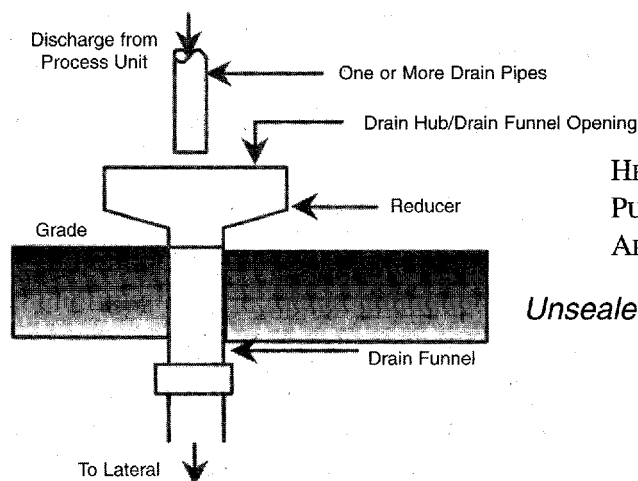
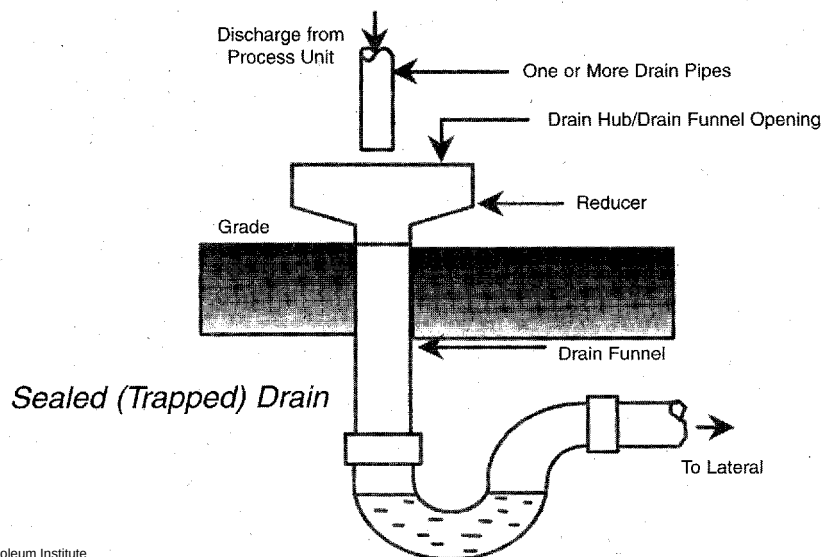


FUGITIVE EMISSIONS FROM REFINERY PROCESS DRAINS VOLUME II

FUNDAMENTALS OF FUGITIVE EMISSIONS FROM REFINERY PROCESS DRAINS



HEALTH AND ENVIRONMENTAL SCIENCES DEPARTMENT
PUBLICATION NUMBER 4678
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Fugitive Emissions From Refinery Process Drains Volume II

Fundamentals of Fugitive Emissions From Refinery Process Drains

Health and Environmental Sciences Department

API PUBLICATION NUMBER 4678

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PREFACE

The results of this study are presented in three separate reports.

- Volume I entitled "*Fugitive Emission Factors for Refinery Process Drains*" (API Publication Number 4677) contains simplified emission factors that can be used to quickly estimate total volatile organic compound (VOC) emissions from refinery process drains.
- Volume II entitled "*Fundamentals of Fugitive Emissions from Refinery Process Drains*" (API Publication Number 4678) describes theoretical concepts and equations that may be used in a model (APIDRAIN) to estimate speciated VOC emissions. The model can provide insight on how to change process drain variables (flow rate, temperature, etc.) to reduce emissions.
- Volume III entitled "*APIDRAIN Version 1.0, Process Drain Emission Calculator*" (API Publication Number 4681) is the computer model with user's guide to estimate emissions from refinery process drains. The software allows users to calculate VOC emissions based on the emission factors in Volume I and equations for speciated emissions in Volume II.

All three volumes of this study can be purchased separately; however, it is suggested that the user consider purchase of the entire set to gain a complete understanding of fugitive emissions from refinery process drains.

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EXECUTIVE SUMMARY

STATEMENT OF NEED

Industry continues to face increasingly stringent regulations related to volatile organic compound (VOC) emissions to the ambient atmosphere. Such emissions cause concern since most VOCs are photochemically reactive and contribute to the formation of ground level ozone in urban airsheds. Furthermore, many VOCs are also classified as hazardous air pollutants (HAPs) that pose risks to workers or the general public. These concerns cause a need for improved estimates of VOC and HAP emissions for many industrial sources, including process drains that serve as the initial point of wastewater collection in on-site industrial sewers. However, the number of process drains in a petroleum refinery can be in the thousands, making direct emission measurements costly and generally impractical. As such, emission factors and predictive models have been developed to estimate such emissions. Many of these factors and models are outdated or employ conservative assumptions that lead to significant overestimates of VOC emissions. There is a clear need for improved models to estimate VOC and HAP emissions from refinery process drains.

IMPROVED MODEL

A two-zone emissions model was developed for estimating VOC emissions from refinery process drains. The model includes estimates of emissions from a water seal (zone 1) and an underlying channel (zone 2). For zone 1, the model includes estimates of air entrainment, degree of chemical equilibrium between entrained air bubbles and surrounding liquid, and gas- and liquid-phase mass transfer coefficients associated with volatilization across the upstream surface of a water seal. For zone 2, the model includes estimates of gas- and liquid-phase mass transfer coefficients in the channel below an active process drain.

