

Estimation of Fugitive Emissions from Petroleum Refinery Process Drains

Phase I Report

Health and Environmental Sciences Department
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API PUBLICATION NUMBER 4639

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ABSTRACT

Fugitive emissions are commonly estimated using USEPA's AP-42 emission factors. The factor for refinery process drains was developed in 1979. Since that time, modifications to drains, carried out in response to regulatory requirements, have reduced emissions, with the result that the AP-42 factor may be over-estimating actual drain emissions. This work was undertaken to address these concerns by developing a protocol to improve estimates of drain emissions. A survey of process drains was conducted at three refineries, and an evaluation carried out of the capability of existing models to predict drain emissions and important variables influencing drain emissions. Laboratory scale and pilot scale equipment were assembled to facilitate the measurement of VOC emissions from simulated drain structures under controlled conditions. Testing demonstrated almost complete mass balance closures, and repeatability of analytical determination of target compounds and their stripping efficiencies, confirming the suitability of the protocol for measuring VOC emissions from drain structures.

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EXECUTIVE SUMMARY

This investigation was initiated by the American Petroleum Institute (API) to address the apparent inadequacy of the AP-42 factor in estimating correctly the fugitive emissions from refinery process drains. Significant modifications have been made to refinery drain installations over the last few years in response to regulatory requirements introduced during this period. These changes have resulted in reductions in emissions from drains such that the AP-42 factor is now thought to overestimate these emissions.

The work reported here was the first phase of an investigation to develop predictive correlations that can be used to improve the estimate of drain emissions. This report presents and discusses a protocol which would facilitate the measurement and modeling of volatile organic compound¹ (VOC) emissions from refinery process drains. It includes a comprehensive literature review on fugitive emissions from process drains, the results of a survey of process drains at three refineries, a review of models that describe VOC emissions from drain structures and the results from a series of tests that were carried out to evaluate, at laboratory scale and pilot scale, the suitability of the equipment and procedures that make up the protocol.

LITERATURE REVIEW

The literature review revealed that, of 220 publications related to VOC emissions, only 19 addressed VOC emissions from process drains. The current base of knowledge on process drain emissions is based on five of these publications, the remaining 14 borrowing heavily from the first five. It was found that current methods for estimating VOC emissions from process drains are both conservative (overestimate) and characterized by a high degree of uncertainty. Factors affecting VOC emissions from drains were divided into those affecting mass transfer and those affecting ventilation. Important factors affecting mass transfer were identified as volatility, liquid concentration, diffusion rate through air and water, and drain diameter. Factors affecting ventilation included wastewater drag, wind eduction, temperature differentials, barometric pressure, wastewater levels, and drain dimensions. The review differentiated between emission

¹ Volatile Organic Compounds (VOC), in general, means any compound of carbon which participates in atmospheric photochemical reactions, excluding certain compounds determined to have negligible photochemical reactivity (e.g., methane and ethane). A more complete and precise definition is given in 40 CFR 51.100 (S).

factors, equilibrium-based models, and kinetics-based models. Existing emission factors were found to be outdated and needed to be revised to reflect advances in process drain configurations. Equilibrium-based models represent the state-of-the-art in emissions estimation methods for process drains. Improvement of such models will depend upon improvements in methods to measure and estimate air exchange rates between drains and the ambient atmosphere.

The USEPA raised the concern that ventilation rate can impact emissions from process drains as a result of air exchange between the drains and a collection system suggesting that a modeling analysis of drain emissions should incorporate the collection system. However, the petroleum industry, through the Petroleum Environmental Research Forum (PERF), intends to address this concern by modeling the collection system and its component parts. This project, sponsored by API, is an integral part of the overall PERF investigation to estimate VOC emissions from petroleum refineries. The drain model to be developed in Phase II of this API study intends to provide boundary conditions to allow the drain model to be incorporated into collection models such as SEAM, or fate models such as WATER 8.

REFINERY SURVEYS

Onsite surveys were conducted at three refineries; approximately 2950 drains were counted at a west coast refinery, 1700 at a mid-west refinery, and 1650 at an east coast refinery. Less than 20 percent of the drains surveyed were not sealed. The other drains were water sealed with P-traps or with a commercially available drain insert that functioned as a P-trap. Approximately one to two percent of the drains surveyed were found to be active in that they were discharging, on a continuous basis, liquids that were neither runoff nor steam condensate. Temperatures of drain discharges ranged from ambient to approximately 200°F. No frost damage to drain structures was reported.

LABORATORY STUDY

Equipment was assembled in laboratory scale at the University of Texas at Austin and in pilot scale at the Wastewater Technology Centre, Burlington, Ontario. The equipment simulates actual drain configurations of the type identified in the drain surveys and facilitates experiments conducted on the emission of VOCs from drains. A series of procedures were developed as a basis for conducting the emission experiments. Collectively, the procedures and equipment were

defined as a protocol to evaluate emissions from refinery process drain structures. Tests were conducted to evaluate the adequacy of the equipment and the procedures to measure VOC emissions from drain structures. Results showed almost complete mass balance closures and close reproducibility in the analysis of target VOCs and stripping rates, confirming the suitability of the protocol in measuring VOC emissions from drain structures.

RECOMMENDATIONS

The following actions could be taken to improve the current AP-42 factor for refinery process drains:

- The verification of a field protocol for measurement of VOC emissions from drains. Five to ten experiments would be required to demonstrate reasonable mass balance closure and reproducibility of procedures. This is a necessary first step required to validate each of the following options.
- Collection of field data on fugitive emissions from refinery drains using the verified field protocol.
- Reassessment of the correlation equation using the verified field protocol.
- The investigation of emissions from simulated drain structures under different operating conditions to generate a matrix of emission factors.
- The development of a model based upon parameter calibration experiments under controlled laboratory conditions.

Section 1 INTRODUCTION

OBJECTIVE

Project objectives included the completion of a comprehensive literature review, a survey of refinery process drains, and the design of an experimental program which incorporates laboratory-, pilot-, and field-scale investigations of process drain fugitive emissions.

PROBLEM DEFINITION

Fugitive emission sources in petroleum refineries are generally defined as VOC emission sources from leaking equipment (valves, flanges, drains, etc.) associated with refinery processes.

Fugitive emissions are difficult to measure because of the diffuse nature of the emitted air pollutants and the high variability in emission rates. In the case of fugitive emissions from refinery process drains, a USEPA sponsored study (USEPA, 1980a), concluded that they represented only 2.2 per cent of fugitive emissions from a hypothetical 330,000 bpd refinery. The study examined 49 process drains at 13 refineries and assumed that the drains were not sealed. Based on that assessment, the USEPA allocated an emission factor of 0.070 total non-methane hydrocarbons (TNMHCs) lb/hr per drain (USEPA, 1977a), despite the high, ten-fold, variability reported by the USEPA contractor (95 per cent confidence limits of 0.023 to 0.20).

Fugitive emissions from refinery drains were first regulated federally through the 1989 New Source Performance Standards (Subpart QQQ). In 1990, the USEPA published the Benzene Waste Operations National Emission Standards for Hazardous Air Pollutants (BW-NESHAP), the objective of which was to reduce emissions of benzene vapors from benzene-containing waste streams. The regulation specifies methods of handling benzene-containing waste streams to prevent emissions of benzene to the air. Refineries have used two approaches in addressing this regulation: the first is an end of pipe strategy in which controls are installed on the process wastewater collection system and at the wastewater treatment plant, and the second is an at-source control strategy in which treatment or waste minimization is applied at the in-plant source of waste. Forty-three per cent of U.S. refineries, representing an estimated 79 per cent of refinery benzene emissions, were addressed by the BW-NESHAP. Under this regulation, process drain

emissions were contained through P-trap water seals or equivalent. Such drains are referred to here as *benzene NESHAP drains* (See Figure 3-1). Those drains discharging to sewer hubs without water seals and which were excluded from the BW-NESHAP rule, may be referred to as *non-benzene NESHAP drains*. Of the individual state regulations reviewed, none were more stringent than the federal regulation. A third category of drain describes the type defined by the Synthetic Organic Chemical Manufacturing Industry--Hazardous Organic NESHAP (SOCMI-HON) rule (promulgated in September, 1994 with compliance in September, 1997) in which the drain pipe discharges below a water surface and in a shrouded environment.

Individual states can implement regulations which are more stringent than federal requirements. Current regulations from three major industrial states, Texas, New Jersey, and California (South Coast Air Quality Management District (SCAQMD)) were reviewed to identify state-specific refinery process drain requirements.

Requirements for refinery process drains in Texas are described in Chapter 115 of the Air Policy and Regulations from the Texas Natural Resource Conservation Commission. On an annual basis, refinery operators are required to measure the emissions from all process drains with a hydrocarbon analyzer. Records of monitoring activities must be maintained.

Title 7, Chapter 27, Subchapter 16 of the New Jersey Administrative Code, titled "Control and Prohibition of Air Pollution by Volatile Organic Compounds", establishes requirements and procedures for controlling VOC emissions in New Jersey. No requirements, in addition to those already required by federal regulations, are included.

In California, Rule 1176 for Sumps and Wastewater Separators contains regulations for the control of VOCs from miscellaneous piping structures including process drains at petroleum refineries and chemical plants. Monitoring of process drains is required to be conducted monthly. According to these regulations, VOC emission concentrations from process drains shall not exceed 500 parts per million (ppm) above background. The initial test measurement is to be made with a portable hydrocarbon analyzer. If the concentration exceeds 500 ppm, a laboratory analysis must be conducted using EPA Reference Method 25.

Presently, emissions from these drains are estimated using the AP-42 factor. This method does not differentiate between sealed and unsealed drains, differences in liquid and air temperatures, and level of activity. This practice may result in inappropriately high estimates of drain emissions.

Unfortunately, there are no validated models or data sets that can improve estimation of fugitive emissions from refinery drains over those generated with the AP-42 factor. The overall project (Phases I and II) is designed to address this shortcoming by developing predictive correlations that can be used to better estimate fugitive emissions from the different categories of refinery drains described above.

