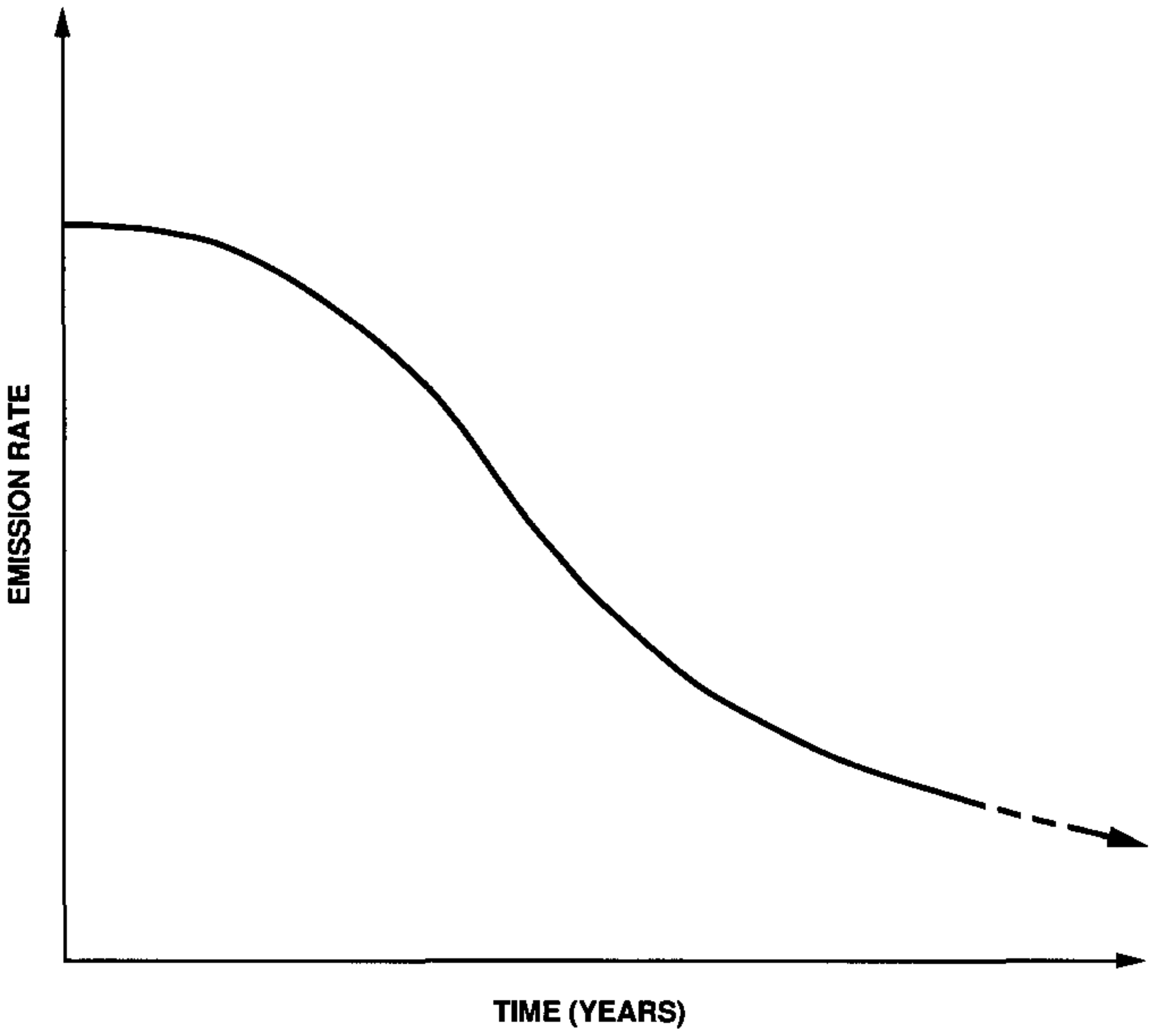


FIGURE 4-7
CHANGE IN EMISSION RATES WITH TIME
FOR AIR STRIPPERS

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APPENDIX A

PHYSIOCHEMICAL PROPERTIES OF CDM SYNTHETIC GASOLINE BLEND
(Source: CDM, 1988b)

Petroleum fuels such as automotive gasoline, jet fuel, diesel, and home heating oil are composed of a wide variety of hydrocarbons. Many petroleum products also contain additives, which not only enhance the performance, but may also modify the physical and chemical properties of the fuel. Additives are generally used in small quantities, however they occasionally compose as much as 10-12% of the fuel.

