DETERGENT ETHANOL EMISSIONS FROM MUNICIPAL WASTEWATER COLLECTION AND TREATMENT SYSTEMS

Prepared for
The Soap and Detergent Association

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Executive Summary

The Soap and Detergent Association (SDA) previously presented a report (Engineering Science 1990) to the California Air Resources Board (CARB) that provided an analysis of the fate of the ethanol from the use and disposal of liquid laundry and hand dishwashing detergents. After review of that report, CARB had further questions concerning the fate of ethanol in municipal wastewater collection and treatment systems. In order to respond to these questions, and to address the issue of ethanol emissions from municipal wastewater collection and treatment systems in more detail, SDA retained CH2M HILL to look at the fate of ethanol specifically in wastewater treatment and collection systems. Most of the conclusions made in this report are based on the findings presented in a series of five volumes of draft reports that the University of California at Davis (UC Davis) prepared for CARB.

UC Davis Reports

The draft reports from UC Davis present findings and research on air toxic emissions from municipal wastewater collection and treatment systems (Guensler 1989; Chang, Schroeder, et al., 1990; Corsi et al., 1990; Chang, Guensler, et al., 1990; Meyerhofer, et al., 1990) and present one of the most complete works on air toxic emissions in municipal wastewater treatment systems that is available today. However, the documents prepared by UC Davis present few quantitative conclusions that could be applied directly to wastewater systems in general. For example, no explicit estimates were made as to the total air toxic emissions originating at wastewater treatment facilities. They were very focused on specific issues and compounds and generally did not extrapolate their findings beyond their specific research. Nonetheless, the following conclusions can be drawn from these documents:

1. Volatile organic compounds (VOCs) often found in wastewater, and studied by UC Davis, include chloroform, perchloroethylene, methylene chloride, and trichloroethylene.

2. All of the above VOCs have Henry's Law (gas/liquid partition) constants between 0.1 and 1.0, using units of mg/l per mg/l (hereinafter called "dimensionless").

3. All of the above VOCs have very similar mass transfer characteristics to each other, and in turn they have very similar mass transfer characteristics to oxygen, because all of these compounds are dominated by liquid phase mass transfer resistance.

4. All of the mass transfer modeling performed in the UC Davis documents extrapolated oxygen mass transfer to predict the mass transfer of these VOCs.
5. These VOCs are predicted to lose between 10 and 100 percent of the original liquid phase mass to the atmosphere while being transported in wastewater collection systems and treated in wastewater treatment systems.

6. This extrapolation of oxygen mass transfer as a predictor of VOC mass transfer does not work for compounds that have Henry's Law constants below 0.1, because compounds that have Henry's Law constants less than this are controlled by gas phase mass transfer resistance. The farther the Henry's Law constant is below 0.1, the more that mass transfer is controlled by gas phase resistance.

7. When processes are well ventilated (no accumulation of gases is assumed, i.e., infinite ventilation), all the compounds studied by UC Davis have similar emission rates, regardless of individual compound Henry's Law constant, because interfacial mass transfer resistance controls and they all have similar interfacial mass transfer resistance. As stated before, for compounds similar to the UC Davis compounds, this mass transfer rate is similar to, and can be modeled from, oxygen. An example of a well ventilated system is an open tank with surface aerators.

8. When processes are poorly ventilated, Henry's Law constant controls emissions because the gas phase will approach saturation. Under these circumstances, each compound will have a different emission rate that is a function of its Henry's Law constant. An example of a poorly ventilated system is a typical wastewater sewer pipe system. When the gas phase is saturated, no net mass transfer takes place, because the VOC is being transferred from the gas phase back to the liquid phase at the same rate that it is being transferred from the liquid to the gas phase.

Specific Findings About Ethanol Emissions

Based on the findings of UC Davis, and further study of ethanol, the following conclusions are drawn in this report:

1. The Henry's Law constant for ethanol is 0.00044, about three orders of magnitude (1,000 times) below the compounds studied by UC Davis.

2. For poorly ventilated systems, the rate of loss due to volatilization for ethanol will be about three orders of magnitude (1,000 times) less than the compounds studied by UC Davis.

3. For well ventilated systems, the rate of loss due to volatilization of ethanol will range between 2 times less for quiescent surfaces with high wind speeds, to over 100 times less for areas of intense liquid turbulence (weirs), than the compounds studied by UC Davis. Since the majority of wastewater treatment
air emissions occur at points of intense turbulence, in general, ethanol should volatilize from wastewater treatment plants at a rate of over 100 times less than the compounds studied by UC Davis.