Section 2

LITERATURE REVIEW

INTRODUCTION

A literature review was completed to assess the state of knowledge related to VOC emissions from industrial process drains. The review is divided into two major components, the first being technical "briefs" for each paper or report that was reviewed. These are included in Appendix A, and generally contain more detail than the information provided below. The second component is an overview of existing knowledge related to VOC emissions from drains. The approach used to complete the literature review is described. Previously noted factors which can affect VOC emissions from drains are reviewed. A summary of previous field studies, including emission measurement procedures is provided. Existing emission estimation methods, both emission factors and models, are summarized. Finally, a summary of existing knowledge and research recommendations is provided.

Objectives

The major objectives were to review and summarize the existing knowledge, theory and practice of estimating fugitive emissions of VOCs from refinery process drains. The use of emission modeling techniques, and the application of these techniques specifically to refinery process drains, was also examined. In order to complete these objectives, an understanding of the origin and development of AP-42 emission factors was required. Reports of studies in which emission factors were determined and/or used to predict emissions were reviewed. An objective of this project was to identify the most important reports on fugitive emissions, to establish a chronology of events and studies, and to eliminate the large degree of redundancy that characterizes existing literature. Finally, an attempt was made to interpret the literature with respect to technical limitations of existing knowledge and practices, and to subsequently identify research needs.

General Approach

The first major task involved identification and compilation of existing literature. Literature was obtained by review of bibliographical computer data bases, cross-referencing of previously obtained literature, communication with industry, and literature obtained from previous research.

An extensive computer search was initiated using available library facilities at the University of Texas at Austin. This search included data bases from CD-ROM Engineering Index and CD-ROM Science and Technology Index, focusing on works published from 1990 to 1994. Literature obtained from previous research was used to determine a base of reports concerning emissions from wastewater.

The second major task was to develop a logical organization of available literature. Three broad categories were identified: VOC emissions from wastewater treatment and collection systems, fugitive emissions, in general, and emissions specifically from industrial process drains.

The third major task was to critically review existing literature. Every relevant manuscript was reviewed, and a one to four page literature "brief" was developed to summarize the general information provided in the manuscript, along with significant findings and technical limitations. The "findings" section includes a description of the important results and conclusions cited in each paper. The "technical limitations" section includes a description of the major assumptions and drawbacks of each paper. Collectively, this information played an important role in identifying research needs related to VOC emissions from process drains.

Summary

Over 220 papers related to VOC emissions from wastewater were obtained. Most of these papers do not deal specifically with process drains, and are thus provided only as a supplemental bibliography in Appendix B. Only 19 papers or reports related to fugitive emissions from drains were identified. A detailed "brief" is provided for each paper in Appendix A. There are five major reports that form the current base of knowledge related to VOC emissions from process drains (Table 2-1). The remaining 14 papers borrow heavily from these five reports.

Table 2-1. Major Reports Related to Emissions from Process Drains.

Title	Author (Year)	Summary
Compilation of Air Pollutant Emission Factors, Third ed. AP-42	USEPA (1977a)	Gives total non-methane hydrocarbon (TNMHC) emission factor for drains (0.07 lb/hour/drain); estimates emissions for a typical refinery.
Assessment of Atmospheric Emissions from Petroleum Refining	USEPA (1980a)	Field studies to estimate emission factors for petroleum refineries.
Fugitive Emission Sources of Organic Compounds - Additional Information on Emissions, Emission Reductions and Costs	USEPA (1982)	Summary of field studies to assess emissions for SOCM1.
Industrial Wastewater Volatile Organic Compound Emissions - Background Information for BACT/LAER Determinations	USEPA (1990)	Equilibrium-based model; three ventilation scenarios for drains
Measurement of Hazardous Air Pollutant Emissions from Wastewater Collection System Components	Enviromega Ltd. (1993)	Kinetics-based model; experimental measurement of emission factors.

FACTORS AFFECTING EMISSIONS

The factors affecting VOC emissions from process drains can be classified into those affecting mass transfer and those affecting ventilation. To calculate the rate of emissions from drains, both of these categories must be clearly quantified because of their interdependency, for example, changing ventilation rate will change VOC concentration gradients which, in turn, will change mass transfer rates. A comprehensive analysis of factors which affect emissions from process drains is provided below.

Important factors which affect mass transfer and which have been reported in existing literature are listed in Table 2-2.

Table 2-2. Factors Affecting Mass Transfer Reported in Existing Literature.

Author (Year)	Factor affecting mass transfer
USEPA (1985), USEPA (1988)	Pollutant properties: pollutant volatility (approximated by Henry's law coefficient) is the most important physical property.
USEPA (1985)	Concentration of compounds in the sewer headspace and in the wastewater.
USEPA (1985)	Rate of molecular diffusion of compounds through air and water. It is suggested that the rate of molecular diffusion is a function of the following: exposed surface area, molar density, diffusion path length, initial and final concentration, and the gas-phase molecular diffusion coefficient.
USEPA (1988)	Drain diameter: a larger diameter corresponds to a larger exposed surface area and higher emissions.

Important factors which affect ventilation and which have been reported in existing literature are listed in Table 2-3. Only one study (Pescod and Price, 1982) confirmed ventilation rates experimentally.

Table 2-3. Factors Affecting Ventilation Reported in Existing Literature.

Author (Year)	Factor affecting ventilation
Pescod and Price (1982)	Wastewater drag: momentum is transferred from wastewater to air at the air-water interface (by the no-slip condition), thus inducing air flow in the sewer.
USEPA (1985), USEPA (1988) Pescod and Price (1982)	Wind eduction: wind blowing across a drain causes a dynamic pressure drop, which can lead to air flow out of a drain, with corresponding fresh air entering from another location.
Alpha-Gamma (1994), USEPA (1985), USEPA (1988), Pescod and Price (1982)	Temperature differentials: this effect occurs when the temperature of the sewer headspace is different from the ambient temperature. Differences in temperature create differences in density which induce air flow through buoyancy.
Alpha-Gamma (1994), USEPA (1985), Pescod and Price (1982)	Barometric pressure: temporal variations in barometric pressure lead to volume expansion and compression of gases, with corresponding air flows into and out of sewers. It should be noted that for typical systems the effect of barometric pressure is minimal (Pescod and Price, 1982).
Alpha-Gamma (1994), Pescod and Price (1982)	Rise and fall of wastewater level: rising water levels can force air out of unsealed drain openings. Conversely, declining water levels can draw air into sewers.
USEPA (1985), USEPA (1988)	Drain dimensions: emissions increase with an increase in drain diameter or a decrease in the length of the drain riser, each of which leads to reduced headloss

FIELD STUDIES

Several studies have been completed in both the petroleum refining and chemical manufacturing industries to assess fugitive emissions. Field evaluations of potential sources have occurred at two levels: screening studies and emissions measurement studies. The former involves the relative proportion of each source that can be qualified as "leaking." The latter uses more sophisticated sampling techniques in an attempt to quantify hydrocarbon emissions from a given source. The two types of studies are summarized below.

Frequency of Outgassing Drains

A "leaking" source is one around which concentrations of hydrocarbon may be detected above a predetermined concentration using a portable organic vapor analyzer (OVA) or similar calibrated device. Some investigators have defined this threshold concentration to be 10,000 ppmv

(USEPA, 1982) while others have used 200 ppmv as a screening value for further examination of a source (USEPA, 1980a). The BW-NESHAP regulation uses 500 ppmv as a threshold concentration for leaks.

Leak frequency data from six screening studies completed at both chemical manufacturing plants and at petroleum refineries were reviewed (USEPA, 1982). Information pertaining specifically to process drains was reported for two studies, in which results showed that from 2 percent to 17 percent of process drains were leaking. This is interpreted as outgassing of the drain. A similar study found 6 percent of process drains inspected to be leaking at a plant in Sweeney, Texas (USEPA, 1980b). Additional information related to these studies is provided in Appendix A. Extensive studies of this type have also been completed in which sources other than process drains were examined as potential sources of fugitive emissions (Ellis and Lackaye, 1989).

Fugitive Emissions Measurements

Typically, measurement of hydrocarbon emission rates from fugitive sources has been determined by enclosing the source, if possible, and by measuring hydrocarbon concentration and volumetric flow rate of gases through a regulated outlet in the enclosure (Chemical Manufacturers Association, 1989). This has been referred to as "bagging" a source, and although some potential sources have been classified as "unbaggable", the technique has been found to be appropriate for process drains.

To quantify emissions from a drain, the source of interest is enclosed using an inert material such as polyester or polyvinylfluoride. Previous studies (USEPA, 1980a) have been based on the use of a vacuum pump to draw air through a bag, which can lead to biased high emissions if the pump induces air flow through the drain system. Sweep gas introduction (positive pressure) has also been suggested (Chemical Manufacturers Association, 1989), but may suppress emissions if positive pressure exists in the bag. An improved method might include gas introduction and vacuum extraction with monitored pressure balancing. Such a method was recently outlined in a memo entitled "SCQAMD- approved protocols for Texaco bagging study" (Wilkniss, 1994). A magnehelic pressure gauge can be used to monitor vacuum differential inside the bag, and can indicate the presence of a leak. It has been suggested that the purge gas flow rate be set to a value representative of ambient wind speed when applying the technique to process drains, or

that a slight positive pressure of no more than 1 psig be established inside the enclosure (Wilkness, 1994). Sampling equipment consists of an OVA, an oxygen/combustible gas meter and a canister for sample collection.

Detailed sampling protocols were reported for a study in which an average emission factor for drains was determined to be 0.070 lb/hr-source (USEPA, 1980a). This study served as the basis for the existing AP-42 emission factor for process drains. A flow-through sampling method was employed in which the sample train consisted of a vacuum pump used to draw gas through the system and to maintain a slight negative pressure inside the enclosure to prevent hydrocarbon leaks. A cold trap was installed to prevent condensation in the lines. During each sampling run, a portable hydrocarbon analyzer was used to monitor the effluent air from the sampling train to ensure that steady-state had been established. A schematic of the sample train is shown in Figure 2-1.