This Appendix contains tables that list the physiochemical properties of a synthetic gasoline blend at different temperatures. By comparing the typical constituents of other fuels to the constituents of the synthetic gasoline, generalizations can be made as to air emission rates that could be expected at sites where fuels other than gasoline have leaked into the ground.

In general, automotive gasoline has a higher vapor pressure than other fuels such as diesel, home heating oil and jet fuel. At the same temperature then, these fuels will evaporate at lower rates than automotive gasoline. Consequently, the air emission rates of these compounds would also be lower than those expected for gasoline. Of these fuels, jet fuel tends to be more volatile than both diesel and home heating oil, and diesel tends to be more volatile than home heating oil. For these reasons, air emission rates for jet fuel would tend to be higher than emission rates for diesel. Emission rates for both jet fuel and diesel would tend to be higher than the emission rates for home heating oil.

Typical categories of fuel additives include lead scavenging agents, octane enhancers, anit-oxidants, metal deactivators, and corrosion and rust inhibitors, to name just a few. For the most part however, only the octane enhancers and lead scavenging agents are found in significant quantities (they commonly make up 2-5% of the composition), and these are only found in automotive gasolines. In general the lead scavenging agents have low vapor pressures, and hence the air emission rates for these compounds would be negligible. The octane enhancers include MTBE (methyl t-butyl ether), t-butyl alcohol, methanol, and ethanol. These compounds have high vapor pressures, and hence the air emission rates for these compounds would be significant. The contribution of these compounds to the total emission rate for gasoline may not be significant however, because they make up a small portion of the total composition of the gasoline.

List of Tables for Appendix A

CHEMICAL PROPERTY ESTIMATION FOR SYNTHETIC
GASOLINE AND CONSTITUENTS AT 0 DEGREES C.