Five volatile tracers and two separate experimental drains systems were used to develop model parameters. A total of 76 experiments were completed with the two experimental systems.

The two-zone model, including a description of all relevant variables and units, is presented in Chapter 5 of this report.

CONCLUSIONS

Specific conclusions that resulted from this study are listed below:

1. Stripping efficiencies in water seals increase with increasing Henry's law constant and may approach 20% at moderate liquid temperatures (20 °C to 30 °C) for chemicals with Henry's law constants similar to or greater than toluene. However, stripping efficiencies for lower-volatility chemicals, e.g., acetone and ethyl acetate, should generally be on the order of 1% or lower.
2. Both air entrainment and surface volatilization are important contributors to mass transfer at water seals. For this study, the effects of surface volatilization were generally greater than those associated with entrained air.
3. Stripping efficiencies in water seals decrease substantially as the jet that impinges on the seal moves from a disintegrated film to a solid (intact) film. This is generally due to the effects of similar air entrainment rates but longer hydraulic residence times for the lower flows associated with disintegrated films.
4. Wind speed above a drain hub affects VOC emissions from drains with disintegrated process flows. However, the effects of wind on intact process flows appear to be small. The specific mechanism by which wind affects emissions during disintegrated flow conditions was not determined but could include increases in mass transfer coefficients, increases in interfacial area due to distortion of the falling film, increased ventilation of the drain throat, or some combination of the above.
5. Air entrainment rates in a water seal are significantly influenced by, and increase with, increases in process flowrate. Entrainment rates do not appear to be significantly influenced by the diameter of a drain throat or corresponding water seal.
6. The degree of chemical equilibrium between entrained air bubbles and surrounding liquid is highly dependent on Henry's law constant, and is also affected by changes in air entrainment rate. The degree of equilibrium increases with decreases in Henry's law constant and entrainment rate. It is reasonable to assume that chemicals with Henry's law constants as low as ethyl acetate and acetone will have a degree of equilibrium that approaches unity. However, highly volatile chemicals, e.g., cyclohexane or 1,3-butadiene, should have degrees of equilibrium that are generally less than 0.1 (10% of equilibrium). For these chemicals, an assumption of equilibrium for bubbles can lead to significant overestimation of emissions.

7. Stripping efficiencies associated with open drains are generally, but not always, greater than those for water seals for similar operating conditions. For this study, stripping efficiencies as high as 45% (cyclohexane) were observed for open drains.
8. Significant variations in stripping efficiency can occur as the operating conditions of open drains are varied. As with water seals, stripping efficiencies for open drains decrease as the process flowrate moves from being a disintegrated to a solid jet.
9. Elevated liquid temperatures can lead to substantial increases in chemical stripping efficiencies, particularly for lower-volatility chemicals. Increases in liquid temperature lead to increases in Henry's law constant, increases in mass transfer coefficients, and increases in buoyancy-induced ventilation.
10. The integrated two-zone model developed for this study should be a valuable tool for estimating VOC emissions from process drains. It is more mechanistic in nature than existing emissions models for process drains, and allows for an investigation of the effects of system operating conditions and chemical properties on VOC emissions.
11. An existing USEPA model (WATER8) may significantly overestimate stripping efficiencies, and subsequently emissions, from process drains that contain water seals.
12. Except in the case of highly-volatile chemicals, e.g., cyclohexane, BACT/LAER may underestimate VOC emissions and does not account for the mechanistic behavior of emissions as process operating conditions are varied.

1. INTRODUCTION

STATEMENT OF NEED

Industry continues to face increasingly stringent regulations related to volatile organic compound (VOC) emissions to the ambient atmosphere. Such emissions cause concern since most VOCs are photochemically reactive and contribute to the formation of ground level ozone in urban airsheds. Furthermore, many VOCs are also classified as hazardous air pollutants (HAPs) that pose risks to workers or the general public. Emissions of such compounds are, or will soon be, regulated by industry-specific National Emission Standards for Hazardous Air Pollutants (NESHAPs).

The concerns listed above pose the need for improved estimates of VOC and HAP emissions for many industrial sources, including process drains that serve as the initial point of wastewater collection in on-site industrial sewers. However, the number of process drains in a petroleum refinery can number in the thousands, making direct emission measurements costly and generally impractical. Emission factors and predictive models have been developed to estimate such emissions. These factors and models are generally outdated, e.g., emission factors based on studies completed in the 1970s, or employ conservative assumptions, e.g., chemical equilibrium, that may lead to significant overestimates of VOC emissions.

There is a clear need for improved models to estimate VOC and HAP emissions from refinery process drains. A model based on fundamental mass transfer principles with mechanistic expressions that relate mass transfer parameters to system conditions should allow improved estimates of VOC and HAP emissions from process drains. Furthermore, such a model could be used to determine the effects of changes in system operating conditions and passive control strategies, e.g., inclusion of water seals and their effects on VOC emissions.

OBJECTIVES

Specific objectives of this study are listed below:

1. Develop a state-of-the-art model to estimate VOC and HAP emissions from refinery process drains.

2. Determine model parameters based on a series of controlled experiments in laboratory-based drain simulators.
3. Develop empirical or semi-empirical relationships between model parameters and system operating conditions, environmental conditions, and chemical properties.
4. Use the experimental results and model to ascertain the relative significance of mass transfer mechanisms in process drains.
5. Compare the model developed for this study with those that have been used to estimate speciated VOC emissions from process drains.