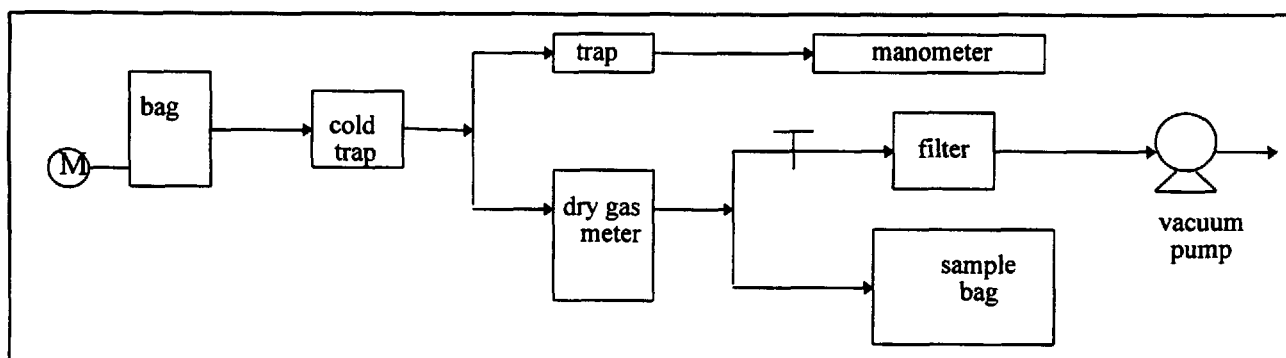


Figure 2-1. Schematic of Sample Train for Baggage Source (Vacuum Method).

For large leaks, the vacuum pump was disconnected and the sample gas was allowed to pass through the cold trap and dry gas meter, where the flow rate through the meter was combined with the amount of organic condensate collected (if any) to “obtain a direct measure of the hydrocarbon vapor leak.”

An alternate emission measurement technique approved by the USEPA is known as the blow-through method (Chemical Manufacturers Association, 1989). It has been described more extensively in Brief #2, and consists of purging the system with nitrogen gas and measuring VOC concentrations in the tent at various nitrogen flow rates. Figure 2-2 illustrates the basic sample system. The drawback to both techniques is that natural ventilation patterns in the drain

are altered when the drain is enclosed in a tent and when a vacuum-induced or nitrogen flow-induced airflow is imposed on the drain. A PERF-sponsored investigation is addressing ventilation patterns and has produced a video illustrating smoke tests conducted in a refinery drain structure (Rabideau, 1995).

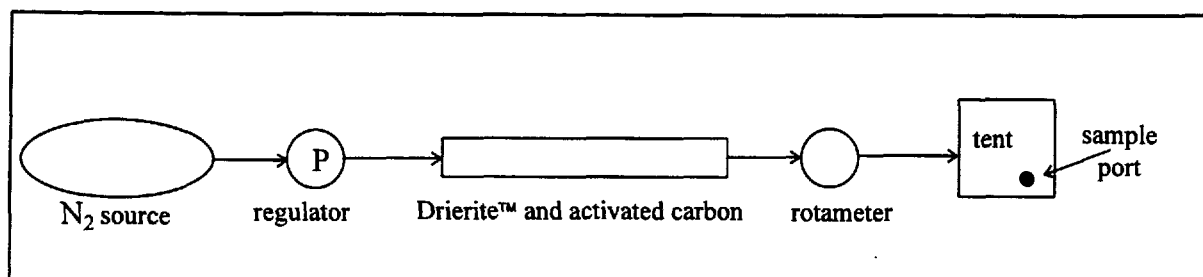


Figure 2-2. Schematic of Sample Train for Blow-Through Method.

A superior method of measuring emissions would be one in which the actual ventilation rate of the drain was measured and multiplied by VOC concentration to give an emission rate. For example, it might be possible to use tracer dilution methods to measure ventilation rates if adequate protocols could be developed to introduce inert tracers into a drain riser.

EMISSION MODELS

There are currently three levels of sophistication for modeling emissions from drains: emission factors, equilibrium-based models, and kinetics-based models. The simplest method for estimating emissions is by using emission factors, which typically gives an emission rate (mass/time/drain) based on an average drain configuration and loading condition. Equilibrium-based models assume that the air and water are in chemical and thermal chemical and thermal equilibrium and are more appropriate in systems with restricted ventilation or low pollutant volatility. The most sophisticated model is kinetics-based, which assumes that equilibrium does not exist and typically requires the determination of an overall mass transfer coefficient.

Emission Factors

In 1977, the USEPA published industry-specific emission factors for hydrocarbons from process unit operations and fugitive sources. The value assigned to process drains was 0.07 lb/hour-source. The most widely used and currently accepted technique for estimating fugitive emissions from process drains and other sources is to determine the number of such sources within a given

plant or refinery and to multiply this value by the appropriate factor. Emission factors have been used for estimating total plant emissions and for evaluating potential control strategies by several researchers. They have been used as a tool for determining appropriate areas for concentrating control efforts. As part of EPA's AP-42 report (USEPA, 1977b), a sample calculation was completed for a hypothetical refinery of 52,500 m³/day (330,000 barrels/d) capacity. Use of emission factors resulted in an estimated 20.4 metric tons (44,880 lb/d) of benzene emissions per day, 2 percent of which were from process drains. A second report identified five alternative regulation strategies for three model plants (USEPA, 1980b). Emission factors played a large role in the analysis of the most effective leak detection and control techniques.

Several researchers have suggested that total emissions will tend to be overestimated by this method (Ellis and Lackaye, 1989), or have advised caution in the use of such factors (Lipton, 1990) for similar processes in other industries than those for which they were developed. A study completed by Radian Corporation (USEPA, 1977b) to revise AP-42 emission factors did not result in changes to values for fugitive factors due to insufficient information. The authors did, however, emphasize the importance of understanding fugitive sources, since they can represent an appreciable contribution to total emissions, and may also have the greatest potential for emission reduction.

Best estimates made for refinery process drain emission factors have not been revised in over 15 years, while design of drains has progressed and emission control techniques have been applied in some cases. Use of potentially outdated AP-42 factors may lead to inaccurate estimation of hazardous air pollutant (HAP) emission rates from process drains. In addition, these factors were intended to provide a means of estimating industry-wide emissions and the relative magnitude of various potential sources within each industry, not for establishing an emissions inventory on a per drain basis. While emission factors are widely used, it is important to recognize that existing factors are likely outdated and conservative. Furthermore, the non-mechanistic or "gross" characteristic of such emission factors should preclude their use for anything other than approximate, industry-wide emission estimates.

Equilibrium-Based Models

The assumption that a VOC reaches chemical equilibrium between water and adjacent air forms the basis for several existing models. Three different cases for emissions from drains have been considered based on an equilibrium assumption (USEPA, 1990): air entering the sewer that is induced by process flow and wastewater flow (case 1), air entering the sewer with only wastewater flow (case 2), and air exiting the sewer with only wastewater flow (case 3), where process flow is flow in the hub and wastewater flow is flow in the channel. An overall fraction emitted was calculated based on the average of these three cases. For case 1, the fraction emitted was based on the ratio of moles of gas to total moles of flow in the sewer. For cases 2 and 3, the fraction emitted was assumed to be induced by wind suction. An equivalent maximum driving force due to ambient wind was defined using Bernoulli's equation. The pressure force from the air velocity was then equated with the frictional losses in the sewer using the energy equation. These calculations were based on three controlling factors: wastewater flow rate, air flow rate, and Henry's law coefficient. Of these factors, the ventilation rate has the most uncertainty. The reader is referred to brief #10 for a more detailed discussion of BACT/LAER calculations.

BACT/LAER calculations (USEPA, 1990) form the basis for two models used to estimate air emissions from process drains: Water8 and Collect. Both of these models generally assume that the air and water are in equilibrium. The two models are identical except that the user is required to specify a ventilation rate for Water8. The documentation for the Water8 and Collect models can be found in "Air Emission Model for Waste and Wastewater" (USEPA, 1994). There is one loading condition that does not assume equilibrium between air and water. This occurs for a P-trap sealed with wastewater that has a continuous discharge of process flow. For this case, empirical mass transfer coefficients were determined using data from Enviromega Ltd. (1993). Refer to brief #4 for a more detailed discussion of these data. Refer to brief #10 and brief #18 for more detailed discussions of the Water8 and Collect models.

Kinetics-Based Models

The assumption that a VOC in air adjacent to a process or waste stream is in chemical equilibrium with the liquid may lead to appreciable overestimates of gaseous emissions. There are several cases in which such an assumption would be inappropriate, e.g., when there is no enclosed headspace adjacent to the liquid (the interfacial contact area is open to the atmosphere),

when the ventilation rate is relatively high and water transport distance is relatively small, or when the compound of interest is highly volatile (having a high Henry's law coefficient).

A more accurate method for estimating fugitive emissions from process drains and other potential sources would include an analysis of mass transfer, that is, an analysis of the kinetic limitations of the process. A mass transfer coefficient would be required for each compound of interest and set of drain operating conditions in order to calculate the emissions from that source.

Currently, no models exist to calculate emissions in this way, or to provide mass transfer coefficients. Some work has been completed to measure mass transfer coefficients for several VOCs under a limited range of operating conditions (Enviromega Ltd., 1993) in an effort to develop a mechanistic model for estimating mass transfer at process drains. When estimating emissions using a mass transfer approach, a quantitative evaluation of ventilation rates and patterns in the drain is required.

EXPERIMENTAL STUDIES

Experimental research related to VOC emissions from process drains has not been widely attempted in the past, with only one study reported in the literature (Enviromega Ltd., 1993). A pilot scale sewer drain system was constructed to investigate the effect of certain parameters on mass transfer, such as compound physicochemical properties, type of drain throat connection and process flow rate. The emission factors presented in the report should be considered system-specific, i.e., caution should be taken in extrapolating such results to other systems. Experiments were completed under conditions of both forced and natural ventilation. Introduction of process flow into the drain greatly increased VOC emissions over the case of an inactive drain, and increasing process flow increased stripping efficiencies slightly. More detailed results have been summarized in the corresponding brief in Appendix A. Some limitations of the study include the fact that an insufficient number of experiments was completed to develop a mechanistic model for VOC stripping at process drains, tests were not completed to ascertain whether complete mixing occurred in the tracer reservoir, and mass closure was not attained when gas and liquid samples were compared.