REPRESENTATIVE CHEMICAL	PERCENT COMPOSITION	GRAM MOL. WEIGHT (GM/MOL)	LIQ. PHASE MOL FRACT.	AIR DIFFUSION COEFFICIENT (CM^2/SEC)	LIQUID DENSITY (GM/CM^3)	PURE CHEMICAL VAPOR PRESSURE (mm Hg)	PARTIAL PRESSURE OVER GASOLINE (mm Hg)	PURE CHEMICAL VAPOR DENSITY (GM/M^3)	CONCENTRATION OVER LIQUID GASOLINE (ppm)	BOILING POINT (deg. K)	HENRY'S LAW CONSTANT (dim.)
Isobutane	2	58.12	0.0326	0.0805	0.5876	1174.26	38.3215	4006.65	50423.0	261.25	24.08
n-Butane	1	58.12	0.0163	0.0805	0.6064	774.09	12.6310	2641.24	16619.8	272.65	18.18
Isopentane	14	72.15	0.1840	0.0722	0.6418	259.30	47.7170	1098.34	62785.6	300.95	23.20
n-Pentane	3	72.15	0.0394	0.0722	0.6465	183.40	7.2320	776.84	9515.8	309.15	19.94
n-Octane	1	114.23	0.0083	0.0528	0.7161	2.86	0.0237	19.16	31.2	398.75	27.35
Benzene	3	78.11	0.0364	0.0800	0.9061	26.34	0.9594	120.79	1262.4	353.25	0.07
Toluene	5	92.14	0.0515	0.0728	0.8844	6.72	0.3459	36.36	455.1	383.75	0.07
Xylene (m)	7	106.17	0.0625	0.0590	0.8761	1.63	0.1017	10.14	133.8	466.25	0.06
n-Hexane	9	86.18	0.0990	0.0628	0.6759	45.32	4.4868	229.31	5904.4	341.85	22.72
2-Methylpentane	8	86.18	0.0880	0.0628	0.6707	67.27	5.9218	340.32	7791.8	333.35	24.10
Cyclohexane	3	84.16	0.0338	0.0636	0.7975	27.85	0.9414	137.60	1238.7	353.85	2.29
n-Heptane	1.5	100.20	0.0142	0.0583	0.6986	11.42	0.1621	67.17	213.3	371.55	25.55
2-Methylhexane	5	100.20	0.0473	0.0583	0.6942	17.59	0.8326	103.49	1095.5	363.15	41.04
Methylcyclohexane	1	98.19	0.0097	0.0589	0.7869	12.11	0.1170	69.83	154.0	374.05	4.67
2,4-Dimethylhexane	8	114.23	0.0664	0.0546	0.7141	7.20	0.4779	48.25	628.8	382.55	32.58
Ethylbenzene	2	106.17	0.0179	0.0648	0.8823	1.89	0.0338	11.79	44.5	409.25	0.07
1-Pentene	1.5	70.14	0.0203	0.0733	0.6620	235.47	4.7757	969.60	6283.8	303.05	6.64
2,2,4-Trimethylhexane	2	128.26	0.0148	0.0537	0.7306	3.20	0.0473	24.07	62.2	399.65	33.29
2,2,5,5-Tetramethylhexane	1.5	142.29	0.0100	0.0510	0.7327	1.68	0.0168	14.00	22.0	410.55	109.49
1,4-Diethylbenzene	5	134.22	0.0353	0.0525	0.8745	0.14	0.0048	1.07	6.3	456.85	0.08
1-Hexene	1.5	84.16	0.0169	0.0636	0.6909	57.64	0.9742	284.77	1281.9	336.55	5.78
1,3,5-Trimethylbenzene	5	120.20	0.0394	0.0555	0.8785	0.38	0.0152	2.71	20.0	437.85	0.04
C12-aliphatic	10	170.00	0.0558	0.0463	0.8711	0.01	0.0005	0.10	0.7	489.15	27.20
Total	100	102.20	1.0000		0.7539		126.1422		165976.6		18.68111

Temperature = 273.15 deg. K
Pressure = 760 mm Hg
Gas Constant = 0.0623 mm Hg*m^3/mol*K

Molecular Weight of Air = 28.96 gm/mol
Average Molecular Weight of Gasoline Vapors = 68.34 gm/mol
Molecular Weight of Gasoline-Air Mixture = 35.50 gm/mol

Vapor Density of Gasoline-Air Mixture = 1583.72 gm/m^3
Weighted Average Air Diffusion Coefficient = 0.0642 cm^2/sec

Weighted average liquid density = 0.736 gm/cm^3
Weighted average gas density = 506 gm/m^3

CHEMICAL PROPERTY ESTIMATION FOR SYNTHETIC
GASOLINE AND CONSTITUENTS AT 10 DEGREES C.

