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STEP
Strategies for Today's
Environmental Partnership

Estimation of Fugitive Emissions from Petroleum Refinery Process Drains

Phase I Report

Health and Environmental Sciences Department
Publication Number 4639
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Strategies for Today's Environmental Partnership

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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 compound[1] (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 recommendatons 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 SOCMI.
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.

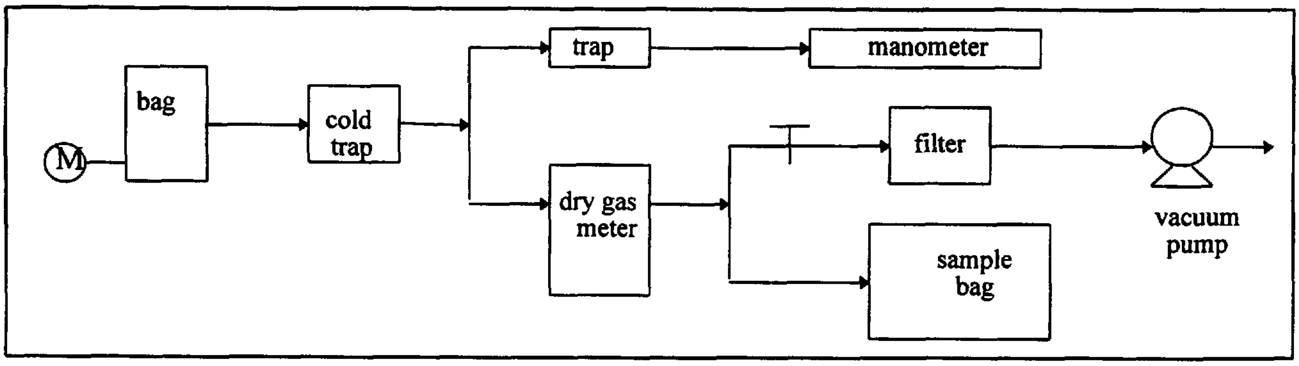


Figure 2-1. Schematic of Sample Train for Baggable Source (Vacuum Method).

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).

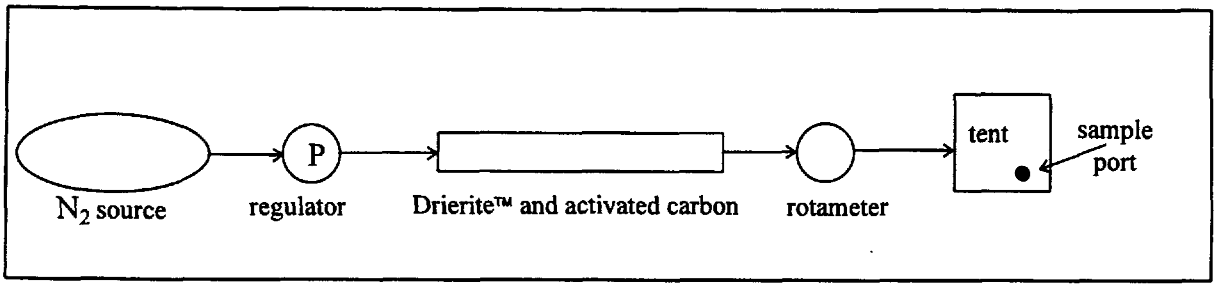


Figure 2-2. Schematic of Sample Train for Blow-Through Method.

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 m^3/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 eduction. 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.

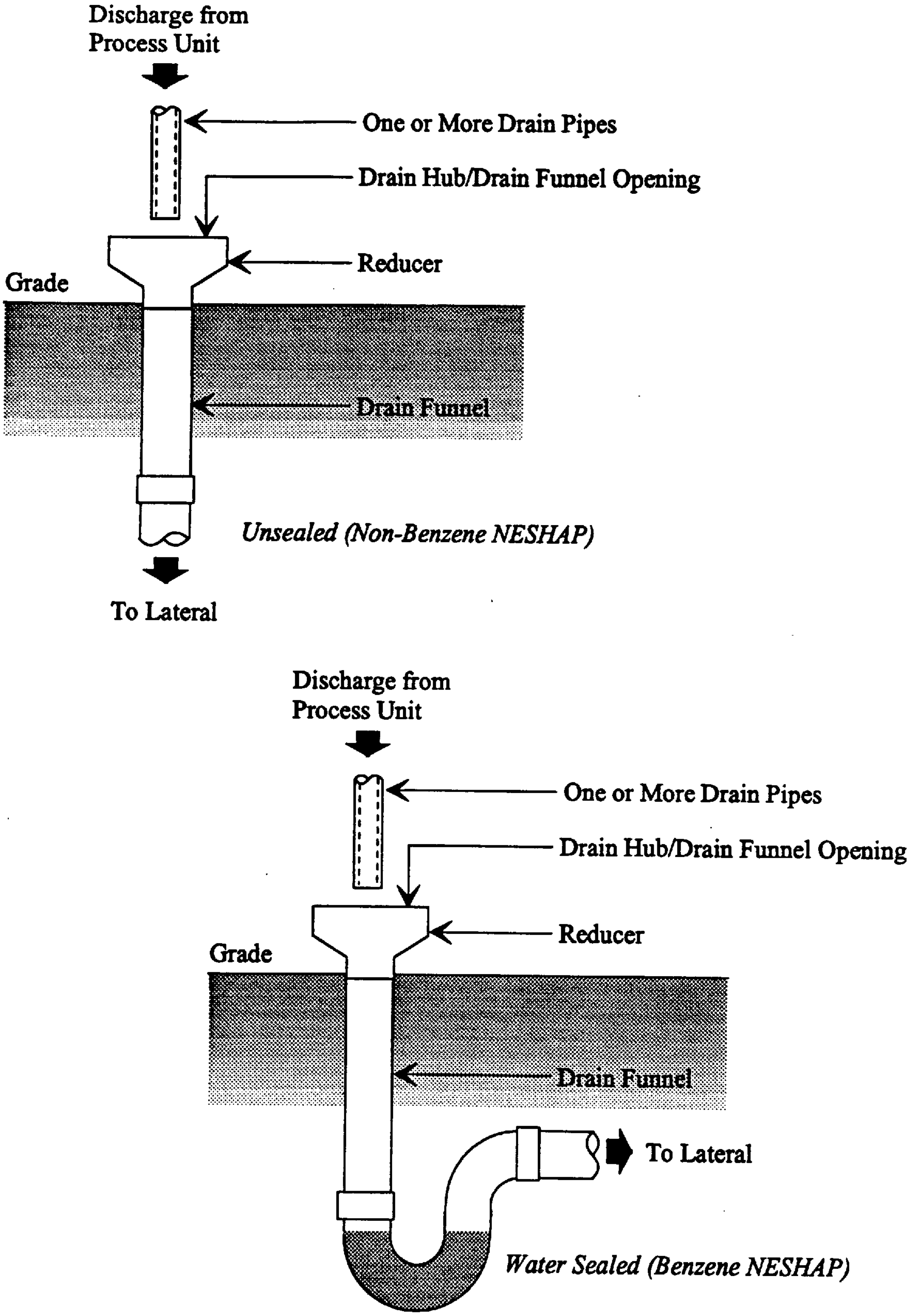


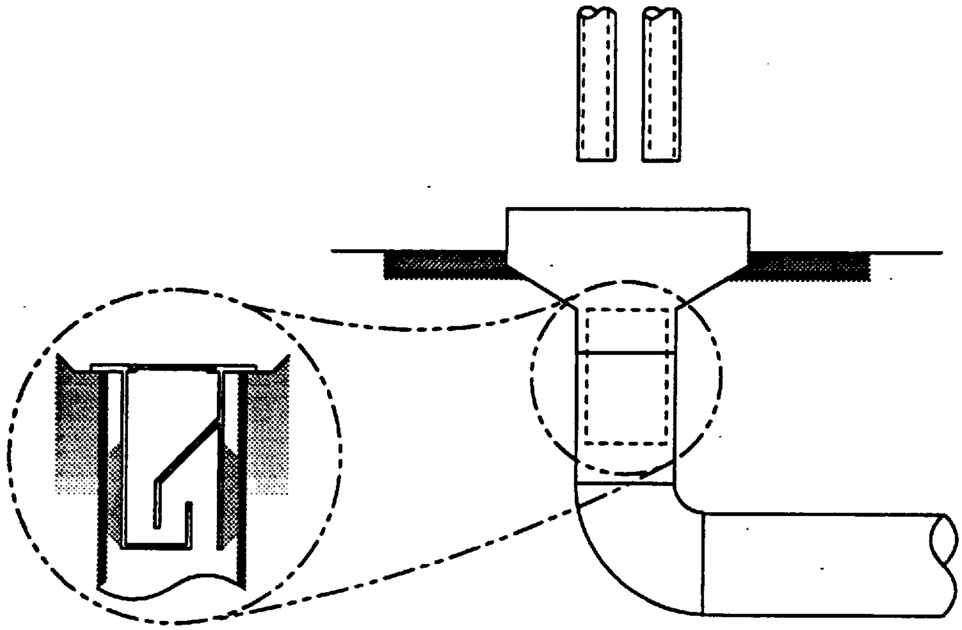
Figure 3-1. Major Components of a Drain Structure (Not to Scale).

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.

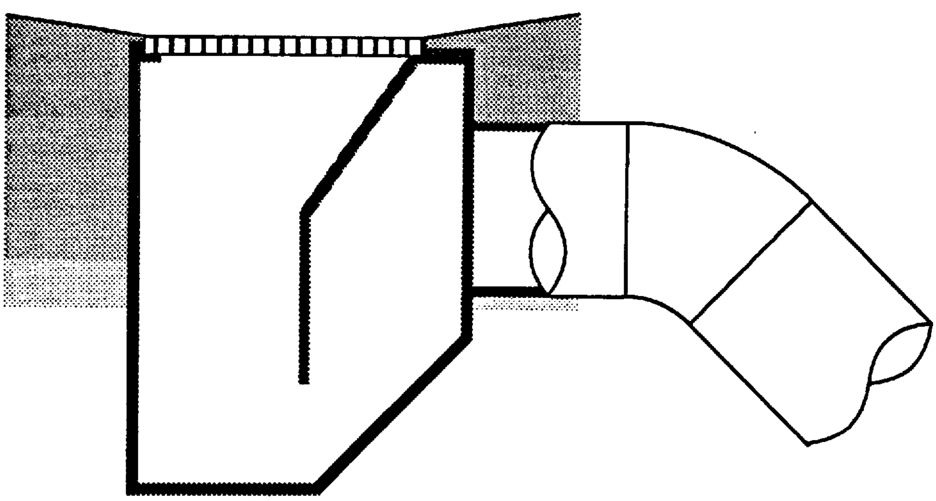
The P-trap was the drain seal used by the mid-west and east coast refineries. Typical dimensions of the P-trap used by the mid-west refinery are shown in Figure 3-3. Most drain funnels were four inches in diameter. The dimensions of the unsealed drain funnels at the mid-west refinery are shown in Figure 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).

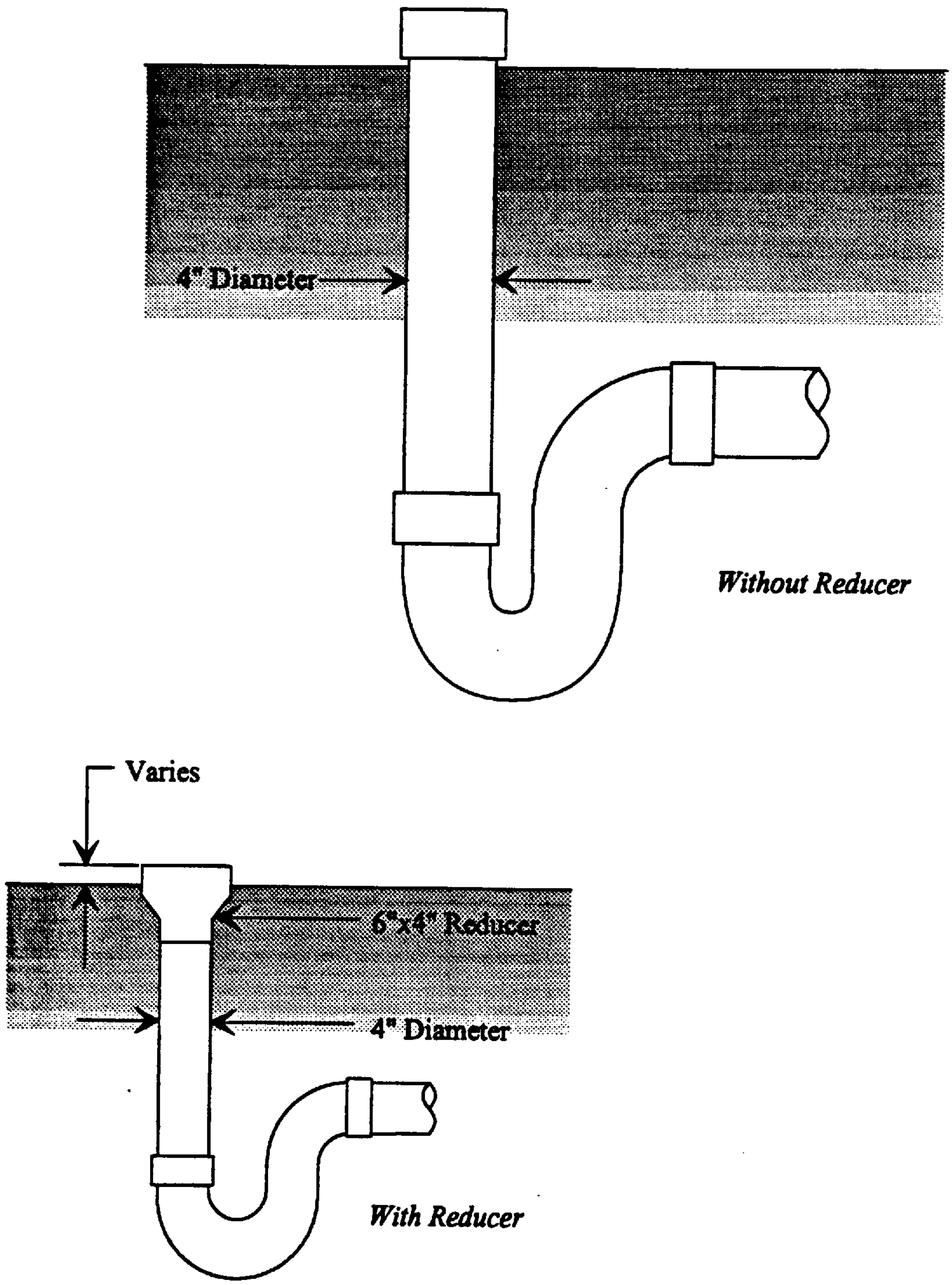


Figure 3-3. P-Trap - Water Sealed Drain at the Midwest Refinery (Not to Scale).

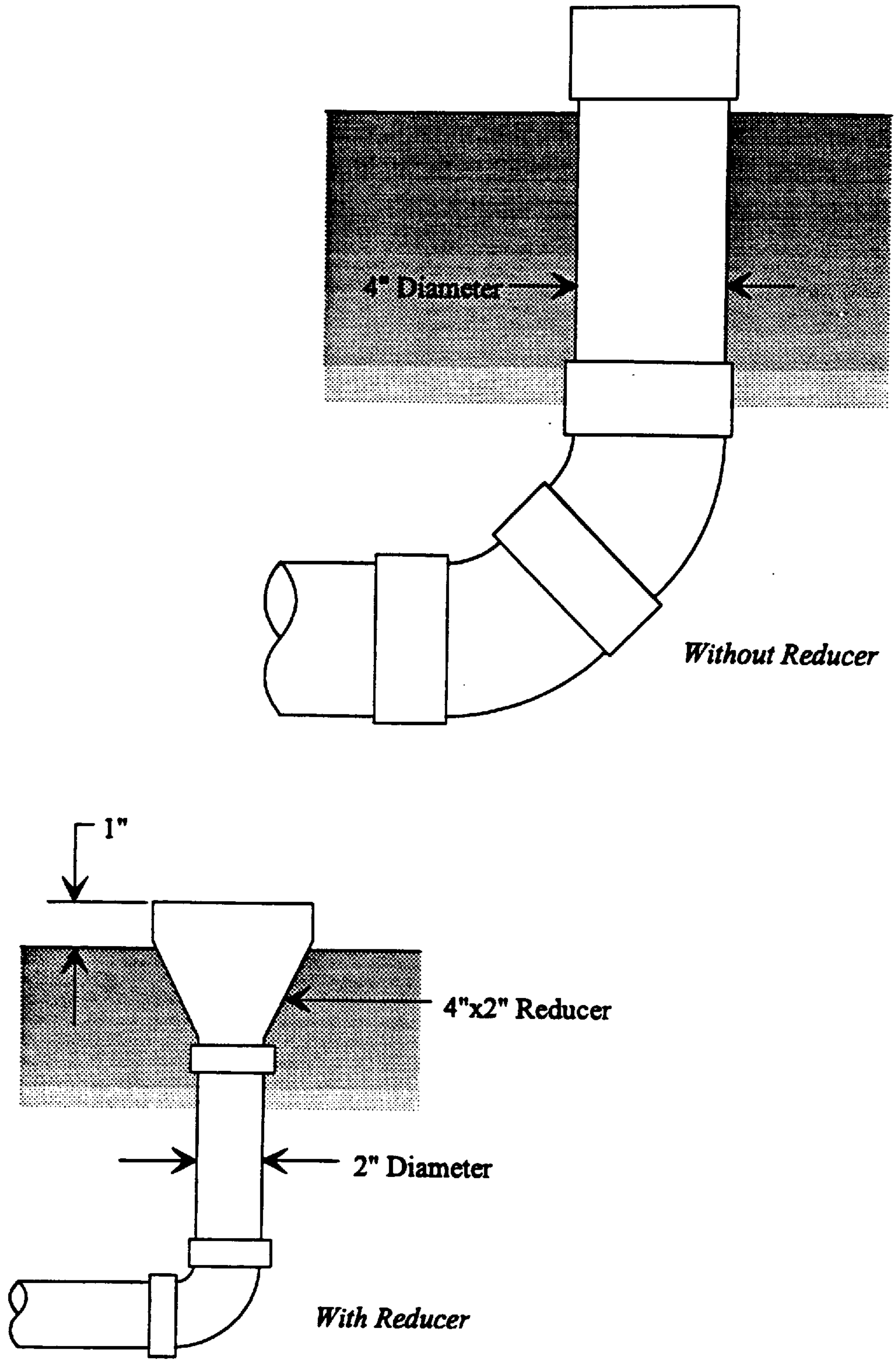


Figure 3-4. Unsealed Drain Funnel at the Midwest Refinery (Not to Scale).

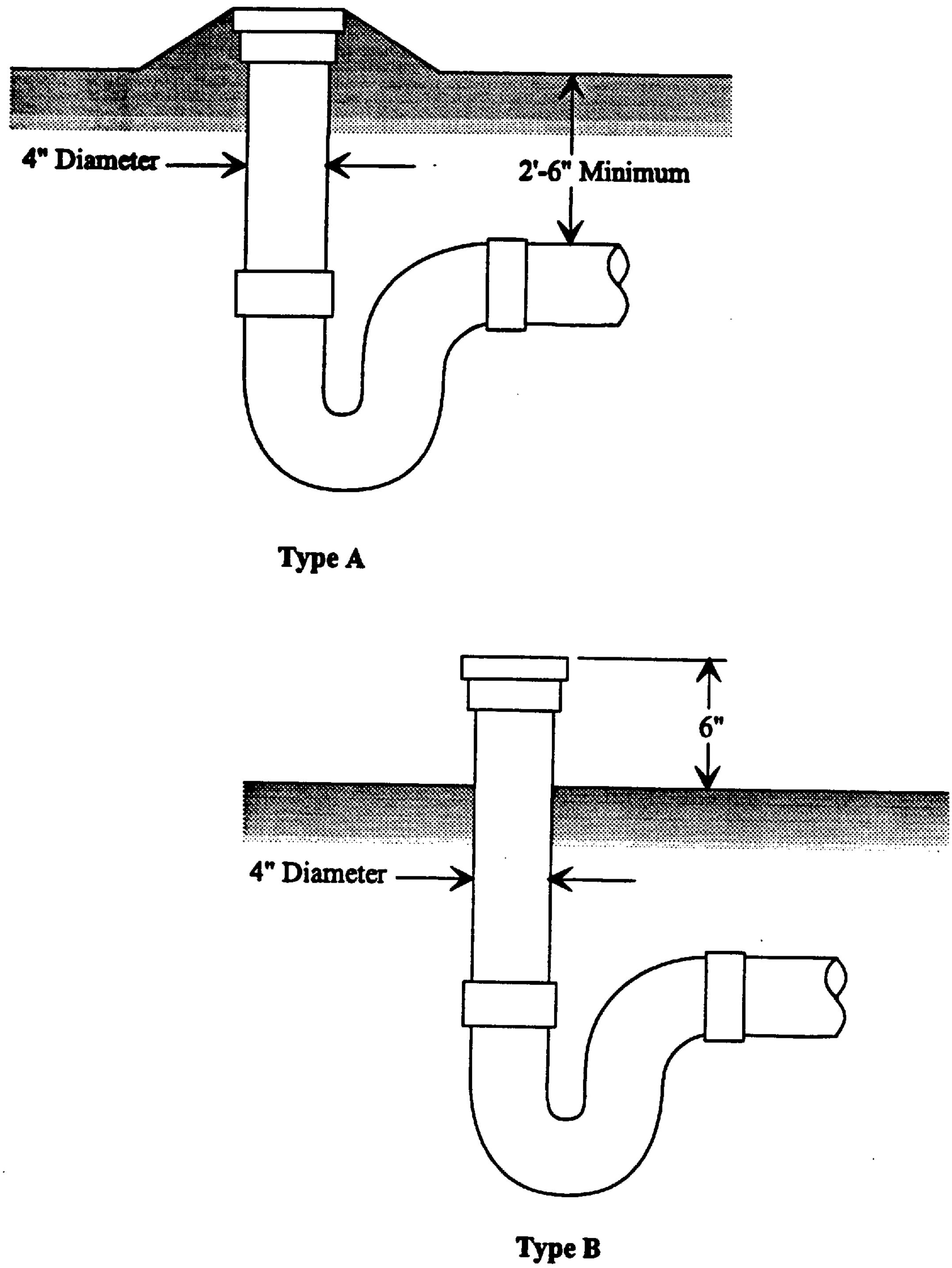


Figure 3-5. P-Trap Types at the East Coast Refinery (Not to Scale).

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

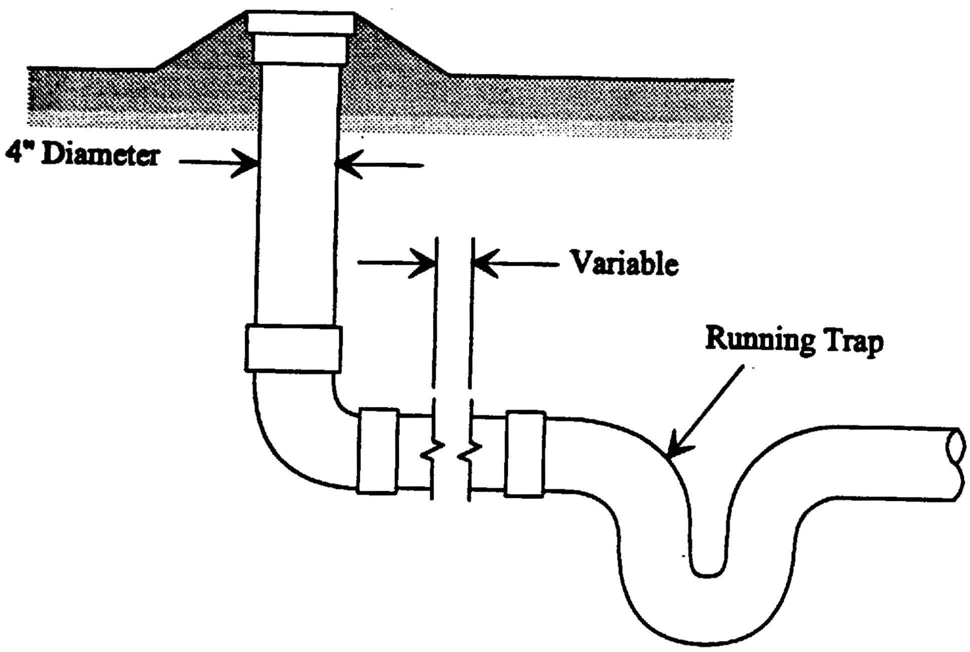
Typical pump drain funnels were fed by up to three drain pipes, normally one inch diameter or less. Pump discharges consisted of pumped (hydrocarbon) material, seal water, steam condensate and blowoff, lube oil drippings from the pumps, and pump pad drainage at flow rates ranging from a few drops per 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.

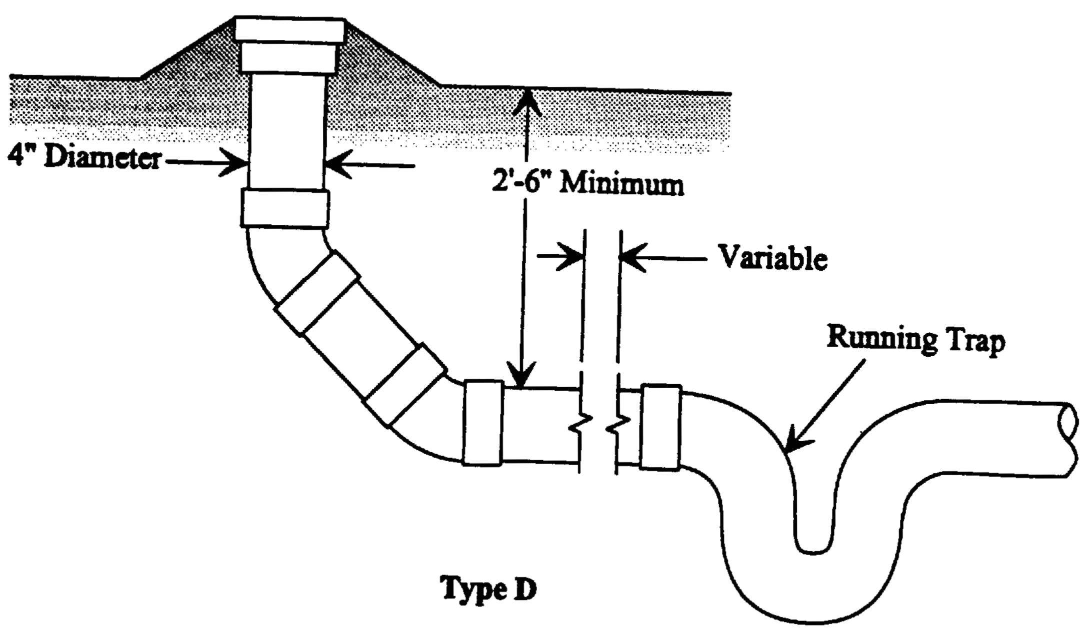
Temperature

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.



Type C



Type D

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.

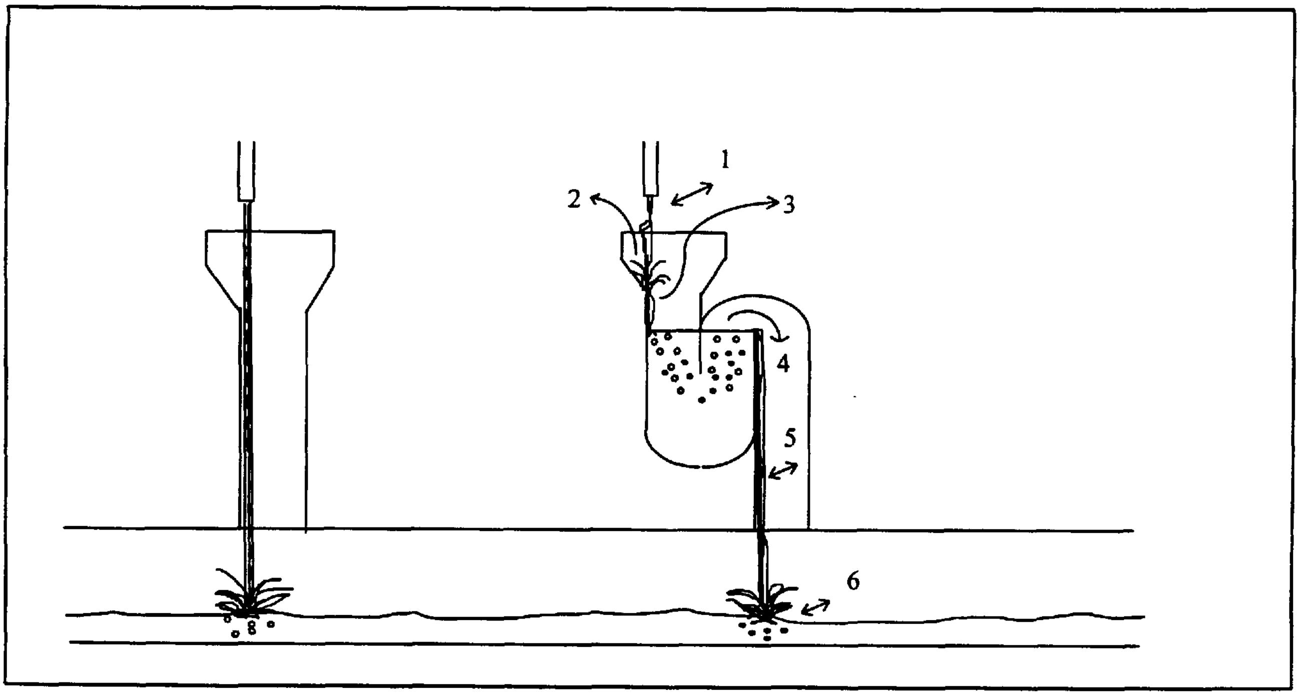


Figure 4-1. Mass Transfer Mechanisms in Process Drains.

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:

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

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.

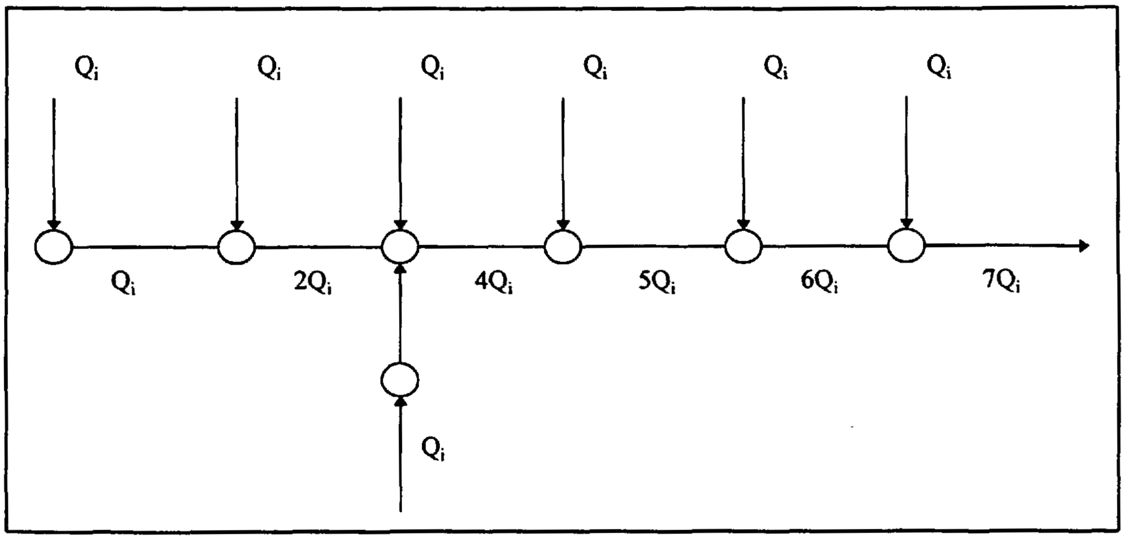


Figure 4-2. Illustration of Co-current, Cumulative Ventilation Model.

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 sampling of drain discharges under controlled conditions and the isolation of the process to allow measurement of VOC emissions. The pilot scale apparatus would serve well to test and validate a refined field procedure alternative to the current bagging procedure.

This section identifies the laboratory and pilot scale portions of the protocol with recommended minimal levels of investigations to generate meaningful information. The levels of effort could be altered if one of the above tasks was identified to be of a greater priority than the others. A description of the field portion of the protocol cannot be detailed at this time since it is contingent upon a refinement of the existing field bagging procedure, and the experimental identification of those variables which are the most critical ones controlling drain emissions. Some alternative options for field measurements are suggested at the end of this section and are evaluated in Section 6.

LABORATORY SCALE

The objective here is to evaluate the effects of a wide range of chemical properties, environmental conditions, and system operating conditions on VOC emissions from process drain structures under closely controlled conditions using an existing laboratory scale drain and sewer facility. Emissions are observed through the behavior of target compounds dosed into the system fluid.

Test System

A small-scale process drain and sewer reach has been constructed in an environmental chamber at the University of Texas. The Laboratory Drain System (LDS) is currently used for tracer studies to investigate mass transfer of VOCs under various operating conditions and is shown in Figure 5-1. The main components of the LDS include a 45 L (12 gallon) glass reservoir, an eight-foot section of six-inch i.d. glass pipe, two variable speed rotary vane pumps and one-inch polytetrafluoroethylene pipe. Water is pumped from the reservoir through the polytetrafluoroethylene process pipe and discharged into a vertical drain riser attached to the six inch sewer pipe. The water then flows along the sewer reach and back into the reservoir through a 1.5-inch vertical discharge pipe that extends into the neck of the reservoir. The second pump transfers water from the reservoir into the sewer channel directly and simulates an upstream component of wastewater flow.

There are a total of three vertical risers along the sewer pipe, the middle of which currently serves as the active drain while the remaining risers simulate inactive drains or other openings in an industrial wastewater collection system. The sewer pipe is comprised of six sections and is assembled with beaded glass couplings. Vertical branches are two-inch i.d. for the risers, and 1.5-inch i.d. for the return pipe. However, since the system is modular, it can easily be retrofitted with branches that include larger risers. The active drain riser is equipped with a glass reducer (4 x 2 inches) which serves as a drain hub. The inactive risers may be vented to a nearby fumehood with dryer hose, sealed to prevent air flow, or left open to natural ventilation patterns.