SUMMARY OF EXISTING KNOWLEDGE BASE

An extensive search of existing literature related to gaseous emissions from process drains was completed. Several relevant papers have been summarized above and individual reviews have been included in Appendix A. A complete bibliography of literature related to emissions from wastewater has been included in Appendix B. A review of relevant literature indicates that current methods for estimating fugitive emissions from process drains rely heavily upon the use of AP-42 factors. Development of these factors was based on one study completed in 1978 where fugitive and process emissions were measured at several petroleum refineries (USEPA, 1977b). Since that time, the emission factor for process drains has not been modified to reflect improved drain design or increased application of control techniques. For example, water seals are commonly implemented as an emission control strategy in current refinery practice (USEPA, 1985). It has been suggested in the literature that use of AP-42 factors for process drains may lead to overestimation of emissions (Ellis and Lackaye, 1989).

Modeling efforts have been largely based on an assumption of chemical equilibrium between process wastewater and adjacent headspace. This technique should generally lead to an overestimation of VOC emissions from process drains. Even if equilibrium-based models are valid, they still require an understanding of ventilation rates and patterns associated with drains in order to predict HAP emission rates. Emission estimates based on a mass transfer approach would also require improved understanding of ventilation rates and patterns in process drains. However, gas flow rates through process drains are poorly understood, and existing measurement techniques can lead to highly uncertain results.

Current methods for estimating VOC emissions from process drains are both conservative (overestimate) and characterized by high degrees of uncertainty. Existing emission factors are outdated and should be revised to reflect advances in drain configurations. Furthermore, even improved emission factors should be reserved for industry-wide, as opposed to process-specific, assessments. Equilibrium-based models reflect the current state-of-the-art in emission estimation methods for process drains. Improvements of such models will depend significantly on improvements in methods to both measure and estimate air exchange rates between drains and the ambient atmosphere. Finally, there is currently a paucity of information related to the mechanistic behavior of VOC emissions from process drains. Significant improvements in

emission estimation methods will only follow improved understandings of the nature of gas-liquid mass transfer kinetics in process drains, and the effects of environmental, chemical, and process operating conditions on such mass transfer.

Section 3

SURVEY OF REFINERY PROCESS DRAINS

A survey of process drains was conducted at three refineries to improve the state of knowledge on refinery process drains. Information was gathered on the number and type of drain structures commonly found in refineries, the proportion of active versus inactive drains, and the types of fluid discharged.

APPROACH

Three candidate refineries were proposed for the drain survey by the API Technical Advisory Committee. They included mid-sized refineries in the mid-west and the east, and a slightly larger refinery on the west coast. The surveys were conducted during the period of February through May, 1995. A similar phased approach was taken at each refinery, the degree of information collected being a function of the time allocated at each refinery and the availability of data. Interviews were held with key refinery environmental and operations personnel to obtain information on the number and types of process drains used at each refinery, the history of drain installation, and the nature of the discharges being routed to the drain structures. Hard-copy and computerized (where available) drawings were then searched, focusing on drain system drawings for various refinery areas. Drawings were collected for process unit drain system layouts and details of the water-sealed drains. Junction boxes and other downstream drain structures were not included in this survey.

Based on these reviews, at least one process unit was inspected for each type of drain identified in the drawings, with the objective of confirming drain configuration and seal mechanism. The presence of a seal was established by visually observing standing water in the drain. When a seal was found, it was assumed that the sealing configuration was as shown in the drawings. Where possible, the inspection also included the evaluation of the discharge type and quantity, level of drain activity, and the existence of high temperature discharges (condensate or steam blowoffs) to the drains. A report describing these findings was prepared for each refinery and reviewed by refinery staff. Appendix C contains copies of these reports. The major findings from these surveys are presented below. To clarify the terminology used in drain structures, Figure 3-1 illustrates the major parts of a generic drain structure.

MAJOR FINDINGS

Number of Drains

Table 3-1 summarizes pertinent data from the surveys. The west coast refinery had already inventoried their process drains enabling a more precise estimate to be made of the number of drains. Such data were not available at the other two refineries and estimates are presented as ranges with a corresponding mean value. Similar ranges were obtained for the mid-west and east refineries which were of similar size with respect to crude consumption.

Table 3-1. Summary of Drain Survey Data.

Refinery Location	Survey Date	Estimated Drains		Drain Type				Active Drains ¹	
		Mean	Range	Not sealed	Sealed				
					Inserts	Catch basin	P-trap	No.	Percent
West Coast	2/7/95 - 2/8/95	2950	-	-	2100	850	-	-	-
Mid-West	5/2/95 - 5/4/95	1700	1465-1935	950- 1260	-	-	515- 675	16	1
East Coast	5/10/95 - 5/12/95	1650	1370- 1930	-	-	-	1370- 1930	40	2

¹ These include drains with continuous flow discharges (excluding condensate discharge from steam turbine pumps). They are expressed as a percentage of the actual drains surveyed.

Types of Drain Structures

The west coast and east coast refineries had sealed drains unlike the mid-west refinery, where the majority of drains were not sealed. This difference occurred as a result of the retrofitting of the drains in the west coast refinery with drain inserts in response to the requirements of the Benzene NESHAP regulation, whereas P-traps were the originally installed process drain at the east coast refinery. The mid-west refinery had responded to the Benzene NESHAP regulation by collecting benzene-containing streams and conveying them in a closed system to a control device, that is, drain sealing activities at this refinery were not associated with the Benzene NESHAP regulation. The use of water seals in process drains was based on safety considerations at this refinery. Nevertheless, the surveys showed that less than 20 percent of all the drains surveyed were not sealed.

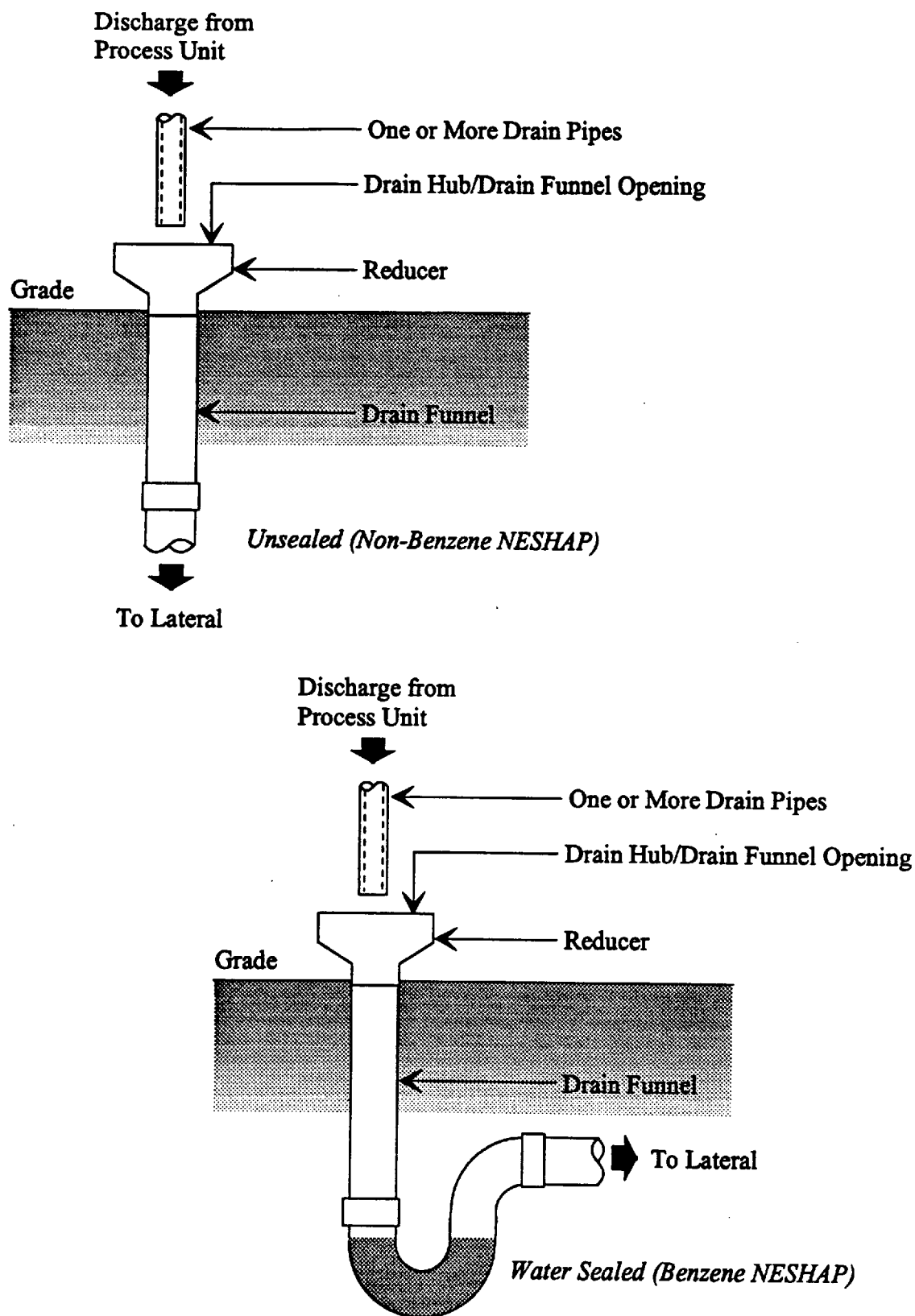


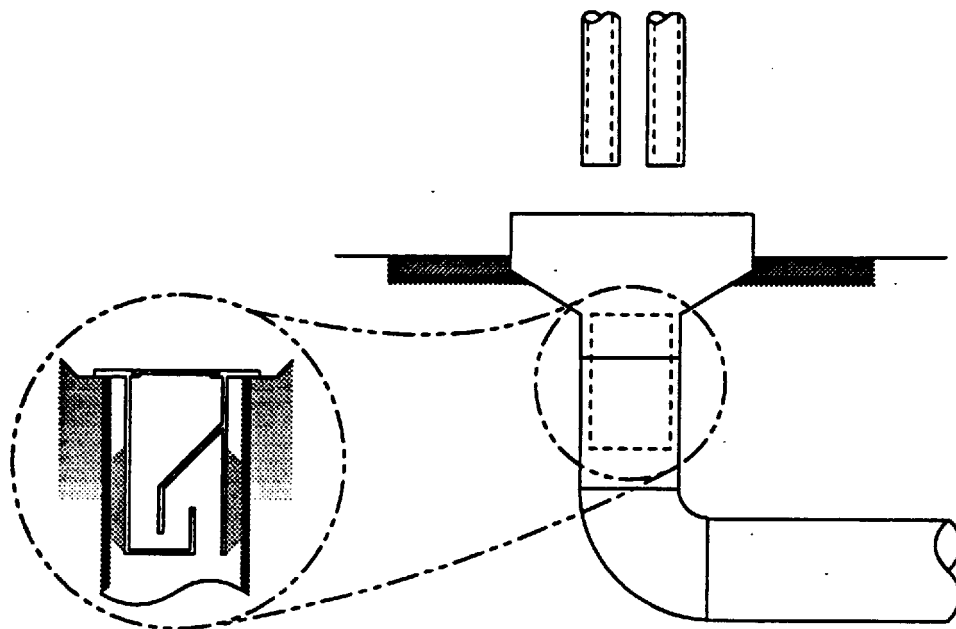
Figure 3-1. Major Components of a Drain Structure (Not to Scale).