REPRESENTATIVE CHEMICAL	PERCENT COMPOSITION	GRAM MOL. WEIGHT (GM/MOL)	LIQ. PHASE MOL FRACT.	AIR DIFFUSION COEFFICIENT (CM^2/SEC)	LIQUID DENSITY (GM/CM^3)	PURE CHEMICAL VAPOR PRESSURE (mm Hg)	PARTIAL PRESSURE OVER GASOLINE (mm Hg)	PURE CHEMICAL VAPOR DENSITY (GM/M^3)	CONCENTRATION OVER LIQUID GASOLINE (ppm)	BOILING POINT (deg. K)	HENRY'S LAW CONSTANT (dim.)
Isobutane	2	58.12	0.0326	0.0857	0.5728	1647.77	53.7745	5423.76	70755.9	261.25	32.60
n-Butane	1	58.12	0.0163	0.0857	0.5931	1112.75	18.1571	3662.69	23890.9	272.65	25.22
Isopentane	14	72.15	0.1840	0.0769	0.6311	392.47	72.2231	1603.70	95030.4	300.95	33.88
n-Pentane	3	72.15	0.0394	0.0769	0.6364	283.84	11.1925	1159.80	14727.0	309.15	29.77
n-Octane	1	114.23	0.0083	0.0563	0.7096	5.63	0.0468	36.43	61.5	398.75	52.00
Benzene	3	78.11	0.0364	0.0851	0.8957	45.53	1.6563	201.40	2182.0	353.25	0.11
Toluene	5	92.14	0.0515	0.0776	0.8758	12.43	0.6397	64.86	841.7	383.75	0.13
Xylene (m)	7	106.17	0.0625	0.0629	0.8701	3.26	0.2039	19.61	268.3	466.25	0.12
n-Hexane	9	86.18	0.0990	0.0669	0.6676	75.70	7.4976	369.48	9865.2	341.85	36.61
2-Methylpentane	8	86.18	0.0880	0.0669	0.6620	109.55	9.6446	534.70	12690.2	333.35	37.86
Cyclohexane	3	84.16	0.0338	0.0677	0.7884	47.51	1.6060	226.44	2113.2	353.85	3.77
n-Heptane	1.5	100.20	0.0142	0.0620	0.6914	20.66	0.2933	117.23	385.9	371.55	44.60
2-Methylhexane	5	100.20	0.0473	0.0620	0.6867	30.94	1.4642	175.57	1926.5	363.15	69.63
Methylcyclohexane	1	98.19	0.0097	0.0627	0.7789	21.45	0.2071	119.26	272.6	374.05	7.97
2,4-Dimethylhexane	8	114.23	0.0664	0.0581	0.7071	13.30	0.8833	86.03	1162.2	382.55	58.08
Ethylbenzene	2	106.17	0.0179	0.0690	0.8748	3.77	0.0673	22.66	88.6	409.25	0.14
1-Pentene	1.5	70.14	0.0203	0.0780	0.6513	359.48	7.2909	1427.99	9593.3	303.05	9.78
2,2,4-Trimethylhexane	2	128.26	0.0148	0.0572	0.7240	6.18	0.0915	44.92	120.3	399.65	62.14
2,2,5,5-Tetramethylhexane	1.5	142.29	0.0100	0.0543	0.7264	3.40	0.0340	27.37	44.7	410.55	214.06
1,4-Diethylbenzene	5	134.22	0.0353	0.0559	0.8683	0.32	0.0113	2.43	14.9	456.85	0.19
1-Hexene	1.5	84.16	0.0169	0.0677	0.6821	94.87	1.6036	452.20	2110.1	336.55	9.18
1,3,5-Trimethylbenzene	5	120.20	0.0394	0.0591	0.8718	0.84	0.0333	5.74	43.8	437.85	0.09
C12-aliphatic	10	170.00	0.0550	0.0493	0.8656	0.03	0.0016	0.27	2.1	489.15	77.43
Total	100	102.20	1.0000		0.7457		188.6252		240191.2		32.02673

Temperature = 283.15 deg. K
Pressure = 760 mm Hg
Gas Constant = 0.0623 mm Hg*m^3/mol*K

Molecular Weight of Air = 28.96 gm/mol
Average Molecular Weight of
Gasoline Vapors = 68.92 gm/mol
Molecular Weight of
Gasoline-Air Mixture = 38.88 gm/mol

Vapor Density of Gasoline-
Air Mixture = 1673.38 gm/m^3
Weighted Average Air
Diffusion Coefficient = 0.0684 cm^2/sec

Weighted average
liquid density = 0.727 gm/cm^3
Weighted average
gas density = 736 gm/m^3

CHEMICAL PROPERTY ESTIMATION FOR SYNTHETIC
GASOLINE AND CONSTITUENTS AT 20 DEGREES C.