SCOPE

It was originally intended that a three-zone emissions model be developed with the ability to estimate VOC emissions from a falling film, water seal, and channel located below a drain. It was impossible to separate (experimentally) the effects of a falling film from volatilization in an underlying channel or water seal. As such, the effects of a falling film were "lumped" into mass transfer in an underlying channel or water seal.

Five volatile tracers were used in determining mass transfer parameters for the two-zone model. These tracers spanned a wide range of Henry's law constants, i.e., $0.0015 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$ to $7.3 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$ at 25 °C.

A total of 76 experiments were completed with the use of two separate experimental systems. Twelve of these experiments were completed to study gas-liquid mass transfer in the channel below a process drain. Forty experiments were completed to determine rates of air entrainment in a water seal. Seventeen experiments were completed to study the degree of chemical equilibrium between entrained air bubbles and surrounding liquid in a water seal. Seven experiments were completed to study volatilization across the upstream surface of a water seal. Four additional experiments were completed to ascertain volatilization from a falling film, but were inconclusive and not reported herein. No experiments were completed to determine emissions from a water seal below an inactive drain. No experiments were completed to assess gas-liquid mass transfer in the channel below inactive drains.

Several variables can affect mass transfer in a process drain. The primary variables that were studied included process flowrate, hydrodynamic regime (disintegrated or intact liquid

flow), and Henry's law constant. The effects of molecular-diffusion coefficients were accounted for in some correlations. The effects of temperature were accounted for through variations in liquid molecular diffusion coefficients, water viscosity and, most importantly, Henry's law constant.

ORGANIZATION OF REPORT

The two-zone emissions model is described in Chapter 2. Chapter 3 includes a detailed description of experimental methods, including the two experimental systems that were employed, sample analysis procedures, and data analysis methods. Experimental results are presented in Chapter 4. The resulting two-zone model and parameter correlations are presented in Chapter 5. Several examples are provided to compare the model developed for this study with existing models for VOC emissions from process drains. An example is also provided to demonstrate the utility of the model for establishing whether water seals effectively reduce VOC emissions from process drains. A set of conclusions is provided in Chapter 6. References are provided in Chapter 7.

2. TWO-ZONE EMISSIONS MODEL

MODEL OVERVIEW

A two-zone mechanistic emissions model is presented in this chapter. The model is intended to serve as a state-of-the-art tool for estimating chemical emissions from process drains. It is based on mass transfer kinetics, with parameters determined from a series of experiments described in Chapter 3. This chapter begins with a brief discussion of mass transfer fundamentals and terminology, as well as a conceptual description of the two-zone model. Mathematical expressions used to estimate gas-liquid mass transfer are then presented for each drain zone.

Mass Transfer Fundamentals

Equation 2-1, derived from a number of different mass transfer theories, can be used to calculate the mass flux across a gas-liquid interface (Lewis and Whitman, 1924; Higbie, 1935; Danckwerts, 1951; Dobbins, 1956):

$$r_a = K_L \left(C_l - \frac{C_g}{H_c} \right) \quad (2-1)$$

where:

r_a	=	flux across interface from liquid to gas (M/L ² T)
K_L	=	overall mass transfer coefficient (L/T)
C_l	=	liquid-phase concentration of compound (M/L ³)
C_g	=	gas-phase concentration of compound (M/L ³)
H_c	=	Henry's law constant (L ³ _{liq} /L ³ _{gas})

The term in brackets is often referred to as a concentration driving force, and represents how far a system is from a state of chemical equilibrium. The overall mass transfer coefficient, K_L , can be further reduced to its gas- and liquid-phase components. This concept, stemming from two-film theory, models mass transfer as a steady-state molecular diffusion process occurring

across two quiescent boundary films, one in the liquid phase and one in the gas phase (Lewis and Whitman, 1924):

$$\frac{1}{K_L} = \frac{1}{k_l} + \frac{1}{k_g H_c} \quad (2-2)$$

where:

- k_l = liquid-phase mass transfer coefficient (L/T)
- k_g = gas-phase mass transfer coefficient (L/T)
- H_c = Henry's law constant (L^3_{liq}/L^3_{gas})

The inverse of the overall mass transfer coefficient is often referred to as an overall resistance to mass transfer. This analogy to electrical resistance illustrates the liquid-phase ($1/k_l$) and gas-phase resistance ($1/k_g H_c$) to mass transfer.

Based on two-film (Lewis and Whitman, 1924), penetration (Higbie, 1935), and surface-renewal (Danckwerts, 1951) theories, the following relationships were developed. These relationships allow comparison of liquid- and gas-phase mass transfer coefficients for two different compounds:

$$\Psi_l = \frac{k_{li}}{k_{lj}} = \left(\frac{D_{li}}{D_{lj}} \right)^n \quad (2-3)$$

$$\Psi_g = \frac{k_{gi}}{k_{gj}} = \left(\frac{D_{gi}}{D_{gj}} \right)^m \quad (2-4)$$

where

- Ψ_l, Ψ_g = mass transfer proportionality constants between compounds (-)
- k_{li} = liquid-phase mass transfer coefficient for compound i (L/T)
- k_{lj} = liquid-phase mass transfer coefficient for compound j (L/T)
- k_{gi} = gas-phase mass transfer coefficient for compound i (L/T)
- k_{gj} = gas-phase mass transfer coefficient for compound j (L/T)
- D_{li} = liquid-phase molecular diffusion coefficient for compound i (L^2/T)