The return pipe has been equipped with a globe valve, which regulates flow from the sewer channel to the reservoir below. This valve is instrumental in controlling the depth of water in the sewer channel and in eliminating air entrainment into the reservoir. Polytetrafluoroethylene and glass were selected for their relative inertness. Threaded polytetrafluoroethylene elbows are used to connect most pipe sections. An acrylic rotameter with a stainless steel float was installed in a vertical section of polytetrafluoroethylene process pipe. A polytetrafluoroethylene stopcock was inserted into the side of the reservoir for sample collection.

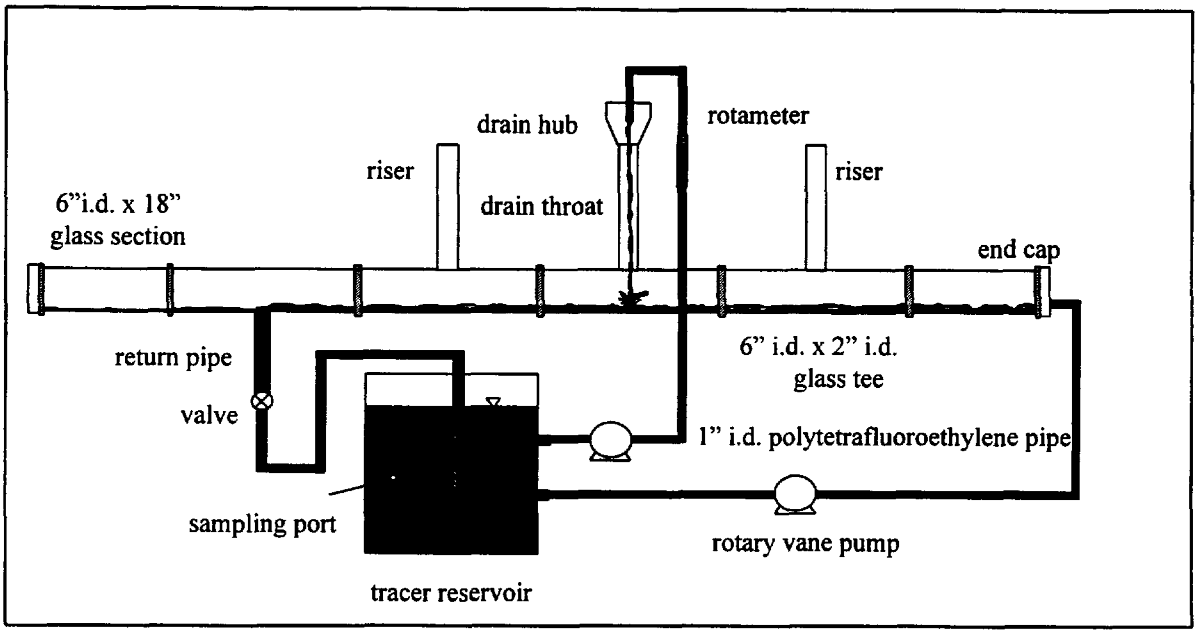


Figure 5-1. Schematic of Pilot Drain System.

The majority of the VOC dosing solution remains in the well-mixed reservoir until it is pumped through the system and returned once again to the reservoir. During each pass through the drain system, a fraction of each dissolved VOC will be stripped out of the water. To facilitate the calculation of the compound specific stripping efficiencies for this system, it is reasonable to conceptualize the LDS as a recirculating and well-mixed batch reactor, as illustrated in Figure 5-2. A mass balance on the system leads to:

$$-V dC_l / dt = QC_l \eta \qquad 5\text{-}1$$

where:

C_l = tracer concentration in liquid phase (mg/m^3)
η = fractional stripping efficiency (-)
t = time (min)
Q = liquid flow rate through the LDS (m^3/min).
V = volume of liquid in the system (m^3)

Separation and integration of Equations 5-1 leads to:

$$-\ln(C_l / C_{lo}) = (\eta / \theta)t \qquad 5\text{-}2$$

where:

θ = V/Q , average time that a molecule spends in the reservoir before being pumped through the drain throat (min).

Plotting the logarithmic decay of normalized liquid-phase tracer concentration versus normalized time allows determination of stripping efficiency, η.

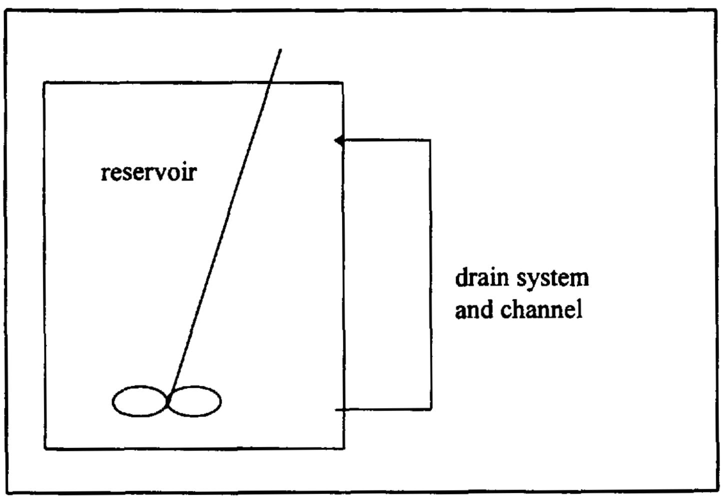


Figure 5-2. Schematic of Recirculating Batch Reactor.

Fluid Simulation

The liquid flowing through the test drain structure is potable water dosed with target VOCs. The temperature of the water may be varied by adjusting the temperature of the environmental chamber. The target VOCs are selected to provide approximately four orders of magnitude range of Henry's Law coefficients (Table 5-1). Toluene is a good surrogate for benzene. Acetone and cyclohexane can also serve as surrogates for correspondingly lower and higher volatility hydrocarbons that may exist in refinery process streams.

Table 5-1. Henry's Law Coefficients for Target VOCs at 22°C (Ashworth *et al.*, 1988).

Target VOC	Hc (m^3_{liq}/m^3_{gas})
Acetone	0.0015
Toluene	0.265
Cyclohexane	7.32
Oxygen	32

Dosing solutions are prepared in three liter polyvinylfluoride bags the day before an experiment. Four bags are filled with two liters of distilled water. Based on solubility limits, 0.13 mL of cyclohexane is injected into each bag. A fifth bag is filled with 1.5 L of distilled water, and acetone (4 mL) and toluene (1 mL) injected into it. A peristaltic pump and polytetrafluoroethylene tubing are used to fill bags with the required amount of distilled water. Pure acetone, toluene and cyclohexane are injected with glass, gas-tight syringes through polytetrafluoroethylene-lined septa into the bags. Bags are agitated by hand to dissolve compounds and then left overnight. Between experiments, bags are rinsed three times each with distilled water.

Dosing Procedure

The polyvinylfluoride bags are inspected visually to verify dissolution of chemicals (i.e., that there is no free phase remaining). A peristaltic pump and polytetrafluoroethylene tubing are used to pump the solution from the bags into the reservoir. The tubing is submerged below the water level in the reservoir and care is taken to prohibit volatilization of compounds at the water surface by reducing air bubbles in the tubing and minimizing surface agitation. Initial concentrations of dissolved VOCs in the reservoir are 25 mg/L toluene, 75 mg/L acetone and 10 mg/L cyclohexane.

Oxygen Uptake Rate Determination

Oxygen mass transfer coefficients are determined since they are used to compute VOC mass transfer coefficients through the diffusional relationship developed by Roberts (1984) (See Appendix B). In order to determine the oxygen mass transfer coefficient or rate of oxygen uptake, the dissolved oxygen concentration (DO) of the water in the reservoir is depleted before beginning an experiment. Sodium sulfite (3.0 - 3.5 g) and a few grains of cobalt chloride are dissolved in 500 mL of distilled water and poured into the reservoir. The rotary vane pump is then turned on to mix the water. Water samples are collected through the sample port in the reservoir and DO measured immediately. The DO will fall to below 1 mg/L, and recirculation with the pump continued until it reaches approximately 2 mg/L to prevent residual sodium sulfite in the water. At this point, the pump is shut down and VOC solutions added.

Liquid Sampling and Analysis

Approximately 10 mL of water is collected for each sample in 20 mL glass crimp top vials. Samples are collected through a short section of polytetrafluoroethylene tubing extending from the sample port. Sample vials are capped and crimped immediately after filling. Duplicate samples are collected immediately following capping. Liquid samples and standards are analyzed using a GC/FID (Hewlett Packard model 5890 Series II Plus) with a Tekmar® headspace autosampler (Tekmar® model 7000) using EPA method 1625.

Gas Sampling and Analysis

The University of Texas at Austin research team has the capability of collecting and analyzing gas samples using adsorbent tubes, polyvinylfluoride bags, or gas-tight syringes, with appropriate desorption and delivery techniques in each case.

Recommendations for Laboratory-Scale Phase II Work

The objectives of Phase II Laboratory scale investigations should include:

- Development of a model to estimate VOC emissions from drains. A rigorous sensitivity analysis of the model should be completed to determine combinations of variables that lead to high VOC stripping efficiencies, and to identify those mechanisms that likely dominate in terms of gas-liquid mass transfer.

- The use of controlled laboratory experiments to estimate model parameters, and to develop mechanistic relationships between those parameters and chemical, environmental and system operating conditions/properties.

- Experimental confirmation of the sensitivity of VOC stripping efficiencies to specific drain configurations.

These objectives could be addressed by the tasks described in Appendix E. A minimum program which could begin to address parameter estimation for the models proposed in Appendix D could consist of the following:

> Nine factorial experiments should be completed (three liquid flows and three wind speeds) to determine variations in K_{L1} and K_{L1}' for the most common case of aligned hubs. Replicate experiments should be conducted at two different temperatures.

Three of the aligned hub experiments should be repeated with a misaligned hub. As liquid flowrate is expected to have a significant influence for misaligned hubs, the three experiments should be completed at different liquid flowrates and a mid-range wind speed. The objective will be to develop a reasonable value of K_{L1}' / K_{L1} for different liquid flow rates. The variables α and γ, should be investigated over six liquid flowrates and two trap volumes (to determine effects of bubble transport time on degree of saturation). Approximately 10 percent of the experiments should be replicated three times to assess reproducibility of data. A thorough QA project plan (QAPP) would be developed including field and analysis blanks, field and analysis spikes, calibration curves, internal audits, and data analysis - including treatment of outliers.

PILOT SCALE

The following represent appropriate measurement procedures for estimating fugitive emissions from process drains for the pilot scale drain facility located at the Wastewater Technology Centre in Burlington, Ontario, Canada and which was available for this work. Portions of this protocol will also be relevant for measurements in the field. The objective would be to evaluate the level of fugitive emissions from a selected drain configuration under specified operating conditions that can be well controlled, using an existing pilot scale drain structure. Emissions are observed through the behaviour of selected target compounds whose properties span a wide range of volatilities. They are dosed into the drain influent and samples are taken of aqueous and gaseous effluents to facilitate mass balance closure calculations and the estimation of the proportion of influent contaminant mass flow emitted to the atmosphere.

Drain Structure

A schematic of the drain structure is presented in Figure 5-3. All materials were constructed of carbon steel. The drain funnel consisted of a standard seven to four inch reducer. The influent wastewater line was one inch diameter and discharged one inch above the plane of the drain opening. Thus, there was a one inch air gap between the inlet line and the plane of the drain opening. The drain funnel was connected to a P-trap with a four inch diameter pipe. There is provision to allow changing the P-trap to a straight drain funnel with or without a drain insert.

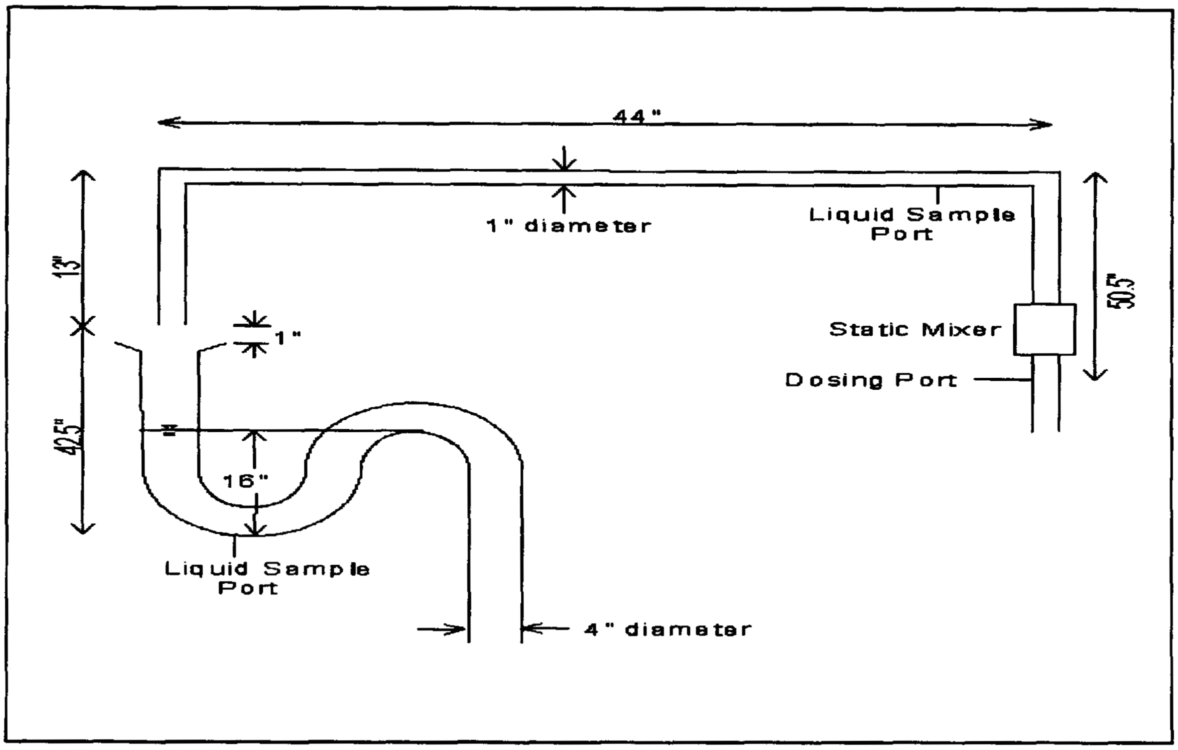


Figure 5-3. Schematic of Pilot Drain Structure.

Fluid Simulation

The influent to the drain structure is potable water, heated to a desired temperature, and dosed with target VOCs. A minimum of three target compounds is required to span the range of volatilities of the compounds typically found in refinery process drain discharges. Their selection is also influenced by the need to facilitate reliable and reproducible analytical determinations of the compounds in both the aqueous and gas phases. The target compounds are prepared a day before experiments are conducted. They are dissolved in water and contained in a polyvinylfluoride bag. Dissolution and equilibration is achieved by mixing with magnetic stirrer for 24 hours. The influent water flow rate is measured with a rotameter at the beginning and end of a sampling period.

Dosing Procedure

The dosing solution is pumped from the polyvinylfluoride bag into the influent water stream, at a controlled rate, through fluoroelastomer tubing. The dosing bag will collapse upon itself as the contents are pumped, preventing the formation of headspace in the bag. The compounds are pumped into a vertical section of pipe because the full pipe encouraged mixing and provided a gas seal for the system. A static, helical mixer is located immediately downstream of the point of entry for the dosed chemicals.

Wastewater Sampling and Analysis

Once steady-state conditions are established, a minimum of three wastewater samples are recommended to characterize emission rates. The samples should be taken at regular intervals over the gas sampling period. All wastewater samples should be collected in 60 mL amber, polytetrafluoroethylene septum top bottles, and analyzed using EPA Method 1625. Samples of the wastewater entering the drain are collected from a sample port in the horizontal section of the influent pipe, downstream of the dosing location. The contents of the P-trap are sampled from a sample port at the bottom of the trap.

Gas Sampling and Analysis

A schematic of the apparatus used to ventilate the headspace above the drain and collect gas samples is presented in Figure 5-4. The procedure is based on that recommended by the CMA (Chemical Manufacturers Assoc., 1989). The procedure is commonly referred to as a bagging - blow through procedure.

A cylinder of ultra-high purity nitrogen is used to provide the blow-through gas. The nitrogen gas flows through a desiccant trap for moisture removal and an activated carbon trap to remove any residual organics. The gas flow rate is measured with a rotameter, before entering the tent enclosure and controlled at four liter/min.

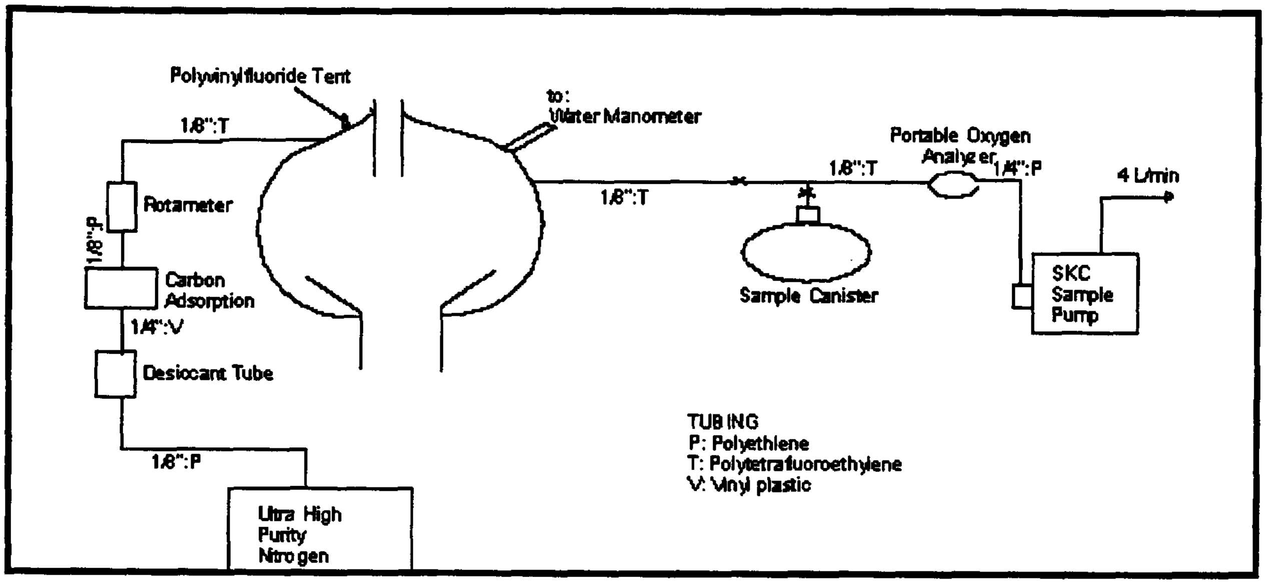


Figure 5-4. Schematic of Gas Sampling Apparatus.

The tent enclosure construction is of polyvinylfluoride sheeting obtained from cutting a 40 L polyvinylfluoride sampling bag. The enclosure is sealed around the drain structure using duct tape. The resulting gas volume enclosed by the tent is approximately three liters. An inlet gas line is inserted into the enclosure via a nickel-plated valve provided with the polyvinylfluoride bag. A fluoroelastomer tube is inserted into the tent enclosure and connected to a water manometer for monitoring gas pressure within the tent enclosure. The gas pressure within the tent enclosure is maintained between +0.5 to +1.0 inches water gauge. The slight positive pressure ensures that air will not leak into the enclosure and dilute the gas stream.

The discharge from the tent enclosure is withdrawn by an SKC sampling pump through polytetrafluorethylene tubing. The sampling pump also has a rotameter used to verify the upstream gas flow rate measurement. An oxygen probe, installed in the gas discharge line upstream of the sampling pump, monitors oxygen concentration for two reasons. At the start of an experiment, a decline in oxygen concentration to a zero value indicates that the existing gas in the system has been adequately purged. During the experiment, an increase in oxygen concentration would indicate a leak in the system.

A polytetrafluoroethylene T-valve connects an evacuated six liter, stainless steel gas sampling canister to the gas discharge line. To sample the tent enclosure gas discharge, the valve is opened allowing access to the canister. A flow restriction frit on the inlet to the canister allows the canister to fill slowly, over a 20 minute period. The canister is filled slowly to ensure that a vacuum is not created in the tent enclosure when the canister is first opened. Once the canister is filled, the valve is turned off and the canister disconnected.

A minimum of two gas samples are recommended to be collected in six liter stainless steel canisters to characterize emission rates over the course of an experiment. Analysis for the target VOCs is via EPA Method TO-14.

Recommendations for Pilot-Scale Phase II Work

The primary objective of pilot plant investigations should be to measure stripping rates to produce a table of emission factors for refinery process drains under different design and operating conditions. The following variables should be addressed:

- Trapped/straight drains;
- High/low drain flow rate;
- Inactive drains; and
- Drain lines above/below the drain hub plane;
- High/low wastewater temperature;
- High/low volatility compounds.

A minimum set of experiments is illustrated in Table 5-2.

Table 5-2. Number of Experiments at Each Operating Condition.

		Trapped Drain		Straight Drain	
		Drain Below Hub	Drain Above Hub	Drain Below Hub	Drain Above Hub
High Temperatures	High Flow	2	1	1	1
	Low Flow	1	2	1	1
Low Temperatures	High Flow	1	1	2	1
	Low Flow	1	1	1	2
	Inactive	2	1	1	1

A second objective should be to evaluate the effectiveness of the bagging technique for measuring process drain emissions in the field and to modify the bagging procedure until a true measure of air emissions can be reproduced.

ALTERNATIVE PROCEDURES FOR FIELD MEASUREMENTS

Wastewater Sampling and Analysis

Ideally, wastewater samples would be collected from sample ports in the drain pipes. Obtaining a representative wastewater sample in the field may not be as straightforward. A potential method for obtaining a wastewater sample is to pump the contents of the P-trap to the surface and collect samples at the surface. These samples may be obtained by inserting copper tubing into the trap prior to constructing a tent enclosure for measuring off-gas concentrations. The tubing can be connected to a short length of fluoroelastomer tubing for drawing the sample to the surface with a peristaltic pump.

Wastewater samples should be collected in amber, sample bottles. All material in contact with the wastewater should be either glass or polytetrafluoroethylene. The method of analysis will depend on the target compounds. Many VOCs can be analyzed using EPA Method 1625.

Wastewater Flow Rate

The wastewater flow rate is measured by a rotameter during the pilot scale experiments. Obtaining an accurate wastewater flow rate under field conditions may not be as straightforward. In most cases the flow will not be routinely measured. A potential method for measuring wastewater flow rate is a tracer dilution technique. A measurable tracer is continuously injected at a controlled rate into the trap. The turbulence in the trap provides mixing. If there is insufficient turbulence to do this, the technique is invalid. Samples of the wastewater in the P-trap are pumped to the surface and analyzed for the tracer. The wastewater tracer concentration is calculated by performing a mass balance on the tracer around the trap. Lithium is a recommended tracer, although rhodamine dye has been successfully used. Lithium may be more appropriate for aggressive or highly stained wastewaters. Rhodamine has the advantage that the analysis is relatively easy to perform, and can be frequently done on site.

Section 6
TESTING OF PHASE II PROTOCOL

The purpose of these tests was to validate the procedures described in the Phase II protocol using the equipment which had been assembled in the University of Texas laboratory and the Wastewater Technology Centre. This was assessed by performing mass balance closures, where possible, and by assessing reproducibility of experimental replicates, and from the consistency in trends with respect to compound volatility.

LABORATORY SCALE ASSESSMENT

Experimental Conditions

Five experimental conditions were tested using the protocol described in Section 5. A summary of experimental conditions is provided in Table 6.1. Experiments 1 and 2 were completed specifically for this study. Experiments 3 to 5 are provided as in-kind contributions, and are essentially a hybrid of the study described herein and a parallel study using a modification of the protocol.

Table 6.1. Summary of Experimental Conditions.

Expt. #	Type	T (°C)	Q_l (L/min)
1	straight drain	21	4.5
2	straight drain	22	6.1
3	misaligned	22	7.9
4	misaligned	22	7.9
5	misaligned	22	7.9

Experiments 1 and 2 were completed using liquid discharge into a single straight drain, with two adjacent open straight drains. The active drain provided the only flow into the channel. Previous measurements using hot wire anemometry indicated air exchange rates of approximately 0.1 - 0.2 L/min for these conditions. The only major difference between experiments 1 and 2 was an approximate 30 percent increase in flow rate for experiment 2.

Experiments 3 through 5 were completed using the same reservoir and target VOC pumping system as that used for experiments 1 and 2. The major difference was that the liquid discharge was pumped into a splash basin that was intended to represent a misaligned hub. The discharge pipe was situated approximately 10 to 12 inches above the hub. Rather than flowing through a drain throat, with downstream splashing in an underlying channel, the flow was directly reinjected from a hole in the basin back into the reservoir. These experiments can be used to ascertain the significance of a misaligned hub relative to those mechanisms that include stripping below a hub. These experiments were completed in triplicate, with the intent of evaluating the repeatability of experimental operation, sampling and analysis protocols.

Results

Duplicate Sample Analyses. For each experiment, a five-point calibration curve was prepared for each volatile tracer. A typical curve for acetone is provided as Figure 6.1, which had an R^2 value of 0.9995 for a linear fit. Calibration curves for other chemicals and experiments also exhibited excellent linear fits. Over the course of all five experiments, a total of 58 duplicate water samples were collected and analyzed for all three volatile tracers (acetone, toluene, and cyclohexane). For each pair of samples, the relative percent difference in concentration was determined for each tracer. Without removing any outliers, the average percent deviation in liquid samples was only 16 percent, e.g., 22 versus 25 μg/L. The coefficient of variation (COV) for duplicate differences was only 1.5 percent.

Mass Balance Closure

The operation of the LDS in a batch closed loop recycle mode does not lend itself to mass balance closure assessment without many measurements of liquid and gas VOC concentrations over a period of time. Mass balances are estimated by integrating the concentration-time relationship of the liquid and gas phases. Mass balances are more easily calculated by operating in a flow through mode as described in the pilot scale experiments below. The batch mode of operation, however, favors accurate assessment of stripping efficiencies which is described below. The LDS was operated for a period exclusive of the drain nozzle and it was shown that no VOC losses occurred in the conveyance lines.

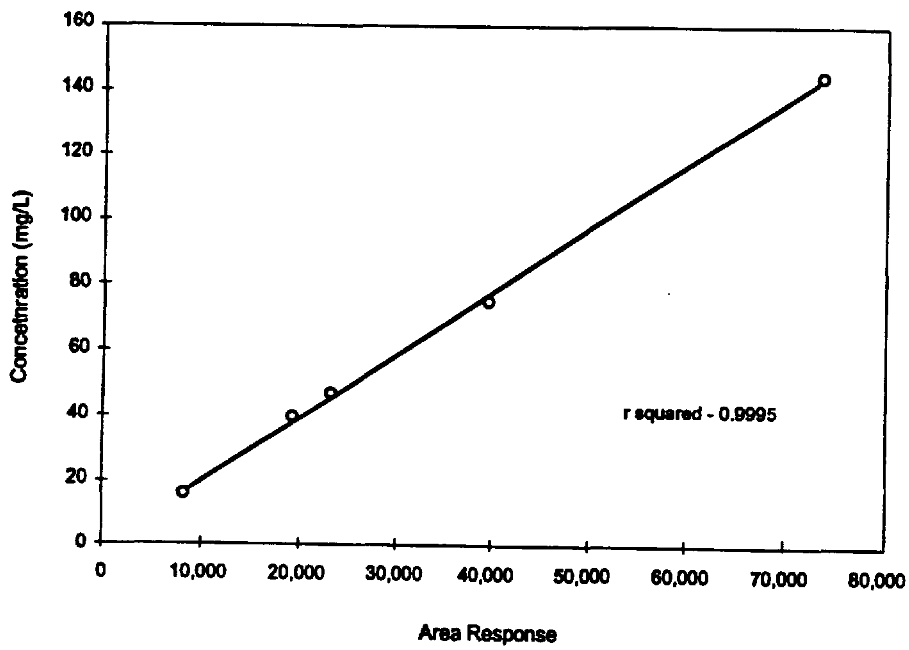


Figure 6-1. Acetone Calibration Curve.

<u>Stripping Efficiencies</u>

Stripping efficiencies determined for each experimental condition are listed in Table 6.2.

Stripping efficiency is defined as:

$$\frac{\text{mass of VOC removed by stripping}}{\text{mass of VOC discharged through drain nozzle}} \times 100$$

Table 6.2. Stripping Efficiencies.

		Stripping Efficiency (percent)		
Expt. #	Type	Acetone	Toluene	Cyclohexane
1	straight	1.5	35	36
2	straight	1.5	26	29
3	misaligned	1.3	17	20
4	misaligned	1.5	18	22
5	misaligned	2.2	17	19

Based on Experiments 1 and 2 it appears that an increase in liquid flow rate led to a slight decrease in stripping efficiencies for toluene and cyclohexane, with little effect on acetone. Furthermore, there was little difference in stripping efficiencies between toluene and cyclohexane, despite a factor of 27 difference in the Henry's law coefficients of the two compounds. This result suggests that air entrainment for the case of no trap (straight drain) was not significant, and that for well-ventilated condition, gas-phase resistance to mass transfer may be negligible for chemicals with volatilities equal to or greater than toluene (or benzene). These results are significant and suggest that equilibrium-based emissions estimates (emissions directly proportional to Henry's law coefficient) are clearly invalid for many conditions. The reduced stripping efficiency for acetone indicates significant gas-phase resistance to mass transfer for this lower-volatility compound, even for the well-ventilated conditions used in this study.

Experiments 3 to 5 represented replicates of a condition involving a misaligned hub without a long drain throat or underlying channel. Stripping efficiencies for acetone were similar to those obtained for Experiments 1 and 2. Stripping efficiencies for toluene and cyclohexane were reduced somewhat relative to Experiments 1 and 2.

Experiments 3 to 5 reflect the fact that the experimental and analytical protocols developed and practiced by the UT research team can lead to a high degree of replication. The coefficient of variation for acetone, toluene, and cyclohexane stripping were only 28 percent, 3.3 percent, and 7.5 percent, respectively.

Finally, the results presented here indicate how the Laboratory Drain System (LDS) can be routinely used to provide insight into the effects of both chemical properties and drain configuration on VOC stripping. For the conditions studied, acetone stripping was relatively insensitive to either water flow rate or drain configuration. Toluene and cyclohexane stripping efficiencies were sensitive to each. The results also suggest that while significant stripping may occur at a misaligned hub, gas-liquid mass transfer may be even greater in the drain throat or channel below a drain. It may be possible to reduce such emissions by suppressing channel or throat ventilation without the use of a water seal, e.g., a shroud around the drain, a condition that could easily be tested with the LDS.

Conclusions

- Analytical procedures used by the University of Texas at Austin (UT) research team lead to very small differences in duplicate sample concentrations (well within the variation of most commercial laboratories).

- Experimental replication can be achieved using the protocols developed in Section 5.

- The LDS can be routinely used to determine VOC stripping efficiencies for a wide range of drain operating conditions.

- The LDS can be used to determine the mechanistic behavior of VOC stripping, i.e. effects of VOC properties and system operating conditions on stripping efficiencies and mass transfer parameters.

- The LDS and associated protocols can be used to ascertain the relative importance of gas and liquid-phase mass transfer coefficients for a wide range of experimental conditions.

- It is possible to use the LDS (as is or with minor modifications) to determine several of the fundamental mass transfer parameters described in Appendix D.

PILOT SCALE ASSESSMENT

Experimental Plan

Three identical experiments were completed on three separate days. Experimental conditions are presented in Table 6-3. The conditions were kept as close as possible between experiments, in order to evaluate reproducibility of results. The system was thoroughly rinsed with clean water and ventilated between experiments to eliminate any risk of contaminant carry over. Five target compounds were used. Henry's Law coefficients for the compounds are presented in Table 6-4. The wastewater flow rate was selected to represent a typical influent wastewater flow rate identified in the drain survey. The gas flow rate was selected to simulate a low wind velocity condition (< 0.1 km/h).

Table 6-3. Experimental Conditions.

Wastewater Flow Rate (L/min)	Wastewater Temperature (^{o}C)	Gas Flow rate (L/min)
4.0	30	4.0

Table 6-4. Dosed Contaminants.

Compound	H (m^3liq/m^3gas) @ 25°C[1]
Cyclohexane	7.17
Tetrachloromethane	1.23
Toluene	0.26
1,4 Dichlorobenzene	0.13
Bromoform	0.02

[1] Ratio of contaminant concentration in gas phase (g/m^3) to contaminant concentration in liquid phase (g/m^3); values taken from Toxchem database.

Table 6-5 presents the sampling schedule for the experiments. For each experiment, the system was operated for one hour before sampling. This provided time for several turnovers of gas in the tent enclosure and wastewater in the P-trap, thus ensuring steady state operation. For each experiment, three samples of the inlet wastewater and wastewater contained in the P-trap, which represented the drain effluent, were collected. Two samples of the gas discharge from the tent enclosure were collected.

Table 6-5. Sampling Schedule.

Time[1] (hour)	Wastewater Samples		Gas Sample
	Inlet	P-trap	
1	X	X	X
1.5	X	X	
2	X	X	X

[1] Time after operation of drain structure initiated

Results

Tables 6-6 to 6-8 summarize concentration data for the three experiments. For each experiment, the coefficient of variation between samples is presented as a percentage of the average concentration.

For wastewater samples, the coefficients of variation were consistently less than 40 percent of the average values and frequently less than 10 percent. The coefficient of variation represents the ratio of the data standard deviation to the data mean. The coefficient of variation increases as data scatter increases. For 1,4-dichlorobenzene, a single value in the first experiment was excluded as an outlier. Average effluent concentrations exceeded average influent concentrations in experiment 2 for 1,4-dichlorobenzene and experiment 3 for bromoform. These apparent anomalies result from data scatter associated with wastewater sampling and analysis. These compounds were emitted to the least extent, and thus influent and effluent wastewater concentrations were not similar for these compounds. This indicates the need for gas sampling to facilitate accurate measurements of emission rates for the less volatile compounds.

For gas samples, the coefficients of variation were consistently less than 40 percent of the average values. As with the wastewater samples, the final experiment displayed the least variability. This was attributed to the technician gaining substantial experience in controlling the wastewater and gas flow rates over the first two experiments. In addition, these samples were analyzed immediately following re-calibration of the analytical instrument.

Table 6-6. Analytical Data - Experiment 1.