REPRESENTATIVE CHEMICAL	PERCENT COMPOSITION	GRAM MOL. WEIGHT (GM/MOL)	LIQ. PHASE MOL FRACT.	AIR DIFFUSION COEFFICIENT (CM^2/SEC)	LIQUID DENSITY (GM/CM^3)	PURE CHEMICAL VAPOR PRESSURE (mm Hg)	PARTIAL PRESSURE OVER GASOLINE (mm Hg)	PURE CHEMICAL VAPOR DENSITY (GM/M^3)	CONCENTRATION OVER LIQUID GASOLINE (ppm)	BOILING POINT (deg. K)	HENRY'S LAW CONSTANT (dim.)
Isobutane	2	58.12	0.0326	0.0911	0.5570	2252.75	73.5170	7162.14	96733.9	261.25	43.04
n-Butane	1	58.12	0.0163	0.0911	0.5790	1555.33	25.3788	4944.83	33393.1	272.65	34.04
Isopentane	14	72.15	0.1840	0.0817	0.6200	574.89	105.7925	2268.97	139200.7	300.95	47.93
n-Pentane	3	72.15	0.0394	0.0817	0.6260	424.38	16.7346	1674.92	22019.2	309.15	43.00
n-Octane	1	114.23	0.0083	0.0598	0.7030	10.46	0.0869	65.37	114.3	398.75	93.30
Benzene	3	78.11	0.0364	0.0905	0.8850	75.20	2.7390	321.31	3604.0	353.25	0.18
Toluene	5	92.14	0.0515	0.0824	0.8670	21.84	1.1237	110.05	1478.6	383.75	0.21
Xylene (m)	7	106.17	0.0625	0.0668	0.8640	6.16	0.3852	35.78	506.8	466.25	0.22
n-Hexane	9	86.18	0.0990	0.0711	0.6590	121.24	12.0080	571.57	15800.0	341.85	56.64
2-Methylpentane	8	86.18	0.0880	0.0711	0.6530	171.50	15.0985	808.51	19866.4	333.35	57.24
Cyclohexane	3	84.16	0.0338	0.0719	0.7790	77.55	2.6218	357.04	3449.7	353.85	5.94
n-Heptane	1.5	100.20	0.0142	0.0659	0.6840	35.55	0.5047	194.86	664.1	371.55	74.13
2-Methylhexane	5	100.20	0.0473	0.0659	0.6790	51.90	2.4563	284.50	3232.0	363.15	112.83
Methylcyclohexane	1	98.19	0.0097	0.0666	0.7707	36.21	0.3497	194.50	460.2	374.05	13.00
2,4-Dimethylhexane	8	114.23	0.0664	0.0617	0.7000	23.32	1.5492	145.75	2038.4	382.55	98.40
Ethylbenzene	2	106.17	0.0179	0.0733	0.8670	7.08	0.1264	41.09	166.3	409.25	0.25
1-Pentene	1.5	70.14	0.0203	0.0829	0.6400	530.80	10.7654	2036.57	14165.0	303.05	13.94
2,2,4-Trimethylhexane	2	128.26	0.0148	0.0608	0.7173	11.30	0.1671	79.30	219.9	399.65	109.70
2,2,5,5-Tetramethylhexane	1.5	142.29	0.0100	0.0577	0.7200	6.47	0.0647	50.35	85.1	410.55	393.73
1,4-Diethylbenzene	5	134.22	0.0353	0.0594	0.8620	0.70	0.0244	5.11	32.4	456.85	0.40
1-Hexene	1.5	84.16	0.0169	0.0719	0.6730	149.97	2.5348	690.40	3335.3	336.55	14.01
1,3,5-Trimethylbenzene	5	120.20	0.0394	0.0628	0.8650	1.73	0.0681	11.36	89.7	437.85	0.18
C12-aliphatic	10	170.00	0.0558	0.0524	0.8600	0.08	0.0042	0.70	5.5	489.15	198.23
Total	100	102.20	1.0000		0.7373		274.1020		360660.5		54.34632

Temperature = 293.15 deg. K
Pressure = 760 mm Hg
Gas Constant = 0.0623 mm Hg*m^3/mol*K

Molecular Weight of Air = 28.96 gm/mol
Average Molecular Weight of Gasoline Vapors = 69.48 gm/mol
Molecular Weight of Gasoline-Air Mixture = 43.58 gm/mol

Vapor Density of Gasoline-Air Mixture = 1811.60 gm/m^3
Weighted Average Air Diffusion Coefficient = 0.0726 cm^2/sec

Weighted average liquid density = 0.718 gm/cm^3
Weighted average gas density = 1042 gm/m^3

APPENDIX B

AIR EMISSION ESTIMATION EQUATIONS

This appendix contains the development of the equations used to estimate the air emission rates for soil excavation, vacuum extraction and air stripping.