D_{lj}	=	liquid-phase molecular diffusion coefficient for compound j (L^2/T)
D_{gi}	=	gas-phase molecular diffusion coefficient for compound i (L^2/T)
D_{gj}	=	gas-phase molecular diffusion coefficient for compound j (L^2/T)
n, m	=	power constants (-)

The power constants n and m can vary from anywhere between unity (for two-film theory) and 0.5 (for penetration and surface-renewal theories). When a compound possesses an extremely large Henry's law constant, it may be possible to neglect the gas-phase resistance to transfer and thereby simplify Equation 2-2 to $K_L \approx k_l$. This is often done for oxygen, a commonly studied compound with an H_c value of $32 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$ at 25°C . Conversely, for very low volatility chemicals such as acetone, it is often possible to neglect the liquid-phase resistance altogether, and to express Equation 2-2 as $K_L \approx k_g H_c$. Once reference chemicals such as oxygen and acetone have been used to estimate liquid- and gas-phase mass transfer coefficients, Equations 2-3 and 2-4 can be used to calculate mass transfer coefficients for any compound.

Overview of Two-Zone Model

Within a specific process drain, there are several locations where mass transfer can occur. In each case, different emission mechanisms are responsible. Figure 2-1 shows two typical process drains, one open and one trapped. Each drain is subdivided into one or two zones from which emissions may occur. Zone 1 extends from the bottom of the discharge nozzle to the water seal (inclusive of the water seal); mass transfer in this region is attributed to surface volatilization and air entrainment. The original intent of this study was to separate surface volatilization associated with the falling film from that associated with the underlying water seal. This proved to be experimentally difficult and, as such, the two surface volatilization components were "lumped" for zone 1. Based on the degree of splashing and the longer residence time within the water seal, i.e., relative to the falling film, it can be reasonably assumed that volatilization at the water seal is significantly greater than from the falling film.

Zone 2, present in both trapped and untrapped drains, follows the falling film as it impacts the underlying channel. In this zone, splashing in the channel is likely the primary emission mechanism.

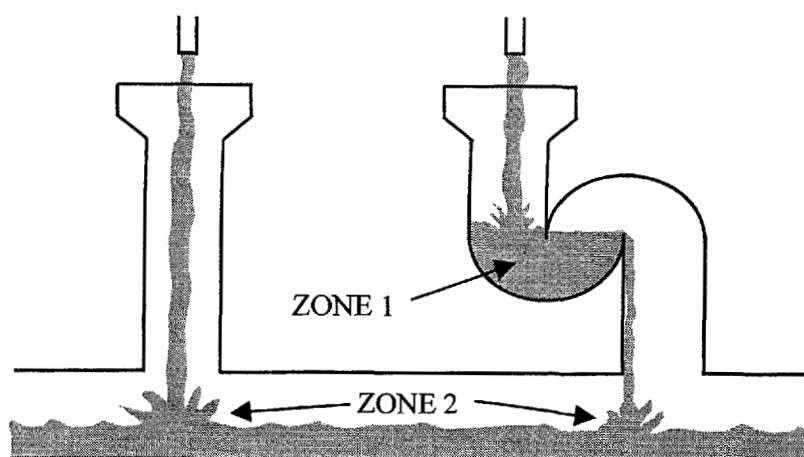


Figure 2-1. Different Emission Zones in an Industrial Process Drain

ZONE 1 SUBMODEL

According to the American Petroleum Institute (API), over 80% of all petroleum refinery process drains are equipped with a water seal, provided by a P-trap, J-trap or similar device (American Petroleum Institute, 1996). As stated earlier, these water seals are designed to minimize the amount of fresh air entering the sewer, thus lowering the concentration driving force in the channel headspace and reducing VOC emissions. Even so, emissions still occur in a trapped drain. Zone 1 encompasses the falling film as well as the water seal (trap).

Within zone 1, it is assumed there are two major mechanisms by which chemicals can volatilize. The first involves surface volatilization which occurs from the falling film and the upstream surface of the water seal. Splashing is the most visible manifestation of this mechanism.

The second major mechanism is air entrainment induced by the boundary layer of air that surrounds the falling film as it descends into the drain. Small undulations along the surface of the film tend to "pull" air along in "pockets." When the falling film strikes the water below, these trapped air pockets are pulled below the water surface (Van de Sande and Smith, 1973). These air parcels break apart into many small air bubbles below the water surface, then return to the surface of the water seal. In larger traps, the bubbles return to the surface of the water seal, where they immediately outgas to the overlying drain throat. In smaller traps, the bubble

rise is often impeded by the impact of the falling film, causing the bubbles to recirculate within the water seal. It is assumed, based on repeated observations, that a negligible fraction of the entrained bubbles actually pass through the entire trap, i.e., most of them move within the upstream portion of the water seal and rupture upon resurfacing on the upstream side.

Several important assumptions were made in the development of the zone 1 model. First, the water seal itself was modeled as a continuous-flow stirred tank reactor (CFSTR). At the beginning of this study, dye (food coloring) was added to water that was pumped into the trapped drain. The dye was visually observed to almost immediately tint the water within the trap, confirming the CFSTR assumption.

Another assumption was that the gas-phase concentration within the drain throat is negligible. The gas boundary layer accompanying the falling film was presumed to ventilate the drain throat, preventing any gas-phase VOC accumulation. This assumption may be valid for high-volatility (high H_o) VOCs, e.g., 1,3-butadiene, but may be violated for low-volatility chemicals, e.g., methanol. However, it was beyond the scope of this study to consider the drain throat as a separate zone.