Compound	Sample 1 (μg/L)	Sample 2 (μg/L)	Sample 3 (μg/L)	Average (μg/L)	Coefficient of Variation (percent)
<u>Influent Wastewater</u>					
Cyclohexane	6.49	5.82	4.77	5.69	15.2
Tetrachloromethane	38.4	33.8	37.7	36.6	6.8
Toluene	392	395	378	388	2.3
1,4-Dichlorobenzene	222	244	103	233[1]	6.7
Bromoform	398	412	442	417	5.4
<u>Effluent Wastewater</u>					
Cyclohexane	3.98	3.90	3.09	3.66	13.5
Tetrachloromethane	24.2	24.2	23.0	23.8	2.9
Toluene	341	351	351	348	1.7
1,4-Dichlorobenzene	199	215	220	211	5.2
Bromoform	369	393	384	382	3.2
<u>Off-gas</u>					
Cyclohexane	1820	2290	--	2055	16.2
Tetrachloromethane	6820	9369	--	8095	22.3
Toluene	33200	58000	--	45600	38.5
1,4-Dichlorobenzene	7850	13700	--	10775	14.2
Bromoform	6820	8340	--	7580	38.4

[1] Sample 3 excluded as outlier for 1,4-dichlorobenzene

Table 6-7. Analytical Data - Experiment 2.

Compound	Sample 1 (µg/L)	Sample 2 (µg/L)	Sample 3 (µg/L)	Average (µg/L)	Coefficient of Variation (percent)
Influent Wastewater					
Cyclohexane	15.0	13.9	6.86	11.9	37.1
Tetrachloromethane	54.5	52.5	31.0	46.0	28.3
Toluene	196	185	152	178	12.9
1,4-Dichlorobenzene	225	143	110	159	31.5
Bromoform	160	166	166	164	2.1
Effluent Wastewater					
Cyclohexane	13.0	9.39	7.18	9.86	29.8
Tetrachloromethane	36.9	35.4	32.7	35.0	6.1
Toluene	154	174	184	171	9.0
1,4-Dichlorobenzene	192	201	248	214	14.1
Bromoform	146	169	178	164	10.0
Off-gas					
Cyclohexane	4200	6160	--	5180	26.8
Tetrachloromethane	11900	16500	--	14200	22.9
Toluene	27500	33300	--	30400	13.5
1,4-Dichlorobenzene	8510	13200	--	10855	30.6
Bromoform	2520	3220	--	2870	17.2

Table 6-8. Analytical Data - Experiment 3.

Compound	Sample 1 (µg/L)	Sample 2 (µg/L)	Sample 3 (µg/L)	Average (µg/L)	Coefficient of Variation (percent)
Influent Wastewater					
Cyclohexane	19.2	21.1	20.3	20.2	4.7
Tetrachloromethane	38.1	41.5	39.3	39.6	4.4
Toluene	43.2	47.5	46.2	45.6	4.8
1,4-Dichlorobenzene	46.2	50.6	49.2	48.7	6.4
Bromoform	46.2	51.0	48.3	48.5	5.0
Effluent Wastewater					
Cyclohexane	11.3	12.1	11.9	11.8	3.5
Tetrachloromethane	29.4	30.8	30.6	30.3	2.5
Toluene	36.7	40.5	39.9	39.0	5.2
1,4-Dichlorobenzene	42.9	47.1	46.0	43.3	4.8
Bromoform	45.2	48.8	46.9	50.0	3.8
Off-gas					
Cyclohexane	7420	7690	--	7555	2.5
Tetrachloromethane	10200	10500	--	10350	2.0
Toluene	6180	6510	--	6345	3.7
1,4-Dichlorobenzene	5680	5470	--	5575	2.7
Bromoform	1190	1260	--	1225	4.0

<u>Mass Balance Closure</u>. For each experiment, the percentage mass balance closure for each compound was calculated by:

$$MC = 100 * (E + F_{ww,out}) / F_{ww,in} \tag{6-1}$$

where:

MC	=	mass balance closure (percent)
E	=	mass of compound emitted from drain (mass/time)
$F_{ww,out}$	=	mass flow rate of compound out of P-trap (mass/time)
$F_{ww,in}$	=	mass flow rate of compound into drain; (mass/time)

The ideal mass balance closure is 100 percent.

The mass emission rate of each compound was calculated by:

$$E = C_g * Q_g \tag{6-2}$$

where:

E	=	emission rate (mass/time)
C_g	=	average concentration of compound in gas discharge from tent enclosure (mass/volume)
Q_g	=	tent enclosure ventilation rate (volume/time)

The mass flow rate of each compound out of the P-trap was calculated by:

$$F_{ww,out} = C_{ww,out} * Q_{ww} \tag{6-3}$$

where:

$F_{ww,out}$	=	mass flow rate of compound out of P-trap (mass/time)
$C_{ww,out}$	=	average concentration of compound in P-trap (mass/volume)
Q_{ww}	=	wastewater flow rate (volume/time)

The mass flow rate of each compound into the drain was calculated by:

$$F_{ww,in} = C_{ww,in} * Q_{ww} \tag{6-4}$$

where:

$F_{ww,in}$	=	mass flow rate of compound into drain (mass/time)
$C_{ww,in}$	=	average concentration of compound in influent wastewater stream (mass/volume)
Q_{ww}	=	wastewater flow rate (volume/time)

Table 6-9 presents mass balance closure results for the three experiments. The average mass balance closure ranged from 98.2 percent for bromoform to 113.6 percent for 1,4-dichlorobenzene. This range is highly satisfactory, given the number of analytical measurements that are input into the mass balance equation, and verifies the precision and accuracy of the sampling and analytical techniques employed.

The mass balance closure results for the third experiment were even better than for experiments 1 and 2, likely because of the technician's increasing experience in controlling the experiment and the very recent calibration of the analytical instrument. On this basis, it is suggested that the third experiment provided the best data set, although all three experiments are highly satisfactory.

Table 6-9. Mass Balance Closures.

Compound	Mass Balance (percent)			
	Exp. 1	Exp. 2	Exp. 3	Average
Cyclohexane	100.3	126.1	95.7	107.2
Tetrachloromethane	87.1	107.0	102.5	98.8
Toluene	101.3	113.2	99.4	104.6
1,4-Dichlorobenzene	95.3	140.9	104.6	113.6
Bromoform	93.3	102.0	99.4	98.2

Table 6-10. Percent Air Emissions/Stripping Efficiency from Drain Structure.

Compound	Stripping Efficiency (percent)				COV[1] (percent)	95 percent CI[2]
	Exp. 1	Exp. 2	Exp. 3	Average		
Cyclohexane	36.1	43.5	37.4	39.0	10.1	34.5 - 43.5
Tetrachloromethane	22.1	30.9	26.1	26.4	16.7	21.4 - 31.4
Toluene	11.7	17.1	13.9	14.2	19.1	11.2 - 17.3
1,4-Dichlorobenzene	4.6	6.8	11.5	7.6	46.2	3.6 - 11.6
Bromoform	1.8	1.8	2.5	2.0	19.9	1.6 - 2.5

[1] COV = coefficient of variation
[2] CI = confidence interval

Stripping Efficiency. Table 6-10 presents stripping efficiency or air emission estimates for each experiment. The emission rates are expressed as a percentage of the influent mass flow of each compound into the drain. The values were calculated using the formula:

$$\text{Percent E} = (100 * E)/F_{ww,in} \tag{6-5}$$

where E and $F_{ww,in}$ were calculated using Equations 6-2 and 6-4. Table 6.10 also presents the coefficient of variation of emission estimates between experiments as a percentage of the average emission estimate and the 95 percent confidence interval for emission estimates.

The average stripping efficiencies ranged from a low of two percent for bromoform to a high of 39 percent for cyclohexane. The magnitude of emissions consistently increased with increasing compound volatility, as indicated by the compound Henry's Law Coefficient. The 95 percent confidence interval ranges for percentage emissions were acceptably narrow, given the number of measurements in the calculated values. 1,4-Dichlorobenzene displayed the largest confidence interval because of the greater scatter in the wastewater analytical data for this compound.

Two of the compounds examined in this study, toluene and 1,4-dichlorobenzene were also investigated in a similar study for the CMA using the same equipment (Enviromega Ltd., 1993). While it is not possible to compare results directly, because the prior study employed greater wastewater flow rates, the magnitude of stripping efficiencies in this study were within the range observed in the prior study.

The data from this work suggest that emissions from a trapped drain could result from two possible mechanisms:

1) Emissions induced by rising bubbles in the p-trap escaping to the atmosphere. The bubbles result from gas entrainment by the falling wastewater stream into the P-trap.

2) Emissions were induced by volatilization directly from the surface of the falling stream and the liquid surface in the trap.

Phase II work will verify this observation.

Conclusions

- The precision of the data produced by the experimental techniques used in this study was highly satisfactory. Data reproducibility was good, both between replicate samples and between separate experiments. The coefficient of variation of emission rates between experiments was less than 20 percent for four of five compounds.

- The average compound mass balance closures ranged from 98.2 to 113.6 percent. The narrow range and proximity to 100 percent suggest accurate emission estimates were made.

- The average percentage emission rates or stripping efficiencies ranged from a low of two percent for bromoform to a high of 39 percent for cyclohexane. The magnitude of emissions consistently increased with increasing compound volatility, as indicated by the compound Henry's Law Coefficient.

ASSESSMENT OF ALTERNATIVE MEASUREMENT PROCEDURES

Wastewater Flow Rate

A total of four experiments were conducted over a range of wastewater flow rates using the procedure described in Section 5. For each experiment, rhodamine dye was injected into the P-trap at a flow rate of 0.0068 L/min. After 10 minutes of dye injection, two samples of the wastewater contained in the P-trap were pumped to the surface and collected. A fluorometer was used to analyze the concentration of dye in the samples. Two replicates were completed for each experiment.

Experimental results are summarized in Table 6-11. For all experiments, the relative differences between the wastewater flow rate measured with the rotameter and the flow rate measured by the dye dilution technique were less than 10 percent. It was concluded that this method is an acceptable alternative for measuring wastewater flow rate under field conditions.

Table 6-11. Comparison of Flow Rate Measurements.

Flow Rate (L/min)		
Rotameter	Dye	Difference (percent)
2.0	1.93	-3.5
	2.09	+4.5
4.0	4.29	+7.2
	4.29	+7.2
6.5	6.91	+6.3
	6.86	+5.5
9	9.69	+7.6
	9.50	+5.5

Wastewater Sampling

The following experiments were conducted to evaluate the accuracy of this technique for obtaining wastewater samples from a trapped drain (Section 5).

For each set of drain emission experiments, a second set of P-trap samples was collected by pumping wastewater from the trap to the surface. Copper tubing was threaded into the trap, prior to constructing the tent enclosure. The copper tubing was connected to a 30 cm length of flexible tubing, which was ran through a peristaltic pump for drawing the samples to the surface. Vinyl plastic tubing was used for the first two experiments and fluoroelastomer tubing was used for the third experiments.

A comparison of sample results is presented in Table 6-12. For the first two experiments, the samples pumped to the surface were substantially lower in concentration than the samples collected from the sample port. This suggests that the compounds permeated the tubing and even a short length of vinyl plastic tubing is unacceptable. For the third experiment, in which fluoroelastomer tubing was used, the relative difference between sample results was consistently less than 10 percent. This suggests that the method may be acceptable if an appropriate selection of flexible tubing is used. Even closer results may have been obtained if a pump that does not require flexible tubing had been used.

Table 6-12. Comparison of Wastewater Sampling Results.

Compound	Avg. Sample Conc. (μg/L)		Percent Difference
	Port	Tubing	
Experiment 1: Vinyl Plastic Tubing			
Cyclohexane	3.66	2.80	- 23
Tetrachloromethane	23.8	18.3	- 23
Toluene	348	277	- 20
1,4 Dichlorobenzene	211	164	- 22
Bromoform	382	322	- 18
Experiment 2: Vinyl Plastic Tubing			
Cyclohexane	9.86	6.22	- 36
Tetrachloromethane	35.0	27.5	- 21
Toluene	171	119	- 44
1,4 Dichlorobenzene	214	120	- 44
Bromoform	164	129	- 21
Experiment 3: Fluoroelastomer Tubing			
Cyclohexane	11.8	10.7	- 09
Tetrachloromethane	30.3	29.5	-03
Toluene	39.0	37.3	- 04
1,4 Dichlorobenzene	45.3	42.0	- 07
Bromoform	47.0	47.8	+ 02

Section 7
RECOMMENDATIONS FOR PHASE II WORK

Industry is concerned that the current AP-42 factor of 0.07 lb TNMHC / hour overestimates the level of fugitive emissions from refinery process drains. Several tasks should be completed to improve drain emission estimates:

1. Recalculate the AP-42 factor using newly collected field drain emission data.

2. Recalculate the empirical correlation equations [which relate emission rates to organic volatile analyzer (OVA) data] using newly collected field drain emission data.

3. Measure stripping efficiencies to assess the effect of specific variables such as drain (in)activity to generate a matrix of emission factors corresponding to different drain conditions.

4. Develop a model that takes into account the major mechanisms of VOC emissions and which will estimate emissions based upon knowledge of the physical conditions of a specific drain.

Laboratory and pilot scale facilities could be utilized to measure emission rates from drain structures with a wide range of operating conditions such as flow rate, water-sealing, liquid and air temperature, and drain configuration. Data on VOC emissions could be collected and grouped to define emission factors for each combination of operating conditions. In this way, a matrix of emission factors could be developed in the form of a look up table.

A modeling approach has been proposed in this report that accounts for the major mechanisms of VOC removal in a drain. Model calibration would require a significant number of experiments to ensure accurate parameter estimation. Experimental data may also reveal potential model simplifications if it is found that the effect of some of the mechanisms are negligible.

The development of both the emission factor matrix and predictive model would require field verification to validate the outputs of these approaches to the satisfaction of the regulatory agencies. In either case, a validated field measurement protocol would be required.

In summary, 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.

REFERENCES

Alpha-Gamma Technologies, Inc. 1994. *Low emission sewer systems for industry.* Water Environment Research Foundation.

Ashworth, R.A., G.B. Howe, M.E. Mullins, and Rogers, T.N. 1988. Air-water partitioning coefficients of organics in dilute aqueous solutons. *Journal of Hazardous Materials* 18: pp 25-36.

Chemical Manufacturers Association. 1989. Improving Air Quality: Guidance for Estimating Fugitive Emissions from Equipment.

Ellis, H.M., and R. Lackaye. 1989. Estimating fugitive emissions of volatile compounds from equipment leaks. *Journal of the Air Pollution Control Association.* 39(12): pp. 1619 - 1622.

Enviromega, Ltd. 1993. *Measurement of hazardous air pollutant emissions from wastewater collection system components, Volume II: Process drains.* Hamilton, Ontario, Canada.

Lipton, S. 1990. Fugitive emissions. *Chemical Engineering Progress.* 85(6): pp. 42 - 47.

Pescod, M.B. and A.C. Price. 1982. Major factors in sewer ventilation. *Journal of the Water Pollution Control Federation.* 54(4): pp. 385-397.

USEPA. 1977a. *Compilation of Air Pollutant Emission Factors.* Third ed. Research Triangle Park, N.C. EPA AP-42, Section 9: Petroleum Industry. pp. 9.1-1 to 9.1-10.

USEPA. 1977b. *Revision of emission factors for petroleum refining.* EPA-450/3-77-030.

USEPA. 1980a. *Assessment of atmospheric emissions from petroleum refining: Volume I, Technical Report.* EPA-600/2-80-075a.

USEPA. 1980b. *Draft environmental impact statement; Benzene fugitive emission - Background information for proposed standards.* EPA-450/2-80-032a.

USEPA. 1982. *Fugitive emission sources of organic compounds - Additional information on emissions, emission reductions and costs.* EPA-502/3-82-010.

USEPA. 1985. *VOC emissions from petroleum refinery wastewater systems - Background information for proposed standards.* EPA-450/3-85-001a.

USEPA. 1988. Control of volatile organic compound emissions from industrial wastewater, preliminary draft.

USEPA. 1990. *Industrial wastewater volatile organic compound emissions - Background information for BACT-LAER determinations.* EPA-450/3-90-004.

USEPA. 1994. *Air emissions models for waste and wastewater.* EPA-453/R-94-080A.

Wilkness, R. 1994. SCAQMD-approved protocols for Texaco bagging study. WSPA, internal memo.

Appendix A

LITERATURE REVIEW BRIEFS

1. Alpha-Gamma Technologies, Inc. 1994. *Low emission sewer systems for industry.* Water Environment Research Foundation.

2. Chemical Manufacturers Association. 1989. Improving Air Quality: Guidance for Estimating Fugitive Emissions from Equipment.

3. Ellis, H.M., and R. Lackaye. 1989. Estimating fugitive emissions of volatile compounds from equipment leaks. *Journal of the Air Pollution Control Association.* 39(12): pp. 1619 - 1622.

4. Enviromega, Ltd. 1993. *Measurement of hazardous air pollutant emissions from wastewater collection system components, Volume II: Process drains.* Hamilton, Ontario, Canada.

5. Lipton, S. 1990. Fugitive emissions. *Chemical Engineering Progress.* 85(6): pp. 42 - 47.

6. Pescod, M.B. and A.C. Price. 1982. Major factors in sewer ventilation. *Journal of the Water Pollution Control Federation.* 54(4): pp. 385-397.

7. USEPA. 1977b. *Revision of emission factors for petroleum refining.* EPA-450/3-77-030.

8. USEPA. 1980a. *Assessment of atmospheric emissions from petroleum refining: Volume I, Technical Report.* EPA-600/2-80-075a.

9. USEPA. 1980c. *Assessment of atmospheric emissions from petroleum refining: Volume III, Appendix B.* EPA-600/2-80-075a.

10. USEPA. 1990. *Industrial wastewater volatile organic compound emissions - Background information for BACT-LAER determinations.* EPA-450/3-90-004.

11. Research Triangle Institute. 1988. *Estimation of air emission factors from airflow in wastewater collection systems.* U.S. EPA Contract No. 68D10118.

12. Schaich, J.R. 1991. Estimate fugitive emissions from process equipment. *Chemical Engineering Progress.* 87: pp. 31-35.

13. USEPA. 1977a. *Compilation of Air Pollutant Emission Factors*. Third ed. Research Triangle Park, N.C. EPA AP-42, Section 9: Petroleum Industry. pp. 9.1-1 to 9.1-10.

14. USEPA. 1980b. *Draft environmental impact statement, Benzene fugitive emission - Background information for proposed standards*. EPA-450/2-80-032a.

15. USEPA. 1982. *Fugitive emission sources of organic compounds - Additional information on emissions, emission reductions and costs*. EPA-502/3-82-010.

16. USEPA. 1985. *VOC emissions from petroleum refinery wastewater systems - Background information for proposed standards*. EPA-450/3-85-001a.

17. USEPA. 1988. Control of volatile organic compound emissions from industrial wastewater, preliminary draft.

18. USEPA. 1994. *Air emissions models for waste and wastewater*. EPA-453/R-94-080A.

19. Wilkness, R. 1994. SCAQMD-approved protocols for Texaco bagging study. WSPA, internal memo.

Brief #1

Alpha-Gamma Technologies, Inc. 1994. *Low emissions sewer systems for industry*. Water Environment Research Foundation, Raleigh, North Carolina.

Overview

This paper described types of process drains and mechanisms for air flow within a sewer line. To reduce emissions and/or to prevent the propagation of explosion fronts, some sewers use water seals or p-traps to separate sewer and ambient atmospheres. It was suggested that water seals and p-traps will not completely eliminate organic emissions, possibly due to swirling air above the drain or splashing water from the process flow. However, it was suggested that drains with a gas-tight cap should have negligible emissions. The authors stated that the replacement of existing drains with p-traps may not be feasible because of space or maintenance requirements. A water seal insert was recommended as the best alternative. However, one problem with these drains was noted to be clogging from solid debris, although this can be avoided by using screen filters across the drain opening. Other potential problems included freezing of water seals and sewer pressure surges.

Factors affecting sewer ventilation were listed as thermal differentials, barometric differentials, and water flow differentials. Temperature differences were noted to create a density gradient which drives air flow from the sewer air space to the ambient. Wind blowing over sewer openings created pressure gradients between sewer components. Higher water levels forced air out of sewer openings. Lower water levels were noted to increase the sewer air space, drawing more ambient air into the sewer. No mechanistic model was presented to account for these factors.

Major findings

The authors cited observations from on-site measurements that p-traps reduce organic emissions by between 33% and 99% (USEPA, 1985), and that more than 50% of p-traps had a greater than 90% reductions in emissions. Further evidence supporting reduced emissions from p-traps was given as the authors cited data suggesting mass transfer rates for sealed drains were more than an order of magnitude lower than mass transfer rates for straight drains (Enviromega Ltd., 1993). The price of carbon steel water seal inserts was estimated to range from $200 to $1000 each. The price of stainless steel water seal inserts was estimated to range from $1000 to $2000. The installation time was estimated to be approximately 1.5 man-hour/drain.

Technical limitations

This report was primarily qualitative. Methods for estimating VOC emissions were not presented.

Brief #2

Chemical Manufacturers Association. 1989. Improving Air Quality: Guidance for estimating fugitive emissions from equipment.

Overview

This document incorporates the protocol established by the U.S. EPA for estimating fugitive emissions from equipment (including drains) in process units in both chemical manufacturing plants and petroleum refineries. The stated goals of the report include the development of emission factors or equations to improve emission estimates and the quantification of various equipment and operating practices on fugitive emissions.

Five techniques for estimating emissions are presented in detail, which require increasing sampling effort and lead to correspondingly increased accuracy. The first is the direct application of AP-42 factors, which requires an accurate inventory of the number of drains in a process unit. The next approach requires an assessment of the percentage of leaking or non-leaking drains and application of two different emission factors to the appropriate fraction of drains. The third estimation technique involves the application of stratified emission factors to the fraction of drains whose screening concentrations fall within specified discrete ranges. The final two methods provide continuous functions relating screening concentration to mass emission rate. The simplest of these methods is to use correlation equations developed by EPA, but additional bag studies and screening may be completed to adjust or validate these equations, or to develop unit-specific correlations. Potential drawbacks to this method include overestimates due to use of 8 ppmv as a default zero value and high cost of emission measurements.

The document then describes EPA's screening procedure (Method 21). A portable hydrocarbon analyzer must be placed near the emission source and a traverse is made of the perimeter. For larger sources, a grid of readings should be taken about the leak area.

Two techniques are presented for measuring mass emission rates of VOCs, which both involve enclosing, or "bagging" the source. The importance of a well-constructed and non-permeable enclosure is stressed. The first method is called the "vacuum" method and is the preferred technique for most applications. The second is referred to as the "blow through" method and the study recommends its use for large leaks, i.e., when the leak rate is greater than the pump capacity.

The vacuum method (also referred to as the dilution method) involves drawing air through the enclosure with a vacuum pump, at a flowrate measured by a dry gas meter. Emission and background samples are collected in bags for laboratory analysis. The sample train is shown below in Figure 1 and major components of the system have been described in Table 1.

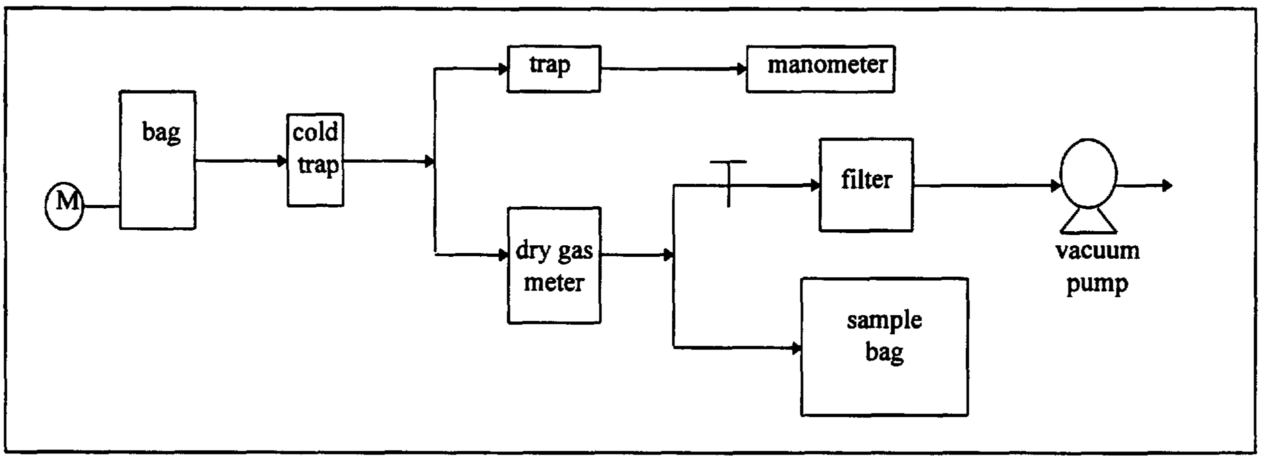


Figure 1. Schematic of sample train for vacuum method.

Table 1. Major components of vacuum method sample train.

Component	Materials/Specifications	Function
enclosure	polyester, polyvinylfluoride, etc.	isolate source from ambient air
cold trap	500 mL flask in ice bath	condense moisture and heavy organics
manometer	n/a	monitor pressure inside enclosure
vacuum pump	approx. 2 - 4 cfm	draw air through sample train
sample bag	polyester, polyvinylfluoride, etc.	collection and transportation of samples

The flowrate through the sample train is controlled by a valve upstream of the pump. At lower flowrates, hydrocarbon concentrations are expected to increase, and therefore, care must be taken to avoid explosive mixtures. Before beginning to sample, the system is thoroughly checked for leaks by conducting a leak test at a high vacuum flowrate (approximately 3" Hg). The flow time is monitored to calculate the leak rate, which should be less than 0.01 cfm.

The basic steps of the procedure are as follows: complete leak check, enclose source and assemble sample train, note initial gas meter readings, start pump and stopwatch, record pressure and temperature inside tent, and gas flowrate and VOC concentration at pump exhaust every 5 - 7 minutes. When VOC concentration in pump exhaust stabilizes, collect sample in bag and also collect background sample from nearby.

The second method described for measuring emission rates was referred to as the "blow-through" method. Nitrogen gas is forced through an enclosure surrounding the source to obtain a constant VOC concentration at a sample port. The sample train is shown below in Figure 2.

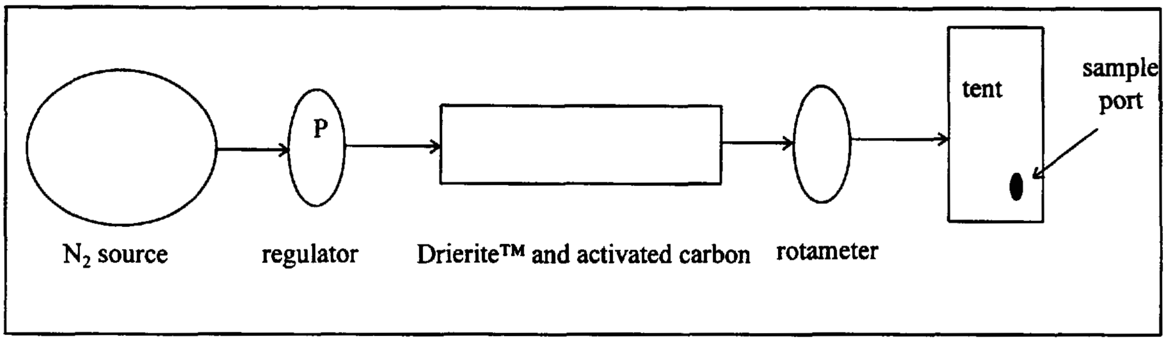


Figure 2. Schematic of sample train for blow-through method.

Important components of the system include a nitrogen gas source and purification system, a rotameter for measuring nitrogen flowrate, an enclosure system as previously described for the vacuum method, and polytetrafluoroethylene tubing to transfer gas sample. Steady-state VOC concentration is measured at the sample port on the enclosure. Temperature and oxygen concentration are measured inside the tent and VOC concentration is measured at various nitrogen flowrates. It is important to use a dilution probe and to calibrate the OVA with nitrogen-diluted gases. Emission rates may then be calculated using response factors determined previously in the laboratory. Alternatively, samples may be collected with a pump and transported to a laboratory for analysis. The oxygen concentration inside the tent is used to calculate total flowrate. The total leak rate may then be calculated using the following expression:

$$tented\ leak\ rate = \frac{(4.836x10^{-5})(Q)(MW)(OVA)(RF)}{T+460}$$

where:	Q	=	total gas flowrate (m^3/hr)
	MW	=	molecular weight of gas (lb/lb-mol)
	OVA	=	organic vapor analyzer reading (ppmv)
	RF	=	response factor for OVA
	T	=	temperature inside tent (°F).

Major findings

The document presented two detailed sampling protocols for determining emission rates from baggable sources. These methods, along with a screening technique for fugitive emission sources, correspond to accepted EPA methods, and are consistent with other research and emission measurement work. The Chemical Manufacturers Association has also provided additional guidance, such as checklists and helpful hints to aid in emission sampling and screening.

Technical limitations

This guidance document was very well-written and clearly illustrated. It should serve as a useful tool to someone who must sample emissions from process drains in a manner consistent with accepted EPA practice. Both the techniques presented, however, are invasive of the natural operating conditions of the source. For example, ventilation patterns in a process drain would be altered by enclosing it with a bag and by imposing a vacuum or nitrogen gas flow.

Brief #3

Ellis, H. M., R. Lackaye. 1989. Estimating fugitive emissions of volatile compounds from equipment leaks, *Journal of the Air Pollution Control Association*. 39(12): pp. 1619-1622.

NOTE: This paper did not mention drains specifically, but the methods for estimating fugitive emissions from other equipment were identical to that of drains.

Overview

Three different methods identified by the EPA for estimating fugitive air emissions from equipment leaks were reviewed in this paper. The three methods were: the average emission factor method, the leak/no leak emission factor method, and the stratified emission factor method. Many federal, state, and local regulations require industries to report annual VOC emissions, and this may include fugitive emissions from equipment leaks. The EPA has recommended these methods (as well as the leak rate/screening value correlations method) in order to estimate emissions from equipment leaks. The average emission factor method categorized each component by type of equipment and type of service (light liquid, heavy liquid, or gas). EPA's average emission factor method was used to find the appropriate emission factor for each category. The other methods used concentration measurements for each piece of equipment using an OVA analyzer. The concentrations were measured by Method 21, which was EPA's recommended procedure for measuring fugitive emissions from equipment leaks.

The leak/no leak method separated concentration measurements into two categories: components with concentrations greater than 10,000 ppm ("leakers") and components with concentrations less than 10,000 ppm ("non-leakers"). The authors counted the number of components that were "leakers' and the number of that were "non-leakers." The total emission rate was calculated by the product of the number of "leakers" times an average emission factor for "leakers" plus the product of the number of "non-leakers" times an average emission factor for "non-leakers." The stratified method used three categories (0-1000 ppm, 1001-10,000 ppm, and over 10,000 ppm) for each type of equipment component. Determination of the average emission factor was identical to the leak/no leak method except that there were three concentration categories.

Major findings

Using field data from 3412 components in four plants, emission factors were determined by each of the three methods. The following components were studied: valves, pump seals, pressure relief seals, flanges, and open ended lines. For many chemicals and facilities, the average emission factor was similar for different types of equipment. This implied that all concentrations were in the same range for the leak/no leak or the stratified method. The average emission factor method was observed to significantly overestimate emissions compared with the other two methods. The average emission factors were 1.1 to 25 times larger than the emission factors determined using the other two methods. The authors concluded that the leak/no leak or the stratified emission factor was the more accurate method and reduced estimated fugitive emissions from equipment leaks.

Technical limitations

Total emission rates could be grossly overestimated or underestimated if concentration measurements were near the boundary between "leakers" and "non-leakers." Furthermore, no distinctions were made for different chemical compositions, which is an important factor in mass transfer calculations. An average emission factor cannot account for differences in operating conditions, drain dimensions, drain configurations, or ventilation rates.

Brief #4

Enviromega Ltd. 1993. Measurement of Hazardous Air Pollutant Emissions from Wastewater Collection System Components, Volume II: Process Drains.

Overview

A pilot-scale sewer drain system was constructed to investigate stripping of hazardous air pollutants (HAPs) from process drains in wastewater collection systems. Emission factors were noted to depend on the following operating conditions: ventilation rate, gas-liquid mass transfer rate of the compound, turbulence in the sewer, characteristics of flow in the drain and compound physicochemical properties such as Henry's law coefficient. The report cautions that, due to such potential variability in the above conditions, any measured emission factors must be considered site-specific. The variable tested in the reported study were: compound Henry's law coefficient, type of drain throat connection (straight or p-trap) and process flow rate.

The experimental system consisted of a recirculating flow through a 50' long, 4" diameter steel sewer pipe connected to a 1250 L reservoir. A portion of this flow was diverted through a process pipe discharging 1.5" above the drain, which extended 6' above the sewer pipe. Experiments were completed under conditions of both passive and forced ventilation through the sewer, and at three process flow rates (0, 15 and 49 L/min). A tracer solution comprised of methanol, 1,4-dichlorobenzene, toluene, trichloroethylene and tetrachloroethylene was used. Figure 1 illustrates the experimental apparatus.

A relatively rigorous discussion of ventilation patterns was presented which listed the following mechanisms that may induce air flow in a sewer or drain: liquid drag, wind eduction, buoyancy effects and rise and fall of wastewater level. These individual phenomenon may work together to increase overall ventilation in the sewer, or may counteract each other to reduce air flow rates. Two experiments were completed in which the pilot sewer reach was force-ventilated at a rate of 12.2 m^3/day, which corresponds to 10 turnovers per day (the number of changes of air in the sewer per day) when the sewer is empty and to 200 turnovers per day when the sewer is half full (air velocity equal to 0.035 m/s).