B-1 Soil Excavation

The transport processes of advection and diffusion contribute to the overall flux of vapors from an excavated soil pile. Although research by Fukuda (1955) has indicated that wind eddies can increase the advection of vapors through soil, this movement has been shown to be small when compared to other transport processes (CDM, 1986). For this reason, it is assumed that the flux of vapors is controlled by the process of diffusion.

Molecular diffusion in one dimension is described by the following form of Fick's First Law (PEI, 1988):

$$J = D_{eff} \left(\frac{dc}{dz}\right) \qquad \text{(B-1)}$$

where: J = the flux of vapors [$lb/(ft^2\text{-}hr)$]
D_{eff} = the effective diffusion coefficient [ft^2/hr]
$(\frac{dc}{dz})$ = the concentration gradient in the vertical direction [lb/ft^4]

The effective diffusion coefficient can be defined in the following manner (PEI, 1988):

$$D_{eff} = D_{air}\ \tau\ \Theta_{air} \qquad \text{(B-2)}$$

where: D_{air} = the diffusion coefficient [ft^2/hr]
τ = tortuosity, $(0 < \tau < 1)$ [dimensionless]
Θ_{air} = the air filled porosity (expressed as a fraction of 1) [dimensionless]

The air diffusion coefficient is adjusted by the tortuosity and air filled porosity in order to account for diffusion through a porous medium. The path length of the diffusing molecule increases as it wanders through the air filled pores of the soil (CDM, 1987b).

It follows that the more tortuous the path, the longer it takes the molecule to diffuse through soil, effectively reducing the air diffusion coefficient by a greater amount (PEI, 1988). There are many expressions that can be used to calculate the tortuosity, however the Millington and Quirk (1961) expression that is used here has a theoretical basis, and tends to be preferred (PEI, 1988):

$$\tau = (\Theta_{air})^{1/3} \left[\frac{\Theta_{air}}{\Theta_{total}}\right]^2 \qquad \text{(B-3)}$$

where: Θ_{total} = the total porosity, $(0 < \Theta_{total} < 1)$
Θ_{air} = the air filled porosity
$= \Theta_{total} - \Theta_{water}$
where Θ_{water} = the moisture content of the soil

Different soil types typically have different values of total porosity and moisture content. For the formulations presented here, a soil type having a medium grain size (such as a sand) was selected. The soil was assumed to have a total porosity of 0.35, and moisture content of 0.08. These numbers correspond to average values that might be expected for a moist sand, and were obtained from graphs and tables given in Freeze and Cherry (1979) and CDM (1986).

The steady state form of the concentration gradient can be written as:

$$\left(\frac{dc}{dz}\right) = (C_{soil\ gas} - C_{atmosphere})/(z) \qquad \text{(B-4)}$$

where: $C_{soil\ gas}$ = concentration of the contaminant in the soil pores $[lb/ft^3]$

$C_{atmosphere}$ = concentration of the contaminant in the air above the soil pile $[lb/ft^3]$

z = the depth of the soil over which the concentration gradient exists [ft]

It is assumed that the wind is sufficient to mix the contaminants that diffuse out of the soil with clean air, thereby reducing the concentration of the contaminants in the air above the soil. Hence, $C_{atmosphere} = 0$. This has the effect of maintaining a steep concentration gradient across the soil-air interface, and consequently a maximum flux of vapors is maintained.

The steady state concentration gradient takes time to establish, however the thinner the soil layer thickness being considered, the less time is required. The assumption of a thin soil layer thickness again allows for the calculation of a maximum flux of vapors. For the calculations presented here, a soil layer thickness of 0.5 inches was assumed.