Finally, it was assumed that all of the mass transfer in a water seal occurs along the upstream liquid-gas interface. Most water seals do have a downstream surface. However, observations have shown it to be very quiescent under most flow conditions, especially when compared to the upstream surface. Additionally, most water seals are installed to facilitate an approach to chemical equilibrium within the underlying channel. With these assumptions, the following expression can be used to represent total stripping efficiency for a water seal:

$$\eta_1 = 1 - \frac{1}{1 + \frac{Q_e}{Q_l} H_c \gamma + \frac{K_L A_s}{Q_l}} \quad (2-5)$$

where:

- η_1 = fractional stripping efficiency for zone 1 (-)
- $K_L A_s$ = mass transfer coefficient for surface volatilization (L^3/T)
- Q_e = air entrainment rate (L^3/T)

Q_i	=	process flowrate into drain (L^3/T)
γ	=	extent of chemical equilibrium in the entrained bubbles (-)
H_c	=	Henry's law constant (L^3_{liq}/L^3_{gas})

The γ term should vary between 0 and 1. A value of $\gamma = 1.0$ corresponds to a condition of chemical equilibrium between gas within the bubble and the surrounding liquid. It is assumed that air that is initially entrained below the water surface is devoid of VOCs.

The mass transfer coefficients and interfacial areas are lumped together and expressed as " $K_L A$ " values in Equation 2-5. From this point forward, the term "mass transfer coefficient" will refer to both K_L and $K_L A$ terms interchangeably.

In zone 1, there are a total of four parameters that must be determined empirically: the liquid and gas-phase mass transfer coefficients for surface volatilization ($k_l A_s$, $k_g A_s$), the degree of equilibrium term (γ), and the volumetric flowrate at which air is entrained into the water seal (Q_e).

Air entrainment as a result of a liquid jet impacting upon a liquid surface has been the subject of several experimental investigations. These studies used high speed pressurized water jets (Bin, 1993 and Van de Sande, 1976), and are thus not applicable for estimation of air entrainment in typical trapped process drains.

ZONE 2 SUBMODEL

Zone 2 accounts for mass transfer which occurs when the process flow enters the sewer reach. Emissions in zone 2 are primarily due to splashing which occurs when the process flow impacts any liquid that might be in the channel or the channel bottom itself. Mass transfer due to air entrainment may also occur in the channel, but only when a sufficient depth of water exists in the sewer reach. For the purpose of the zone 2 model, both the gas and liquid phases were treated as CFSTRs. Simultaneous steady-state mass balances on gas and liquid phases can be used to derive an expression for zone 2 emissions.

Due to shear forces associated with the descending liquid film, it is assumed that an active open drain will always ingas. Once this air has entered the sewer, it will combine with whatever air is flowing down the sewer reach and will continue traveling in the same direction as the channel ventilation. It is further assumed that there is negligible gas-phase VOC entering zone 2 via the drain throat. In a trapped drain, the gas flowrate in the drain throat was assumed to be zero, while in an open drain it was assumed that the gas-phase concentration in the drain throat is negligible, as with zone 1. These assumptions result in the following expressions for stripping efficiency:

$$\eta_2 = 1 - \frac{(Q_i + Q_c) \left(\frac{Q_c C_{co} + Q_i C_{lo} + \frac{K_L A_c Q_{gc} C_{gc}}{H_c Q_{gc} + H_c Q_{gd} + K_L A_c}}{Q_c + Q_i + K_L A_c - \frac{(K_L A_c)^2}{H_c Q_{gc} + H_c Q_{gd} + K_L A_c}} \right)}{Q_c C_{co} + Q_i C_{lo}} \quad (2-6)$$

where:

- η_2 = fractional stripping efficiency for zone 2 (-)
- Q_i = process flowrate into drain (L^3/T)
- Q_c = upstream liquid channel flowrate (L^3/T)
- C_{lo} = liquid-phase concentration entering the zone (M/L^3)
- C_{co} = upstream liquid channel concentration (M/L^3)
- $K_L A_c$ = mass transfer coefficient for channel effects (L^3/T)
- C_g = gas-phase concentration in channel headspace (M/L^3)
- Q_{gc} = upstream headspace gas flowrate (L^3/T)
- C_{gc} = upstream headspace gas concentration (M/L^3)
- Q_{gd} = gas flowrate drawn down process drain throat (L^3/T)
- C_{gd} = gas concentration of gas drawn down process drain throat (M/L^3)
- H_c = Henry's law constant (L^3_{liq}/L^3_{gas})

Only in zone 2 does the stripping efficiency include channel flow as well as process flow. Aqueous phase chemicals, entering the region of the drain from some point upstream, may volatilize as they pass through the channel splash zone. There are several possible factors contributing to emissions from zone 2. As with zone 1, liquid velocity may be an important factor. Emission rates may also be a function of whether or not the process flow is aligned with the drain throat. When the flow is misaligned, it strikes the drain hub and adheres to the walls of the throat as it descends into the sewer reach. A similar effect is observed when a J-trap is in place above the channel. The extent of air flow into the mass transfer zone should have an effect on gaseous accumulation, and thus mass transfer, but may also affect gas-phase resistance to mass transfer.