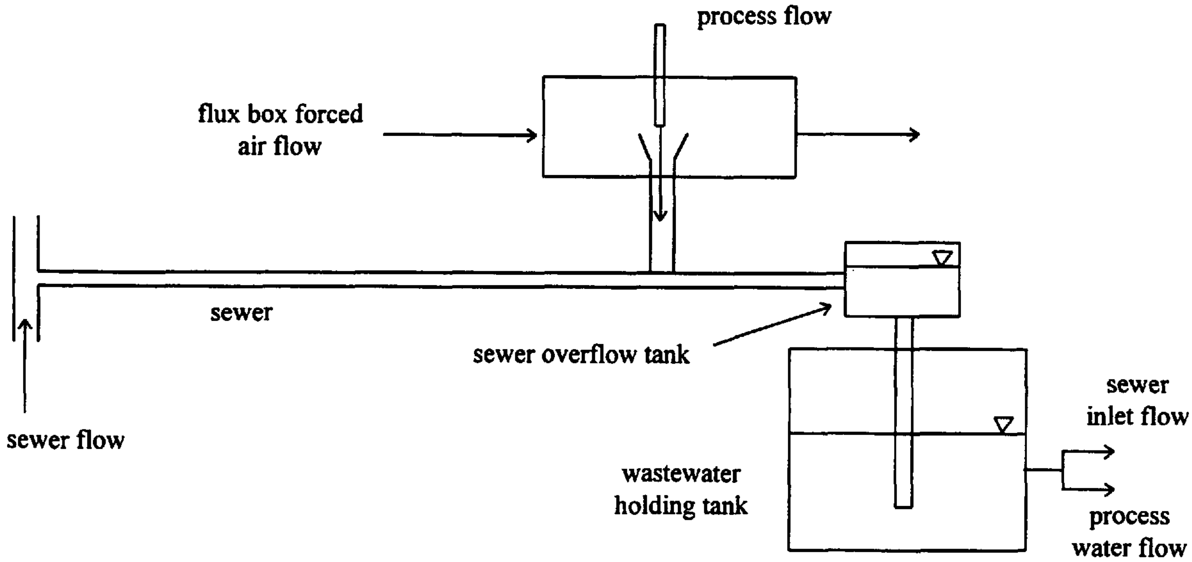


Figure 1. Schematic of experimental apparatus.

Major findings

The presence of a p-trap in the drain throat effectively reduced ventilation in the sewer to below measurable velocity. When the straight drain throat was in place and there was no process flow, extremely high velocities were measured in the sewer headspace (1.3 m/s at the inlet and 1.0 m/s in pipe), due likely to the fact that liquid drag and wind eduction were inducing air flow in the same direction, from sewer inlet to drain. The introduction of process flow led to a reduction in ventilation. This may have been due to liquid drag from process flow counteracting wastewater drag and wind eduction. Velocities for all free-ventilation experiments (except that with a straight drain and no process flow) were found to be from 0.1 to 0.2 m/s in the sewer headspace. For inactive drains without the p-trap, the emission rate of the four compounds ranged from 1.1 to 2.7 percent of the influent mass flow of the compound along the sewer. The p-trap reduced emission rates by approximately two orders of magnitude.

Process flow into the drain greatly increased HAP emissions, with flux box concentrations an order of magnitude higher for experiments which had process flow than for those that did not. Overall mass transfer coefficients, K_La, for experiments with low process flow (0.1 to 0.2 h^{-1}) were an order of magnitude greater than those for experiments with no process flow (0.02 to 0.07 h^{-1}). Increased process flow resulted in slight increases in mass transfer coefficients. For active drains, the emission rates of the four volatile compounds ranged from 3.6% to 53% of the influent mass flow of the compound into the drain funnel. The p-trap reduced emission rates slightly. It is postulated that emissions were primarily induced by rising bubbles in the p-trap escaping to the atmosphere. The bubbles result from gas entrainment by the falling wastewater stream into the p-trap. A model consistent with an air entrainment mechanism adequately simulated the observed emission rates.

Technical limitations

This study led to a novel characterization of HAP emissions from drains and related interactions of mass transfer mechanisms. However, an insufficient number of experiments was completed to be able to develop empirical relationships for extrapolating results to other drain operating conditions. There were difficulties with experimental results in that mass closure was not attained for the volatile tracer compounds used. Furthermore, it has been suggested that incomplete mixing of the tracer reservoir led to overestimation of stripping efficiencies, particularly at lower process flow rates. However, inlet and outlet ports in the reservoir were located to minimize short-circuiting. Also, if liquid volume measurements account for the freeboard in the tank, emission estimates based on liquid losses and gas measurements are similar.

These technical limitations are not large enough to refute a principal study finding of significant stripping losses from active trapped drains.

Brief #5

Lipton, S. 1990. Fugitive emissions. *Chemical Engineering Progress*. 85(6): pp. 42-47.

Overview

The principal discussion was a comparison between fugitive emission factors from refineries and chemical plants for sources such as valves, flanges, pump seals, and drains. The EPA's formulation for estimating chemical emissions was based largely on refinery emission factors. The authors suggested that this method overestimates chemical emissions. The Chemical Manufacturers Association (CMA) reasoned that emissions were overestimated because the EPA method did not account for differences in process design, operation, maintenance practices, and exposure standards between petroleum refining and chemical processing facilities. One example was that non-ethylene chemical plants have much lower emissions because of lower valve emission rates. There was no discussion regarding factors affecting drain emission rates, but it was concluded that emissions from chemical drains differ significantly from refinery drains.

Major findings

The average emission rate from drains at refineries was 0.07 pounds/hour/source (cited from AP-42 estimates). The average emission rate from drains at chemical plants was 0.0037 pounds/hour/source, cited from a revised set of emission factors at chemical plants (Radian, 1980).

Technical limitations

The emission factor gave no distinction to chemical composition, an important factor in mass transfer kinetics. An average emission factor cannot account for differences in operating conditions, drain dimensions, drain configurations, or ventilation rates. There was no quantitative discussion regarding factors that might cause the different emission rates between chemical drains and refinery drains. Other than differences in operating practices, chemical plants also differ from refineries since they are typically much smaller. Many chemical plants only have one or two process units. The average emission rates from similar process units may differ significantly from refineries since the emission rates for refineries are averaged over a larger number of units.

Brief #6

Pescod, M.B., and A.C. Price. 1982. Major factors in sewer ventilation. ***Journal of the Water Pollution Control Federation.*** **54(4): pp. 385-397.**

NOTE: This article did not deal specifically with drains, but the factors affecting drain ventilation are identical to sewer ventilation and should be included in the literature review.

Overview

The authors noted that the mechanisms that affect sewer ventilation included: wind eduction, wastewater drag, rise and fall of the wastewater level, temperature differences, and barometric pressure differences. The first two factors were approached experimentally. A model sewer reach was constructed, and it was determined analytically that a slotted extractor was the most practical vent design. Experiments were conducted to quantify the effects of wastewater drag, and qualitative observations were made using smoke tests. The combined effect of liquid drag and eduction was also considered, as well as the applicability of the ventilation model to field conditions.

Major findings

Within a sewer headspace, the air velocity decreased exponentially with increasing vertical distance from the water surface, and the air velocity at the water surface was always slightly less than the average water velocity. With higher water levels, the airflow was less affected by changes in the water velocity (although there was no mechanistic explanation for this phenomenon). Since energy transfer to the air space was considered to be an important parameter, a shape ratio was defined which includes the mean water surface velocity, the water surface width in the pipe, and either the unwetted perimeter or the hydraulic radius of the air space.

The average air velocity was plotted versus WVs/L and WVs/R, where W is the width of the water surface, Vs is the average water surface velocity, L is the unwetted perimeter of the air flow, and R is the hydraulic radius of the air space. The shape ratio was defined as either WVs/L or WVs/R. Both graphs (Vair vs. WVs/L or Vair vs. WVs/R) showed a reasonable correlation for the conditions tested. The values of WVs/L ranged from 0 to 0.6 and the values of WVs/R ranged from 0 to 5.0. In both cases the average air velocity increased with increasing shape ratio, and the mean air velocity approached a limiting value of approximately 0.2 m/s.

Tests indicated that when smoke was injected near the water surface the smoke tended to move close to the surface, indicating a low degree of diffusion. When smoke injection was evenly distributed, the entire air stream was filled with smoke far enough downstream, indicating air flow in the upper air space. At higher water velocities, the smoke velocity was less than the water velocity, suggested the presence of turbulent eddies.

The combined effects of liquid drag and wind eduction were not additive. When the wind effect was greater than the liquid drag and both were acting in the same direction, the air flow was approximately the same as with no liquid drag present. When the effects were operating in opposite directions, it was expected that the air flow would be reduced, although no experiments were conducted to verify this conclusion. The experimental results were reasonably consistent with field data.

Technical limitations

The major shortcoming of this study was that the sewer reach was constructed such that it would always be well-ventilated; the risers were a short distance apart, the manhole covers were well-ventilated, and the water flowrates were relatively high.

Brief #7

Radian Corporation. 1977. *Revision of Emission Factors for Petroleum Refining.* EPA-450/3-77-030.

Overview

This report describes a study completed by the Radian Corporation to revise AP-42 emission factors, some of which had not been revised since 1958. Although several adjustments were made to unit operations emission factors, fugitive emission factors were not revised due to insufficient data. It was acknowledged that good maintenance practices resulted in lower emission factors than current AP-42 factors. Additions were made to the existing fugitive emission factors, in so much as controlled emission rates were reported and appropriate control technologies were listed where available. Fugitive emissions were given high priority because they were stated to represent the second largest source of refinery emissions and the source with the highest potential for emission factor improvement.

Major findings

The most important results presented in this report did not concern fugitive emissions, but instead focused on unit operation emissions. The authors only alluded to the importance of investigating and controlling fugitive emissions.

Technical limitations

The major limitation of this work was the omission of revised fugitive emission factors. Process drains were not specifically included in the discussion.

Brief #8

Radian Corporation. 1980. ***Assessment of Atmospheric Emissions from Petroleum Refining: Volume I, Technical Report.*** **EPA-600/2-80-075a.**

Overview

This report presents the findings of a three year study carried out at 13 refineries to assess the environmental impact of fugitive and process emissions. Nonmethane hydrocarbon emission rates were measured from drains and several other sources, and emission factors were calculated for major fugitive sources. Nomographs were developed to illustrate the relationship between hydrocarbon concentration at a leaking source (screening value) and the leak rate.

Emissions were measured from both "baggable" and "non-baggable" sources; process drains were classified as the former. In each of the 13 refineries, 6 - 9 process units were selected for the study and a total of 257 drains were screened. The choice parameter for drains was "service," i.e., each drain was either classified as active or wash-up. A portable hydrocarbon analyzer was used for the screening study and was positioned around the perimeter of the drain as well as across a traverse. If the maximum concentration reading from either of these techniques was greater than 200 ppmv hydrocarbon, the drain was bagged for further sample collection.

The sample method used was termed a "dilution" or "flow-through" method. Major components included a 2.5 cfm vacuum pump to draw air through the system, a cold trap to condense water and hydrocarbons upstream of sample collection, a polyester bag for source enclosure and a magnehelic to monitor pressure inside the enclosure. A schematic of the sample train is provided in Figure 1.

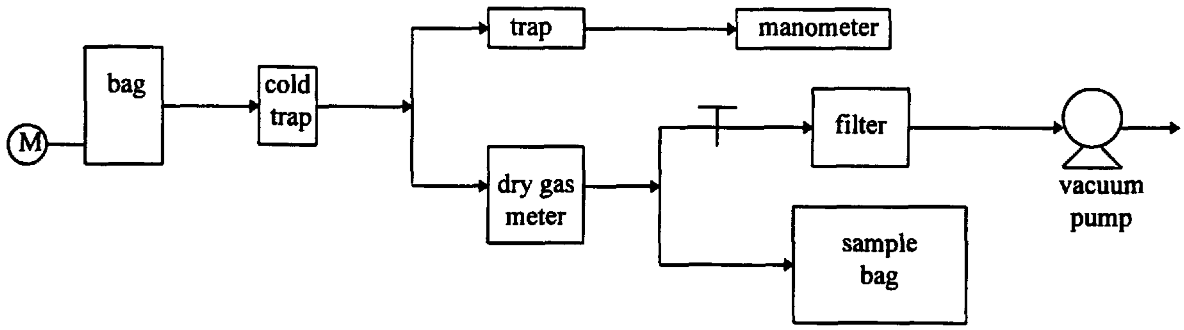


Figure 1. Schematic of sample train for baggable source.

The enclosure was kept at a slight negative pressure to prevent escape of hydrocarbons from the bag. To begin sampling, the pump was turned on and the portable hydrocarbon analyzer was used to determine when steady-state was reached in the system. Air flowrate, temperature and pressure were monitored at all times and the sample bag was flushed once prior to being filled. Background air samples, condensate from the cold trap and the sample bag were all transported to a laboratory for analysis. For large leaks, the vacuum pump was disconnected and the passive air flowrate through the system was measured. In this case, the emission rate was assumed to be the product of the flowrate and the concentration of organics in the cold trap.

Results indicated that 49 drains had screening values greater than 200 ppmv (19.1%), and the 95% confidence interval for this value was 14 - 24%. Due to a high level of skewness in the data, a log-normal distribution was used to characterize the leak rate of drains. Since many drains were found to not be leaking, a mixed distribution was modeled (a lognormal distribution with a discrete probability mass at zero). The emission factor estimated for drains was 0.070 lb/hour-source, as reported in AP-42. An attempt was made to investigate the effect of process variables on emission factors, but was unsuccessful due to the lack of independence between process variables as they naturally occurred.

Major findings

A linear relationship was proposed to determine the leak rate of a source, based on its screening value:

$$\log_{10} L = B_0 + B_1 \log_{10} M$$

where:

L	=	nonmethane hydrocarbon leak rate, lb/hr
B_0, B_1	=	constants, intercept and slope respectively
M	=	maximum screening (or rescreening) value, ppmv

Regression of data for 13 drains in light liquid service allowed the following determination of constant values: $B_0 = -2.38$ and $B_1 = 0.60$, with an r^2 value of 0.10. For drains in heavy liquid service (17 were sampled), $B_0 = -3.35$, $B_1 = 0.51$ and $r^2 = 0.60$. While this correlation is better than the former, both correlations may be regarded statistically as weak. When investigating correlations between leak rate and screening value for the broad category of drains, 61 data pairs were used and $B_0 = -4.9$, $B_1 = 1.10$.

Technical limitations

The sampling technique used to measure emissions from drains was invasive and altered the natural ventilation rate and patterns of the drain. By maintaining a negative pressure in the bag enclosure, the concentration driving force for mass transfer of contaminants to the gas phase was enhanced. By forcing air through the system, hydrocarbon emission rates were increased.

The only parameter of interest in characterizing process drains was service type (i.e., whether a drain was active or in washup mode). The fraction of straight versus trapped drains was not provided, and therefore, no differentiation between controlled and uncontrolled emission rates was made.

An investigation of the effects of various source operating conditions was unsuccessful.

Brief #9

Radian Corporation. 1980. Assessment of Atmospheric Emissions from Petroleum Refining: Volume III, Appendix B. EPA-600/2-80-075c.

Overview

This document provides a compilation of the raw data collected to determine EPA's AP-42 emission factors for process drains. All sampling methods and data analysis have been described in previous volumes of the report. This appendix provides several tables, including leakage rates and frequencies, confidence intervals for calculated leak rates and an estimation of the total number of process drains and other source types in 15 specific process units.

Major findings

A total of 257 process drains was screened and the measured leak rate for each of these has been summarized in Table 2 according to several leak range categories.

Table 1. Summary of source leakage rates and total leakage from process drains.

	Leaking sources within range			Total leakage within range	
Leak range (lb/hr)	No.	% of leaking sources	% of total sources screened	Total leakage (lb/hr)	% of total source of leakage
> 1.0	4	8.2	1.6	7.3958	61.6
0.1 - 1.0	12	24.5	4.7	3.9615	33.0
0.01 - 0.1	17	34.7	6.6	0.5939	4.9
0.001 - 0.01	13	26.5	5.1	0.0630	0.5
0.00001 - 0.001	3	6.1	1.1	0.0013	0.0
	49	100	19.1	12.0155	100

Confidence intervals were also included in the report for calculated leakage rates for drains and other source types. The data for process drains has been presented below in Table 2.

Table 2. Confidence intervals for mean and individual leak rates.

Value (ppmv)	Predicted mean leak rate (lb/hr)	90% confidence interval	
		Mean leak (lb/hr)	Individual leak (lb/hr)
1	$8.1x10^{-5}$	($1.5x10^{-5}$, 0.00045)	($2.0x10^{-6}$, 0.0032)
200	0.028	(0.016, 0.048)	(0.0010, 0.76)
500	0.077	(0.050, 0.12)	(0.0029, 2.1)
1,000	0.16	(0.11, 0.25)	(0.0061, 4.4)
3,000	0.55	(0.32, 0.95)	(0.020, 15.0)
5,000	0.97	(0.51, 1.8)	(0.035, 27.0)
10,000	2.1	(0.96, 4.5)	(0.073, 59.0)

A brief discussion of estimating the number of drains and other source types in a process unit was included in the report. The recommended technique for estimating the number of process drains was to multiply the number of pumps by a factor of 2.6.

Technical limitations

The limitations of the study were discussed in Brief #8. It is important to indicate the relatively large confidence intervals for individual sources as listed in Table 2. This may suggest the difficulty in applying an empirically determined leak rate or emission factor to a specific drain.

Brief #10

Radian Corporation. 1990. *Industrial wastewater volatile organic compound emissions - background information for BACT/LAER determinations.* EPA-450/3-90-004.

Overview

Emissions for ten different cases were considered in this report. The cases encompassed emissions from the following structures: drains, manholes, and sewer lines. Three different cases pertained to drains (see Figure 1): air induction by process flow and wastewater flow (case A1), air induction with only wastewater flow (case A2), and air exhaust with only wastewater flow (case A3). The drain dimensions and wastewater flowrate were chosen from "typical values" observed in chemical plants. The fraction emitted from drains was determined for five different pollutants. The overall fraction emitted was considered to be the average of the three drain cases.

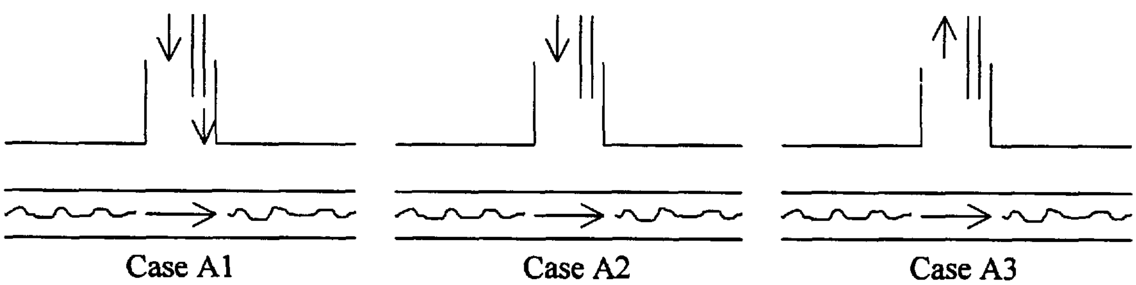


Figure 1. Three drain cases for BACT/LAER calculations.

Major findings

For case A1, the fraction emitted (F) was calculated as:

$$F = \frac{(Arr)(0.25)(0.0121 / Ta)K}{(Arr)(0.25)(0.0121 / Ta)K + 0.0555}$$

where:

Arr = area ratio in sewer headspace (area of air/area of water)

K = partition coefficient

Ta = air temperature (K)

Water density = 0.0555 mol/cm^3

Air density = P/RT = (1 atm)/(82.06 cm^3-atm/g-mol K)(T) = 0.0121/Ta mol/cm^3

The fraction emitted was therefore based on the ratio of moles of gas to total moles of flow in the sewer (see technical limitations). Air flow was estimated as a linear fraction of water flow.

For cases A2 and A3, the fraction emitted was assumed to be induced by wind eduction. An equivalent pressure driving force due to ambient wind was defined using Bernoulli's equation. The pressure driving force from the air velocity was then equated with the frictional losses in the sewer using the energy equation:

$$dP = (V_{wind})^2(\rho)/2g_c$$
$$dP = (1 + Ke + 4FL/D\ Arr^2 + 4FL2/D2 + K1)(V_{drain})^2(\rho)/2g_c$$

where:

dP = pressure driving force

V_{wind} = wind velocity

V_{drain} = air velocity in the drain

ρ = density of air = 0.0012 g/cm^3

g_c = 981 g-cm/g_f-s^2

Ke = diameter change coefficient (assumed to be 0.31)

F = friction factor of air (assumed to be 0.006). Although not defined, this is assumed to be Fanning's friction factor which is applicable to laminar and turbulent regions of flow.

L = length of sewer

D = hydraulic diameter of sewer headspace (four times hydraulic radius)

Arr = area ratio (area of air/area of water)

L2 = combined height of entrance and exit drain risers

D2 = diameter of drain riser

K1 = loss coefficient (assumed to be 4)

Symbols for all variables are reproduced exactly as defined in the Bact-Laer report.

The fraction emitted was then based on the simultaneous solution of the two equations (see technical limitations).

Using "typical" values observed in chemical plants for drain dimensions and operating conditions, the fraction emitted was determined for five pollutants as illustrated in Table 1.

Table 1. Emission estimates for drains

Compound	Fraction Emitted, F (T=40° C)
1,3-Butadiene	0.57
Toluene	0.061
Naphthalene	0.011
1-Butanol	0.000087
Phenol	0.0000044

Technical limitations

The VOC was assumed to be in chemical equilibrium between water and air. This assumption tends toward overestimation of emissions. The calculations for each case appeared to double count emissions, since individual emissions were added together such that all flows were considered to be exiting the drain. For case A1 the air velocity was assumed to be one-fourth the water velocity, so that

$$Q_G/Q_L = (V_G A_G)/(V_L A_L) = (Arr)(V_G/V_L) = (0.25)(Arr)$$

Substituting this expression in the equation for F (case A1) and multiplying through by Q_G leads to:

$$F = \frac{Q_G \rho K}{Q_G \rho K + \rho w Q_L}$$

This equation was the ratio of (molar) air flow to total (molar) flow. The assumption that the air velocity was one-fourth the water velocity was larger than typical values given for the entrainment rate of a free jet.

For cases A2 and A3, two of the headloss terms were not identified explicitly (K1 and the loss term equal to 1.0). These terms presumably accounted for entrance and exit losses, respectively. The entrance loss coefficient was assumed to be 4.0, a value that was higher than typical values given for entrance losses. The loss through the elbow was approximated by the change in diameter. A more appropriate method would be to use an elbow loss coefficient or to treat the elbow as branch flow across a tee. The elbow headloss was only counted once, thus not accounting for the exit elbow. Another limitation was that the friction factor was assumed to be a value of 0.006 irrespective of the air velocity, when in reality it was a function of the air velocity (based on the equivalent Reynolds number). An iterative solution should have been used to find the air velocity in the drain. This drawback will be most significant for long distances between drains since the headloss in the channel becomes more important for this case.

The overall fraction emitted was limited in utility since it was assumed to be the average of three cases with specific operating conditions. This average emission factor did not include all possible flow scenarios (e.g. process flow with no wastewater flow, buoyancy driven emissions, etc.). The ventilation calculations did not account for the fact that the combination of ventilation mechanisms can be additive or counteractive.

Brief #11

Research Triangle Institute. 1988. ***Estimation of air emission factors from airflow in wastewater collection systems.*** **USEPA Contract No. 68D10118.**

This paper was identical to the discussion of ventilation rates from EPA-450/3-90-004.

Brief #12

Schaich, J.R. 1991. Estimate Fugitive Emissions from Process Equipment. *Chemical Engineering Progress*. Vol. 87: pp 31-35.

Overview

This paper listed and described five methods for estimating fugitive emissions from process equipment in the synthetic organic chemical manufacturing industry (SOCMI). The relative accuracy of each method was discussed, as well as the degree of monitoring requirements, in order to aid the reader in choosing the most appropriate method. The first of these methods, and the least complex, is to employ SOCMI emission factors which have been defined for various emission sources, such as pumps, flanges and valves. Similar emission factors from the petroleum refining industry have been adapted for this purpose. The estimation technique has no monitoring requirements, and simply involves multiplication of the appropriate factors with the number of each type of source in the unit or plant. It was noted that an improvement on this technique may be made by attempting to characterize all of the potential emission sources in a plant as either leaking or not leaking, and by employing the correct proportion of "leak/no leak" factors to each source category. However, some sampling of potential sources is required in order to estimate the percentage of each source that may be considered to be leaking. The third technique which was presented involved the use of stratified factors, where further sampling must be completed in order to ascertain the proportion of sources that is emitting in the low, medium and high ranges, and by applying the appropriate emission factor to the corresponding number of sources. Correlation curves were also presented which provide a continuous relationship between concentration measured at the source and emission rate. Finally, the most accurate and most sampling-intensive approach described for estimating fugitive emissions involved development of unit-specific correlations. The author stated that this method should provide the most accurate emission estimate, but requires further bagging and screening data. Actual emission rates were determined for a specific process in ranges below, within, and above the upper detection limit of the screening instrument. It was noted that correlation curve of leak rate vs. screening value can then be developed that is specific to the unit tested.

Major findings

There was no original work presented in this paper. However, it did provide a concise and useful summary of EPA's currently recommended method for estimating fugitive emissions from equipment leaks, such as flanges and valves. Information was provided for obtaining a guidance document from the Chemical Manufacturing Association, which has also been included in this literature review.

Technical limitations

There was no specific discussion of emissions from process drains, nor were emission factors and correlation curves presented for this source type. It may be assumed, however, that such values would correspond to those listed in EPA's AP-42 document. Although most likely beyond the intended scope of work, a brief description of acceptable sampling techniques would have proven helpful to the reader.

Brief #13

USEPA. 1977. *Compilation of Air Pollutant Emission Factors. Third ed.* Research Triangle Park, N.C. EPA AP-42. Section 9 - Petroleum Industry.

Overview

This document provides a list of emission factors for various processes included in petroleum refineries, and for fugitive emissions associated with waste streams and product handling. Process emission factors for particulates, sulfur oxides, carbon monoxide, total hydrocarbons, nitrogen oxides, aldehydes and ammonia were provided for the following refinery components: boilers and process heaters, catalytic cracking units, coking units, compressor engines, blowdown systems and column condensers. Fugitive emission factors in units of lb/hr-source and kg/day-source were provided for pipeline and open-ended valves, flanges, pump and compressor seals, process drains, relief valves, cooling towers and oil/water separators.

Process drains were listed as having an emission factor of 0.070 lb/hr-source (range: 0.023 - 0.20), or 0.76 kg/day-source (range: 0.25 - 2.2). This factor is higher than those listed for all of the following sources: pipeline valves, open-ended valves, flanges, pump seals (heavy liquid) and compressor seals. The report stated that sources in gas/vapor service have higher emission rates than those in heavier stream service, and that the size of the source (valves, flanges, seals and drains) does not affect leak rates. It was also stated that emission factors are independent of process unit or refinery throughput.

Analysis of a hypothetical refinery coupled with emission factors found valves to be the greatest source of fugitive emissions due to their number and relatively high emission factors. The total quantity of fugitive VOC emissions in a typical oil refinery with a capacity of 330,000 barrels (52,500 m^3) per day was estimated to be 45,000 lb (20.4 MT) per day. This refinery was assumed to have 11,500 valves, 46,500 flanges, 650 process drains, uncovered oil/water separators and cooling towers, as well as pump seals, relief valves and compressors. The uncovered oil/water separators were responsible for 71% of total emissions, while valves accounted for 15%, and drains accounted for only 2%. Nevertheless, the 2% contribution was estimated to be 365 tons/year.

Major findings

This document currently provides regulators and industry with the simplest means of predicting fugitive VOC emissions from refinery process drains. It includes drains as a potential source of emissions and assigns a relatively high emission factor. However, in the context of an entire refinery, the total emissions from drains appears to be less important than other potential sources listed due to their number. The use of traps and covers were briefly mentioned as possible emission control measures.

Technical limitations

By assigning a fixed emission factor to a source with such potential variability as a process drain, the authors have over-simplified a complex situation. The large range of values for which emission factors are within a 95% confidence level is indicative of the high degree of uncertainty associated with the factors. Characteristics including operation patterns, flowrate, discharge position, process flow temperature and ventilation should be understood before assuming a given emission rate of VOCs from an industrial process drain. There was no description given of how the emission factors were calculated, or under what conditions they were obtained.

Brief #14

USEPA. 1980. *Draft Environmental Impact Statement, Benzene Fugitive Emissions - Background Information for Proposed Standards, Final.* EPA 450/3-80-032a.

Overview

This report provided a discussion of the logic used to develop benzene emission standards from leaks and spills at petroleum refineries, assuming that these were the major fugitive sources. Drains were discussed briefly and listed as a potential source, and it was stated that, "...if leakage and spills are minimized, benzene emissions from drains are expected to be slight." Emission factors for various types were listed as referenced from Wetherold and Provost (1979), with the emission rate for process drains given as 0.032 kg/hr-source.

The bulk of the report involved application of five alternative regulation strategies applied to three model plants to examine potential fugitive emission reductions. Factors were then developed to represent "controlled" and "uncontrolled" sources. There was minimal discussion of drains in this section, which dealt primarily with leak detection and repair strategies. There was, however, reference to drains in the sense that they could be leaking or non-leaking, and one study completed at a Phillips plant in Sweeny, Texas, found 6% of inspected process drains to be leaking (9 of 150).

Major findings

Results from several inspections of chemical plants and refineries were presented which illustrated the relative frequency of detectable leaks from equipment. Only one reference to process drains was provided.

Technical limitations

The major flaw of this study was that the use of single emission factors to estimate fugitive emissions from process drains was encouraged. There was no discussion of parameters affecting emission rates, other than to characterize a drain as either leaking or not leaking. The definition of a leaking drain was not provided, and may refer to a drain in service as opposed to one that is not in service. Process drains were given much less attention than valves and flanges.

Brief #15

USEPA. 1982. ***Fugitive Emission Sources of Organic Compounds - Additional Information on Emissions, Emission Reductions and Costs.*** **EPA 450/3-82-010.**

Overview

The purpose of this report was to provide information regarding the methods used to determine fugitive emission factors for the synthetic organic chemical manufacturing industry (SOCMI). The authors summarized several studies intended to assess emission rates from various sources within the petroleum refining industry. They attempted to develop emission factors for SOCMI based on these results. The following studies were presented:

1) Petroleum refinery study (1980, EPA 600/2-80-075c): 15 units were studied at 9 refineries and 20 - 40 drains were examined. Sources were enclosed, presumably by using a bagging technique, and an organic vapor analyzer (OVA) was used to screen for leaking sources. Leak frequencies were reported for some types of sources, but not for drains.

2) EPA 4-unit study (1980): Four SOCMI units were studied, but not enough information was collected for results to be technically sound. Results were not used in developing standards.

3) EPA 6-unit study (1978): Data were collected on the percent of tested sources that were found to be leaking (concentrations greater than 10,000 ppmv methane). Of the 39 drains tested in one unit, 10% were leaking. An OVA was placed as near to the sources as possible, but no enclosure method was described.

4) DuPont study: Only pumps and valves were tested at two plants, using polyvinylfluoride bags and an OVA.

5) Exxon cyclohexane study: Valves and seals were tested at Exxon's Baytown plant.

6) EPA 24-unit study (1980): Leak screening was completed at 24 SOCMI units whose boundaries were defined to include feed streams and product/byproduct delivery lines.

The following results for drains were presented:

Service	Number screened	% not screened	% screened with 10,000 ppmv	95% confidence interval
gaseous	83	23.1	2.4	(0.3, 8.4)
light liquid	527	1.9	3.8	(2.3, 5.8)
heavy liquid	28	0.0	7.1	(0.9, 23.5)

Overall, 4% of SOCMI sources had screening values >10,000 ppmv OVA-methane and 5% had >10,000 ppmv OVA-hexane.

Information from five new studies was also provided, but four of these (German Study, Union Carbide, Radian maintenance study and Allied & Kemron) did not measure emissions from drains. The fifth was completed by the South Coast Air Quality Management District (SCAQMD), which screened two petroleum refineries. The following results were presented:

Service	Sources subject to rule			Sources exempt from rule		
	screened	>10,000	%	screened	>10,000	%
light liquid	87	2	2.3	6	1	16.7
heavy liquid	-	-	-	31	0	0.0

It was determined that the Petroleum Refinery study and the 24-unit study were the most appropriate for development of SOCMI emission factors. Some differences existed between the two industries, and a method was presented to account for such differences when adopting petroleum refining factors for use in SOCMI. The preferred method for obtaining SOCMI emission factors was to determine leaking and non-leaking source emission factors from the refinery data set and to apply these factors to SOCMI leak frequencies to yield SOCMI factors for an average unit.

Major findings

This report provided a concise and seemingly complete summary of all relevant screening studies that assessed fugitive emissions from petroleum refineries and from SOCMI units. Process drains were evaluated in several of these studies and information on relative leak frequency for drains was presented.

Technical limitations

Sampling techniques were not described in detail for each study, and so it is difficult to fully evaluate the results. It appears that use of a bagging method with an organic vapor analyzer was used in some cases. However, the term "emissions" is a misnomer in most cases in this document, since natural air flow rates through process drains were not measured. Quantification of both VOC concentration and ventilation rate are required for calculation of emission rates from drains. A clear definition of a "leaking" drain was not provided, and therefore it must be assumed to be a drain in service around which organic vapors were measured at concentrations greater than 10,000 ppmv.

Brief #16

USEPA. 1985. ***VOC Emissions from Petroleum Refinery Wastewater Systems - Background Information for Proposed Standards.*** **EPA-450/3-85-001a.**

Overview

This paper presented a description of typical process drain systems. A large refinery could have several thousand drains, many of which are open to the atmosphere. Drain openings are often used for more than one piece of equipment. Some drains are closed to the atmosphere and are connected directly to lateral sewer lines. Four different types of drain configurations were discussed: straight riser, p-type drain, seal pot drain, and a closed drain. The straight riser was stated to be the only drain configuration that does not provide a liquid seal to prevent emissions to the atmosphere.

The following factors were noted to affect VOC emissions from drains: rate of molecular diffusion through air and water, rate of convection, volatility of compounds in the wastewater stream, characteristics of the wastewater discharge, wastewater temperature, ambient temperature, wind speed, drain and pipe dimensions, and concentration of compounds in the air and water. A model was presented to account for the transport of volatile compounds by diffusion.

Two additional sections of this document have relevance to emissions from process drains: a discussion in Chapter 3 dealing with previous studies where emissions from drains were measured, and an analysis in Chapter 4 of techniques for controlling emissions from process drains.

A 1958 study in Los Angeles County was described, in which an emission factor for drains was presented. However, the factor was based more on qualitative observation than on quantitative information, and data presented were insufficient to estimate VOC emissions from drains. A study published by the EPA in 1980 was stated to be the only exercise in which emissions from drains were actually measured. A total of 49 drains in 13 refineries were sampled, and the ratio of sealed to unsealed drains was unknown. Since the refineries sampled were representative of late 1970's design practice, a time when it was not common to seal drains, it was assumed that the majority of drains were uncontrolled. Finally, a screening study completed in 1983 was presented. No sources were bagged for this study, and no emission measurements were made.