When liquid gasoline and air are present in the soil pores, concentrations in the vapor phase are controlled by the gasoline composition and the vapor pressures of the constituents (Stephanatos, 1988). These concentrations are temperature dependent, as is the air diffusion coefficient. For temperatures of 32°F, 50°F, 68°F, and 86°F the values of the maximum gasoline VOC and benzene concentrations in (mg/l) are:

	32°F	50°F	68°F	86°F
gasoline concentration	757	1091	1532	2099
benzene concentration	4.4	7.3	11.7	17.9

Values for the air diffusion coefficients for different gasoline constituents are tabulated in Appendix A.

Substituting the definitions for the effective diffusion coefficient and the concentration gradient allows Equation B-1 to be rewritten in the following form:

$$J = D_{air}\ \Theta_{air}\ (\Theta_{air})^{1/3} \left(\frac{\Theta_{air}}{\Theta_{total}} \right)^2 \frac{C_{soil\ gas}}{z} \qquad \text{(B-5)}$$

Equation B-5 allows the calculation of the flux in units of [lb/(hr-ft^2)]. In order to obtain the emission rate in units of [lb/hr], the flux must be multiplied by the surface area of the soil pile, as follows:

$$ER = J \times A \qquad \text{(B-6)}$$

where: ER = emission rate [lb/hr]
J = vapor flux [lb/(hr-ft^2)]
A = surface area of the soil pile [ft^2]

In order to simplify this process, it is assumed that the soil pile can have one of two basic shapes: a horizontal layer, or cone. For the horizontal layer it is also assumed that there is no flux of vapors out of the sides of the pile. One of the following two equations can be used to calculate the surface area of a horizontal pile:

$$\text{Surface area} = (\text{total volume})/(\text{height}) \qquad \text{(B-7)}$$

$$\text{Surface area} = (\text{length}) \times (\text{width}) \qquad \text{(B-8)}$$

The following equation can be used to calculate the surface area of conical soil piles:

$$\text{Surface area} = 3.142 \times r \times \sqrt{r^2 + h^2} \qquad \text{(B-9)}$$

Here, r is equal to one-half of the diameter at the base of the soil pile.

If the height of the pile is approximately equal to the radius at the base of the soil pile, the equation for the surface area can be simplified considerably:

$$\text{Surface area} = 1.11 \times (\text{diameter})^2 \qquad \text{(B-10)}$$

B-2 Vacuum Extraction

The following equation is used frequently by industry to estimate air emission rates from a single vacuum extraction well (Johnson, 1988):

$$ER = (Q \times C_{\text{soil gas}} \times MW \times 1.581 \times 10^{-7}) \qquad \text{(B-11)}$$

where: ER = emission rate [lb/hr]
Q = pumping rate [cfm]
C = soil gas concentration [ppm-v]
MW = molecular weight of contaminant [lb/lb-mole]

The constant (1.581×10^{-7}) has units of [(lb-mole min)/(ft^3 ppm-v hr)] and was derived in the following manner:

$$\frac{1}{10^6 \text{ ppm-v}} \times \frac{60 \text{ min}}{1 \text{ hr}} \times \frac{1 \text{ lb-mole}^*}{379.5 \text{ ft}^3} = 1.581 \times 10^{-7}$$

*(Source: Perry's Chemical Engineers' Handbook, 1984)

API (1985) gives a similar form of this equation to calculate emission rates.

B-3 Air Stripping

Emission rates are a function of influent concentrations and the rate of flow to the air stripper. The form of the equation that can be used to calculate emission rates is (Radian, 1987):

$$ER = (Q \times C \times RE \times 5.042 \times 10^{-4}) \qquad \text{(B-12)}$$

where: ER = the emission rate in [lb/hr]

Q = the groundwater pumping rate in [gpm]

C = the concentration of the contaminant in the groundwater in [mg/l]