THE INTEGRATED MODEL

By sequentially applying the stripping efficiencies for zones 1 and 2, the total fractional stripping efficiency associated with a process drain can be estimated. The stripping that occurs in one emission zone is accounted for when calculating stripping effects from the downstream zone:

$$\eta_d = \eta_1 + \eta_2(1 - \eta_1) \quad (2-7)$$

where:

- η_d = total stripping efficiency for process drain (-)
- η_1 = stripping efficiency for zone 1 (-)
- η_2 = stripping efficiency for zone 2 (-)

In situations where there are fewer than two active emission zones, Equation 2-7 is still valid, providing that the stripping efficiency term for the missing emission zone is set to zero. This would be the case for an open drain, or even a trapped drain, if the user was confident that a state of chemical equilibrium existed in the underlying channel. Calculating the total stripping efficiency is complicated somewhat by the possible presence of chemicals flowing into zone 2 from upstream drains. Equation 2-7 becomes inapplicable under such conditions; it can only be

used to calculate the stripping from one waste stream. For the more complex scenario of mass flow from upstream drains, the following expressions should be used:

$$\eta_d = 1 - \frac{(1 - \eta_2)(Q_c C_{\infty} + Q_l C_{lo}[1 - \eta_1])}{Q_c C_{\infty} + Q_l C_{lo}} \quad (2-8)$$

where:

η_d	=	total stripping efficiency (process drain with channel flow) (-)
η_1	=	stripping efficiency for zone 1 (-)
η_2	=	stripping efficiency for zone 2 (-)
Q_c	=	upstream liquid channel flowrate (L ³ /T)
Q_l	=	process flowrate into drain (L ³ /T)
C_{lo}	=	liquid-phase concentration in process discharge to drain (M/L ³)
C_{∞}	=	upstream liquid channel concentration (M/L ³)

If either Q_c or C_{∞} is zero, Equation 2-8 reverts to the simpler Equation 2-7. Once the fractional stripping efficiency has been determined, the gaseous emission rate from a process drain is easily calculated. It is simply equal to the total stripping efficiency multiplied by the mass rate at which a VOC enters the drain in the liquid phase:

$$E = \eta_d (Q_c C_{\infty} + Q_l C_{lo}) \quad (2-9)$$

where:

E	=	process drain emission rate (M/T)
η_d	=	total stripping efficiency for process drain (-)
Q_c	=	upstream liquid channel flowrate (L ³ /T)
Q_l	=	process flowrate into drain (L ³ /T)
C_{lo}	=	liquid-phase concentration in process discharge to drain (M/L ³)
C_{∞}	=	upstream liquid channel concentration (M/L ³)

3. EXPERIMENTAL METHODOLOGY

EXPERIMENTAL SYSTEMS

Two experimental systems were constructed in an environmental chamber at The University of Texas at Austin. A laboratory drain system (LDS) and three trap simulators were designed to isolate different VOC emission mechanisms and to allow the determination of important mass transfer parameters. Originally, all of the experiments except those investigating temperature effects were to be conducted at a temperature of 20 °C. However, during the course of the study, the climate control equipment in the environmental chamber housing the LDS and trap simulators failed. The remainder of the experiments were completed at liquid and air temperatures ranging between 21 and 25 °C.

Laboratory Drain System (LDS)

A pilot-scale process drain and sewer reach was constructed at The University of Texas at Austin. The system, as shown on Figure 3-1, consisted of a channel, a tracer reservoir, and accompanying pumps, piping, and miscellaneous equipment. It was similar to the system used previously by Shepherd (1996).

The channel was comprised of six or seven glass pieces: three reach sections, two end caps, a drain hub, and sometimes a J-trap, all of which were connected to one another by beaded glass couplings. The channel sections each had an inside diameter (i.d.) of 15 cm and a length of 46 cm. Two channel sections were fitted with 5 cm i.d. vertical risers, each extending 30.5 cm above the crown of the sewer channel. The upstream riser served as the active drain throat. During open drain experiments, a removable glass reducer (10 cm by 5 cm) was attached to this riser to help simulate an actual drain hub. During experiments where a water seal was desired, the hub shown on Figure 3-1 was removed and a 5 cm i.d. glass J-trap was fastened in its place. The reducer (hub) was then re-attached to the top of the J-trap to complete the drain arrangement. The downstream riser allowed for the outgassing of air drawn into the channel headspace by falling process flow. For experiments where channel ventilation was not desired, glass end caps were placed over the downstream riser.

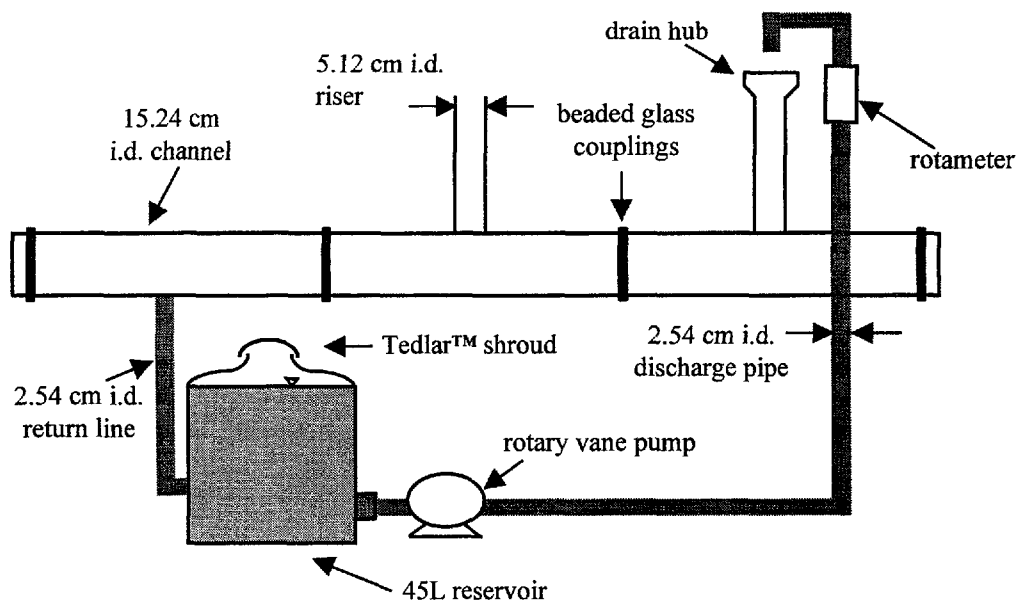


Figure 3-1. Schematic of Laboratory Drain System (LDS)