The results of the above screening study were used to examine the potential effectiveness of various types of control techniques for process drains. The following factors which affect the performance of water seals were listed: 1) drainage rate, 2) temperature and composition of liquid entering the drain, 3) diameter of the drain, and 4) ambient atmospheric conditions. An anecdotal description of a completely closed drain was given, in which the vertical riser was closed with a flange. VOC emissions were assumed to be completely eliminated within that process unit.

The effectiveness of controls was evaluated using two techniques: physical comparison of leak rates from controlled and uncontrolled drains, and a theoretical analysis of mass transfer rates under controlled and uncontrolled conditions.

For the first method, three refineries were visited and three types of drains were identified: controlled, uncontrolled with a water seal and controlled with removable caps. The first comparison was made between controlled and uncontrolled drains, in which the average leak rates from each were determined to be 0.00353 lb/hr and 0.00592 lb/hr, respectively. This indicated a control effectiveness of 40%. The authors then compared leak rates from capped drains with those associated with a removed cap. Data pairs were obtained for 76 such drains and leak rates were reduced by 50% on average (the reduction would be 74% with the removal of an outlying data point).

Next, a theoretical analysis was completed for three drain scenarios: an uncontrolled drain, a p-trap water sealed drain with no contaminated water and a p-trap water sealed drain saturated with benzene from a contaminated stream. Two mass transfer mechanisms were modeled. These included molecular diffusion through the water seal and convection. The latter was assumed to be 150 times more effective than the former. It was also assumed that the vapor in the sewer headspace was saturated with hydrocarbons. The following results were obtained:

Configuration	Emissions due to diffusion (g/day)	Emissions due to convection (g/day)	Total emissions (g/day)
uncontrolled	2.1	312	315
uncontaminated controlled	0.0026	-	0.0026
contaminated controlled	3.7	551	555

These results suggest that a clean water seal could reduce emissions by 99.9%. A contaminated water seal was predicted to lose its effectiveness, with 1.7 times the emissions of uncontrolled drains. These results concur with observations from the screening study, in which 73 of 76 capped drains had little contamination and also had screening values of less than 100 ppm.

Major findings

The following factors were noted to affect diffusion through the air: temperature, drain dimensions, solution density, and concentration gradient. The rate of molecular diffusion for volatile organics through air was given as:

$$N_A = \frac{A D_v \rho_m}{BT} \ln\left(\frac{1-Y}{1-Y_i}\right)$$

where:

- N_A = Flux (mol/s)
- A = exposed surface area (cm^2)
- D_v = diffusion coefficient (cm^2/s)
- ρ_m = molar density (mol/cm^3)
- BT = diffusion path length
- Y_i = initial concentration (atm)
- Y = final concentration (atm)

This document also provided a detailed discussion of the potential effectiveness of control measures for reducing VOC emissions from process drains. Several techniques were used to determine emissions reductions. Screening studies indicated that 40 - 50% emission reductions could be obtained with a water seal or cap, and theoretical analyses showed that even great reduction is possible if controlled drains are well-maintained.

Technical limitations

Estimating emissions by modeling molecular diffusion is not useful for most practical applications. Advection is also a dominant mechanism for most process drains.

Actual emission measurements were not made for this report, and all conclusions were based on drain screening values. It was assumed that the following relationship, presented in "Assessment of atmospheric emissions from.....1980", (Brief #8, p. A-21) accurately predicted leak rates:

$$\log_{10}(\text{leak rate}) = -4.9 + 1.10 \log_{10} (\text{maximum screening value}).$$

The model used to theoretically calculate emissions from sealed and unsealed drains was not derived in the report and was therefore difficult to interpret and evaluate.

Brief #17

USEPA. 1988. Control of volatile organic compound emissions from industrial wastewater, preliminary draft.

Overview

The mechanisms associated with VOC emissions from industrial process drains were described in this report. Although many factors affect the rate of VOC emissions, it was estimated that roughly 90 percent of the VOCs entering the wastewater will volatilize during collection and treatment. Wastewater entered the collection system through process drains, many of which were open to the atmosphere. The authors noted that emissions can occur when drains were open to the atmosphere since pollutants in the wastewater stream volatilized in an attempt to reach equilibrium with the surrounding air. One common control strategy was to retrofit all open drains with p-traps or water seal pots.

Emissions from drains occured via diffusion and/or advection. It was noted that in the wastewater stream, organics will tend to volatilize, increasing the concentration of the sewer headspace. The resulting concentration gradient between the sewer headspace and the ambient air was noted to induce diffusion to the atmosphere. Similarly, it was suggested that a temperature gradient between the wastewater and the ambient atmosphere will induce air flow from the sewer, causing convective mass transfer of VOCs.

Factors affecting drain emission rates were noted to include pollutant properties, drain dimensions, wastewater temperature, and ambient conditions. Pollutant volatility was noted to be the most important physical property. Emissions were noted to increase with an increase in drain diameter (more exposed surface area and lower resistance to air flow) or a decrease in the length of the drain riser (reduced headloss). Emission rates were affected by the ambient temperature and wind speed. Wind created a pressure gradient by developing a dynamic pressure drop across a drain opening.

Major findings

No major findings were presented in this report.

Technical limitations

Methods for estimating VOC emission were not presented.

Brief #18

USEPA. 1994. *Air emissions models for waste and wastewater.* EPA-453/R-94-080A.

Overview

This report considered emissions for nineteen different cases. The cases included emissions from the following structures: drains, manholes, conduits, stacks, trenches, lift stations, sumps, and weirs. Five different cases pertained to drains: air entering the sewer that was induced by process flow and wastewater flow (case A1), air entering the sewer with only wastewater flow (case A2), air exiting the sewer with only wastewater flow (case A3), a j-trap drain with no process flow (case E1), and a j-trap drain with process flow (case E2). The first three cases were identical to those used for the BACT/LAER calculations (Radian Corporation, 1990). The remaining two cases (see Figure 1) assumed that the j-trap was sealed with wastewater. For cases A1-A3, a fraction emitted was determined (see brief #10). For case E1 an emission rate was determined and for case E2 a fraction emitted was determined.

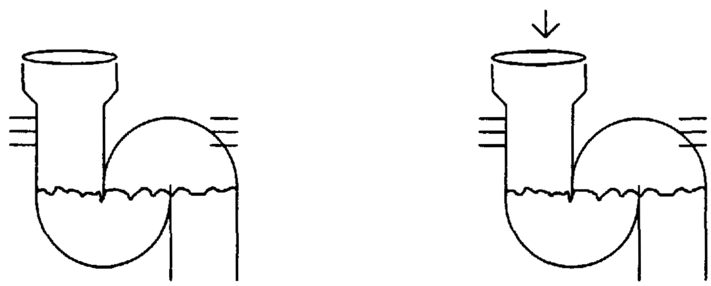


Figure 1. Two j-trap drain cases.

Major findings

Air emissions from a j-trap sealed with wastewater and with no process flow was estimated from the following equations:

$$D_{eff} = \frac{h^2}{t}$$

$$E = K\frac{18}{24400}\frac{D_{eff}}{d}A$$

where:

D_{eff} = effective diffusivity (cm^2/s)
h = waste displacement (cm)
t = period of displacement (s)
E = emission rate (g/s per weight fraction in the wastewater)
K = partition coefficient
18 = weight of a mole of water (g/mol)
24400 = volume of a mole of gas (cm^3/mol)
d = distance from the waste level to the top of the hub (cm)
A = hub cross-section area (cm^2)

For air emissions from a j-trap sealed with wastewater and with continuous process flow, empirical correlations for mass transfer coefficients were determined using data from Enviromega Ltd. (1993). It was noted that extrapolation beyond the experimental range of the data should be done with caution. The gas diffusion coefficient was given by:

$$k_g = 0.178\left(\frac{D_g}{0.088}\right)^{0.66}$$

where:

K_g = gas phase mass transfer coefficient (m/s)
0.088 = reference gas diffusion coefficient (cm^2/s). The report does not specify whether this is the diffusivity coefficient for benzene in air.
D_g = gas phase diffusion coefficient (cm^2/s)

The liquid diffusion coefficient was given by:

$$k_l = 0.0041\left(\frac{D_l}{0.0000088}\right)^{0.66}$$

where:

k_l = liquid phase mass transfer coefficient (m/s)
V = process flow velocity (cm/s)
0.0000088 = reference liquid diffusion coefficient (cm^2/s). This report does not specify whether this is the diffusivity of benzene in water.
D_l = liquid phase diffusion coefficient (cm^2/s)

The overall mass transfer coefficient was given by the combined gas and liquid phase resistances:

$$K_o = \left(\frac{1}{K_l} + \frac{1}{40.9\,K_g K} \right)^{-1}$$

where:

K_o = the overall mass transfer coefficient based on the liquid concentration (m/s)
K = partition coefficient

The fraction of pollutant emitted was given by:

$$f_{air} = 1 - \exp\left(-\frac{K_o A}{q} \right)$$

where:

f_{air} = fraction of the component emitted to the air
A = the area of the exposed surface (cm^2)
q = liquid flow rate (cm^3/s)

The area of the exposed surface was assumed to be the surface area of the falling film of the process flow.

Technical limitations

A major limitation was that mass transfer coefficients were based on empirical correlations rather than on fundamental principles. The Enviromega Ltd. (1993) data included only a few loading conditions and drain configurations. Refer to brief #4 for a more detailed discussion of technical limitations of the Enviromega Ltd. (1993) data. Refer to brief #10 for a more detailed discussion of technical limitations of BACT/LAER calculations. For calculations for a j-trap with process flow, the model only accounted for emissions from the falling film. Emissions will also occur from splashing within the trap.

For calculations with no process flow, the emission rate was based on the rate of molecular diffusion of volatile compounds through air. This approach assumed a uniform displacement of wastewater in the water seal of the j-trap. In reality, this water seal was probably more susceptible to shock loads such as barometric pumping. Air emissions will tend to be more concentrated but less frequent. A modified form of this equation was used in USEPA (1985). Refer to brief #16 for a more detailed discussion of this molecular diffusion equation.

Brief #19

Wilkness, R. 1994. SCAQMD-approved protocols for Texaco bagging study. WSPA, internal memo.

Overview

A method was presented for sampling and reducing emissions from specific sites such as flange, valves, seals, compressors, caps elbows, tees and drains, among others. The method consisted of covering the source with a tent or bag and then sealing the enclosure to isolate the leak from the ambient air. A vacuum aspirator was used to pull gas through the system while monitoring pressure and temperature. Reactive organic gases (ROGs) were measured using an organic vapor analyzer (OVA), and oxygen content was measured using an oxygen/combustible gas meter. Canisters may be used to collect emitted gases. Nitrogen was a preferred purge gas and was controlled by a pressure regulator to maintain a slight positive pressure inside the enclosure. A procedure was provided that describes calibration and sampling techniques. Figure 1 illustrates the major components of the sampling system for an enclosed drain.

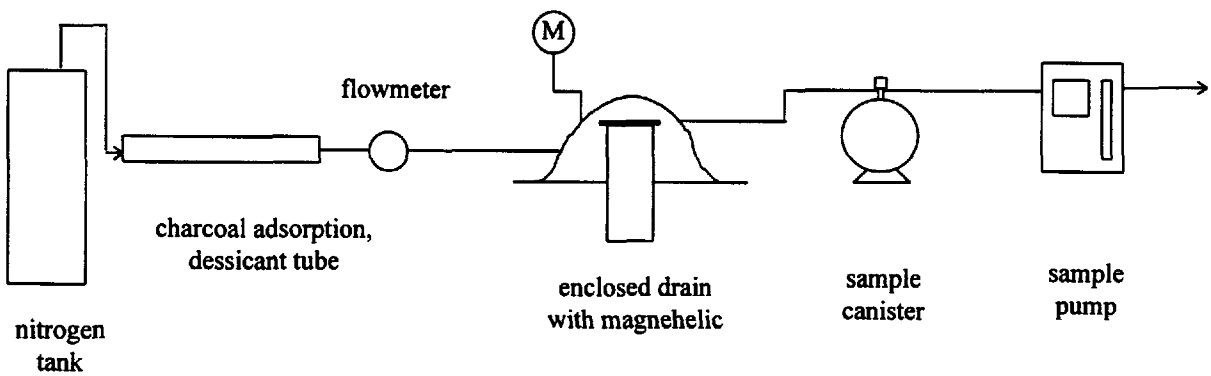


Figure 1. Schematic of sample train for bagging study.

A statement regarding adaptation of this procedure for drains suggested setting the flow rate of the pump equal to the ambient wind speed since "fugitive emissions from drains is primarily driven by local wind velocities."

Major findings

The memorandum provides a well-defined method for determining VOC emission from process drains.

Technical limitations

By covering the drain and isolating it from the natural environment, several mass transfer mechanisms will be affected, the most important of which involve ventilation patterns around a drain. Attempting to simulate wind effects is a step in the right direction, but may not adequately represent a true situation. Otherwise, the "bagging" method described by the author appears to be as valid and rigorous as other measurement methods, and may well serve as the most appropriate method for further studies.

Appendix B

SUPPLEMENTARY REFERENCES

Adams, W.V. (1991) Control Fugitive Emissions from Mechanical Seals. *Chemical Engineering Progress*, **87**, 36.

Allen, C.C., Green. D.A., White, J.B., and Coburn, J.B. (1986) Preliminary Assessment of Air Emissions from Aerated Waste Treatment Systems at Hazardous Waste Treatment. U.S. EPA, Hazardous Waste Engineering Research Laboratory, Office of Research and Development, Cincinnati.

Anderson, P.H., and Greenberg, M.H. (1989) Estimating Chemical-specific Fugitive Emissions from Chemical Processing Equipment, *Proceedings of the 82nd Annual Meeting of the Air and Waste Management Association*, Anaheim, California.

Ashworth, R.A., Howe, G.B., Mullins, M.E., and Rogers, T.N. (1988) Air-Water Partitioning Coefficients of Organics in Dilute Aqueous Solutions, *Journal of Hazardous Materials*, **18**, 25.

BAAQMD (1989) Controlling VOC Emissions from Oil-water Separators in the Bay Area, Staff Report, Regulation 8, Rule 8.

Backman, R.C., Blanc, F.C., Siino, F.J., and O'Shaughnessy, J.C. (1987) Chemical Enhancement and Depression of Oxygen Transfer in Industrial Wastewaters, *Proceedings of the 42nd Industrial Waste Conference*, Purdue University, Lewis Publishers, Inc.

Baillod, C.R., Crittenden, J.C., Mihelcic, J.R., and Rogers, T.N. (1990) Critical Evaluation of the State of Technologies for Predicting the Transport and Fate of Toxic Compounds in Wastewater Facilities, *Water Pollution Control Federation Research Foundation*, Alexandria, Virginia.

Ball, W.P., Jones, M.D., and Kavanaugh, M.C. (1984) Mass Transfer of Volatile Organic Compounds in Packed Tower Aeration, *Journal of the Water Pollution Control Federation*, **56**(2), 127.

Barsky, J.B., Hee, S.S.Q., Clark, S., and Trapp, J.H. (1986) Simultaneous Multi instrument Monitoring of Vapors in Sewer Headspaces by Several Direct-reading Instruments, *Environmental Research*, **39**, 307.

Barton, D.A. (1987) Intermedia Transport of Organic Compounds in Biological Wastewater Treatment Processes, *Environmental Progress*, **6**(4), 246.

Barton, D.A., and McKeown, J.J. (1991) Field Verification of Predictive Modeling of Organic Compound Removal by Biological Wastewater Treatment Processes, *Environmental Progress*, **10**(2), 96.

Bell, J., Corsi, R.L., and Melcer, H. (1992) Fate and Transport Model Considerations. Chapter 5 in Water Pollution Control Federation Special Publication on VOCs in Wastewater, *Proceedings of the Water Environment Federation Pre-Conference Workshop*, New Orleans.

Bell, J.P. (1990) Development of a Computer Based Model and Data Base for Predicting the Fate of Hazardous Wastes at POTWs. *Proceedings of the U.S. Environmental Protection Agency 1990 Municipal Wastewater Treatment Technology Forum*, Orlando, Florida.

Bell, J.P. *et al.* (1988) Investigation of Stripping of Volatile Organic Contaminants in Municipal Wastewater Treatment Systems--Phase I, Ontario Ministry of Environment, Toronto.

Bell, J.P., Melcer, H., Thompson, D.J., and Dickens, J. (1991) Estimating Treatability Parameters for Predicting the Fate of VOC's in Wastewater Treatment Plants, *Proceedings of the 84th Annual Meeting of the Air and Waste Management Association*, Vancouver.

Berglund, R.L., *et al.* (1989) Equipment Leaks. Results of Industry-wide Studies of 1,3-Butadiene, Ethylene Oxide, and Phosgene Production Facilities, *Proceedings of the 82nd Annual Meeting of Air and Waste Management Association*, Anaheim, California.

Berglund R.L. and Whipple, G.M. (1987) Predictive Modeling of Organic Emissions, *Chemical Engineering Progress*, **83**, 46.

Bhattacharya, R.V.R., *et al.* (1989) Fate and Effects of Selected RCRA and CERCLA Compounds in Activated Sludge Systems, *Proceedings of the EPA 15th Annual Research Symposium on Remedial Action, Treatment, and Disposal of Hazardous Wastes*, Cincinnati.

Bhattacharya, S.K., Angara R.V.R., Hannah, S.A., Bishop, D.F., Dobbs, R.A., and Austern, B.M. (1989) Fate and effects of selected RCRA and CERCLA compounds in activated sludge systems. U.S. EPA Report, Cincinnati.

Birch, R.R. (1991) Prediction of the Fate of Detergent Chemicals during Sewage Treatment, *Journal of Chemical Technology and Biotechnology*, **50**, 411.

Bishop, D.F. (1982) The Role of Municipal Wastewater Treatment in Control of Toxics. *Proceedings of the NATO/CCMS meeting*, Bari, Italy.

Bishop, W., Witherspoon, J., Card, T., Chang, D., and Corsi, R.L. (1990) VOC Vapor Phase Control Technology Assessment, report to the WPCF Research Foundation.

Blackburn, J.W. (1987) Prediction of Organic Chemical Fates in Biological Treatment Systems, *Environmental Progress*, **6**, 217.

Blackburn, J.W. *et al.* (1985) Organic Chemical Fate Prediction in Activated Sludge Treatment Processes. EPA-600/S2-85/102.

Blackburn, J.W., *et al.* (1984) Technical Background and Estimation Methods for Assessing Air Releases from Sewage Treatment Plants. Memorandum, Versar, Inc.

Blackburn, J.W., Troxler, W.L., Sayler, G.S. (1984) Prediction of the Fates of Organic Chemicals in a Biological Treatment Process--an Overview. *Environmental Progress*, **3**(3), 163.

Bouwer, E.J. and McCarty, P.L. (1983) Transformation of 1- and 2-Carbon Halogenated Aliphatic organic Compounds Under Methanogenic Conditions, *Applied and Environmental Microbiology*, **45**(4), 1286.

BP Research (1993) Fugitive Emissions from an Offshore Oil and Gas Production Platform. *Proceedings of the SPE/EPA Exploration and Production Environmental Conference*, San Antonio.

Brestel, R. *et al.* (August 1991) Minimize Fugitive Emission with a New Approach to Valve Packing, *Chemical Engineering Progress*, **87**, 42.

Buchanan, D.L., *et al.* (1992) Fugitive Emissions from Control Valves. *Proceedings of the 47th Annual Symposium on Instrumentation for the Process Industry*, College Station, Texas.

Burnham, N., Corsi, R.L., Zytner, R., and Stiver, W. (1993) Mechanistic Model for VOC Emissions at Hydraulic Structures in WWTPs. *Proceedings of the 1993 Joint CSCE-ASCE National Conference on Environmental Engineering, Montreal.*

Burns and Roe Industrial Services Corporation (1982) Fate of Priority Toxic Pollutants in Publicly-owned Treatment Plants. EPA 1440/1-82/303.

Caballero, R. (1990) VOC Emissions from POTWs. *Appendix I of Workshop Report and Proceedings: Air Toxic Emissions and POTWs*, WPCF and U.S. EPA.

Cadee, K. (1984) Predicted Oxygen Transfer Characteristics Riser Pipes at Wastewater Pumping Stations, *Water*, 23.

California Air Resources Board (1985) Source Tests for Vinyl Chloride and other VOCs at Sewage Treatment Plants, California Air Resources Board Internal Memorandum.

California Air Resources Board (1988) Suggested Control Measure for the Control of Organic Compound Emissions from Sumps Used in Oil Production Operations, California Air Resources Board Staff Report.

Card, T.R., and Corsi, R.L. (1992) A Flexible Fate Model for VOCs in Wastewater, *Water Environment and Technology*, **4**(3), 40.

Card, T.R., Corsi, R.L., and Witherspoon (1991) Toxic Air Contaminant Emissions from Wastewater: Estimation Methods. *Proceedings of the Air and Waste Management Association Conference on Air Toxics Issues in the 1990s: Policies, Strategies and Compliance*, King of Prussia, Pennsylvania.

Chang, D.P.Y., Guensler, J.A., Kim, J.O., Chou, T.L., Uyeminami, D., Teague, S., Schroeder E.D., Corsi, R.L., Meyerhofer, J.A., and Raabe, O.G. (1992) Emissions of Volatile and Potentially Toxic Organic Compounds from Wastewater Treatment Plants and Collection Systems (Phase II)--Volume 3--Wastewater Treatment Plant Emissions--Experimental Phase, report the California Air Resources Board, Contract No. A7-32-085.

Chang, D.P.Y., Schroeder E.D., and Corsi, R.L. (1987) Emissions of Volatile and Potentially Toxic Organic Compounds from Sewage Treatment Plants and Collection Systems, report to the California Air Resources Board, Contract No. A7-32-085.

Chang, D.P.Y., Schroeder E.D., Corsi, R.L., Guensler, J.A., Meyerhofer, J.O., Uyeminami, D., Teague, S., and Raabe, O.G. (1992) Emissions of Volatile and Potentially Toxic Organic Compounds from Wastewater Treatment Plants and Collection Systems (Phase II)--Volume 1--Project Summaries, report the to California Air Resources Board, Contract No. A7-32-085.

Clark, B., Henry, G., Mackay, D., and Salenieks, S. (1986) The Fate of Toxic Organic Chemicals in Sewage Treatment Plants, *Proceedings of the Technology Transfer Conference*, Toronto.

Colyer, R.S. and Meyer, J. (1991) Understanding the Regulation Governing Equipment Leaks, *Chemical Engineering Progress*, **87**, 22.

Corsi, R.L. (1991) Estimation of Air Toxics Emissions Using the Bay Area Sewage Toxics Emissions (BASTE) Model, *Proceedings of the 1991 Summer National Meeting of the AIChE, Pittsburgh.*

Corsi, R.L. (1989) Prediction of Cross-Media VOC Mass Transfer Rates in Sewers Based Upon Oxygen Reareation Rates, *Proceedings of the 82nd Annual Meeting of the Air and Waste Management Association*, Anaheim, California, 89-10.5.

Corsi, R.L. (1991) VOC Emissions from Sewers, *Proceedings of the WEF Conference*, Ontario.

Corsi, R.L. (1989) Volatile Organic Compound Emissions from Wastewater Collection Systems, Ph.D. Dissertation, University of California.

Corsi, R.L., and Birkett, S. (awaiting publication) A Multi-parameter Analysis of VOC Emissions from Sewers, *Water Environment Research*.

Corsi, R.L., and Card T.R. (1991) A Multi-Process General Fate Model for VOCs in Wastewater, *Proceedings of the 84th Annual Meeting of the Air and Waste Management Association*, Vancouver, 91-92.1.

Corsi, R.L. and Card, T.R. (1991) Estimation of VOC Emissions Using the BASTE Model, *Environmental Progress*, **10**(4), 290.

Corsi, R.L., and Card, T.R. (1991) VOCs in Wastewater: State of Understanding, *Proceedings of the 84th Annual Meeting of the Air and Waste Management Association*, Vancouver, 91-92.12.

Corsi, R.L., Chang, D.P.Y., Schroeder, E.D. (1989) Assessment of the Effects of Ventilation Rates on VOC Emissions from Sewers, *Proceedings of the WPCF/EPA Workshop on Air Toxics Emissions and POTWs*, Alexandria, Virginia.

Corsi, R.L., Chang, D.P.Y., and Schroeder E.D. (1989) Assessment of the Effect of Ventilation Rates on VOC Emissions from Sewers, *Proceedings of the 82nd Annual Meeting of the Air and Waste Management Association*, Anaheim, California, 89-10.5.

Corsi, R.L., Chang, D.P.Y., and Schroeder E.D. (1992) Emissions of Volatile and Potentially Toxic Organic Compounds from Wastewater Treatment Plants and Collection Systems (Phase II)--Volume 2--Wastewater Collection System Study, report to the California Air Resources Board, Contract No. A7-32-085.

Corsi, R.L., Chang, D.P.Y., and Schroeder, E.D. (1992) A Modeling Approach for VOC Emissions from Sewers, *Water Environment Research*, **64**(5), 734.

Corsi, R.L., Chang, D.P.Y., Schroeder, E.D., and Qingzeng, Q. (1987) Estimation of Volatile and Potentially Toxic Organic Compounds from Municipal Wastewater Treatment Plants, *Proceedings of the Annual Meeting of the Air Pollution Control Association*, New York.

Corsi, R.L., Chang, D.P.Y., Schroeder E.D., and Qiu, Q. (1987) Emissions of Volatile and Potentially Toxic Organic Compounds from Municipal Wastewater Treatment Plants, *Proceedings of the 80th Annual Meeting of the Air Pollution Control Association*, New York, 87-95.7.

Corsi, R.L., Chang, D.P.Y., Schroeder E.D., and Qiu, Q. (1987) Modeling the Emissions of Volatile and Potentially Toxic Organic Compounds from Municipal Wastewater Treatment Plants, *Proceedings of the 80th Annual Meeting of the Air Pollution Control Association*, New York, 87-95.A.5.

Corsi, R.L., *et al.* (1994) Fate of Volatile Organic Compounds in Wastewater Collection Systems, Volumes I through VIII, report submitted to the Ontario Ministry of Environment and Energy, RAC Project No. G577.

Corsi, R.L., and Griffes, D.A. (1990) VOC Emission Estimation Methods Applied to POTWs in the San Francisco Bay Area, *Proceedings of the American Institute of Chemical Engineers 1990 Summer National Meeting*, San Diego.

Corsi, R.L., Quigley, C., Bell, J., Yendt, M., and Melcer, H. (1994) Design of Low Emission Sewers, *Proceedings of the 87th Annual Meeting of the Air and Waste Management Association*, Cincinnati.

Corsi, R.L., Quigley, C., Mandani, M., and Zytner, R. (1994) VOC Emissions from Industrial Sewers: An Improved Estimation Method Based on Oxygen Transfer Potential, *Proceedings of the 87th Annual Meeting of the Air and Waste Management Association*, Cincinnati.

Corsi, R.L., Schroeder, E.D., Chang, D.P.Y. (1989) Discussion of Estimating Volatile Organic Compound Emissions from Publicly Owned Treatment Works, *Journal of the Water Pollution Control Federation*, **61**, 95.

Corsi, R.L., Schroeder, E.D., Chang, D.P.Y. (1987) The Fate of Volatile Priority Pollutants during Municipal Wastewater Treatment, *Proceedings of the 59th Annual Meeting of the California Water Pollution Control Association*, San Diego.

Corsi, R.L., Shepherd, J., Kalich, L., Monteith, H., and Melcer, H. (1992) VOC and Semi-Volatile Organic Compound Emissions from Sewer Drop Structures, *Proceedings of the 85th Annual Meeting of the Air and Waste Management Association*, Kansas City, paper 92-94.04.

Corsi, R.L., Shepherd, J., Kemp, K. Quigley, C., Monteith, H., and Melcer, H. (1993) VOC Emissions from Small Sewer Drop Structures, *Proceedings of the 86th Annual Meeting of the Air and Waste Management Association*, Denver.

Corsi, R.L., Shepherd, J., Monteith, H., and Melcer, H. (1992) Oxygen Transfer and VOC Emissions from Sewer Drop Structures, *Proceedings of the 1992 ASCE National Conference on Hydraulic Engineering--Water Forum '92.*

Corsi, R.L., and Whitmore, A. (1993) Gas-Liquid Mass Transfer along Sewer Reaches, *Proceedings of the 1993 Joint CSCE-ASCE National Conference on Environmental Engineering*, Montreal.

Corsi, R.L., and Whitmore, A. (1992) Municipal and Industrial Wastewater Collection Systems as Sources of VOC Emissions, *Proceedings of the 9th World Clean Air Congress*, Montreal, paper IU-15.02.

Cowan, C.E., Larson, R.L., Feijtel, T.C.J., and Rapaport, R.A. (1992) An Improved Model for Predicting the Fate of Consumer Product Chemicals in Wastewater Treatment Plants, *Water Research*, **27**(4), 561.

Cox, R.D., Steinmetz, J.I., Lewis, D.L., and Wetherold, R.G. (1984) Evaluation of VOC Emissions from Wastewater Systems (Secondary Emissions), EPA 600/S2-84-080.

Davis, B.C. (1989) Comparison of the Fugitive Emissions from Two Butadiene Plants, *Proceedings of the 82nd Annual Meeting of the Air and Waste Management Association*, Pittsburgh.

Dobbins, W.E. (1964) Mechanism of Gas Absorption by Turbulent Liquids. Advance in Water Pollution Research, Volume 2, W.W. Eckenfelder, ed., Pergamon Press, Ltd., New York.

Dobbs, R., Govind, R., and Lai, L. (1990) Integrated Model for Predicting the Fate of Organics in Wastewater Treatment Plants, *Proceedings of the 4th WPCF/JSWA Joint Technical Seminar on Sewage Treatment Technology*, Japan.

Drews, R.J.L.C. (1981) Biodegradability testing of Industrial Wastes and Intractable Substances, Final report, Pretoria, South Africa: Council for Scientific and Industrial Research, National Institute for Water Research. Report No. PB83-106732.

Dunovant, V.S., Clark, C.S., Que Hee, S.S., Hertzberg, V.S., and Trapp, J.H. (1986) Volatile Organics in the Wastewater and Airspaces of Three Wastewater Treatment Plants, *Journal of the Water Pollution Control Federation*, **58**(9), 886.

Eklund, B. (1992) Practical guidance for flux chamber measurements of fugitive volatile organic emission rates, *Journal of the Air & Waste Management Association*, **42**, 1583.

Eklund, B., Green, D., Blaney, B., and Brown, L. (1988) Assessment of Volatile Organic Air Emissions from an Industrial Aerated Wastewater Treatment Tank. *Proceedings of the 14th Annual Research Symposium on Land Disposal, Remedial Action, Incineration and Treatment of Hazardous Waste,* Cincinnati.

Ellis, H.M., and Lackaye, R. (1989) Comparison of Fugitive Emissions from Equipment Leaks Using U.S. EPA's Published Emission Factors and Field Measurements, *Proceedings of the 82nd Annual Meeting of the Air and Waste Management Association*, Anaheim, California.

EPA (1982) Fate of Priority Pollutants in Publicly Owned Treatment Works. EPA 440/1-82/303.

EPA (1985) In-Situ Methods to Control Emissions from Surface Impoundments and Landfills. EPA 600/2-85-124.

EPA (1982) Measurements of VOC Emissions from Wastewater Basins in the Paper Industry. EPA 600/2-85-095.

EPA (1985) Organic Chemical Fate Prediction in Activated Sludge Treatment Processes. EPA 600/S2-85/102

EPA (1974) Process Design Manual for Sulfide Control in Sanitary Sewerage Systems. EPA 440/1-82/303.

EPA (1986) Report to Congress on the Discharge of Hazardous Wastes to Publicly Owned Treatment Works. EPA /530-SW-86-004.

EPA (1982) Volatilization of Organic Pollutants from Water. EPA 600/3-82-019.

EPA issues clarification on rule governing benzene emissions (1993), *Oil & Gas Journal*, **91**, 24.

Fingas, M.F., Hughes, K.A., and Bobra, A.M. (1988) Fuels in Sewers: Behaviour and Countermeasures, *Journal of Hazardous Materials*, **19**, 289.

Fochtman, E.G., and Eisenberg, W. (1979) Treatability of Carcinogenic and other Hazardous Organic Compounds. Final report, U.S. EPA Contract No. CI-68-03-2559.

Games, L.M., King, J.E., and Larson, R.J. (1982) Fate and Distribution of a Quanternary Ammonium Surfactant, Octadecyltrimehylammonium Chloride (OTAC) in Wastewater Treatment, *Environmental Science and Technology*, **16**, 483.

Gardner, J.F., and Spock, T.F. (1992) Control Emissions from Valves. *Hydrocarbon Processing*, **71**(8), 49.

Geating, J. (1981) Literature Study of the Biodegradability of Chemicals in Water. EPA-600/2-81-175.

Govind, R., Desai, S., and Tabak, H. (1989) Prediction and Modeling of Biodegradation Kinetic of Hazardous Waste Constituents, *Proceedings of the EPA Biosymposium*, Cincinnati.

Govind, R., Lei, L., and Dobbs, R. (1991) Integrated Model for Predicting the Fate of Organics in Wastewater Treatment Plants, *Environmental Progress*, **10**(1), 13.

Hannah, S.A. *et al.* (1986) Comparative Removal of Toxic Pollutants by Six Wastewater Treatment Processes, *Journal of the Water Pollution Control Federation*, **58**(1), 27.

Hao, O.J., Davis, A.P., Wu, Y.C., and Hsueh, K.P. (1991) Modeling Volatile Organic Compound Stripping in a Rotating Disk Contractor System, *Environmental Science and Technology*, **25**, 1891.

Henderson, R.K., Kittleman, T.A., and Doyle, J.D. (1988) Results of Fugitive Emissions Testing at a Chemical Plant, *Proceedings of the National Meeting of the American Institute of Chemical Engineers*, New Orleans.

Holler, A.G. (1971) The Mechanism Describing Oxygen Transfer from the Atmosphere to Discharge through Hydraulic Structures, *Proceedings of the XIV Congress, International Association for Hydraulics Research*, **A45**, 373.

Hwang, S.T. (1982) Measuring Rates of Volatile Emissions from Non-point Source Hazardous Waste Facilities, *Proceedings of the 75th Annual Meeting of the Air Pollution Control Association*, New Orleans.

Hwang, S.T. (1981) Treatability and Pathways of Priority Pollutants in the Biological Wastewater Treatment, AIChE Symposium Series 77:316-326.