In 80 percent of all the drains surveyed, sealing was achieved in one of three ways, retrofitted water seal inserts, P-traps (with minor variations), and water-sealed catch basins. A vertical P-trap drain insert, available commercially, contains design features intended to promote flowthrough while maintaining a water seal in the vertical section of the drain. This type of insert is available in a range of sizes to fit different diameter drain funnels although typically, the drain funnel diameter was four inches (Figure 3-2). It constituted over 70 percent of the drains surveyed at the west coast refinery. The remainder of the drains in the west coast refinery were water-sealed catch basins (Figure 3-2) which were used as area drains for collecting storm water runoff and infrequent (turnaround) maintenance drainage. Their use as process drains was rare and only noted on one occasion. For this reason, the water-sealed catch basin was not considered as one of the alternative drain structures to be evaluated in this project.

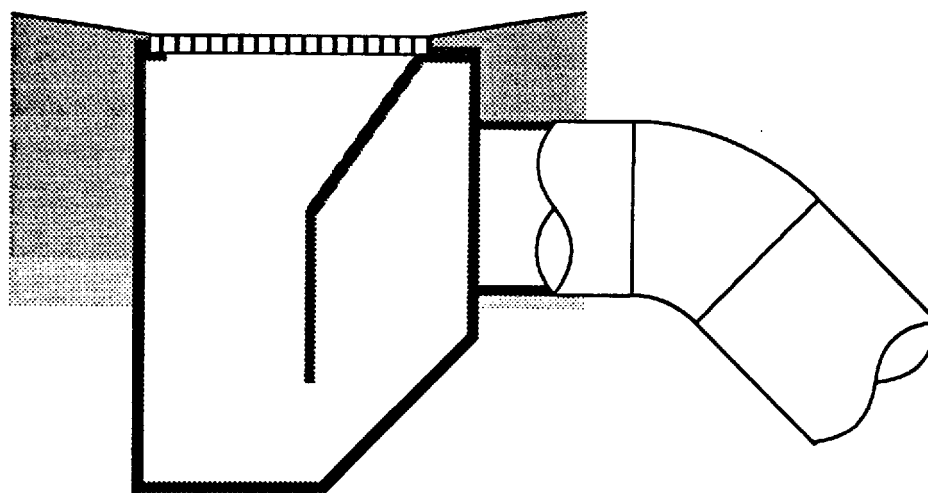
The P-trap was the drain seal used by the mid-west and east coast refineries. Typical dimensions of the P-trap used by the mid-west refinery are shown in Figure 3-3. Most drain funnels were four inches in diameter. The dimensions of the unsealed drain funnels at the mid-west refinery are shown in Figure 3-4. All drains in the east coast refinery were sealed with P-traps of various types. Figure 3-5 illustrates P-traps with and without surface sloping to the drain hubs. Both types were designed to eliminate the inclusion of surface runoff. Figure 3-6 illustrates running P-traps with different downpipe orientations to accommodate different arrangements of concrete footings.

Active Drains

Most drain funnels served pumps, with a small proportion dedicated to process towers, condensers, and compressors. Tower and condenser drains were inactive, as were more than half of the pump drains. The opportunity to conduct the most systematic analysis of drain activity was afforded at the mid-west refinery. Data were available or were collected for almost all process units in the refinery (Appendix C) which allowed a good estimate of drain activity to be made. Active drains were defined as those in which there was a continuous discharge. Table 3-1 shows that approximately 16 drains were designated to be active by this definition. This represented approximately one percent of all the drains in the refinery.



(A) Drain Funnel with Insert



(B) Sealed Catch Basin

Figure 3-2. Drain Structures at the West Coast Refinery (Not to Scale).

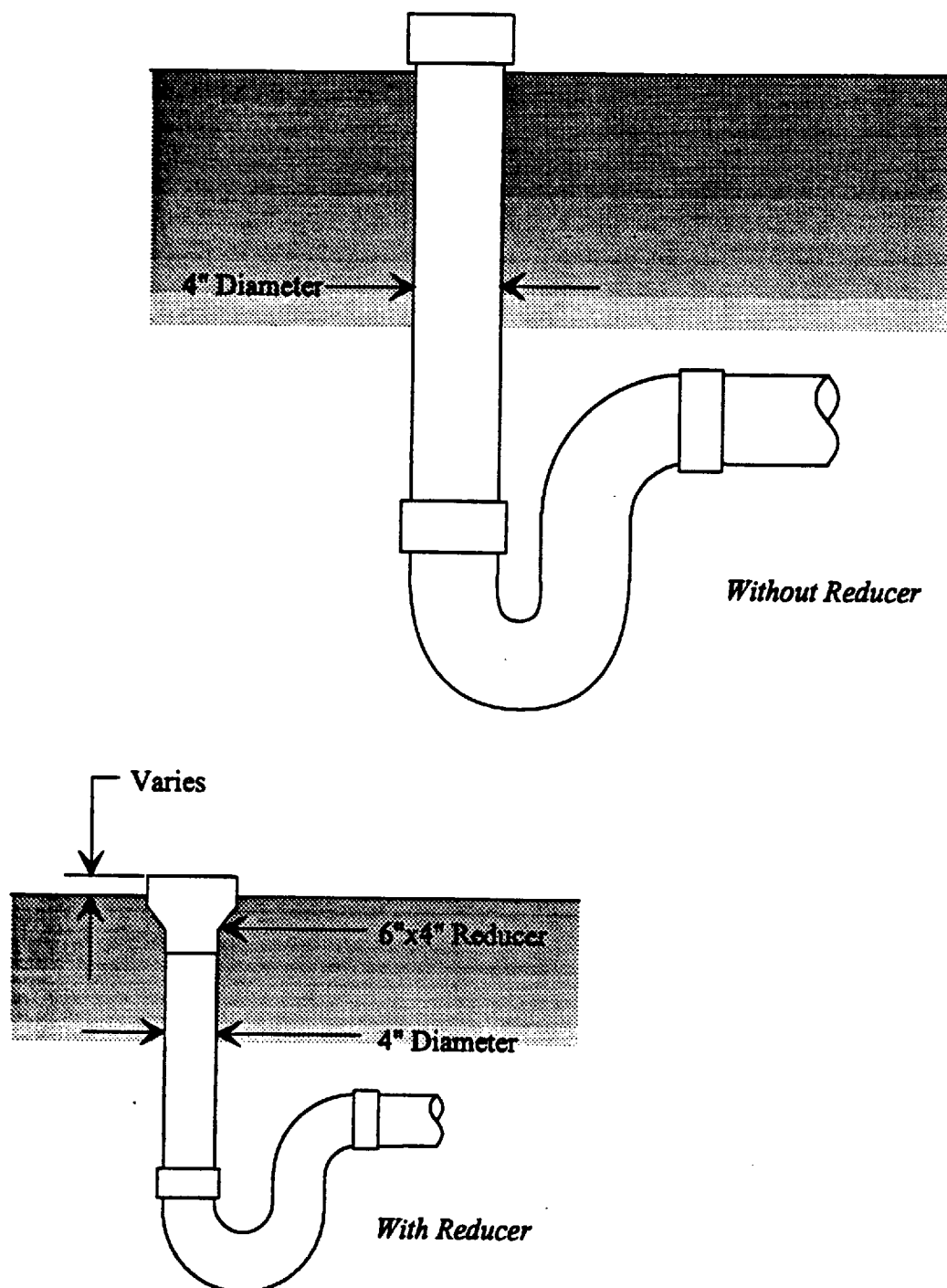


Figure 3-3. P-Trap - Water Sealed Drain at the Midwest Refinery (Not to Scale).