These findings show that the volatilization behavior of ethanol will be quite different than the VOCs studied by UC Davis, and that ethanol will have substantially lower air emissions than the VOCs studied by UC Davis. Quantitatively, the estimated fate of ethanol from municipal wastewater collection and treatment systems in California, as a percentage of ethanol that is discharged from the home, is:

- Biodegraded in POTWs 99.66 percent
- Volatilized 0.24 percent
- Discharged from POTWs in Liquid Phase 0.10 percent

The volatilization estimate should be considered a conservative, worst-case value, with the probable value being substantially less. Examples of the more significant conservative assumptions that were made to produce this value include:

1. The sewer gas headspace was saturated in ethanol.
2. Average sewer gas velocities were assumed to be 20 times greater than measured in previous studies.
3. Up to 20 sewer ventilation barriers (pump stations or siphons) in series could exist in collection systems.
4. No significant adsorption of ethanol was anticipated or assumed.
5. No biological or chemical transformation of ethanol was assumed, except in processes designed for biological treatment.

In general, conclusions drawn about the volatilization of ethanol can be extended to other compounds having similar Henry’s Law constants.

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Section 1
Introduction

The purpose of this study is to estimate the magnitude of ethanol emissions resulting from the collection and treatment of municipal wastewater containing liquid laundry and hand dishwashing detergents. The Soap and Detergent Association (SDA) previously presented a report (Engineering Science, Inc./ESI 1990) to the California Air Resources Board (CARB) that provided an analysis of the fate of the ethanol from the use and disposal of household cleaning products. After review of that report, CARB had further questions concerning the fate of ethanol in municipal wastewater collection and treatment systems. In order to respond to these questions, and to address the issue of ethanol emissions from municipal wastewater collection and treatment systems in more detail, SDA retained CH2M HILL to look at the fate of ethanol specifically in wastewater treatment and collection systems.

The fate of compounds in wastewater collection and treatment systems can be quite complex. However, in the case of ethanol (and substances having similar chemical characteristics), many conservative simplifying assumptions can be made that do not affect conclusions regarding the fate of ethanol in these systems, but that allow for a reduction in the level of detail required to demonstrate its fate. To the extent that the conservative assumptions used in this report may deviate from actual emissions, the assumptions result in the over-estimation of ethanol emissions. Application of more detailed approach, while leading to more accurate emission estimates, would predict lower levels of volatilization. Even though assumptions that would cause ethanol emissions to be over-estimated were used in the analysis presented in this report, the estimated emissions are inconsequential with regard to air pollution issues.

This report presents an explanation of applicable emissions mechanisms, and a conservative estimate of ethanol emission rates. Section 2 describes characteristics of typical municipal collection and treatment systems in California, and uses that information to develop prototype systems for subsequent analyses. Section 3 describes ethanol characteristics and summarizes ethanol emissions calculations for municipal wastewater collection and treatment systems in the state of California.
Section 2
Wastewater Collection and Treatment in California

An understanding of emission pathways is necessary to develop reasonable emission factors. This section describes wastewater collection and treatment operations in California, and uses that information to develop prototype collection and treatment systems. Emissions from wastewater collection and treatment systems are a function of wastewater turbulence, ventilation rates, and the properties of the substances being examined. This section focuses on the physical characteristics of the wastewater systems. The chemical properties of ethanol that effect volatilization will be discussed in the next section.

Collection Systems

In wastewater collection systems turbulence is caused by drops, junctions, and by the flow of wastewater itself. Ventilation is a function of the number of openings that allow for gas exchange between sewer and ambient atmospheres. These openings include manhole covers, vents at building connections, and stormwater gutter drains (the latter for combined sanitary/storm sewers only).

UC Davis, under contract to CARB, studied the impacts of individual ventilation mechanisms occurring within municipal wastewater collection systems (Corsi et al., 1990). It was determined that the velocity of the overlying air in a sewer pipe is an important characteristic of the collection system for the estimating of volatilization rates of semi-volatile compounds. Although ethanol was not discussed specifically by UC Davis, it would be considered such a semi-volatile compound. In this report, compounds that are called semi-volatile are defined as those having Henry's Law constants of between 0.01 and 0.0001 mg/l per mg/l. In general, the conclusions drawn about the volatilization of ethanol can be extended to other semi-volatile compounds.

Municipal Wastewater Treatment Technology

Municipal wastewater treatment plants, commonly referred to as POTWs (publicly owned treatment works) treat a combination of residential, industrial, and commercial wastewater flows. The wastewater is treated using physical, chemical, and biological processes and then discharged to a body of water such as an ocean, bay, or river. The solids removed from the wastewater are usually disposed of in a landfill.