Jacobsen, B.N. (1987) Behavior of Organic Micropollutants in Biological Wastewater Treatment.

Jagiella, T., and Klickman, M. (June 1994) Volatile Emissions from wastewater are regulated, too, *Chemical Engineering*, **101**, 7.

Jones, A.L. (1993) Arresting Runaway Fugitive Emissions. *Pollution Engineering*, **25**(10), 18.

Karickhoff, S.W., Brown, D.S., and Scott, T.A., (1979) Sorption of Hydrophobic Pollutants on Natural Sediments, *Water Research*, **13**, 241.

Kincannon, D.F., *et al.* (1983) Removal Mechanisms for Toxic Priority Pollutants, *Journal of the Water Pollution Control Federation*, **55**, 157.

Kirsch, E.J., Grady, C.P.L., Wukasch, R.F., and Tabak, H.H. (1986) Protocol Development for the Prediction of the Fate of Organic Priority Pollutants in Biological Wastewater Treatment Systems, EPA/600/S2-85/141.

Kyosai, S., Houthoofd, J., and Petrasek, A. (1981) Desorption of Volatile Priority Pollutants in Sewers. Internal report, Office of Research and Development, U.S. EPA, Cincinnati.

Kyosai, S., and Rittmann, B.E. (1991) Effect of Water-Surface Desorption on Volatile Compound Removal Under Bubble Aeration. *Journal of the Water Pollution Control Federation*, **63**(6), 887.

Lawson, C.T., and Siegrist, S.A. (1981) Removal Mechanisms for Selected Priority Pollutants in Activated Sludge Systems, *Proceedings of the ASCE Environmental Engineering Division Specialty Conference*, 356.

Leong, L.Y.C., Kuo, J.F., Regan, M.M., Wong, E. (1991) A Pooled Emission Estimation Program for Wastewater Treatment Facilities, *Proceedings of the 84th Annual Meeting of the Air and Waste Management Association*, Vancouver.

Levins, P., *et al.* (1979) Sources of Toxic Pollutants Found in Influents to Sewage Treatment Plants 6. Integrated Interpretation. EPA 440/4-81/007

Ludzack, F.J., Ettinger, M.B. (1960) Chemical Structures Resistant to Aerobic Biochemical Stabilization, *Journal of the Water Pollution Control Federation*, **32**, 167.

Lurker, P.A., Clark, C.S., and Elia, V.J. (1982) Atmosphere Release of Chlorinated Organic Compounds from the Activated Sludge Process, *Journal of the Water Pollution Control Federation*, **54**(12), 1566.

Lurker, P.A., Clark, C.S., Elia, V.J., Gartside, P.S., and Kinman, R.N. (1984) Aerial Organic Chemical Release from Activated Sludge, *Water Research*, **18**(4), 489.

Mackay, D., and Yuen, T.K. (1980) Volatilization Rates of Organic Contaminants from Rivers, *Water Pollution Research Journal of Canada*, New Series **5**, 83.

Madani, M., Zytner, R., and Corsi, R.L. (1994) Emissions of Volatile Organic Compounds from Clarifier Wiers, *Proceedings of the 1994 Purdue Industrial Waste Conference*.

Madden, M., and Tittlebaum, M. (1983) Biological Treatability of Pentachlorophenol Wastewater, *Journal of Environmental Science and Health*, **A18**, 583.

Mason, A.M., and Supple, P.M. (1988) Overview of CMA's Fugitive Emissions Database, *Proceedings of the National Meeting of the American Institute of Chemical Engineers*, New Orleans.

Matter-Muller, C. *et al.* (1980) Non-biological Elimination Mechanisms in a Biological Sewage Treatment Plant, *Progress in Water Technology*, **12**, 299.

Matthews, P.J. (1975) Limits of Volatile Organic Liquids in Sewers: Part 1, *Effluent and Treatment Journal*, 15(11), 565.

Melcer, H. (1994) Monitoring and Modeling VOCs in Wastewater Facilities, *Environmental Science & Technology*, **28**(7), 328A.

Melcer, H., Bell, J.P., and Corsi, R.L. (1994) Stripping and Volatilization in Wastewater Facilities: Status Report on WERF Project, *Proceedings of the 66th Annual Meeting of the California Water Pollution Control Association*, Santa Clara, California.

Melcer, H., Bell, J.P., and Corsi, R.L. (1994) Stripping and Volatilization in Wastewater Facilities, *Proceedings of the Water Environment Federation Specialty Conference Series: Control of Emissions of Odors and Volatile Organic Compounds*, Jacksonville, Florida.

Melcer, H., Bell, J.P., Thompson, D., and Monteith, H. (1989) Calibrated Steady State and Dynamic Models for Predicting the Fate of Volatile Organic Compounds in Wastewater Treatment Plants, *Proceedings of the 10th Annual Meeting of the Society of Environmental Toxicology and Chemistry*, Toronto.

Melcer, H., Parker, W.J., and Monteith, H.D. (1994) Estimating Emissions of Toxic Pollutants, *Water Environment & Technology*, 50.

Melcer, H., Thompson, D., Bell, J., Monteith, H. (1989) Stripping of Volatile Organic Compounds at Municipal Wastewater Treatment Plants, *Proceedings of the AWM/EPA International Symposium on Hazardous Waste Treatment: Biosystems for Pollution Control*, Cincinnati.

Meyerhofer, J. *et al.* (1990) Control of Volatile Organic Compound Emissions During Preliminary and Primary Treatment, Appendix L of Workshop Report and Proceedings: Air Toxic Emissions and POTWs, WPCF and USEPA.

Mihelcic, J.R., Baillod, C.R., and Crittenden, J.C. (1993) Estimation of VOC emissions from wastewater facilities by volatilization and stripping, *Journal of the Air & Waste Management Association*, **43**, 97.

Miles, M. (1990) Design Qualification of Fugitive Emission Stem Seals, *Proceedings of the 1990 Pressure Vessels and Piping Conference*, Nashville.

Miller, M. (1991) Fugitive Emission Regulations Change Valve Selection/Care, *Pollution Engineering*, **23**(13), 80.

Modeling Wastewater VOC Emissions (1992), *Public Works*, **123**, 80.

Monnig, E., and Zweidinger, R.A. (1980) Treatability Studies of Pesticide Manufacturing Wasterwaters: Dinoseb and Atrazine. Final report, U.S. EPA Contract No. 68-02-2668.

Munz, C., and Roberts, P.V. (1989) Gas- and Liquid-phase Mass Transfer Resistances of Organic Compounds during Mechanical and Surface Aeration, *Water Research*, **23**(5), 589.

Namkung, E. and Rittmann, B.E. (1987) Estimating Volatile Organic Emissions from Publicly Owned Treatment Works, *Journal of the Water Pollution Control Federation*, **59**(7), 670.

Nielsen, P.H., Raunkjaer, K., Norsker, N.H., Jensen, A., and Hvitved-Jacobsen, T. (1992) Transformation of Wastewater in Sewer Systems--a Review, *Water Science and Technology*, **25**, 17.

Noll, K.E., and DePaul, F.T. (1990) Emission of Volatile Organic Compounds from the Sewage Treatment Facilities of the Metropolitan Sanitary District of Greater Chicago, Appendix P of Workshop Report and Proceedings: Air Toxics Emissions and POTWs, WPCF and U.S. EPA.

O'Neill, K., Corsi, R.L., and Dobbins, W.E. (1991) Process Modifications to Reduce VOC Emissions from Wastewater, *Proceedings of the 84th Annual Meeting of the Air and Waste Management Association*, Vancouver.

Parker, W., Corsi, R.L., and Bell, J. (1994) Modeling the Fate of Volatile Organic Compounds in Fixed Film Wastewater Treatment Processes, *Proceedings of the 1994 WEFTEC Meeting*, Chicago.

Parker, W., Thompson, D. Harvey, T., Monteith, H., and Corsi, R.L. (1994) Fugitive Air Emissions of Volatile Organic Compounds from Fixed Film Treatment Processes, *Proceedings of the Water Environment Federation Specialty Conference Series: Control of Emissions of Odors and Volatile Organic Compounds*, Jacksonville, Florida.

Parkhurst, J.D., and Pomeroy, R.D. (1972) Oxygen Absorption in Streams, *Journal of the Sanitary Engineering Division*, **98**, 101.

PEEP Joint Powers Agencies (1990) Pooled Emission Estimation Program (PEEP), Final Report for Publicly Owned Treatment Works (POTWs), prepared by J.M. Montgomery, Consulting Engineers, Inc.

Pellizzari, E.D. (1981) Volatile Organics in Aeration Gases at Municipal Treatment Plants, U.S. EPA, Cincinnati.

Petrasek, A.C., Austern, B.M., and Neiheisel, T.W. (1983) Removal and Partitioning of Volatile Organic Priority Pollutants in Wastewater Treatment, *Proceedings of the 9th U.S.-Japan Conference on Sewage Treatment Technology*, Tokyo.

Petrasek, A.C. *et al.* (1983) Fate of Organic Compounds in Municipal Wastewater Treatment Plants, *Journal of the Water Pollution Control Federation*, **55**, 1286.

Pincince, R.L. (1991) Effect of Aeration Method on Emissions from Aeration Tanks, *Proceedings of the 84th Annual Meeting of the Air and Waste Management Association*, Vancouver.

Pincince, R.L. (1991) Transfer of Oxygen and Emission of Volatile Organic Compounds at Clarifier Wiers, *Journal of the Water Pollution Control Federation*, **63**, 114.

Pomeroy, R. (1945) The Pros and Cons of Sewer Ventilation, Sewage Works Journal, **17**(2), 203.

Quigley, C., and Corsi, R.L. (awaiting publication) Emissions of VOCs from a Municipal Sewer, *Journal of the Air and Waste Management Association*.

Quigley, C., Corsi, R.L., Melcer, H., and Bell, J. (1994) Aromatic VOC Emissions from a Municipal Sewer Interceptor, *Proceedings of The Sewer as a Physical, Chemical and Biological Reactor--a IAWQ International Specialty Conference*, Aalborg, Denmark.

Randall, J.L. (1992) Fugitive Emissions Monitoring in the Nineties, *Proceedings of the Conference on Advances in Instrumentation and Control*, Houston.

Renn, C.E. (1974) Biodegradation of NTA Detergents in Wastewater Treatment System, *Journal of the Water Pollution Control Federation*, **46**, 2363.

Roberts, P.V. (1984) Modeling Volatilization Organic Solute Removal by Surface and Bubble Aeration, *Journal of the Water Pollution Control Federation*, **56**, 157.

Roberts, P.V., Dandliker, P. and Matter-Muller C. (1984) Volatilization of Organic Pollutants in Wastewater Treatment--Model Studies. EPA-600/2-84-047, U.S. Environmental Protection Agency, Cincinnati.

Rogers, T.N., and Mullins, M.E. (1987) Evaluation and Prediction of Henry's Law Constants Applicable to Air Stripping of Volatile Organics. Final Report prepared under Air Force Contract No. F08635-85-C-0054.

Saleh, F.Y., Lee, G.F., and Wolf, H.W. (1982) Selected Organic Pesticides, Behavior and Removal from Domestic Wastewater by Chemical and Physical Properties, *Water Research*, **16**, 479.

Sayler, G.S., Breen, A., Blackburn, J.W., and Yagi, O. (1984) Predictive Assessment of Priority Pollutant Bio-oxidation Kinetics in Activated Sludge, *Environmental Progress*, **3**(3), 153.

Shannon, E.E. (1975) Effects of Detergents Formulation on Wastewater Characteristics and Treatment, *Journal of the Water Pollution Control Federation*, **47**, 2371.

Shell International Petroleum (1991) Elimination of Waste Emissions from Oil and Gas Production Operation, *Proceedings of the First International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production Part 2*, Hague, Netherlands.

Silverman, G. (1985) Air Emissions Associated with Publicly Owned Treatment Works in Santa Clara Valley. Memorandum from Association of Bay Area Governments to the U.S. EPA Integrated Environmental Management Project.

Skippon, S.M., and Roberts, I.R. (1991) Monitoring of Fugitive Hydrocarbon Emissions Using Open-path Infra-red Sensors, *Proceedings of the First International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production Part 2*, Hague, Netherlands.

Smith, J.H., Bomberger, D.C., and Haynes, D.L. (1980) Prediction of the Volatilization Rates of High-Volatility Chemicals from Natural Water Bodies, *Environmental Science and Technology*, **14**(11), 1332.

Stenstrom, M.K. and Hsieh, C.C. (April 1991) Considering VOC emissions, *Water/Engineering & Management*, **138**, 27.

Stover, E.L., *et al.* (1983) Biological Treatability of Specific Organic Compounds Found in the Chemical Industry Wastewaters, *Journal of the Water Pollution Control Federation*, **55**, 97.

Studley, E.G. (1939) Experimental Ventilation of the North Outfall Sewer of the City of Los Angeles, *Sewer Works Journal*, **11**(2), 264.

Sun, P.T., and Compernolle, R.V. (1990) Behavior of Volatile Organics and other Compounds in Refinery Activated Sludge Systems--a Review, *Proceedings of the California WPCA Industrial and Hazardous Waste Conference*.

Taggart, R.H. (1988) Review of CMA Recommended Fugitive Emissions Estimation Methodologies, *Proceedings of the National Meeting of the American Institute of Chemical Engineers*, New Orleans.

Thibodeaux, L.J., Parker, D.G., Heck, H.H. (1982) Measurements of Volatile Chemical Emissions from Wastewater Basins. EPA-600/2-82-095.

Thistlethwayte, D.K.B. (1972) The Control of Sulphides in Sewerage Systems. 1st Edition, Ann Arbor Science Publishers, Inc. Ann Arbor.

Thompson, D., Bell, J.P., and Melcer, H. (1989) A Calibrated Model for Predicting the Fate of Selected Volatile Organic Compounds in Municipal Wastewater Treatment Plants, *Proceedings of the 62nd Annual Conference of the Water Pollution Control Federation*, San Francisco.

Truelove, R.D. (February 1992) Control of Benzene Waste NESHAP Emissions from a Petroleum Refinery, *Environmental Progress*, **11**, 58.

Truong, K.N., and Blackburn, J.W. (1984) The Stripping of Organic Chemicals in Biological Treatment Processes, *Environmental Progress*, **3**(3), 143.

Tsezos, M., and Bell, J.P. (1989) Comparison of the Biosorption and Desorption of Hazardous Organic Pollutants by Live and Dead Biomass, *Water Research*, **23**(5), 561.

Wang, L., Shan, Y., Lai, L., Govind, R., and Dobbs, R. (1989) Prediction of the Fate of Toxic Organic Compounds in Wastewater Treatment System, *Proceedings of the AIChE Summer National Meeting*, Philadelphia.

Weber, W.J. and Jones, B.E. (1986) Toxic Substance Removal in Activated Sludge and PAC Treatment Systems. EPA 600/2-86/045.

Weber, W.J., Jones, B.E., and Katz, L.E. (1987) Fate of Toxic Organic Compounds in Activated Sludge and Integrated PAC Systems, *Water Science Technology*, **19**, 471.

Whitmore, A., and Corsi, R.L. (1994) Measurement of Gas-liquid Mass Transfer Coefficients for Volatile Organic Compounds in Sewers, *Environmental Progress*, **13**, 114.

Whitmore, D., Corsi, R.L., Shepard, J., and Thompson, D. (1992) Examining Gas-Liquid Mass Transfer of Volatile and Semi-Volatile Organic Compounds along Sewer Reaches, *Proceedings of the 85th Annual Meeting of the Air and Waste Management Association*, Kansas City, paper 92-98.01.

Wierich, P. (1985) The Fate of Soluble, Recalcitrants, and Adsorbing Compounds in Activated Sludge Plants, *Ecotoxicology and Environmental Safety*, **5**, 161.

Witherspoon, J.R. (1989) VOC and Toxic Emissions from Dissolved Air Flotation Units in the Bay Area, *Proceedings of the 82nd Annual Meeting of the Air and Waste Management Association*, Anaheim, California.

Witherspoon, J.R., Bell, J.L., Suzuki, S.J., and Wallis, M.J. (1993) Use of a Fate Emissions Model to Analyze Operational Feasibility and Cost Effectiveness of Design Modifications to Reduce Toxic Air Contaminants at a Wastewater Treatment Plant, *Proceedings of the 86th Annual Meeting of the Air and Waste Management Association*, Denver.

Wolstenholme, P.L., and Finger, R.E. (1993) Air Toxics Modeling and Control at a large Wastewater Treatment Plant, *Proceedings of the 86th Annual Meeting of the Air and Waste Management Association*, Denver.

Wukasch, R.F., Grady, C.P.L., and Kirsch, E.J. (1981) Prediction of the Fate of Organic Compounds in Biological Wastewater Treatment Systems. AIChE Symposium Series 77:134-143.

Appendix C
SURVEY OF PROCESS DRAINS REPORTS
WEST COAST REFINERY

SUMMARY

A two day survey of process drains was conducted at this refinery. The procedures followed included a review of drain drawings, discussions with key refinery environmental engineers and operations field personnel and a visual inspection of the seven process units selected. Two types of drains were found. Of the 2950 drains surveyed, approximately two-thirds were of the drain funnel type retro-fitted with inserts and the rest were gas-sealed catch basins.

PROCEDURES

The process drains at a west coast petroleum refinery were surveyed on February 7 and 8, 1995. Drain systems in the process units were inspected. The survey was conducted in a series of steps. Interviews were held with key refinery environmental engineers and operations field personnel to obtain information on the number and type of process drains used in this refinery, the history of drains and seals installation, the nature of wastewater being routed to the different drains, and the regulations which motivated the sealing efforts. Access was provided to hard-copy and computerized engineering drawings, including drain system drawings for various refinery areas. Drawings were assembled showing process unit drain system layouts and details of drain funnels and gas-sealed catch basins.

Based on these reviews, seven process units of different ages were selected as representative of refinery operations for the survey. A visual inspection was conducted of these units to confirm drain configuration, seals, types of discharges, quantities of discharge, level of activity, and the existence of high temperature discharges (condensate or steam blowoffs) to the drains.

MAJOR FINDINGS

The refinery staff estimated there were 2950 process unit drains (drain funnels and gas-sealed catch basins) in the refinery. Visual observations indicated that approximately 70 percent (or 2100) are drain funnels, and 30 per cent (or 850) are gas-sealed catch basins.

With respect to the process unit drains, some were drain funnels dedicated to receiving specific discharges from above-grade hardpipe, and some were area drains intended to collect surface flow. Of the area drains, nearly all were for collecting storm runoff and infrequent (turnaround) maintenance drainage, while some were located in trenches, originally designed to collect surface flows of process wastewaters. Minimal time was spent inspecting the area drains intended for storm runoff.

Drain Funnels

Drain funnels are unsealed pipes connected to laterals leading to trunk sewers (Figure A1). All those observed were 4-inch diameter. Most of the drain funnel openings (drain hubs) in this refinery are raised above grade to exclude surface flow. Often, but not always, an 8-to-4-inch reducer is attached to the drain funnel to create a larger opening for collecting discharges. The use of reducers can cause the height of the opening to vary from 2 to 10 inches above grade. In more recently constructed process units, the reducer funnels were completely above grade.

All drain funnels have been sealed with inserts. Inserts are commercially available, with design features intended to promote flowthrough while maintaining a water seal in the vertical section of the drain. Insert designs are the same for funnels with and without reducers, but installation in reducers must account for the insert being seated low in the reducer at a 4-inch diameter location. The inserts were recessed, with grated covers resting on the insert to prevent trash and debris from entering the drain. The grate holes were approximately ¼ inch circular openings.

Most drain funnels were associated with pumps, with a small percentage dedicated to the tower, condensers, and compressors. Tower and condenser drains were inactive, as were about one-half of the pump drains. Pump discharges were pumped (hydrocarbon) material, steam condensate, seal water, cooling water, and lube oil drippings from pumps (ranging from a few drops per minute to steady discharges not normally exceeding 1 gpm). Typical pump drains were fed by 2 to 3 hardpipes, normally 1-inch diameter or less, carrying sealing discharges, steam blowoff, and pump pad drainage. Most discharge pipes did not break the plane of the drain hub. Steam blowoffs were associated with about 25 percent of the observed drains.

Most of the major process wastewater streams in this refinery, including desalter brine and tank draws, are hard-piped directly to below-grade penetrations into junction boxes.

Gas-Sealed Catch Basins

Area drains for both the functions described above are gas-sealed catch basins (Figure A2). Although referred to as gas-sealed, the seal is actually provided by water. This type of drain is located at low points to collect runoff. The catch basin openings are about 12 inch diameter and are grated to exclude trash and debris.

Nearly all observed catch basins function to collect surface runoff. Their use as process wastewater drains was rare and only noted in one crude unit. Most of these wastewater-collecting catch basins were located in trenches that directed surface flow of process discharges to the catch basins. At one location, a catch basin received a hardpiped discharge with a flow of 10 gpm or more; the catch basin may have been used in place of a drain funnel because of the high flow.

Where catch basins were located in trenches, the original design of receiving surface flow was modified in response to the benzene waste operations NESHAP regulation. The wastewater discharges were prevented from overflowing to the trench and collected into hardpipe extending into the catch basins.

Detailed observations made in each process unit inspected are presented in Appendix 1.

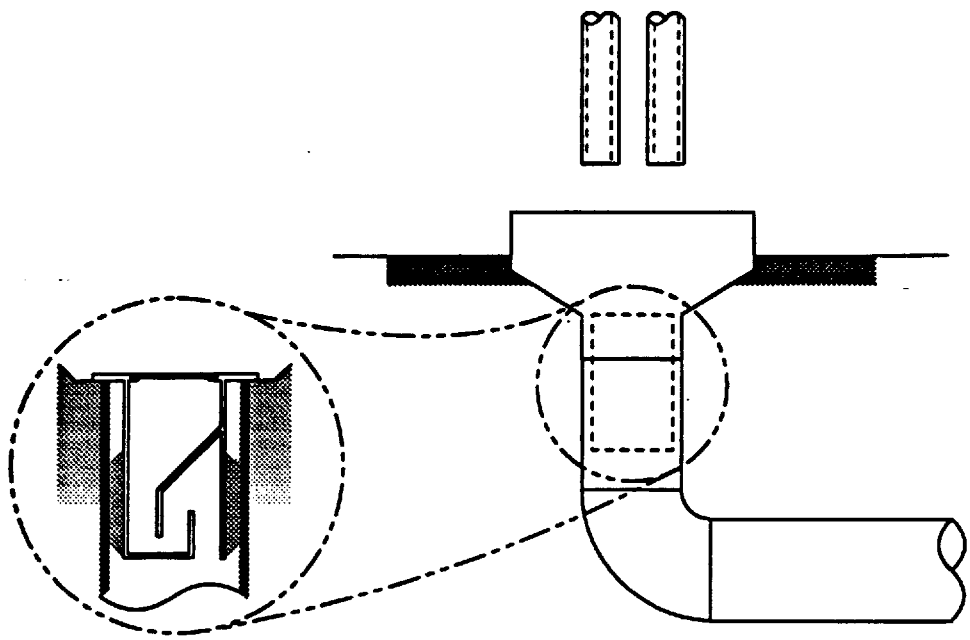


Figure C-1. Drain Funnel with Insert (not to scale).

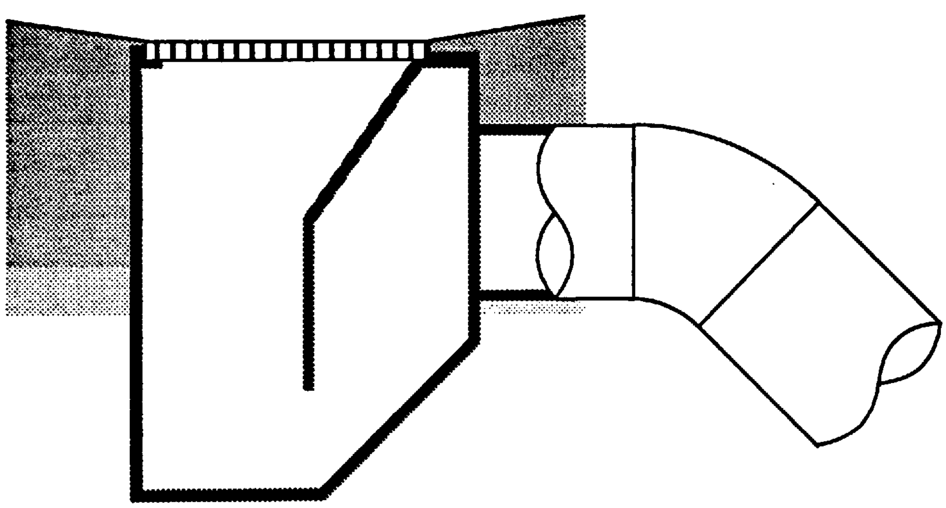


Figure C-2. Sealed Catch Basin (not to scale).

Appendix 1

OBSERVATIONS OF DRAINS AT SPECIFIC PROCESS UNITS

CRUDE UNITS "A"

Drain Funnels

- Generally receiving pump discharges.
- Were not raised funnels, and thus could collect runoff.
- Most appeared to be fitted with inserts. The inserts were recessed, with a small grate catch basin resting on the insert as a trap for large grit. Grate openings were ~¼ circular openings.
- Discharges were normally small. About a third were normally inactive; more than 10 percent of those observed had a stream of ambient water flowing into them at 1 to 2 gpm; steam breathing common; lube oil or hydrocarbon discharges less than slow drip.
- The various discharges were from separate pipes, normally about 0.5 inch diameter. Some discharge pipes broke the plane of the drain.

Gas-Sealed Catch Basins

- Some located on the pad, draining runoff.
- Some located in trenches along pump rows. These originally drained runoff and process wastewater discharged to the trench. Sealing modifications involved hardpiping (with 1 to 2 inch pipe) the pump discharges to the surface drain, usually breaking the plane of the drain. Pump discharges include seal water (an almost continuous stream, well under 1 gpm) and smaller drips of lube oil or seal water. Steam breathing frequently occurred directly into surface drains.
- A few located directly under a discharge (from tower area and individual pumps). Discharge normally did not break the plane of the drain.

OXYGENATE PLANT

Drain Funnels

- All raised funnels were 8 inch x 4 inch reducers.
- Discharges from pumps hard piped (1 to 2 inch pipes).
- Discharge pipes may not break the plane of the drain funnel.

- Very small discharge flows (a few drops per minute) in about 30 percent of the drains. Other drains showed no activity.

- All drains fitted with inserts and grate covers.

Gas-Sealed Catch Basins
- Drains had water seals intact.

- The drains were catch basins at low points for collecting runoff.

- Weirs did not have any grate openings.

- Very minimal discharge activity.

FCC UNIT

Drain Funnels
- Discharges from pumps hard piped (1 to 2 inch pipes).

- Discharge pipes usually did not usually break the plane of the drain hubs.

- Consistent drippings (less than 1 gpm) from pumps appeared to be entering drains.

- All drains fitted with inserts and grate covers.

- About 25 percent of the drains seemed to have steam breathing.

Gas-Sealed Catch Basins
- Drains had water seals intact.

- The drains were catch basins at low points for collecting runoff.

- Some of the weirs had grate openings.

- Overflows from clogged drain hubs and other process drainage seemed to be entering a few catch basin locations.

CCR UNIT

Drain Funnels
- All raised funnels fitted with 8 x 4 inch reducer funnels.

- Discharges from pumps hard piped (1 to 2 inch pipes).

- Discharge pipes did not usually break the plane of the drain funnel.
- Very small discharge flows (few drops per minute) in about 20 percent of the drains. Other drains showed no activity.
- All drains fitted with inserts and grate covers.

Gas-Sealed Catch Basins
- Drains had water seals intact.
- The drains were catch basins at low points for collecting runoff.
- Weirs did not have any grate openings.
- Very minimal discharge activity.

CRUDE UNIT "B"

Drain Funnels
- Discharges from pumps hard piped (1 to 2 inch pipes).
- Discharge pipes did not usually break the plane of the drain hubs.
- Consistent drippings (less than 1 gpm) from pumps appeared to be entering drains.
- All drains fitted with inserts and grate covers.
- A few drains seemed to have steam breathing.

Gas-Sealed Catch Basins
- Drains had water seals intact.
- The drains were catch basins at low points for collecting runoff.
- The weirs did not have grate openings.
- Overflows from clogged drain funnel openings and other process drainage seemed to be entering a few catch basin locations.

TANK DRAWS

Tank draws were hardpiped through a 4 inch pipe to the process wastewater collection system.

There were no drains.

SURVEY OF PROCESS DRAINS REPORTS
MID-WEST REFINERY

SUMMARY

A three-day survey of process drains was conducted at a mid-sized, mid-west refinery. The survey involved a review of drain drawings, discussions with key refinery environmental engineers and operations field personnel, and a visual inspection of process units. A mean value of 1700 drains was estimated to be present in the refinery. The estimates ranged from 1,465 to 1,935. Two types of drains were identified. Approximately two-thirds were of the unsealed drain funnel type, and the rest were sealed drain funnels with p- or s-trap water seals.

PROCEDURES

The process drains at a mid-west petroleum refinery were surveyed on May 2, 3, and 4, 1995. Junction boxes and any other downstream drain structures downstream of process unit drains were not included in this investigation. The survey was conducted in a series of steps. Interviews were held with key refinery environmental engineers to obtain information on the number and types of process drains used in this refinery, the history of drain installation, and the nature of wastewater being routed to the different drains. Hard-copy and computerized engineering drawing files were then searched, focusing on drain system drawings for various refinery areas. Drawings were collected of process unit drain system layouts and details of drain funnels and water-sealed drains.

Based on these reviews, at least one process unit was inspected for each type of drain identified in the drawings to confirm the presence of a seal in those drains identified in the drawings as being sealed. The presence of seals 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. The inspection also included the evaluation of types of discharges, quantities of discharge, level of activity, and the existence of high temperature discharges (condensate or steam blowoffs) to the drains.

MAJOR FINDINGS

An estimated 1,465 to 1,935 process unit drains (unsealed drain funnels and water-sealed drains) were in the refinery. Approximately 950 to 1,260 were unsealed drain funnels and 515 to 675 water-sealed drains. Table 1 presents a breakdown of drains by process unit inspected. The information in Table 1 was developed by counting the drains shown on the drawings (where drawings were available), asking unit operators for their estimates of drain counts, and visually estimating drain counts during the unit inspections. The number of active drains were estimated to be approximately 16 which represents one percent of the total drains in the refinery. The active drains were defined to be those from which there was continuous discharge.

Unsealed Drain Funnels

These drain funnels consisted of unsealed 4-inch pipes connected to laterals leading to trunk sewers (Figure C-3a). Most of the drain funnel openings (drain hubs) were raised above grade to exclude surface flow. Often, but not always, an 6-to-4-inch reducer was attached to the drain funnel to create a larger opening for collecting discharges (Figure C-3b). The use of reducers can cause the height of the opening to vary from 2 to 6 inches above grade. In more recently modified units, the reducer funnels were completely above grade and the sewer pipes were in open trenches.

Most drain funnels were associated with pumps, with a small percentage dedicated to towers, heat exchangers, condensers, and compressors. Tower, heat exchanger, and condenser drains were normally inactive, as were about one-half of the pump drains. Pump discharges were pumped (hydrocarbon) material, steam condensate, seal water, cooling water, and lube oil drippings from pumps (ranging from a few drops per minute to steady discharges not normally exceeding 2 gpm). Typical pump drains were fed by 2 to 3 hardpipes, normally 1-inch diameter or less, carrying sealing discharges, steam blowoff, and pump pad drainage. Most discharge pipes did not break the plane of the drain hub. Steam blowoffs from hot water condensate were associated with about 20 to 30 per cent of the observed drains.

Water-Sealed Drain Funnels

These drains were similar in size and configuration to the funnel type drains described above, except that these were provided with p- or s-traps (Figure C-4a). Observations about positions of the hubs above grade (Figure C-4b), discharge types, and drain activities were the same as with the unsealed drain funnels.

In four process units, there were a total of six water-sealed drains of a different configuration, details of which were not found in the drawings reviewed. These drain hubs were larger and cylindrical, apparently constructed from cast iron pipe, 0.5 to 1.5 feet in diameter and 1 to 2 feet deep. The presence of standing water in the cylinders indicated that water seals existed. The drains received multiple discharges from three to four pipes, a larger number of discharges than the other water-sealed and unsealed drain configurations.

Other Issues and Observations

This refinery addressed the benzene NESHAP regulations by collecting benzene-containing streams and conveying them in a closed system to a control device. Thus, the benzene NESHAP regulations were not associated with drain sealing activities at this refinery. The refinery addressed NSPS Subpart QQQ regulations for a recently constructed drain system in the wastewater treatment plant, where the drains had water seals. The use of water seals elsewhere in the refinery was based on safety considerations, not environmental regulations.

More recent sewer installations--for example, at the wastewater treatment plant--involved placing the sewer pipe in trenches, but not backfilling the trenches. This allows for visual inspection of the pipe for leaks. At the wastewater treatment plant, there was a concern that water seals could freeze; therefore, oily water sample lines flowed continuously through these drains during the winter. At the new, unbackfilled alkylation acid sewers, where some water traps exist, such continuous draining did not occur.

Tanks were not drawn to the sewer system. Tank draws were collected in vacuum trucks and transported to the wastewater treatment plant.

A list of drains in each of the process units is presented in Table 1, and detailed observations made in each process unit inspected are presented in Appendix 1.

Table 1. List of Process Drains in Various Refinery Units.

Unit Name	Total Drains	Active Drains[1]	Funnel Type	
			Unsealed	Sealed
Distillation Units 1 and 2	250 - 300	5	200 - 240	50 - 60
Cat Cracking Units 1 and 2	90 - 135	2	80 - 120	10 - 15
Cat Ref. Unit 3 & Hydrodesulfurization Unit 2	120 - 140	4	48 - 56	72 - 84
Distillate Hydrotreater Unit	10 - 15	0	10 - 15	0
Tank Drawdowns	0	0	0	0
Hydrocracker Unit	80 - 100	0	64 - 80	16 - 20
Saturates Gas Plant	60 - 80	0	54 - 72	6 - 8
Steam Methane Reformer Unit	40 - 60	2	32 - 48	8 - 12
Cat Reforming Unit 1	60 - 70	0	54 - 63	6 - 7
Cat Ref. Unit 2 & Hydrodesulfurization Unit 1	80 - 100	1	56 - 70	24 - 30
Kerosene Hydrotreating Unit	15 - 30	2	3 - 6	12 - 24
Benzene and Kerosene Extraction Units	50 - 60	0	20 - 24	30 - 36
Alkylation Unit	100 - 150	0	70 - 105	30 - 45
Light Oils Treatment Unit	70 - 80	0	7 - 8	63 - 72
Lube Fractionation and Extraction Unit	60 - 80	0	48 - 64	12 - 16
Compounding Unit	40 - 60	0	28 - 42	12 - 18
Catalytic Dewaxing and Deasphalting Units	100 - 120	0	40 - 48	60 - 72
Asphalt Plant	20 - 40	0	20 - 40	0
Rectified Absorber Unit and Gas Plants	150 - 200	0	90 - 120	60 - 80
Sulfur Recovery Units and SCOT Plant	20 - 40	0	4 - 8	16 - 32
Visbreaker Unit	40 - 60	0	20 - 30	20 - 30
Wastewater Treatment Plant	10 - 15	-	0	10 - 15
Total Drains in the Refinery	1465 - 1935	16	948 - 1259	517 - 676

[1] These include drains with continuous flow discharges and drains with frequent periodic purging flows.