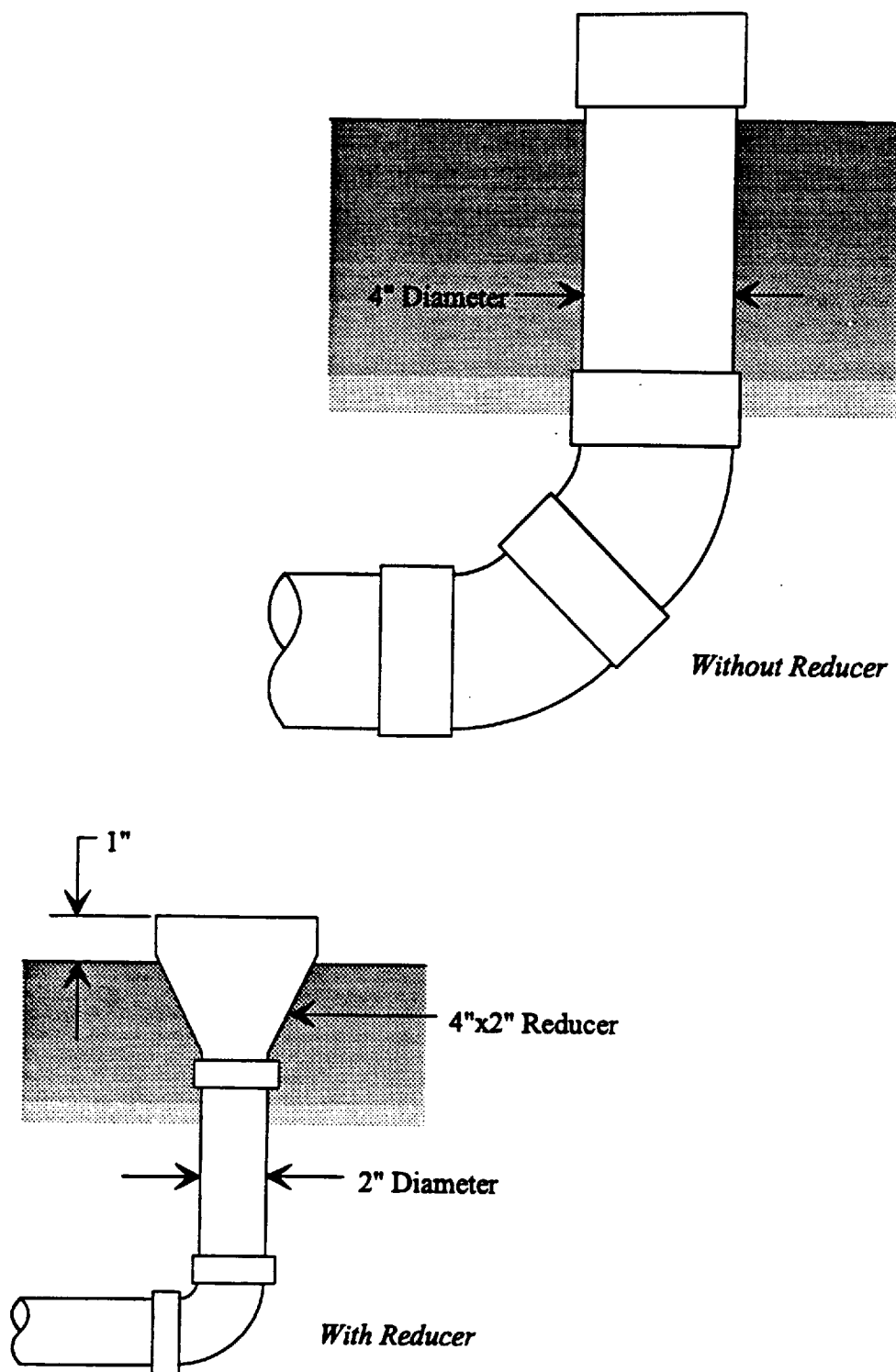
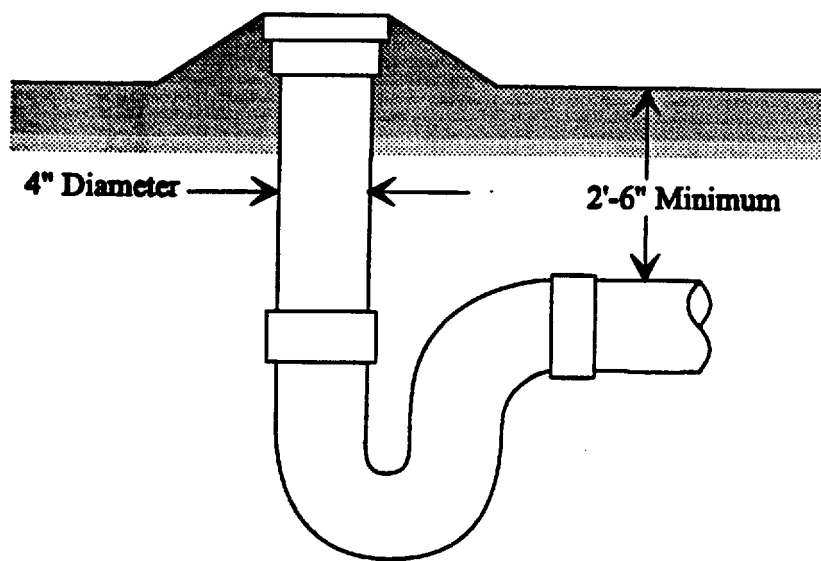
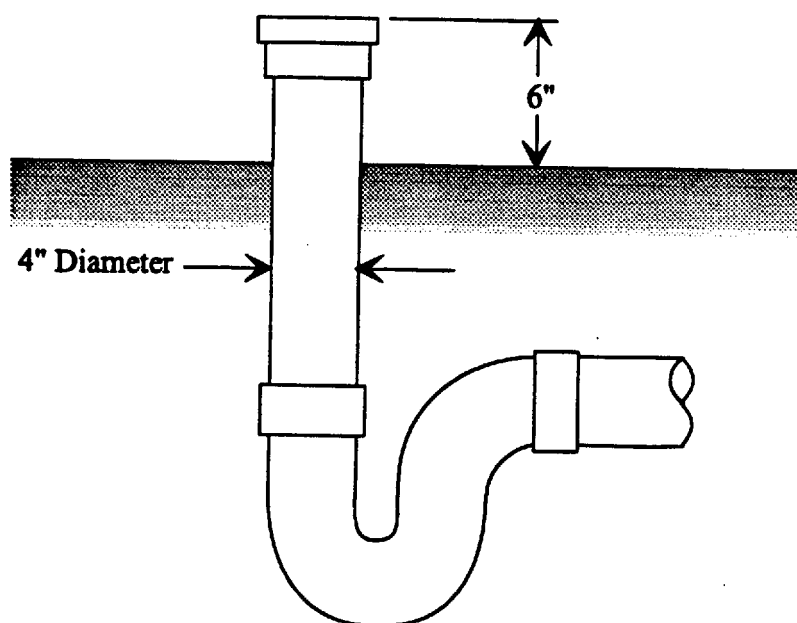


Figure 3-4. Unsealed Drain Funnel at the Midwest Refinery (Not to Scale).



Type A



Type B

Figure 3-5. P-Trap Types at the East Coast Refinery (Not to Scale).

At the east coast refinery, estimates were made of the active drains in the six process units surveyed (Appendix C). Approximately 40 active drains were observed which constituted approximately two percent of the drains in the six process units. While more than half of the drains inspected did discharge continuously, these discharges were condensates from steam turbine pumps and unlikely to contain VOCs, so were omitted from the count of active drains.

Type of Discharge

Typical pump drain funnels were fed by up to three drain pipes, normally one inch diameter or less. Pump discharges consisted of pumped (hydrocarbon) material, seal water, steam condensate and blowoff, lube oil drippings from the pumps, and pump pad drainage at flow rates ranging from a few drops per minute to steady discharges not normally exceeding one gallon per minute (gpm) (Appendix B). The exception to this was the east coast refinery at which most drains received continuous flows of steam condensate at three to five gpm from steam turbine pumps.

Most drain pipes did not break the plane of the drain hub even when the drain hubs were raised six inches above grade. Steam blowoffs were associated with about 25 percent of the observed drains.

Temperature

The temperature of drain pipe discharges varied over a wide range, from ambient temperature to more than 200°F, depending upon the nature of the discharge. Pump drippings were usually hot with frequent steam blowoffs. Discharges from the purging of sampling ports at process units were at the unit operating temperature which ranged from ambient to 200°F (Appendix B).

The temperature of the water seal in drain funnels at the mid-west and east coast refineries was sufficiently high to prevent freezing of the drain structure. Frost was not an issue during winter months at the west coast refinery.

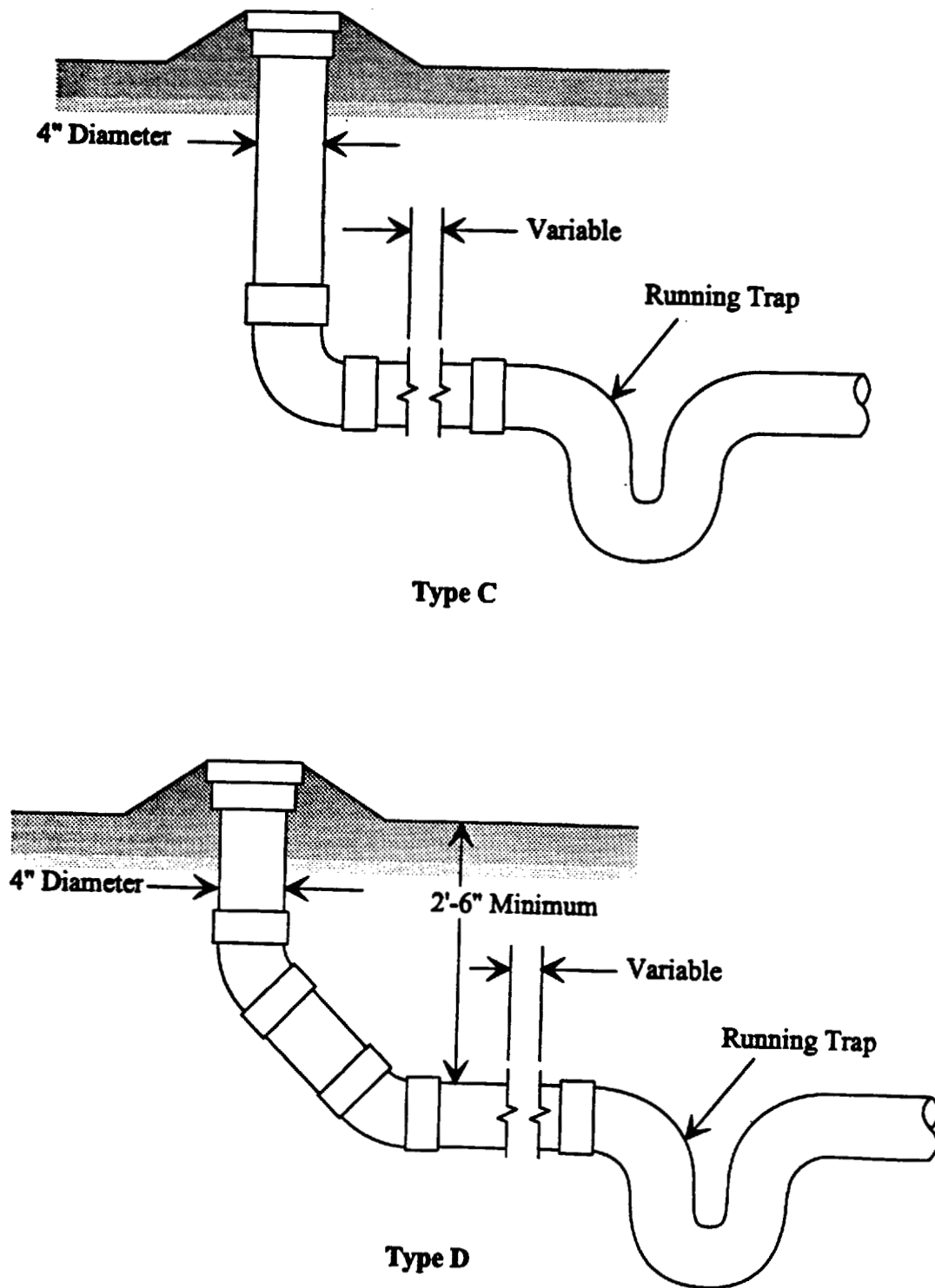


Figure 3-6. Running P-Traps at the East Coast Refinery (Not to Scale).