The final channel section had a 4 cm i.d. riser. This riser, which was further reduced to a 2.5 cm diameter, was pointed downwards, and served as the channel drain. A 4 cm² section of stainless steel mesh was placed at the inlet of the return pipe; its purpose was to prevent the formation of drain vortices, which were observed to occur when there was a high process flowrate and/or low water level in the channel. Both ends of the channel were sealed with a glass end cap. As volatilization from the quiescent water surface of the sewer channel was competing with drain emissions as a mass transfer mechanism, an effort was made to minimize its effect. To reduce the channel surface area across which volatilization could occur, the reach was made as short as possible. The total reach length was 1.5 meters.

The tracer reservoir was a 45 liter glass carboy, narrowed at the top to minimize the air-water interfacial area. During experiments, the top opening was covered with a sheet of inert Tedlar™, secured with duct tape. This minimized the amount of air exchange between the reservoir headspace and the ambient air. The entire reservoir was placed on top of cinder blocks and plywood spacers. By adding or removing spacers, the carboy could be raised or

lowered slightly, allowing complete control over the depth of water in the channel. Three ports were fitted to the reservoir. The return water from the channel entered the reservoir via one of these ports. Another port drew water into the process pump. The final port was a small Teflon™ stopcock inserted in a small hole in the side of the carboy and sealed with silicone. As described later, this stopcock was used for the collection of liquid samples.

A mixing motor (Cole Parmer, Stir Pak), supported by a stand, was used to rotate a stainless steel shaft and propeller that were inserted into the reservoir to mix the water. This mixing ensured that the behavior of the reservoir approached that of a CFSTR. To prevent vortexing, the shaft was tilted at a slight angle and closely controlled.

A variable speed rotary vane pump (PROCON, Model 7116-15) was used to convey water through the system. It drew water from the reservoir and pumped it up a 1.7 m stretch of 2.5 cm i.d. Teflon™ pipe equipped with an in-line rotameter (King, Model K72-05-0161), for flow measurements. Several Teflon™ elbows then redirected this flow so it was aligned with the drain hub.

A wind tunnel was used to simulate the effects of wind passing over a process drain (Figure 3-2). The tunnel was composed of wire mesh wrapped with plastic sheeting, and could be placed over the drain riser when necessary. A small fan (Tatung, Model LC-12) was used to force a flow of air over the drain riser. A rheostat was used to control the wind speed. A thermoanemometer (Alnor® model 8565) was used to determine wind speeds within the tunnel. Anemometer traverses completed immediately upstream of the drain hub indicated uniform velocity profiles for all wind speeds.

Whenever possible, inert materials such as Teflon™ and glass were selected for use in the experimental system. Threaded 2.5 cm i.d. Teflon™ pipes comprised the majority of the process conduits, i.e., leading from the reservoir to the process drain nozzle. However, in some locations where physical flexibility was required to ensure structural integrity, short (2 - 3 cm) sections of Tygon™ tubing were used. Examples of such locations included the process pump inlet and return pipe reservoir inlet. Both connections were subjected to some bending and flexing.

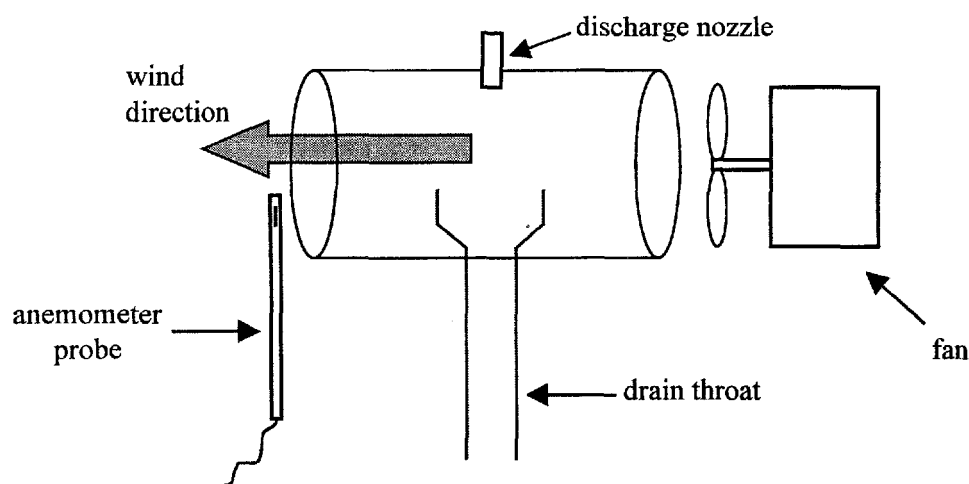


Figure 3-2. Wind Tunnel in Place Over the Drain Hub

The channel and reservoir were each composed of glass. The flow rotameter was comprised of an acrylic polymer casing and a stainless steel float. Stainless steel was also used in the pump impeller, the return pipe vortex suppresser, a pipe fitting, and the mixer shaft and propeller. Silicone caulk was used to seal the sampling and return ports on the reservoir. Previous research on an earlier version of the LDS indicated that incidental losses due to chemical sorption to solid surfaces were small relative to chemical stripping, and could be neglected (Shepherd, 1996). Nearly the same group of chemical tracers was used in each research effort.