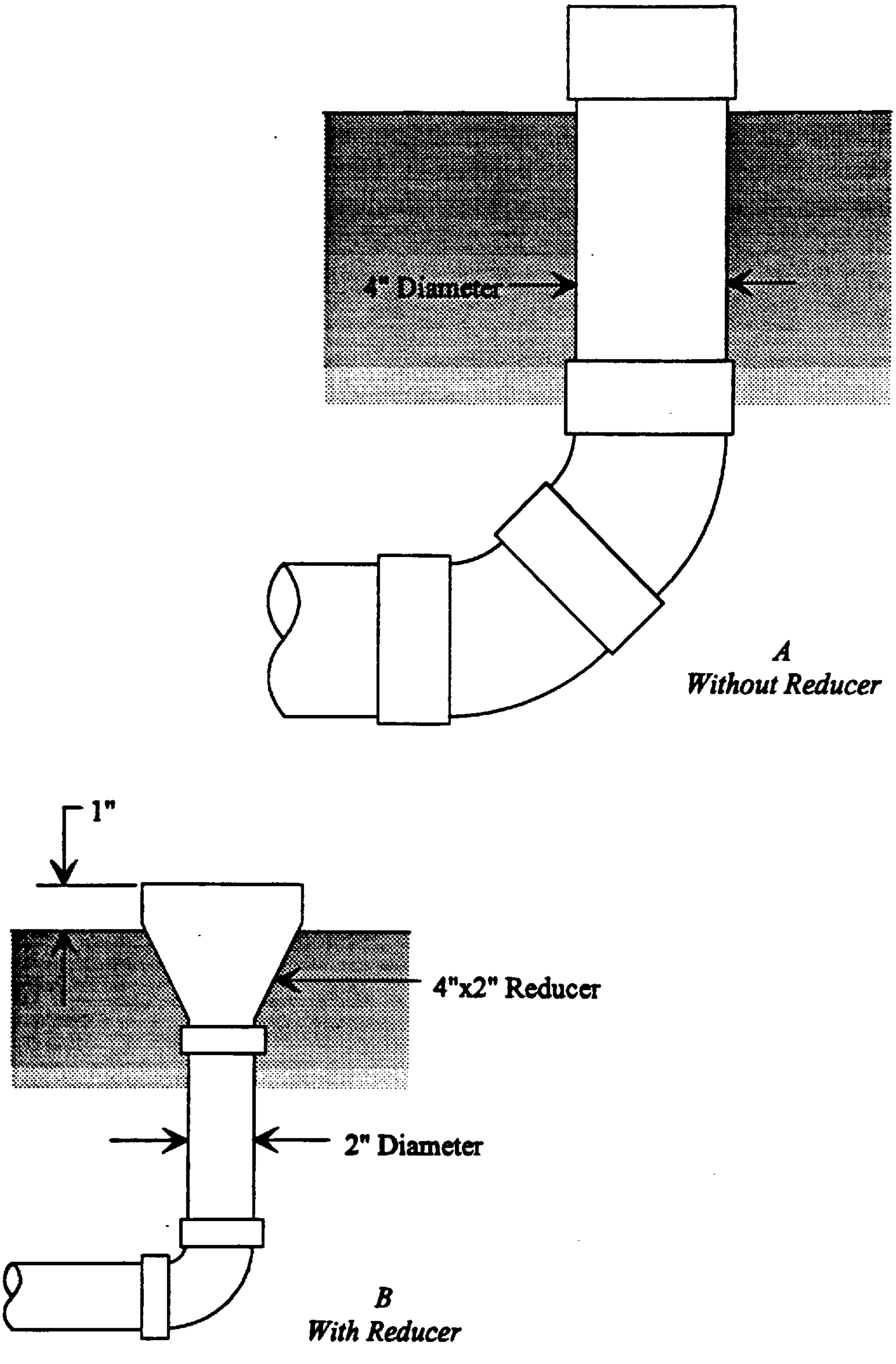


Figure C-3. Unsealed Drain Funnel (not to scale).

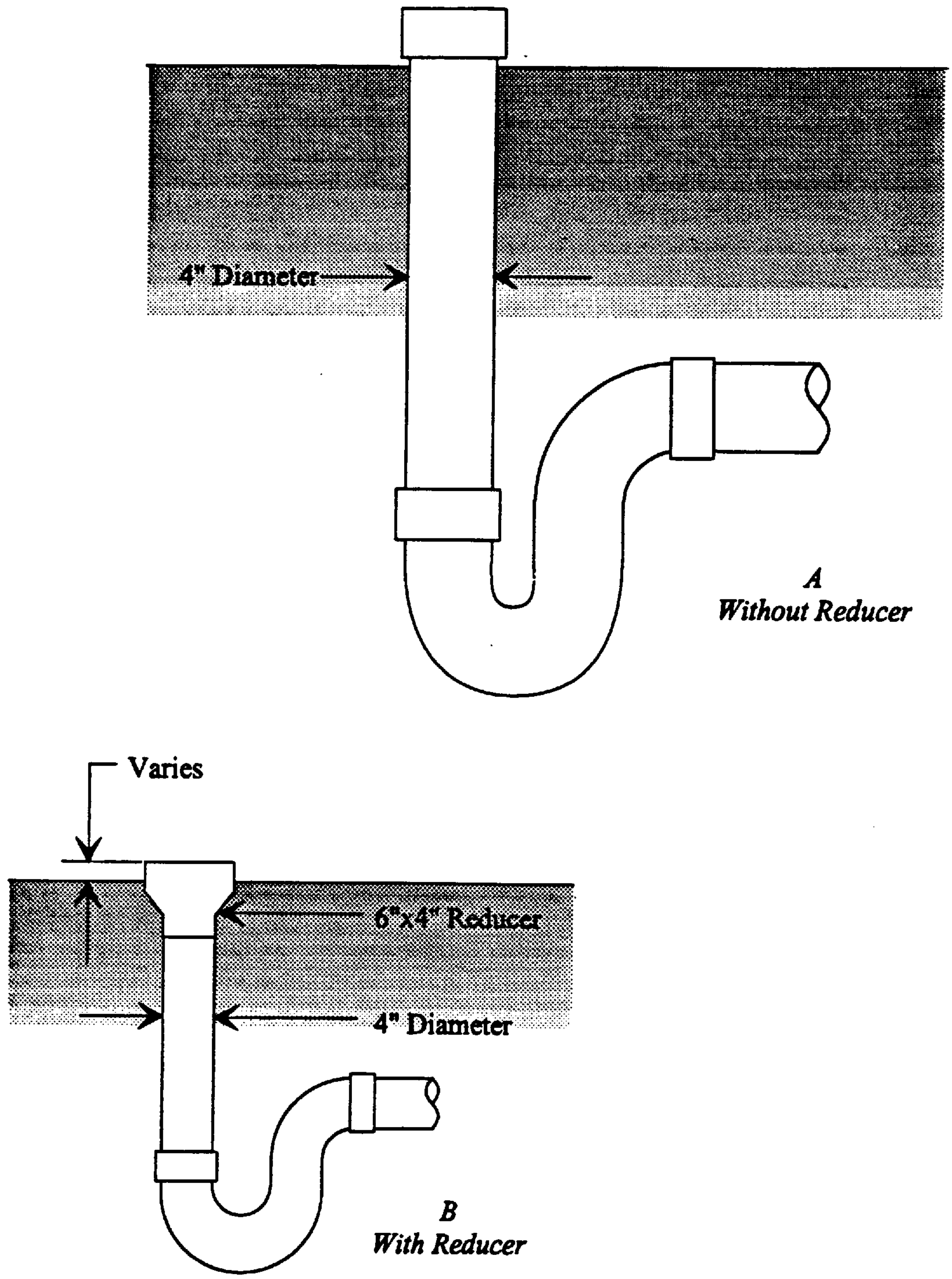


Figure C-4. "p" ("S") Trap - Water-Sealed Drain (not to scale).

Appendix 1

OBSERVATIONS OF DRAINS AT SPECIFIC PROCESS UNITS

DISTILLATION UNITS 1 AND 2

These process units date from the 1940s era. There are a total of approximately 250 to 300 drains in these units. Per operators interviewed, no major drain modifications occurred in the past 5 to 10 years.

Unsealed Drain Funnels

- This type of drain accounts for approximately 80 percent of the total drains.
- These drains generally receive pump discharges.
- Many did not have raised hubs, and thus could collect runoff.
- Most appeared not to be water-sealed.
- Discharges were normally small. Twenty-five percent of the drains observed were normally inactive; approximately 5 drains had a stream of ambient temperature water flowing into them at 1 to 2 gpm; approximately 70 percent of the drains received drips of hot water, and steam breathing was common in these drains; lube oil or hydrocarbon discharges were less than a slow drip.
- There were three drains that received discharges from purging sampling ports (10 to 20 seconds at approximately 5 to 10 gpm). Samples were collected twice daily from these ports. The sample temperatures ranged from 100 °F to 150 °F.

Water-Sealed Drains

- Approximately 20 percent of the drains observed had raised hubs (0.5 to 1 inch) above pad, hence could not receive surface runoff.
- Most of these drains appeared to have water seals (not evident in the drawing details collected during the search). Many of these drains were located along exchanger and pump rows.
- Discharges to these drains were drips from lube oil or seal water. None of these drains received continuous flows.

Catalytic Cracking Units 1 and 2

These process units date from the 1940s era. There are a total of approximately 90 to 135 drains in these units. Per operators interviewed, no major drain modifications occurred in the past 10 years.

Unsealed Drain Funnels

- This type of drain accounts for approximately 90 percent of the total drains.
- These drains generally receive pump discharges.
- Many have raised hubs (1 to 2 inch above pad), and thus could not collect runoff.
- Most appeared not to be water-sealed.
- Discharges were normally small. Fifty percent of the drains observed were normally inactive; approximately 2 drains had a stream of ambient temperature water flowing into them at 3 to 4 gpm; approximately 30 percent of the drains received drips of hot water, and steam breathing was common in these drains; lube oil or hydrocarbon discharges were less than a slow drip.
- There were five drains that received discharges from purging sampling ports (10 to 20 seconds at approximately 5 to 10 gpm). Samples were collected twice daily from these ports. The sample temperatures ranged from 150 °F to 450 °F, according to operators.

Water-Sealed Drains

- Appear to be similar to funnel type drains. This type of drain accounts for 10 percent of the drains observed.
- Most of these drains appeared to have water seals. Many of these drains were located along pump rows.
- Discharges to these drains were drips from lube oil or seal water. None of these drains received continuous flows.

Catch Basin

- There was one catch basin that collects seal water drips, sampling purge (2 sampling ports), and lube oil from four pumps. The basin was approximately 6 feet long, 1 to 2 feet deep and 1 feet wide and covered with grating. Basin could collect runoff water.
- Observed continuous seal water discharge (3 to 5 gpm) to basin from one of the pumps. The discharges seem to be at ambient temperature.

There is one drain located west of the CCU-1 control room that collects storm water and seal and lube oil discharges from a pump. The pump discharges are collected by an above ground pipe which discharges to this grated drain. Surface runoff also enters this grated drain.

CATALYTIC REFORMING UNIT 3 AND HYDRODESULFURIZATION UNIT 2

This is a 1960s era unit. There are approximately 120 to 140 drains in these units. Per operators interviewed, no major drain modifications occurred in the past 10 years.

Unsealed Drain Funnels

- This type of drain accounts for approximately 40 percent of the total drains.
- These drains generally receive pump discharges.
- Many have raised hubs (2 to 3 inch above pad), and thus could not collect runoff.
- Most appeared not to be water-sealed.
- Discharges were normally small. Thirty percent of the drains observed were normally inactive; approximately 4 drains had a stream of ambient temperature water flowing into them at 5 to 10 gpm; all these drains received drips of hot water, and steam breathing was common in these drains; lube oil or hydrocarbon discharges were less than a slow drip.
- There were 4 to 5 drains that received discharges from purging sampling ports (10 to 20 seconds at approximately 5 to 10 gpm). Samples were collected twice daily from these ports. The sample temperatures ranged from 80 °F to 120 °F.

Water-Sealed Drains

- Appear to be similar to funnel type drains. This type of drain accounts for 60 percent of the drains observed.
- Most of these drains appeared to have water seals with p-trap. Many of these drains were located along pump rows.
- Discharges to these drains were drips from lube oil or seal water. None of these drains received continuous flows.

DISTILLATE HYDROTREATER UNIT

This is a 1960s era unit. There are approximately 10 to 15 drains in this unit. Per operators interviewed, no major drain modifications occurred in the past 10 years.

Unsealed Drain Funnels

- This type of drain accounts for approximately all drains in this unit.
- These drains generally receive pump discharges.
- Many have raised hubs (2 to 3 inch above pad), and thus could not collect runoff.
- Most appeared not to be water-sealed.
- Discharges were normally small. Almost all the drains observed were normally inactive.
- There were 2 drains that received discharges from purging sampling ports (10 to 20 seconds at approximately 3 to 5 gpm). Samples were collected twice daily from these ports. The sample temperatures were ambient.

TANK DRAWDOWNS

Tank draws were collected by vacuum trucks and transported to the process wastewater treatment system. There were no drains. Purges before product sample collection from tanks are discharged to 5-gallon buckets and stored in off-spec tanks for recycling.

HYDROCRACKER UNIT

There are approximately 80 to 100 drains in this unit. Per operators interviewed, no major drain modifications occurred in the past 10 years.

Unsealed Drain Funnels

- This type of drain accounts for approximately 80 percent of the drains in this unit.
- These drains generally receive pump discharges.
- Many have raised hubs (1 to 2 inch above pad), and thus could not collect runoff.
- Most appeared not to be water-sealed.

- Discharges were normally small. Almost all the drains observed were normally inactive. Many were breathing steam.

- There were 3 drains that received discharges from purging sampling ports (10 to 20 seconds at approximately 3 to 5 gpm). Samples were collected twice daily from these ports. The sample temperatures were ambient.

Water-Sealed Drains

- Appear to be similar to funnel type drains. This type of drain accounts for 20 percent of the drains observed.

- Most of these drains appeared to have water seals with p-traps. These observations were made by placing long dry wooden sticks in the drain and noting the water mark on the stick. Many of these drains were located along pump rows.

- Discharges to these drains were drips from lube oil or seal water. None of these drains received continuous flows.

SATURATES GAS PLANT

There are approximately 60 to 80 drains at this unit. Per operators interviewed, no major drain modifications occurred in the past 10 years.

Unsealed Drain Funnels

- This type of drain accounts for approximately 90 percent of the total drains.

- These drains generally receive pump discharges.

- Many have raised hubs (2 to 3 inch above pad), and thus could not collect runoff.

- Most appeared not to be water-sealed.

- Discharges were normally small. All the drains observed were normally inactive; all these drains received drips of hot water, and steam breathing common in these drains; lube oil or hydrocarbon discharges were less than a slow drip.

- There were 5 to 6 drains that received discharges from purging sampling ports (10 to 20 seconds at approximately 5 to 10 gpm). Samples were collected twice daily from these ports. The sample temperatures were ambient.

Water-Sealed Drains

- Appear to be similar to funnel type drains. This type of drain accounts for 10 percent of the drains observed.
- Most of these drains appeared to have water seals with p-trap. These observations were made by placing long dry wooden sticks in the drain and noting the water mark on the stick. Many of these drains were located along pump rows.
- Discharges to these drains were drips from lube oil or seal water. None of these drains received continuous flows.

STEAM METHANE REFORMER UNIT

There are approximately 40 to 60 drains at this unit. Per operators interviewed, no major drain modifications occurred in the past 10 years. The drain system in this unit consists of the process wastewater collection system and sulfinol collection system.

Unsealed Drain Funnels

- This type of drain accounts for approximately 80 percent of the total drains.
- These drains generally receive pump discharges.
- Many have raised hubs (1 to 2 inch above pad), and thus could not collect runoff.
- Most appeared not to be water-sealed.
- Discharges were normally small. Most drains observed were normally inactive; all these drains received drips of hot water, and steam breathing was common in these drains; lube oil or hydrocarbon discharges were less than a slow drip. Two drains had a stream of ambient temperature water flowing into them at 2 to 4 gpm.
- There were 3 drains that received discharges from purging sampling ports (10 to 20 seconds at approximately 5 to 10 gpm). Samples were collected twice daily from these ports. The sample temperatures ranged from 80 °F to 120 °F.

Water-Sealed Drains

- Appear to be similar to funnel type drains. This type of drain accounts for 20 percent of the drains observed.

- Most of these drains appeared to have water seals with p-traps. These observations were made by placing long dry wooden sticks in the drain and noting the water mark on the stick. Many of these drains were located along pump rows.

- Discharges to these drains were drips from lube oil or seal water. None of these drains received continuous flows.

CATALYTIC REFORMING UNIT 1

There are approximately 60 to 70 drains in this unit. Per operators interviewed, no major drain modifications occurred in the past 10 years.

Unsealed Drain Funnels

- This type of drain accounts for approximately 90 percent of the total drains.

- These drains generally receive pump discharges.

- Many have raised hubs (2 to 3 inch above pad), and thus could not collect runoff.

- Most appeared not to be water-sealed.

- Discharges were normally small. All of the drains observed were normally inactive; all these drains received drips of hot water, and steam breathing was common in these drains; lube oil or hydrocarbon discharges were less than a slow drip.

- There were 2 to 3 drains that received discharges from purging sampling ports (10 to 20 seconds at approximately 5 to 10 gpm). Samples were collected twice daily from these ports. The sample temperatures ranged from 80 °F to 120 °F.

Water-Sealed Drains

- Appear to be similar to funnel type drains. This type of drain accounts for 10 percent of the drains observed.

- Most of these drains appeared to have water seals with p-traps. Many of these drains were located along pump rows.

- Discharges to these drains were drips from lube oil or seal water. None of these drains received continuous flows.

CATALYTIC REFORMING UNIT 2 AND HYDRODESULFURIZATION UNIT 1

There are approximately 80 to 100 drains in these units. Per operators interviewed, no major drain modifications occurred in the past 10 years.

Unsealed Drain Funnels

- This type of drain accounts for approximately 70 percent of the total drains.
- These drains generally receive pump discharges.
- Many have raised hubs (2 to 3 inch above pad), and thus could not collect runoff.
- Most appeared not to be water-sealed.
- Discharges were normally small. Eighty percent of the drains observed were normally inactive; one drain had a stream of ambient temperature water flowing at 3 to 5 gpm; all other drains received drips of hot water, and steam breathing was common in these drains; lube oil or hydrocarbon discharges were less than a slow drip.
- There were 3 to 5 drains that received discharges from purging sampling ports (10 to 20 seconds at approximately 5 to 10 gpm). Samples were collected twice daily from these ports. The sample temperatures ranged from 90 °F to 120 °F.

Water-Sealed Drains

- Appear to be similar to funnel type drains. This type of drain accounts for 30 percent of the drains observed.
- Most of these drains appeared to have water seals with p-traps. Many of these drains were located along pump rows.
- Discharges to these drains were drips from lube oil or seal water. None of these drains received continuous flows.
- There were two drains that were cylindrical. The cylinders were 0.75 to 1 ft diameter, 1.5 to 2 ft deep (long) cast iron pipes. These drains appeared to have water seals with p-traps. These cylindrical drains collected discharges from 3 to 4 pipes. The discharge point of these pipes were 0.5 to 1 inch below the top of the cylinder. No drawing details collected showed such drains.

KEROSENE HYDROTREATING UNIT

There are approximately 15 to 30 drains in this unit. Per operators interviewed, no major drain modifications occurred in the past 10 years.

Unsealed Drain Funnels

- This type of drain accounts for approximately 20 percent of the total drains.
- These drains generally receive pump discharges.
- Many have raised hubs (2 to 3 inch above pad), and thus could not collect runoff.
- Most appeared not to be water-sealed.
- Discharges were normally small. Eighty percent of the drains observed were normally inactive; two drains had streams of ambient temperature water flowing at 3 - 5 gpm; all other drains received drips of hot water, and steam breathing was common in these drains; lube oil or hydrocarbon discharges were less than a slow drip.
- There were 5 drains that received discharges from purging sampling ports (10 to 20 seconds at approximately 3 to 5 gpm). Samples were collected twice daily from these ports. The sample temperatures ranged from 80 °F to 120 °F.

Water-Sealed Drains

- Appear to be similar to funnel type drains. This type of drain accounts for 80 percent of the drains observed.
- Most of these drains appeared to have water seals with p-traps. Many of these drains were located along pump rows.
- Discharges to these drains were drips from lube oil or seal water. None of these drains received continuous flows.
- There were four drains that were cylindrical. The cylinders were 0.5 to 0.75 ft diameter, 1 to 1.5 ft deep (long) cast iron pipes. These drains appeared to have water seals with p-traps. These cylindrical drains collected discharges from 3 to 4 pipes. The discharge point of these pipes were 0.5 to 1 inch below the top of the cylinder. No drawing details collected showed such drains.

BENZENE AND KEROSENE EXTRACTION UNITS

There are approximately 50 to 60 drains in these units. Per operators interviewed, no major drain modifications occurred in the past 10 years.

Unsealed Drain Funnels

- This type of drain accounts for approximately 40 percent of the total drains.
- These drains generally receive pump discharges.
- Many have raised hubs (2 to 3 inch above pad), and thus could not collect runoff.
- Most appeared not to be water-sealed.
- Discharges were normally small. All the drains observed were normally inactive; all these drains received drips of hot water, and steam breathing was common in these drains; lube oil or hydrocarbon discharges were less than a slow drip.
- There were 2 drains that received discharges from purging sampling ports (10 to 20 seconds at approximately 3 to 5 gpm). Samples were collected twice daily from these ports. The sample temperatures ranged from 90 °F to 120 °F.

Water-Sealed Drains

- Appear to be similar to funnel type drains. This type of drain accounts for 60 percent of the drains observed.
- Most of these drains appeared to have water seals with p-traps. Many of these drains were located along pump rows.
- Discharges to these drains were drips from lube oil or seal water. None of these drains received continuous flows.

ALKYLATION UNIT

This process unit dates from the 1940s era. There are approximately 100 to 150 drains in this unit. The drain system in this unit consists of the process wastewater collection system and acid discharge collection system.

The acid sewer system in this unit was modified in early 1990s. The acid sewer pipes, made of CPVC (chlorinated polyvinyl chloride), were placed in grated open trenches to facilitate identification of leaking pipes. The ratio of unsealed-to-sealed drains in the new acid sewers is the same 70/30 percent ratio described below for the entire unit.

Unsealed Drain Funnels

- This type of drain accounts for approximately 70 percent of the drains in this unit.
- These drains generally receive pump discharges.
- Many have raised hubs (1 to 2 inch above grating). Runoffs collected in the trenches.
- Most appeared not to be water sealed.
- Discharges were normally small. Almost all the drains observed were normally inactive. Most drains appeared to receive discharges at ambient temperatures.
- There were 4 to 6 drains that received discharges from purging sampling ports (10 to 20 seconds at approximately 3 to 5 gpm). Samples were collected twice daily from these ports. The sample temperatures were ambient.

Water-Sealed Drains

- Appear to be similar to funnel type drains. This type of drain account for 30 percent of the drains observed.
- Most of these drains appeared to have water seals with p-traps. These observations were made by placing long dry wooden sticks in the drain and noting the water mark on the stick. Many of these drains were located along pump rows.
- Discharges to these drains were drips from lube oil or seal water. None of these drains received continuous flows.

LIGHT OILS TREATMENT UNIT

There are approximately 70 to 80 drains in this unit. Per operators interviewed, no major drain modifications occurred in the past 10 years. The drain system in this unit consists of the process wastewater collection system and caustic collection and recycling system.

Unsealed Drain Funnels

- This type of drain accounts for approximately 10 percent of the total drains.
- These drains generally receive pump discharges. There were no continuous discharges.
- Many have raised hubs (3 to 4 inch above pad), and thus could not collect runoff.
- Most appeared not to be water-sealed.
- Discharges were normally small. More than 90 percent of the drains observed were normally inactive; all these drains received drips of hot water, and steam breathing was common in a few of these drains; lube oil or hydrocarbon discharges were less than a slow drip.
- There were 2 to 3 drains that received discharges from purging sampling ports (10 to 20 seconds at approximately 5 to 10 gpm). Samples were collected two or three times daily from these ports. The sample temperatures ranged from 100 °F to 140 °F.

Water-Sealed Drains

- Appear to be similar to funnel type drains. This type of drain accounts for 90 percent of the drains observed.
- Most of these drains appeared to have water seals with p-traps. These observations were made by placing long dry wooden sticks in the drain and noting the water mark on the stick. Many of these drains were located along pump rows.
- Discharges to these drains were drips from lube oil or seal water. None of these drains received continuous flows.

LUBE FRACTIONATION AND EXTRACTION UNIT

There are approximately 60 to 80 drains in this unit. Per operators interviewed, no major drain modifications occurred in the past 10 years. However, the unit underwent modifications in the early 1980s.

Unsealed Drain Funnels

- This type of drain accounts for approximately 80 percent of the total drains.
- These drains generally receive pump discharges. There were no continuous discharges.

- Many have raised hubs (0.75 to 4 inch above pad), and thus could not collect runoff.

- Most appeared not to be water-sealed.

- Discharges were normally small. More than 90 percent of the drains observed were normally inactive; all these drains received drips of hot water, and steam breathing was noticed in a few of these drains; lube oil or hydrocarbon discharges were less than a slow drip.

- There were 2 drains that received discharges from purging sampling ports (10 to 20 seconds at approximately 5 to 10 gpm). Samples were collected twice daily from these ports. The sample temperatures ranged from 100 °F to 160 °F.

Water-Sealed Drains

- Appear to be similar to funnel type drains. This type of drain accounts for 20 percent of the drains observed.

- Most of these drains appeared to have water seals with p-traps. These observations were made by placing long dry wooden sticks in the drain and noting the water mark on the stick. Many of these drains were located along pump rows.

- Discharges to these drains were drips from lube oil or seal water. None of these drains received continuous flows.

COMPOUNDING UNIT

There are approximately 40 to 60 drains in this unit. Per operators interviewed, no major drain modifications occurred in the past 10 years.

Unsealed Drain Funnels

- This type of drain accounts for approximately 70 percent of the total drains.

- These drains generally receive pump discharges.

- Many have raised hubs (2 to 4 inch above pad), and thus could not collect runoff.

- Most appeared not to be water-sealed.

- Discharges were normally small. All the drains observed were normally inactive; all these drains received drips of hot water, and steam breathing was common in these drains; lube oil or hydrocarbon discharges were less than a slow drip.

- There were 2 drains that received discharges from purging sampling ports (10 to 20 seconds at approximately 3 to 5 gpm). Samples were collected twice daily from these ports.

Water-Sealed Drains

- Appear to be similar to funnel type drains. This type of drain accounts for 30 percent of the drains observed.

- Most of these drains appeared to have water seals with p-trap. Many of these drains were located along pump rows.

- Discharges to these drains were drips from lube oil or seal water. None of these drains received continuous flows.

CATALYTIC DEWAXING AND DEASPHALTING UNITS

There are approximately 100 to 120 drains in these units. Due to lack of time, operator interviews were not possible in these units.

Unsealed Drain Funnels

- This type of drain accounts for approximately 40 percent of the total drains.

- These drains generally receive pump discharges.

- Many have raised hubs (1 to 2 inch above pad), and thus could not collect runoff.

- Most appeared not to be water-sealed.

- Discharges were normally small. All the drains observed were normally inactive; all these drains received drips of hot water, and steam breathing was common in these drains; lube oil or hydrocarbon discharges were less than a slow drip.

Water-Sealed Drains

- Appear to be similar to funnel type drains. This type of drain accounts for 60 percent of the drains observed.

- Most of these drains appeared to have water seals with p-traps. Many of these drains were located along pump rows.
- Discharges to these drains were drips from lube oil or seal water. None of these drains received continuous flows.

ASPHALT PLANT

There are approximately 20 to 40 drains in this plant. Due to lack of time, operator interviews were not possible in this plant.

Unsealed Drain Funnels

- This type of drain accounts for approximately all drains in this plant.
- These drains generally receive pump discharges.
- Many have raised hubs (2 to 4 inch above pad), and thus could not collect runoff.
- Most appeared not to be water-sealed.
- Discharges were normally small. All the drains observed were normally inactive; all these drains received drips of hot water, and steam breathing was common in these drains; lube oil or hydrocarbon discharges were less than a slow drip.

RECTIFIED ABSORBER UNIT AND GAS PLANTS

There are approximately 150 to 200 drains in these units. Due to lack of time, operator interviews were not possible in these units.

Unsealed Drain Funnels

- This type of drain accounts for approximately 60 percent of the total drains.
- These drains generally receive pump discharges.
- Many have raised hubs (2 to 3 inch above pad), and thus could not collect runoff.
- Most appeared not to be water-sealed.
- Discharges were normally small. All the drains observed were normally inactive; all these drains received drips of hot water, and steam breathing was common in these drains; lube oil or hydrocarbon discharges were less than a slow drip.

Water-Sealed Drains

- Appear to be similar to funnel type drains. This type of drain accounts for 40 percent of the drains observed.

- Most of these drains appeared to have water seals with p-traps. Many of these drains were located along pump rows.

- Discharges to these drains were drips from lube oil or seal water. None of these drains received continuous flows.

SULFUR RECOVERY AND *SCOT* UNITS

There are approximately 20 to 40 drains in these units. Due to lack of time, operator interviews were not possible in these units.

Unsealed Drain Funnels

- This type of drain accounts for approximately 20 percent of the total drains.

- These drains generally receive pump discharges.

- Many have raised hubs (2 to 3 inch above pad), and thus could not collect runoff.

- Most appeared not to be water-sealed.

- Discharges were normally small. All the drains observed were normally inactive; all these drains received drips of hot water, and steam breathing was common in these drains; lube oil or hydrocarbon discharges were less than a slow drip.

Water-Sealed Drains

- Appear to be similar to funnel type drains. This type of drain accounts for 80 percent of the drains observed.

- Most of these drains appeared to have water seals with p-traps. Many of these drains were located along pump rows.

- Discharges to these drains were drips from lube oil or seal water. None of these drains received continuous flows.

VISBREAKER UNIT

There are approximately 40 to 60 drains in these units. Due to lack of time, operator interviews were not possible in this unit.

Unsealed Drain Funnels

- This type of drain accounts for approximately 50 percent of the total drains.
- These drains generally receive pump discharges.
- Many have raised hubs (2 to 3 inch above pad), and thus could not collect runoff.
- Most appeared not to be water-sealed.
- Discharges were normally small. All the drains observed were normally inactive; all these drains received drips of hot water, and steam breathing was common in these drains; lube oil or hydrocarbon discharges were less than a slow drip.

Water-Sealed Drains

- Appear to be similar to funnel type drains. This type of drain accounts for 50 percent of the drains observed.
- Most of these drains appeared to have water seals with p-traps. Many of these drains were located along pump rows.
- Discharges to these drains were drips from lube oil or seal water. None of these drains received continuous flows.

WASTEWATER TREATMENT PLANT

There are approximately 10 to 15 drains in this plant. The sewer system in this plant was modified in early 1990s. The sewer pipes were placed in grated open trenches to facilitate identification of leaking pipes. Most of these drains have water seals with a p-trap. Many of these drains were located along wastewater tanks. The above observations were made by a refinery employee. Due to lack of time, a plant visit was not possible.

SURVEY OF PROCESS DRAINS REPORTS
EAST COAST REFINERY

SUMMARY

A three-day survey of process drains was conducted at a mid-sized east coast refinery. The survey involved a review of drain drawings, brief discussions with key environmental and field operations personnel, and visual inspections of selected process units. Only one basic type of drain system was identified in the refinery, the p-trap, with minor variations. Approximately 1,370 to 1,930 drains (with a mean value of 1650) were estimated to be in the refinery, almost all of which had p-trap water seals.

PROCEDURES

The process drains at an east coast petroleum refinery were surveyed on May 10, 11, and 12, 1995. Junction boxes and any other downstream drain structures were not included in this survey. The survey was conducted in a series of steps. Brief interviews were held with key refinery environmental and field operations personnel to obtain information on the types of process drains used in this refinery, the history of drain installation, and the nature of wastewater being routed to the different drains. Hard-copy 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.

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. The inspection also involved evaluating the types of discharges, quantities of discharge, level of activity, and the existence of high temperature discharges (condensate or steam blowoffs) to the drains.

MAJOR FINDINGS

An estimated 1,370 to 1,930 process unit drains were present in the refinery. Visual observations of drains in process units indicated that almost all are water-sealed. Table 1 presents the breakdown of the estimated number of drains in refinery process units. The information in Table 1 was estimated by counting drains shown on drawings, asking unit operators for their estimates of drain counts, and visually estimating drains during unit inspections. Active drains were defined to be those from which there was a continuous discharge. While more than half of the drains inspected did discharge continuously, these discharges were condensate from steam turbine pumps and were, therefore, omitted from the count of active drains. Based on this definition, the number of active drains were estimated to be approximately 40 for the units inspected. This represented approximately two percent of the drains at the units inspected.

Type A Drains

These drains consist of a 4 inch cast iron soil pipe (CISP) with a p-trap type water seal connected to laterals leading to trunk sewers (Figure C-5). The drain hubs associated with this type of drain were typically raised 1 inch above grade, with the aid of surface sloping, to exclude surface flows. These drains were usually associated with pump seal discharges and sampling ports. Typical pump drains were fed by two to three hardpipes, normally 1 inch diameter or less, carrying sealing discharges, steam blowoff, steam condensates, and pump pad drainage. Many of these drains received steady or intermittent flows. During winter months, the seal water has not been known to freeze.