POTWs in California treat wastewater flows ranging from less than 1 mgd (million gallons per day) to greater than 350 mgd. However, the basic wastewater treatment processes are very similar at most of these POTWs. To arrive at a profile of the typical POTW in California, POTWs throughout the state were telephone surveyed by CH2M HILL in August, 1991, regarding specific characteristics such as influent flow.
rate and unit processes present. The results of the survey are provided in Appendix D. The survey reflects impending changes at some of the POTWs such as increasing capacity or process changes. The survey accounts for 48 POTWs, which treat a total of 2.2 billion gallons per day of wastewater (roughly 73 percent of the total wastewater treated by POTWs in California). The conclusions reached as to the typical characteristics of POTWs in California are summarized below.

**Headworks**

Wastewater enters the POTW at the headworks where preliminary treatment occurs. In California, the headworks are usually enclosed, with the ventilation air collected and treated with odor control equipment. It is not anticipated that the odor control equipment will have any significant effect on the type or quantity of VOC emissions. The first step in the headworks is the removal of coarse solids, usually by allowing the wastewater to flow through bar racks or coarse screens. An alternative to the use of bar racks or screens is comminution, in which the large solids are ground up and allowed to remain in the wastewater to be removed farther downstream.

Following coarse solids removal, grit consisting of sand, gravel, and large organic particles is removed. There are two general types of grit removal chambers: horizontal-flow and aerated. Horizontal-flow grit chambers allow grit to settle to the bottom of the tank. In aerated grit chambers, air is introduced to remove the grit through a spiral flow pattern.

**Primary Treatment**

The wastewater then enters the primary treatment stage. Like grit removal, primary treatment uses physical processes to remove solids from the wastewater. In the primary sedimentation tanks, which may be circular or rectangular, readily settleable solids and floating material are removed. These tanks are usually quite large with a 2- to 6-hour detention time. The water in these tanks is quiescent. In fact, turbulence and agitation are minimized to avoid disruption of the settling process. The floating material is skimmed off the water surface and the settled solids are removed from the bottom of the tank. This material is usually stabilized and disposed of either in landfills or used in agriculture.

There is very little difference in the primary treatment process between different POTWs. However, in California, approximately 80 percent of the total wastewater flow is treated in covered primary sedimentation basins (see Appendix D).

**Secondary Treatment**

Following primary treatment, secondary treatment occurs that uses biological processes in conjunction with physical and chemical processes to remove organic substances. There is more variety in the type of secondary treatment system than primary
treatment system in California. On the basis of sewage flow, 91 percent of all wastewater treated by POTWs in California undergoes treatment in an activated sludge process. Approximately 60 percent of the total California POTW wastewater flow is treated in covered activated sludge basins.

In the activated sludge process, microorganisms that decompose organic waste in an aerobic environment are maintained in the activated sludge tanks. In these tanks, biodegradable organic substances are broken down into carbon dioxide and water. The aerobic environment is achieved by introducing air into the wastewater using diffused or mechanical aeration. High-purity oxygen may also be used to aerate the activated sludge. Aeration not only provides oxygen but also provides the turbulence necessary to keep the bacterial culture in suspension and maintain a well mixed environment. The activated sludge tanks may be circular or rectangular. The surplus organisms, called waste activated sludge, are usually treated and disposed of in the same manner as the primary solids.

A small portion of the wastewater flow in California (roughly 6 percent) is treated with trickling filters followed by activated sludge. Trickling filters consist of beds of highly permeable media on which microorganisms are encouraged to grow. Wastewater trickles down over the media, allowing the microorganisms to degrade the organics in the wastewater. The filter media may consist of rocks or plastic media (which may be either loose or constructed in modules). Trickling filters are usually circular with the wastewater distributed over the top of the bed by a rotary arm. The depth of these filters varies greatly from roughly 3 to 40 feet depending on the media used. In California, trickling filters are frequently used as a preliminary secondary treatment step, which is followed by the activated sludge process. Trickling filters are normally used in smaller wastewater treatment plants and are most often located in small communities in the California central valley, outside of the extreme ozone non-attainment areas.

Stabilization ponds and aerated lagoons are typically large, shallow earthen basins that contain bacteria and algae in suspension and use natural processes to degrade organic substances. Aerated lagoons differ from stabilization ponds in that they have surface aerators and aerobic conditions are maintained throughout.

Following secondary treatment, the wastewater is sent to final clarification tanks. Biodegradable compounds, such as ethanol, are completely biodegraded before this process. Therefore, there are no emissions of degradable compounds from this process.

Disinfection

Finally, the wastewater is disinfected (usually through the application of chlorine gas). Dechlorination to remove the chlorine residual remaining after disinfection is usually
accomplished through the use of sulfur dioxide. Following dechlorination, the wastewater is discharged to the receiving water.

**Prototype Collection and Treatment Systems**

In order to estimate an ethanol emission factor for the state of California, it is first necessary to develop a prototype collection and treatment. Conservative assumptions were made during prototype development in order to reduce the calculation effort, and to interpolate, rather than extrapolate, from existing data. The use of these assumptions will present worst-case results for the volatilization of ethanol. The development of the prototypes is intended to provide a mechanism for tracking ethanol-containing consumer detergent products from the point of discharge into a drain to discharge from a municipal wastewater treatment plant.