RE = the removal efficiency, expressed as a fraction of 1 (for example, a removal efficiency of 95% = 0.95)

and (5.042×10^{-4}) is a constant having units of [(lb liters min)/(mg gal hr)] and is derived in the following manner:

$$\frac{2.2 \text{ lb}}{10^{6} \text{ mg}} \times \frac{1000 \text{ liters}}{261.8 \text{ gal}} \times \frac{60 \text{ min}}{1 \text{ hr}} = 5.042 \times 10^{-4}$$

APPENDIX C

SOIL GAS CONCENTRATION MEASUREMENTS

To convert soil gas concentrations given in $\mu g/l$ to ppm-v (parts per million-volume) the following equation should be used (Geoscience Consultants Limited, 1988):

$$\text{ppm-v} = C \times \frac{(RT)}{P} \times \frac{(1)}{MW} \times 1000\,\frac{\text{liters}}{m^3} \qquad \text{(C-1)}$$

where: C = soil gas concentration of contaminant [μg/liter]
R = gas constant
= .06236 (mm Hg m^3)/(mole °K)
T = temperature [°K]
= 273.15 + °C
= $273.15 + (°F-32)(\frac{5}{9})$
P = atmospheric pressure [mm Hg]
= 760 mm Hg approximately
MW= molecular weight of contaminant
= 78.11 g/mole for benzene
= 102.2 g/mole for gasoline

To calculate soil gas concentrations from total soil concentrations:

Assume that there is equilibrium partitioning of the chemical (gasoline or benzene) between the soil air, soil moisture and the soil organic carbon. Under this assumption there will be no sorption of the chemical vapors onto the dry soil. The total soil concentration is therefore composed of the concentration in the soil gas, soil moisture and the amount sorbed onto the soil organic matter. This relationship can be expressed as follows:

$$C_{total} = C_{gas} + C_{moisture} + C_{soil} \qquad \text{(C-2)}$$

or by rearranging terms:

$$C_{gas} = C_{total} - C_{moisture} - C_{soil} \qquad \text{(C-3)}$$

The following relationships can be used to determine the contaminant concentrations in the gas, moisture and soil:

$$\frac{C_{gas}\ [\text{atm}]}{C_{moisture}\,[\text{g/m}^3]} = \frac{H\ [\text{atm-m}^3/\text{mol}]}{MW\ [\text{g/mol}]} \qquad \text{(C-4)}$$

where: H = Henry's Law Constant
MW = molecular weight of the contaminant

$$\frac{C_{soil}\ [\text{mg/kg}]}{C_{moisture}\ [\text{mg/l}]} = (f_{oc})\ K_{oc}\,[\text{l/kg}] \qquad \text{(C-5)}$$

where: f_{oc} = organic carbon content of the soil, $(0 < foc < 1)$
K_{oc} = organic carbon normalized soil/water partition coefficient

$$\frac{C_{soil}\ [\text{mg/kg}]}{C_{gas}\ [\text{atm}]} = \frac{(foc)\ K_{oc}\,[\text{l/kg}]\ MW[\text{g/mol}]}{H\ [\text{atm-m}^3/\text{mol}]} \qquad \text{(C-6)}$$

An estimate for K_{oc} can be obtained from the following expression:

$$\log K_{oc} = \log K_{ow} - .21$$

where: K_{ow} = octanol/water partition coefficient

Experimental values of K_{ow} are tabulated in the literature. The fraction of organic material in the soil can be measured in the field, or it can be roughly approximated. The molecular weight and Henry's Law constants for the synthetic gasoline blend are listed in Appendix A.

APPENDIX D

UNITS CONVERSION TABLE

To convert	in	to	ft	Multiply by	.083
	cm				.033
	m				3.3
To convert	in^2	to	ft^2	Multiply by	.069
	cm^2				.0011
	m^2				10.89
To convert	ft^3/sec	to	ft^3/min	Multiply by	60.
	gal/min				.134
	$\frac{\text{liters}}{\text{min}}$				.035
	$\frac{\text{liters}}{\text{sec}}$				2.1
To convert	gal/sec	to	gal/min	Multiply by	60.
	ft^3/min				7.48
	ft^3/sec				448.8
	$\frac{\text{liters}}{\text{min}}$				.26
	$\frac{\text{liters}}{\text{sec}}$				15.6