Type B Drains

These drains are similar in construction to type A drains, but the drain hub was raised 6 inches above grade. These drains typically collect discharges from equipment sampling ports and heat exchangers (Figure C-6). Many of these drains received intermittent discharges or no discharges at all under normal operating conditions. During winter months, the seal water has not been known to freeze.

Type C Drains

These drains typically consist of a 4 inch CISP connected to a 90° elbow followed by a straight pipe run with a p-trap type water seal (running trap) before connecting to laterals leading to trunk sewers (Figure C-7). The water seals in these drains could not be seen during the inspections. The drain hubs associated with this type of drain were typically raised 1 inch above grade, with the aid of surface sloping, to exclude surface flows. Most of these drains were associated with towers, heat exchangers, condensers, and compressors. Tower, heat exchanger, and condenser drains were normally inactive.

Type D Drains

These drains are similar to Type C running-trap drains, but with a 45° connector rather than a 90° connector (Figure C-8). Drain locations and activities were the same as with Type C drains.

Detailed observations from each inspected process unit are presented in Appendix 1, at the end of this section.

Table 1. List of Process Drains in Various Refinery Units.

Unit Name	Estimated Number of Drains	Active Drains[1]
Crude Unit 1	200 - 250	0
Coker Unit 2 (shutdown for turn around)	100 - 150	-
Cracker and Fractionator Unit	100 - 150	37
Gas Plant	100 - 150	-
Reformer Unit	80 - 140	-
Poly Plant	40 - 80	-
Alky Plant	60 - 90	-
Sulfur Plant	30 - 40	-
Desulfurizer Unit	50 - 70	3
Process Unit	50 - 70	-
Process Plant	70 - 90	-
Process Plant	30 - 50	-
Butadiene Plant	40 - 60	-
Hydrocracker Unit	80 - 100	-
Hydrogen Plant-II	70 - 90	-
Tank Farm and Blenders	50 - 80	0
Process Plant	80 - 100	-
New Reformer Unit	60 - 90	-
Process Plant	60 - 70	0
Wastewater Treatment Plant	10 - 20	-
Total Drains in the Refinery	1370 - 1930	

[1] These include drains with continuous flow discharges (excluding steam turbine pump condensate discharges).

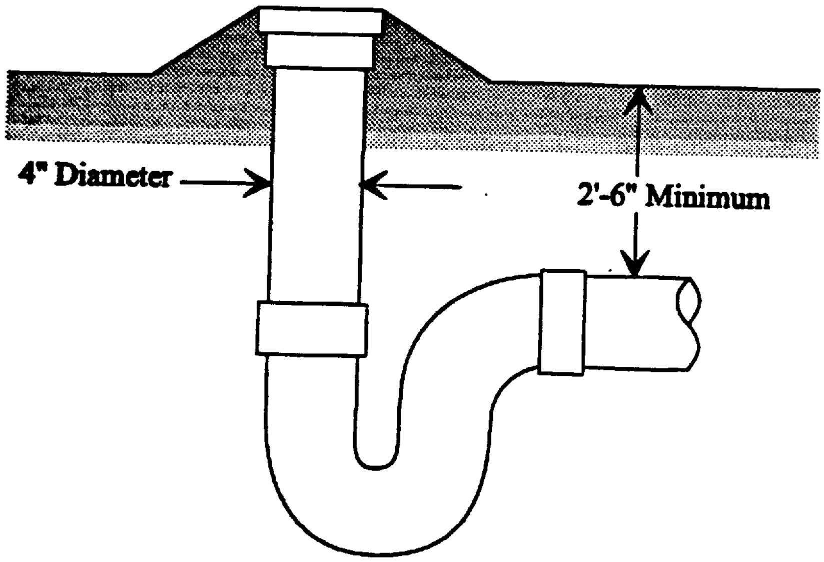


Figure C-5. "p" Trap - Type A (not to scale).

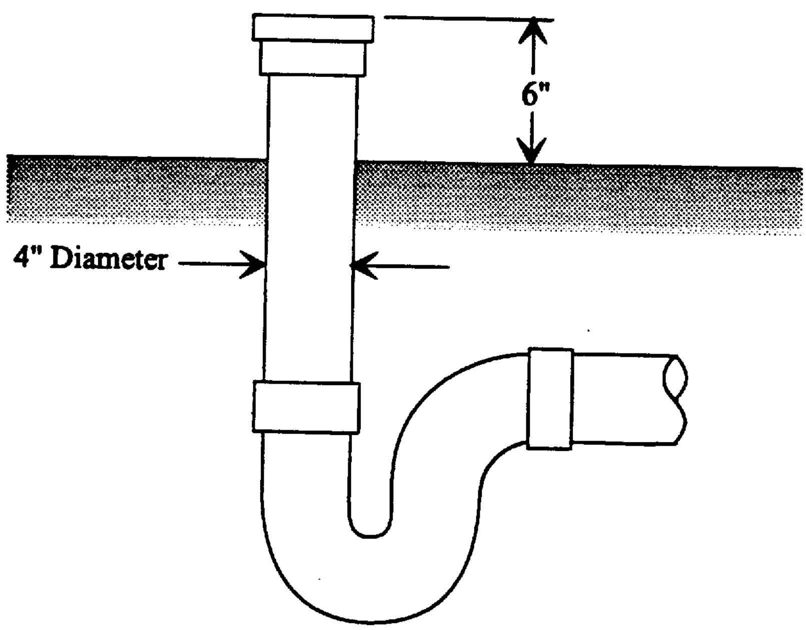


Figure C-6. "p" Trap - Type B (not to scale).

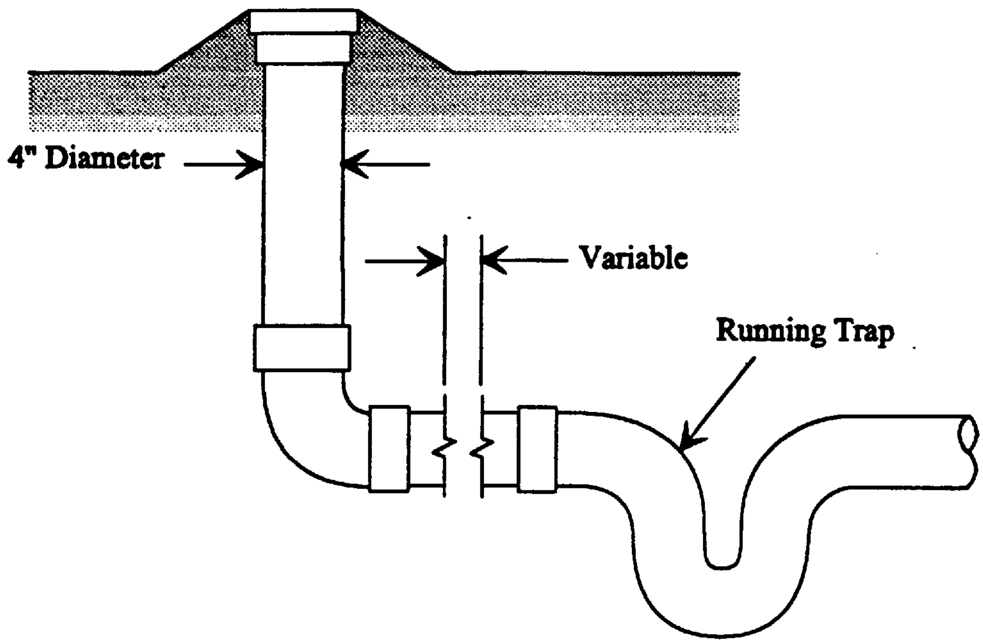


Figure C-7. "p" Trap - Type C (not to scale).

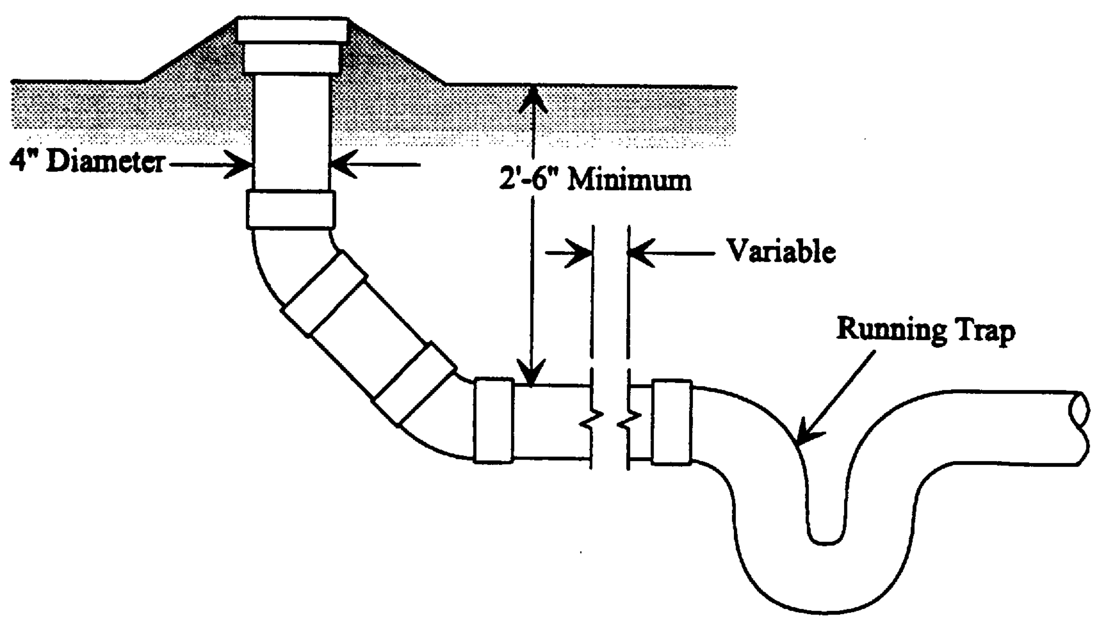


Figure C-8. "p" Trap - Type D (not to scale).

Appendix 1

OBSERVATIONS OF DRAINS AT SPECIFIC PROCESS UNITS

CRUDE UNIT 1

This process unit dates from the mid-1950s era. There are approximately 200 to 250 drains in this unit. Per operators interviewed, no major drain modifications occurred in the past 10 years.

Type A Drains

- This type of drain accounts for approximately all the drains in this unit. These drains were with p-trap type water seal.
- These drains generally receive pump discharges.
- Many had raised hubs above-grade connection with top of drain hub located 1 inch above surface elevation, and thus could not collect surface runoff.
- Most appeared to be water-sealed.
- Discharges were normally small. Approximately 25 percent of the drains observed were normally inactive. The remaining 75 percent of the drains received drips of hot water, and steam breathing was also common in these drains. Most of the drains received continuous flows from steam turbine pumps, typically in the range of 3 to 5 gpm. Lube oil or hydrocarbon discharges were less than a slow drip.
- There were 10 to 12 drains that received discharges from purging sampling ports (10 to 20 seconds at approximately 5 to 10 gpm). Samples were collected once daily from these ports. The sample temperatures ranged from ambient to 90 °F.

CRACKER AND FRACTIONATOR UNITS

This process unit dates from the mid-1950s era. There are approximately 100 to 150 drains in this unit. Per operators interviewed, no major drain modifications occurred in the past 10 years.

Type A Drains

- This type of drain accounts for approximately 70 percent of the drains in this unit. These drains had p-trap type water seals.
- These drains generally received pump discharges.
- Many did not have raised hubs, and thus could collect runoff.

- Most appeared to be water-sealed.
- Discharges were normally small. Approximately 50 percent of the drains observed were normally inactive. The remaining 50 percent of the drains received drips of hot water, and steam breathing was common in these drains. Most of these drains received continuous flows from steam turbine pumps, typically in the range of 3 to 5 gpm. Lube oil or hydrocarbon discharges were less than a slow drip.
- There were 8 to 10 drains that received discharges from purging sampling ports (10 to 20 seconds at approximately 5 to 10 gpm). Samples were collected once daily from these ports. The sample temperatures ranged from ambient to 100 °F to 200 °F.

Type C Drains

- This type of drain accounts for approximately 30 percent of the drains in this unit. These drains had running traps (p-traps in a running pipe).
- These drains generally receive discharges from heat exchangers, compressors, and condensers.
- This type had raised hubs (1 inch above finished surface), and thus could not collect runoff.
- Discharges were normally small. Most of the drains observed were normally active receiving continuous flows at 1 to 2 gpm.

HYDRODESULFURIZATION UNIT

This process unit dates from the mid-1950s era. There are approximately 50 to 70 drains in this unit. Per operators interviewed, no major drain modifications occurred in the past 10 years.

Type A Drains

- This type of drain accounts for almost all the drains in this unit. These drains had p-trap type water seals.
- These drains generally received pump discharges.
- Many did not have raised hubs, and thus could collect runoff.
- Most appeared to be water-sealed.
- Discharges were normally small. Most of the drains observed were normally inactive. Of the remaining drains (< 5 percent), some received drips of hot water, and steam breathing was common; most, however, received continuous flows from steam turbine

pumps, typically in the range of 3 to 5 gpm. Lube oil or hydrocarbon discharges were less than a slow drip.

- There were 4 to 6 drains that received discharges from purging sampling ports (10 to 20 seconds at approximately 5 to 10 gpm). Samples were collected once daily from these ports. The sample temperatures ranged from ambient to 70 °F to 100 °F.

Type D Drains

- This type of drain accounts for less than 5 percent of the drains in this unit. These drains had running traps. Most had type 3 above-grade connections.
- These drains generally receive discharges from heat exchangers, towers, and vessels.
- This type had raised hubs (1 inch above finished surface), and thus could not collect runoff.
- Discharges were normally small. Most of the drains observed were normally active receiving continuous flows at 2 to 5 gpm.

PROCESS UNIT

This is a recent addition to the refinery. There are approximately 60 to 70 drains in this unit.

Type A Drains

- This type of drain was similar to Type B and accounted for approximately all drains in this unit.
- These drains generally received pump discharges.
- Most had raised hubs (2 to 3 inch above pad), and thus could not collect runoff. The discharge pipes in most cases were 2 to 3 inch below the top of the drain hub; that is, discharge pipes broke the plane of the drain hub.
- Almost all appeared to be water-sealed.
- Discharges were normally small. Almost all the drains observed were normally inactive.
- There were 2 drains that received discharges from purging sampling ports (10 to 20 seconds at approximately 3 to 5 gpm). Samples were typically collected twice a week from these ports. The sample temperatures were at operating conditions.

TANK DRAWDOWNS

Tank draws were discharged to the process wastewater treatment system through the underground drainage system. There are approximately 50 to 80 drains associated with tank draws.

Type A Drains

- This type of drain accounts for approximately all the drains associated with tanks. These drains had p-trap type water seals.
- These drains generally received pump discharges.
- Many did have raised hubs (1 inch above finished surface), and thus could not collect runoff. However, there were area drains in some tank containment areas that were connected to the process sewer system. At these tanks, an enclosed separation system exists to segregate dry weather flow from wet weather flow, with vapor control for the dry weather system.
- Most appeared to be water-sealed.
- Tank draw drains were normally inactive. During tank draws, operators normally drained water for about 10 to 30 minutes, depending on the amount of water in the tank. Refinery-wide averages are in the range of 10 to 50 gallons per tank, drawn once per week.
- Most tanks are sampled, and the sampling frequency varies widely. The sample purges are discharged to the drains. The discharges typically last 10 to 20 seconds at approximately 5 to 10 gpm. The sample temperatures ranged from ambient to 200 °F.

Appendix D

MODEL DEVELOPMENT FOR REFINERY PROCESS DRAINS

MASS TRANSFER ABOVE HUB

Mass transfer above a drain hub includes mechanisms 1-2 in Figure D-1. For the purposes of simplification, it is assumed that the concentration of a VOC in air (C_g) adjacent to the falling or splashing liquid stream is negligible. This should be a conservative, but generally reasonable assumption. Furthermore, two specific conditions are modeled. The first involves a process stream that flows into an aligned hub, with minimal surface contact prior to entering the drain throat. In this case, mass transfer is assumed to occur entirely between the falling film surface and adjacent air. The second condition involves a misaligned hub. In this case, it is likely that splashing and the subsequent increase in liquid-air contact area will dominate the mass transfer process.

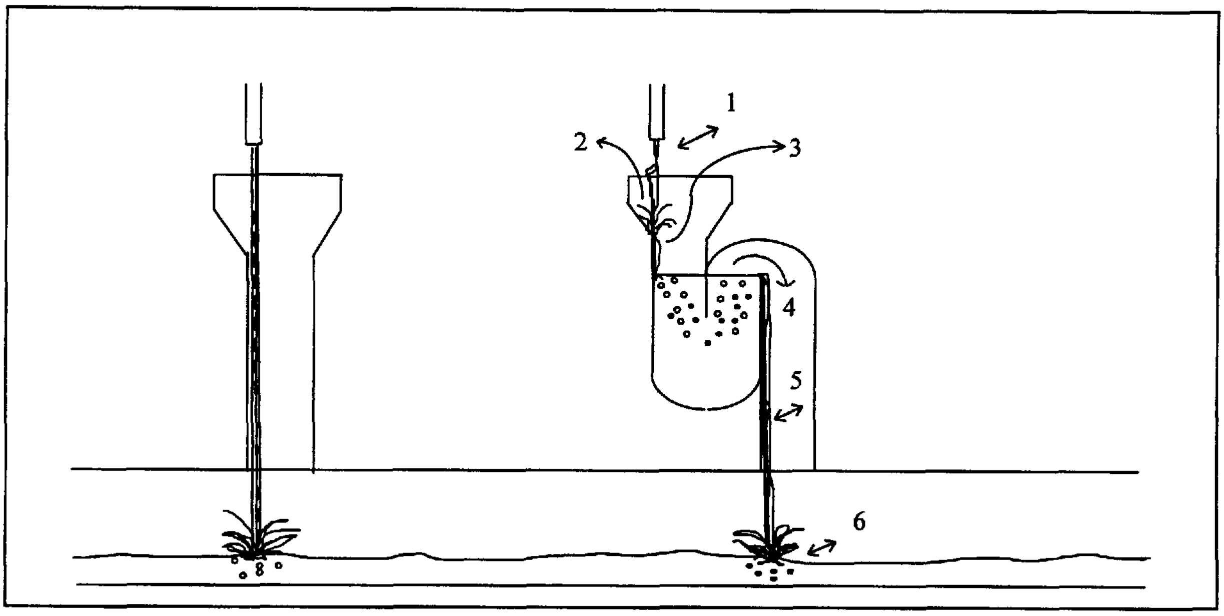


Figure D-1. Mass Transfer Mechanisms in Process Drains.

For the assumptions listed above, a mass balance on the falling film leads to the following equation:

$$C_f = C_o \exp\left\{-\frac{K_{L1}A_1}{Q_l}\right\} \quad \text{(D-1)}$$

where,

C_f = final concentration (concentration of VOC at end of film). (mg/m^3)
C_o = initial concentration of VOC exiting the pipe nozzle (mg/m^3)
K_{L1} = overall mass transfer coefficient for falling jet (m/hr)
A_1 = interfacial contact area for falling jet (m^2)
Q_l = liquid flowrate (m^3/hr)

It is assumed that the falling film remains intact (not disintegrated) during its descent. The interfacial contact area is therefore determined as:

$$A_1 = P_1 l_1 \quad \text{(D-2)}$$

where,

P_1 = perimeter of falling jet (m)
l_1 = distance to hub contact point or drain throat (m)

Thus, equation D-1 becomes

$$C_f = C_o \exp\left\{-\frac{K_{L1}P_1 l_1}{Q_l}\right\} \quad \text{(D-3)}$$

It is assumed that P_1 is also equal to the exit diameter of the drain pipe. Finally, it is assumed that K_{L1} is comprised of both liquid and gas-phase resistance terms in accordance with two-film theory:

$$\frac{1}{K_L} = \frac{1}{k_l} + \frac{1}{k_g H_c} \quad \text{(D-4)}$$

where,

k_l = liquid-phase mass transfer coefficient (m/hr)
k_g = gas-phase mass transfer coefficient (m/hr)
H_c = Henry's law coefficient for a specific VOC (m^3_{liq}/ m^3_{gas}).

Hereafter, it is assumed that all overall mass transfer coefficients can be determined in terms of both liquid and gas-phase mass transfer coefficients. Furthermore, C_o and C_f will always denote the concentrations of a VOC in the stream flowing into and out of a region, respectively. Thus C_f becomes C_o for the next region in a series, and so forth.

For mass transfer within a misaligned hub, the hub is assumed to approach a continuous stirred-tank reactor (CSTR) at steady-state with $C_g = 0$. A mass balance on the hub leads to:

$$C_f = \frac{C_o}{1 + \left\{\dfrac{K_{L1}A_1}{Q_L}\right\}} \qquad \text{(D-5)}$$

where,

K_{L1} = overall mass transfer coefficient for a VOC in a misaligned hub (m/hr)
A_1 = interfacial contact area (liquid-air) in hub (m^2).

For the purposes of this study, K_{L1} and A_1 are "lumped" into a single term $K_{L1}A_1 = K'_{L1}$ (m^3/hr).

MASS TRANSFER BELOW HUB AND ABOVE TRAP/CHANNEL

The region below the hub but above an underlying trap, or channel for a straight drain, is characterized by a falling film or jet. Within this region, it is not necessarily valid to assume that $C_g = 0$. Thus, the following plug-flow mass balance equations must be solved simultaneously for both the liquid and gas-phases at steady-state:

$$Q_l \frac{dC_l}{dz} = -K_{L2}\left(C_l - \frac{C_g}{H_c}\right)P_2 \qquad \text{(D-6)}$$

$$Q_g \frac{dC_g}{dz} = +K_{L2}\left(C_l - \frac{C_g}{H_c}\right)P_2 \qquad \text{(straight drain)} \qquad \text{(D-7)}$$

$$C_g = \frac{Q_l}{Q_v}\left(C_o - C_f\right) \qquad \text{(trapped drain)} \qquad \text{(D-8)}$$

where,

K_{L2} = overall mass transfer coefficient for a VOC and the specific process (m/hr)
C_g = concentration of VOC in air (mg/m^3)
P_2 = perimeter of falling jet or plume (m)
Q_g = air flowrate within drain hub (m^3/hr)
Q_v = air circulation rate in "trapped" drain throat (m^3/hr)
z = distance below mouth of drain (m).

The following boundary conditions are prescribed for solving Equations D-6 and D-7 for co-current air-water flow:

$C_g = 0$ at $z = 0$
$C_l = C_o$ at $z = 0$.

Solution of Equations D-6 and D-7 using the method of elimination then yields:

$$C_f = C_o\left[1 + \frac{Q_g H_c}{Q_g H_c + Q_l}\left(1 - e^{-az}\right)\right] \qquad \text{(D-9a)}$$

$$C_{gf} = \frac{Q_l H_c C_o}{Q_l + Q_g H_c}\left(1 - e^{-az}\right) \qquad \text{(D-9b)}$$

where: $$a = \frac{K_{L2} P_2 \left(Q_g H_c + Q_l\right)}{Q_g Q_l H_c}$$

Similarly, Equations D-6 and D-8 can be solved subject to $C_l = C_o$ at $z = 0$ to yield:

$$C_f = C_o\left\{\frac{b}{a}\left(1 - e^{-az}\right) + e^{-az}\right\} \qquad \text{(D-10a)}$$

$$C_{gf} = C_o \frac{Q_l}{Q_v}\left\{1 - e^{-az} - \frac{b}{a}\left(1 - e^{-az}\right)\right\} \qquad \text{(D-10b)}$$

where:

$$a = \frac{K_{L2} P_2 \left(Q_v H_c + Q_l\right)}{Q_v Q_l H_c}$$

$$b = \frac{K_{L2} P_2}{Q_v H_c}$$

For D-9a, C_f denotes the VOC concentration in liquid which exits the drain throat, i.e., into the underlying channel. For D-10a, C_f denotes the VOC concentration in liquid immediately prior to impact with the trap surface. For D-9b, C_{gf} denotes the VOC concentration in air which exits the drain throat, i.e., into the underlying channel headspace. For D-10b, C_{gf} denotes the well-mixed gas concentration which exists everywhere in the throat above the trap surface.

The variable P_2 is assumed to either equal the perimeter of the falling jet (drain pipe nozzle perimeter), or perimeter of the drain throat (in the case of an attached film).

MASS TRANSFER WITHIN A TRAP

For purposes of simplification, the trap is assumed to be a CSTR at steady-state. Furthermore, it is assumed that air entrainment is the dominant mass transfer mechanism, and that air bubbles which enter the trap exit downstream, i.e., on the channel side. A mass balance on the well-mixed trap leads to:

$$C_f = \frac{C_o + \alpha\gamma\, C_{go}}{1 + \alpha\gamma\, H_c} \tag{D-11}$$

where,

α	=	Q_e/Q_l (-)
Q_e	=	rate of air entrainment (m^3/hr)
γ	=	degree of chemical equilibrium between bubbles and surrounding liquid in a trap (-)
C_{go}	=	concentration of VOC in the space above the trap (mg/m^3).

MASS TRANSFER BELOW A TRAP

Mass transfer below a trap includes mechanisms 5 and 6 in Figure 4-1. For the purpose of simplification, it is assumed that mass transfer within the channel serves as the dominant mass transfer mechanism. The effects of a falling film or jet above the channel (pre-impact) are effectively "lumped" into channel effects.

It is assumed that air entrainment is the dominant mass transfer mechanism. Furthermore, it is assumed that α is the same in the channel as it would be in a trap. A mass balance on the underlying channel must account for mass flow through the drain as well as mass transported to the point of jet impact from upstream in the channel. Finally, it is assumed that entrained air bubbles are initially contaminated by gas in the drain throat and channel, but that they rise out of the water far enough downstream to not affect the gas concentrations at the point of impact.

Given these assumptions, a steady-state mass balance on the underlying drain channel leads to:

$$C_f = \frac{Q_{ld}C_{od} + Q_{lc}C_{oc} + \alpha\gamma\ Q_{ld}C_{go}}{Q_{ld} + Q_{lc} + \alpha\gamma\ Q_{ld}H_c} \tag{D-12}$$

Here, the subscripts d and c are used to distinguish between flows entering from the overlying drain throat and upstream channel, respectively (Figure D-2).

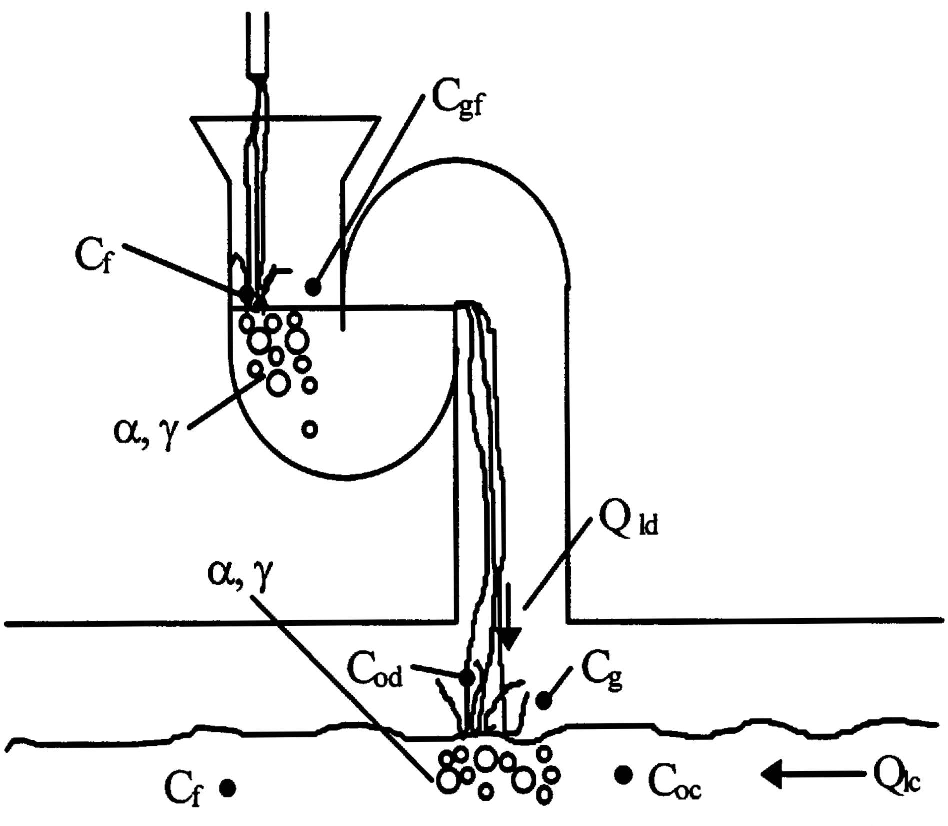


Figure D-2. Model Drain Characteristics.

Appendix E

RECOMMENDED LABORATORY SCALE TASKS FOR PHASE II

TASK 1: MODEL DEVELOPMENT AND SENSITIVITY ANALYSIS

The equations presented in Section 4 should be organized and solved in an appropriate sequence with initial coding and appropriate compilation or incorporation into a standard spreadsheet package. It is recommended that a rigorous sensitivity analysis be completed using Monte Carlo or frequency array techniques to determine those mechanisms that likely dominate in terms of gas-liquid mass transfer, and to focus parameter estimation experiments on those conditions which are most sensitive to changes in specific variables.

TASK 2: MODEL PARAMETER ESTIMATION

The following parameters and their functional relationship to several influencing factors (Section 4) should be determined experimentally: K_{L1}, K'_{L1}, K_{L2}, α, and γ. The mass transfer coefficients associated with the falling jet (K_{L1}) and misaligned hub (K'_{L1}) should be distinguished by completion of experiments using an exposed film versus one enclosed within a non-pressurized shield (tube with diameter slightly greater than the film). Wind speed, liquid flowrate, drain nozzle diameter, hub misalignment, chemical properties, and water temperature should each be varied. Separate empirical or semi-empirical relationships between these variables and the gas and liquid-phase contributions to K_{L1} and K'_{L1} should be developed.

The parameter K_{L2} corresponds to a mass transfer coefficient within a drain throat. It should be distinguished from mass transfer in an underlying channel by repeating experiments in a flow through system with (1) contaminated drain water and clean channel water and (2) clean drain water and contaminated channel water. The would allow a determination of channel (splashing, etc.) contributions to VOC stripping. These experiments should be repeated with variations in liquid flowrate, adjacent air flowrate (which can be controlled in the LDS), and nozzle diameter. They should also reflect flow regimes associated with a contained jet (not impacting walls of drain throat) and an attached film flowing down the drain throat. Relationships should be developed to estimate the gas and liquid-phase contributions to K_{L2} (k_{l2} and k_{g2}) as functions of VOC physicochemical properties, nozzle diameter, water flowrate, air flowrate through the drain throat, liquid flow regime, and chemical properties.

The parameters α and γ correspond to normalized air entrainment rate (Q_e/Q_l) and degree of saturation of entrained air bubbles. These parameters are important for estimating VOC emissions from p-traps and underlying sewer channels. Given knowledge of entrainment rates and Henry's law coefficients, γ can also be used to determine an effective mass transfer coefficient ($K_{lb}a$) for conditions involving air entrainment.

Determination of α and γ will require measurements of air entrainment rates and gas concentrations within bubbles under controlled laboratory conditions. Dr. Corsi and his research team have developed a unique method for estimating α and γ in the laboratory. It is based on the capture of entrained bubbles in a confined headspace which is isolated from the air in contact with a plunging jet (see Figure 5.3). Bubbles have been observed to move radially outward from the point of impingement, allowing them to exhaust into a headspace with an outlet port leading to a calibrated bubble flowmeter or rotameter. If target VOCs are added to the inlet water supply and the system is allowed to reach steady-state, effluent air and water samples can be used to determined $\gamma = C_g$ (actual) / ($C_l H_c$). If $\gamma < 1$, its value can be used to estimate $k_{lb}a$. In conjunction with oxygen transfer measurements, gas and liquid-phase mass transfer coefficients could also be readily determined.

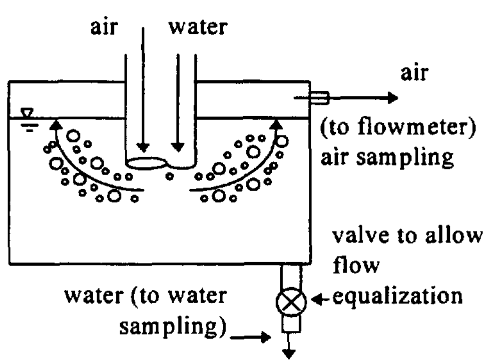


Figure E-1. Recommended Experimental System for Determining Air Entrainment Rates and Degrees of Bubble Saturation.

The system illustrated in Figure E-1 could easily be designed to simulate a p-trap or reservoir with a geometry similar to a drainage channel. It is suggested that α and γ be determined for each type of configuration, and for a range of pool volumes, liquid flowrates, nozzle diameters and fall heights. Experimental results could then be used to develop relationships between α and influencing factors, to determine whether γ is ever significantly less than unity and, if so, to determine an expression allowing its calculation.

TASK 3: EVALUATION OF THE EFFECTS OF DRAIN CONFIGURATIONS AND CHEMICAL EQUILIBRIUM

Separate experiments should be completed using active straight drains and active drains which incorporate a p-trap. Each type of drain should be studied with (a) all adjacent drains being open (non-active) straight drains, (b) only one adjacent drain being an open straight drain and the others being sealed, and (c) no other open drains in the system. Experiments should also be repeated with and without a shroud around the discharge pipe and hub, i.e., to minimize air flow into or out of the active drain. Finally, each condition should be tested using two liquid flowrates (< 1 L/min and > 10 L/min).

For every condition, chemical stripping efficiencies should be determined, along with the degree of chemical equilibrium associated with gases exhausting from the system. Overall, liquid and gas-phase mass transfer coefficients could also be determined for the system.

With replicates, this task would likely require approximately 30 experiments of the type defined in the Phase II protocol.

FINAL PRODUCTS

These tasks will require a large number (likely between 80 and 120) of experiments. At least 15 months should be allowed for all experiments, with an additional 3 months required for model development and data analysis.

The major product that should result from the recommended Phase II research will be a state-of-the-art model to allow estimation of VOC emissions from process drains and corresponding channels within process units. Unlike existing models, the model should be based on fundamental mass transfer kinetics, and should allow for the effects of a wide range of chemical properties, and system operating and environmental conditions on VOC emissions. The model could be designed to be easily incorporated into existing models such as WATER8 or SEAM. It should also be user-friendly, distancing the user from the complex physical and mathematical nature of the emissions algorithm.

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