RECOMMENDATIONS

Observations made during the drain surveys suggest that the protocol should evaluate the emission of VOCs from the three major groups of process drains identified: unsealed drain funnels, drain funnels sealed with a P-trap and a commercially available drain insert. Although the proportion of active drains was low, emissions from both active and inactive modes should be evaluated to determine the impact of drain usage on fugitive emissions. The impact of high temperatures should be evaluated since it was evident that the fluid from many drains was close to the temperature of saturated steam. This may affect fugitive emissions from unsealed drain funnels. No observations were made of wind velocities in the vicinity of drain structures so no recommendation can be made regarding the impact of drain pipe position with respect to the plane of the drain hub.

Section 4

MODEL AND INFLUENCING FACTORS

CONCEPTUAL SYSTEM

Existing models, whether they are based on simple AP-42 emission factors or equilibrium-based equations, are believed to overestimate VOC emissions from industrial process drains.

Furthermore, such models do not fully account for the mechanistic behavior of VOC emissions, e.g., as a function of system operating or environmental conditions. There is clearly a need for improvements to existing models related to VOC emissions from drains. Such improvements should lead to: (1) more accurate VOC emission estimates, and (2) a mechanistic tool that can be used for purposes of VOC control strategies.

A state-of-the-art model for predicting VOC emissions from process drains is described below. The model is based on a mass transfer kinetics approach for grouped regions of a drain system at steady-state. Determination of model parameters, over a wide range of system operating and environmental conditions, should serve as a basis for future (Phase II) research.

A generalized process drain which incorporates a P-trap is denoted in Figure 4-1. Six mass transfer mechanisms are denoted in the figure. These include: (1) falling film above the drain hub, (2) splashing within a drain hub, (3) falling film below a hub, (4) splashing and air entrainment within a trap, (5) falling film below a trap, and (6) splashing and/or air entrainment in a channel which underlies a drain. The relative importance of each mechanism should vary as system operating conditions, environmental conditions, and chemical properties vary. In some cases (straight drains), one or more mechanisms may be irrelevant (splashing and air entrainment within a trap).

It is unlikely that any attempt to model the mass transfer associated with every mechanism in Figure 4-1 would ever be successful. A logical set of simplifications leads to a revised drain system consisting of four major regions: (1) above hub, (2) above trap, (3) in trap, and (4) below trap. Models to estimate emissions from each region are described below. Mass transfer models for each region, and variables that affect relevant mass transfer parameters are described in Appendix D.

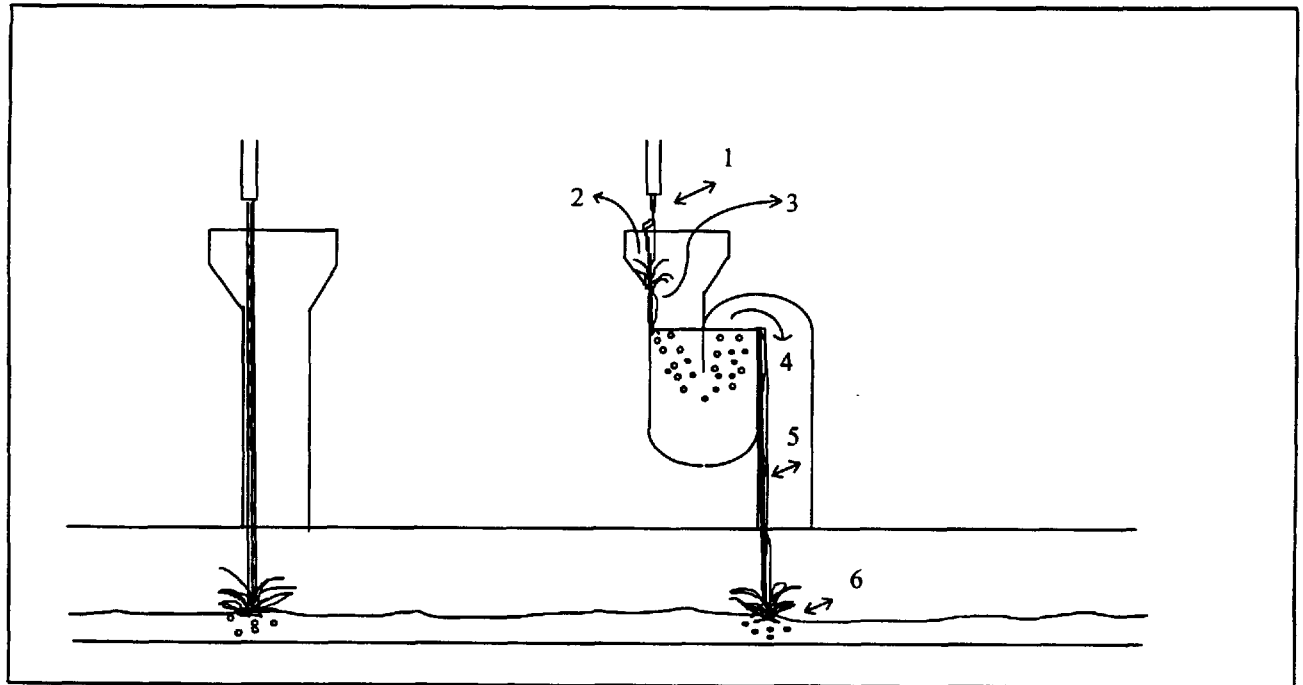


Figure 4-1. Mass Transfer Mechanisms in Process Drains.

AIR EXCHANGE WITHIN A PROCESS UNIT

In order to estimate VOC emissions from industrial process drains, it is important to understand the ventilation rate through drains and underlying channels, i.e., inside the battery limit of a process unit. Some simple classifications of drain operating conditions that affect ventilation rates are trapped (or sealed) versus untrapped (or open), and active (with process flow) versus inactive (without process flow). This classification system leads to four separate categories of drain configurations.

All open drains, whether active or inactive, are subject to mechanisms such as wind eduction, temperature differentials and liquid drag that will induce air flow through the system. A concurrent project at the University of Texas at Austin and sponsored by the Chemical Manufacturers Association addresses the relative importance of ventilation mechanisms in process drains. Based on the results of that research, a maximum possible ventilation rate through an open drain will be possible to estimate. This gas flow rate will henceforth be denoted as $Q_{open,max}$. The use of a maximum air exchange rate should lead to conservative (overestimated) emission rates.

Air entrainment occurs when a plunging jet impinges on an underlying pool, as in an active, trapped drain where process flow impinges on water collected in the trap. For the purpose of this model, all of the entrained air is assumed to flow through the trap and into the underlying channel headspace. This gas flow rate will contribute to system ventilation, and will henceforth be denoted as Q_{ent} . No ventilation is assumed to occur through a trapped, inactive drain.

A total (maximum) air flow rate into and out of a process unit area can be determined based on the number of drains in each category, as defined above. This ventilation rate, Q_{tot} , is the sum of all the contributing air flow rates from individual drains in the system:

$$Q_{tot} = \sum_{i=1}^n Q_{open, max} + \sum_{j=1}^m Q_{ent, j} \quad (4-1)$$

where,

n = the number of open (no trap) drains

m = the number of active, trapped drains

Within a process unit area, the pattern of air exchange is likely to be complex and highly transient. At this time, it is not feasible to reasonably predict such patterns. Therefore, a simplified air flow pattern is suggested for the proposed model. It is assumed that all drains that contribute to Q_{tot} (all but inactive, trapped drains) ingas continuously. Inflowing air is allowed to accumulate in the direction of wastewater flow, and is eventually exhausted at an arbitrary opening downstream of all drains in the system. An illustration of the cumulative flow model is provided in Figure 4-2.

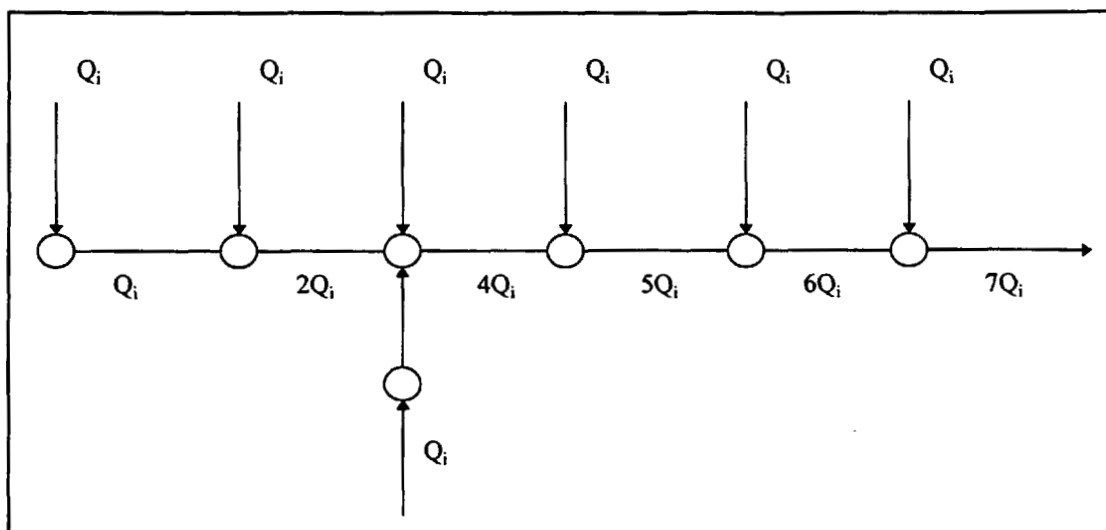


Figure 4-2. Illustration of Co-current, Cumulative Ventilation Model.