Trap Simulators

Three full-scale P-traps were purchased and modified for use in this research. These polyvinyl chloride (PVC) traps, referred to as trap simulators, were used to determine two important operating parameters for zone 1: the degree of equilibrium of entrained air bubbles (γ) and the volumetric rate at which air is entrained within the water seal (Q_e). The three trap simulators had inside diameters of 5, 7.6, and 10 cm. An example of a trap simulator is illustrated on Figure 3-3.

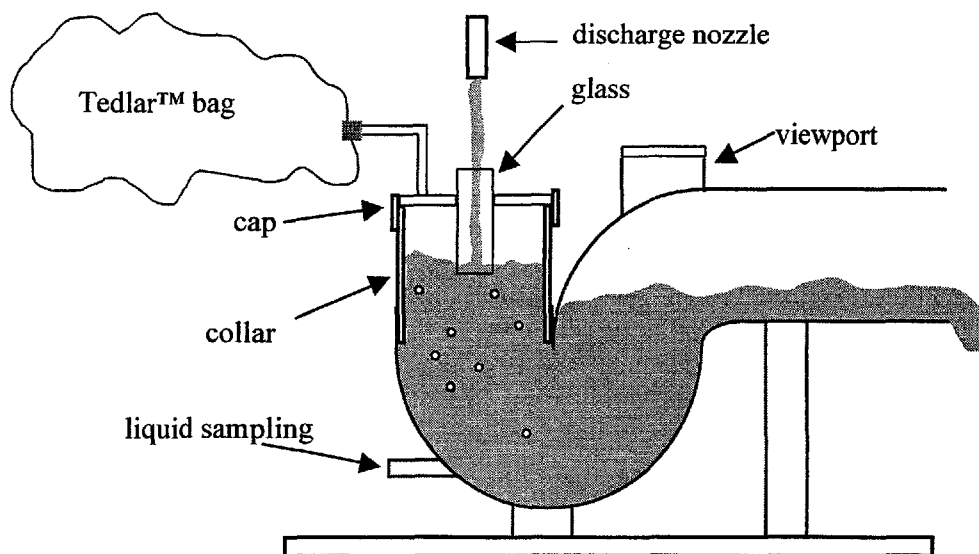


Figure 3-3. Schematic of Trap Simulator

The traps were mounted on small blocks of wood, which in turn were mounted on sections of water-resistant particle board. Steel straps held the traps in place and ensured that they were upright at all times. A small viewing port was attached to each trap simulator allowing for the determination of whether or not entrained air bubbles were passing through to the downstream surface of the water seal.

Water was drawn from the 45 L glass reservoir by means of a variable speed rotary vane pump (PROCON, Model 7116-15). Water was pumped through a section of Teflon™ pipe and rotameter before discharging into the trap. A mixing motor and propeller were used to assure a uniform tracer concentration in the reservoir. The water delivery arrangement was almost identical to that used for the LDS, but there were several important differences. The trap simulator was a “flow through” system; once water had passed through the pump and the trap, it would discharge into a laboratory sink. Each experiment lasted only as long as there was water in the reservoir, typically less than six minutes. However, this flow-through configuration allowed a steady-state condition to be reached within the J-trap as the influent liquid concentration was observed to remain constant over time.

When falling toward the water seal, the process flow would pass through a small glass cylinder inserted in a plexiglass cap and extending just below the surface of the water seal. As the falling film impacted the underlying water surface, air bubbles were entrained within the water seal. This cylinder served several important purposes. First, it was large enough to allow for the gaseous boundary layer that is dragged along a falling film to impinge upon the underlying trap, thus allowing for the entrainment of air bubbles. Secondly, it was small enough in diameter such that most of the entrained air bubbles would not rise back up into the impingement zone defined by the cylinder. Finally, the cylinder acted to suppress agitation (splashing) within the enclosed headspace thus suppressing the effects of surface volatilization, or conversely isolating the effects of mass transfer due to air entrainment. These bubbles then surfaced and ruptured within an enclosed headspace, confined by the water seal on one end and the cap on the other. This led to a pressurization of the headspace; to relieve this pressure, the gas was allowed to exit through a small relief port built into the plexiglass cap. The gas then flowed through a small section of 6 mm i.d. Teflon™ tubing and several Swagelok™ fittings before filling an attached Tedlar™ bag. Liquid samples were collected from a Teflon™ stopcock (liquid sampling port) inserted into the body of the trap.

For the purpose of the emissions model, both the water seal and enclosed headspace were assumed to behave as CFSTRs. Whenever possible, the volume of the enclosed headspace was minimized. Because these were flow-through experiments, samples could not be collected until a steady-state condition was achieved in both the water seal and the headspace. Reaching steady-state conditions usually required the throughput of two or three gas turnovers in the headspace. By minimizing the volume of the enclosed headspace, the time required to reach steady-state conditions was reduced. This was particularly important considering that each experiment lasted only a few minutes. However, there was a minimum bound to the headspace volume. If the volume was too small, plugs of water would be drawn into the gas sampling line, thus rendering the gas sample inaccurate. To closely control the headspace volume, a set of PVC collars were used. These collars, cut to length in 6 mm increments, were placed between the actual body of the trap and the plexiglass cap. Each trap simulator had its own set of collars, with an outside diameter equal to that of the trap's inside diameter.