PARAMETERS AND INFLUENCING FACTORS

The physical design of a drain system (system configuration) should have a significant influence on VOC emissions. For example, additional mass transfer mechanisms occur for drains with P-traps as opposed to straight drains without traps. This is exemplified by the need to include expressions to account for mixing phenomena (Equation D11, Appendix D) in drains with traps. However, the increased potential for mass transfer that may occur with P-trapped drains is countered by a reduction in system ventilation. The degree of air exchange and its dependency on the number and types of drains is accounted for by the air exchange model described previously.

Drain dimensions are important for specific mass transfer mechanisms. In particular, distances from a drain nozzle to hub (l_1 in Equation D-3), total distance from hub to trap or channel (measured as z in Equations D-9 and D-10), drain nozzle diameters and drain throat diameters (to measure jet and throat perimeters) are all required in order to determine surface areas over which mass transfer can occur. These parameters could be easily determined through a complete accounting of a process unit's drain system, or through a routine (representative) survey of a number of drains within a process unit.

The physicochemical properties of a VOC should have a significant influence on liquid-to-gas mass transfer. For example, Henry's law coefficient (H_c) is a critical property for determining the extent of gas-phase resistance to mass transfer (Equation D-4). It is also an important factor in regions where gas-phase accumulation can occur, e.g., within a drain throat (Equation D-9a through D-10b), or where air entrainment occurs, e.g., within a trap or channel (Equations D-11 and D-12). In addition, Henry's law coefficient has a direct influence on the degree of equilibrium terms (γ in Equation D-11 and D-12). Finally, gas and liquid-phase molecular diffusion coefficients (k_g and k_l in Equation D-4) are important for relating mass transfer coefficients between contaminants. Physicochemical properties of most VOCs are known or can be readily determined. From a practical standpoint, they can be effectively "hidden" from a model user by being accessed from any of a number of existing data bases.

Two important environmental conditions that can affect VOC emissions are ambient temperature and wind speed above a drain hub. The primary influence of ambient temperature should be on buoyancy-driven air exchange rates. It may also affect k_g for mass transfer above a drain hub. Wind speed may also affect k_g above a hub. However, its greatest influence is likely to be on air exchange rates between drain channels and the ambient atmosphere, and on the turnover rate (Q_v in Equation D-10b) within a drain throat confined by an underlying water seal (P-trap). The effects of air temperature and wind speed on air exchange are the focus of a parallel study funded by the Chemical Manufacturer's Association.

For the purposes of this modeling exercise, the most important properties of the wastewater stream are VOC concentration, fluid temperature, and wastewater flow rate leaving a drain nozzle. The effects of concentration are obvious and will not be discussed further. Fluid temperature affects the physicochemical properties described previously, as well as the mass transfer coefficients required in Equations D-1 (K_{L1}) and D-6 through D-10b (K_{L2}), and subsequent liquid and gas-phase mass transfer coefficients described previously (Equation D-4). Wastewater temperature should have an influence on adjacent air temperature, with subsequent effects on both k_g and air exchange rates (buoyancy-driven ventilation). Finally, wastewater flow rate is a significant parameter that appears in equations for nearly all regions of a drain system. In addition to its explicit occurrence in several of the previously-described mass transfer

equations, it should also have an influence on the liquid-phase mass transfer coefficients for falling films and misaligned hubs, and should affect the rate of air entrainment in traps and underlying channels.

For practical purposes, a model user should know the approximate concentrations of VOCs, a typical wastewater temperature within a process unit, and typical wastewater flow rates for drains.

SUMMARY OF PROPOSED MODEL

The model described above is an improvement to existing models for two important reasons. First, it is based on fundamental mass transfer kinetics which will allow an improved understanding of the mechanistic behavior of VOC emissions at process drains. Experimental determination of fundamental mass transfer parameters will ultimately allow for significantly improved predictions of VOC emissions. Second, it is based on a rigorous accounting of air flow contributions and accumulation within a process unit's collection system. Although simplified, this approach is more rigorous than others which are applied in existing models. It allows for a "platform" for future improvements, and provides for an important link between air exchange and mass transfer processes.

A mechanistic model estimating VOC emissions from process drains can easily be incorporated into subroutines of existing models such as SEAM, Water8, or Collect. It would be unnecessary for the user to thoroughly understand the theoretical basis for the model, except to recognize that this model will lead to improved estimates of VOC emissions and will be much more useful for control strategy purposes.

Section 5

PHASE II PROTOCOL

A protocol is defined here as being a series of procedures to facilitate the conduct of experiments at different levels or scales of operation to evaluate fugitive emissions from refinery process drains.

The EPA protocol for bagging equipment components (valves, flanges, etc.) for quantifying emissions has been applied to refinery process drains. This procedure was used by investigators in the original work that formed the basis of the AP-42 emission factor for process drains and the first correlation equation that provided a relationship between emission rates and total hydrocarbon gas phase concentrations in the vicinity of a drain (referred to as screening values) (USEPA, 1980a). Both the emission factor and the correlation equation were based upon multiple field measurements of drain emissions using a drain bagging procedure. An average of these emission rates was computed and served as the emission factor. The emission rates were regressed against the screening values to generate the correlation equation. This approach has received USEPA endorsement through several further investigations primarily oriented to the organic chemical manufacturing sector (USEPA, 1982, 1986, 1988), culminating in the document now referred to as the USEPA Protocols Document (USEPA, 1993). Other organizations provided further endorsement through the publication of guidelines which utilized the USEPA approved bagging procedure for measuring process drain emissions in the organic chemical manufacturing sector (CMA, 1989) and in the refinery sector (API, 1994).

Significant efforts have been made in the statistical analysis of these data bases of bagged drain emissions. Further efforts in advancing the refinement of emission factors or correlation equations would best be served by addressing the method by which drain emissions are measured. Bagging techniques were developed to measure emissions from structures such as valves and flanges. The drawback to using the bagging procedure for a drain structure is that it will alter the hydrodynamics of the drain environment causing the natural ventilation patterns to be altered. The PERF-sponsored investigation into drain ventilation patterns showed how complex they are (Rabideau, 1995). Also, the action of imposing a "flow through" sampling

method can contribute further to a distortion of ventilation patterns. Flow balancing is critical to avoid withdrawing vapors from the drain riser when using a vacuum pump to draw vapors through the bag, and to avoid forcing emitted vapors down a drain riser when using nitrogen to purge the bag of emitted vapors.

A modification of the bagging procedure could utilize tracer dilution methods to measure ventilation rates if an adequate procedure could be developed to introduce inert tracers into a drain riser. Tracer dilution methods could also be used to measure liquid flow rates through a drain structure. If emissions were significant, it would be simpler and more accurate to measure changes in liquid concentration if an adequate procedure could be developed to sample liquid moving through a drain system.

Neither the emission factor nor the correlation equation makes a distinction between different drain configurations, whether the drains are active or not, and whether they are sealed or not. The drain survey showed that a majority of drains surveyed were water sealed and that the majority of surveyed drains were not active. This would suggest that refinery process drains would not generate large emissions. However, the technical support document for the SOCMI-HON rule indicated the fraction of VOCs lost in uncontrolled collection systems can be greater than 40 percent (RTI, 1994). The CMA-sponsored drain study (Enviromega Ltd., 1993) showed the emission rates of four VOCs from active uncontrolled drains ranging from four to 53 percent of the influent mass flow of the compound into the drain funnel. The presence of a P-trap reduced emissions only slightly. It was postulated that emissions were primarily induced by rising bubbles in the P-trap escaping to the air. The bubbles result from air entrainment by the falling wastewater stream into the P-trap water seal.

To address these concerns, a multistage approach is recommended which takes advantage of existing equipment and personnel who are skilled in drain emission investigative work. Work at laboratory scale, pilot scale, and field scale is recommended as the most cost effective utilization of resources. Several tasks are visualized as being a part of the solution to refine the AP-42 emission factor:

- Refine a field test procedure for measuring emissions from a drain structure.
- Collect new field data for drain emissions using a refined field test procedure. Recalculate AP-42 emission factor based on new field data.
- Collect new field data as above but also include total hydrocarbon concentration data. Refine correlation equation based on new field data.
- Measure effect of major variables such as flow rate, water sealing, liquid and air temperature, volatility of discharge, and drain configuration in a simulated drain structure where controlled experiments can be conducted to make accurate assessments of system responses to changes in these variables. Use these data to compute a series or matrix of emission factors which are specific to different combinations of the above variables. Validate new emission factors in field tests.
- Make parameter estimates for model described in Section 4 from controlled experiments in a simulated drain apparatus. Validate model estimates of emissions in field tests.

One or more of these tasks could be pursued to generate a more refined emission estimate.

Testing is proposed at different scales of operation so as to maximize the number of variables which can be tested while at the same time generating information which is representative of field conditions. Laboratory scale testing is advantageous from the perspective that equipment costs are low, steady state conditions can be maintained, the size of apparatus lends itself to enclosure to facilitate mass balance closures, process parameters may be varied over a desired range of study, and emissions from different types of process wastewater may be studied. For these reasons, it is recommended that a substantial fraction of the work proposed for Phase II be conducted at the smaller laboratory scale.

In the field, emissions occur under non-steady state conditions with respect to VOC concentration and mass flow. Some level of field testing will be required to ensure acceptance of model predictions by the regulatory authorities. However, the utility of a pilot scale drain facility becomes evident in that it provides the opportunity to evaluate, at field scale but under controlled conditions, the impact of those variables which laboratory scale investigations will demonstrate to be critical to predicting the level of VOC emissions from process drains. It also allows the resolution of difficulties in the measurement of some variables such as drain flow rate, the