**Collection Systems**

Ethanol emissions from wastewater collection systems occur when ethanol is volatilized from wastewater into the air flowing in the sewer headspace, and that air is then discharged to the atmosphere. Mechanisms for VOC emissions include diffusive mass transfer from the wastewater surface, and mass transfer due to surface turbulence. Surface turbulence may be caused by the flow of wastewater, or by drops and other components of the collection system. Air is emitted from wastewater collection systems at manholes, drains and at the entrance to the wastewater treatment plant.

For this report a prototype wastewater collection system was developed consisting of an average-size sewer pipe 1.0 meter in diameter, half full, with wastewater flowing at 1.0 meter per second. This average-diameter sewer pipe was conservatively estimated to be 100,000 meters long. This is equivalent to a collection system pipe length of about 70 miles. Average collection systems have maximum pipe lengths of about 5 miles and very large collection systems (Los Angeles and San Diego) have maximum pipe lengths of about 50 miles. Based on modeling calculations, the wastewater ventilation air is near saturation (in equilibrium with the liquid phase) at this length, so it was assumed that the ventilation air in collection systems was completely saturated. If saturation is assumed, then it is immaterial what the size or turbulence level (weirs, drops, junction boxes, etc.) of the collection system is. This is a worse case assumption. Concentrations less than saturation would result in less emissions.

Based on the UC Davis report (Corsi et al., 1990) wastewater ventilation air was assumed to flow concurrently. The UC Davis report (Corsi et al., 1990) found that actual measurements had been made for ventilation rates in wastewater collection systems (Pescod and Price, 1981) and it was found that the maximum rate was in small diameter sewers and was equivalent to a headspace velocity of 0.05 meters per second. The analysis completed for this report assumed that the ventilation rate was equivalent to a headspace velocity of 1.0 meter per second, for reasons described in the next paragraph. The assumption regarding ventilation rate is critical since it is
conservatively assumed that the air is saturated, and thus the mass flow of ethanol in
the ventilation air is directly proportional to the mass flow of the ventilation air.

Since it was assumed that the wastewater ventilation air is saturated, any combination
of gas velocities and ventilation barriers that multiplied out to 1.0 would not affect the
results of this report. For example, if the reported air velocity value of 0.05 meter
per second was used as the prototype velocity, then 20 ventilation barriers (pump
stations or siphons, for example) could be assumed, and the answer would be identi-
cal to assuming a 1.0-meter-per-second air velocity and no ventilation barriers. A
ventilation barrier is where the total headspace of the sewer is exhausted to the at-
mosphere with the downstream ventilation air being drawn in as fresh air. The as-
sumption of 20 ventilation barriers (i.e., pump stations or siphons) is extreme. For
example, Los Angeles County and Orange County have no major pump stations; the
City of Los Angeles has one significant pump station; and the City of San Diego has
two major pump stations. Thus, the conservative assumption of a 1.0 m/s ventilation
rate will probably overestimate actual collection system ethanol emissions by a factor
of 10.

**Wastewater Treatment**

Emissions from wastewater treatment plants were estimated using the Hyperion
Wastewater Treatment Plant in Los Angeles as a prototype facility, the same facility
that was used in the UC Davis reports (Meyerhofer, 1990). This facility is a good
example because of the large flow rate, 370 million gallons per day, about 17 percent
of the total wastewater in California. In addition, the process type and configuration
represents the vast majority of treatment facilities in California. The total emissions
for the State were calculated by multiplying the Hyperion emissions times the ratio of
the total State flow to the Hyperion flow, with adjustments made to increase emis-
sions to reflect the fact that while the processes at Hyperion are covered, which
represent the majority of the sewage in the State treated, some of the wastewater
treatment capacity in California is uncovered. In addition, only part of the flow
treated at Hyperion undergoes secondary treatment. Secondary treatment emissions
were calculated for one process unit, and then extended as if the entire flow was
treated by the secondary treatment process. However, Hyperion will have full sec-
ondary treatment in 5 years, using a process that has extremely low air emissions
(high purity oxygen activated sludge). No credit was taken for this, and Hyperion
emissions were calculated as if it was full secondary with open basins.
Emissions Calculations

This section describes the calculations performed to estimate ethanol emissions from wastewater collection and treatment systems within the state of California.

Chemical Properties of Ethanol

Ethanol has been reported to have a Henry’s Law constant of $1.07 \times 10^{-5}$ atm-m$^3$/gmole (ESI 1990). There are discrepancies in the reported values for ethanol due to ethanol’s high degree of solubility in water. An EPA contractor reported a Henry’s Law constant for ethanol of $3.03 \times 10^{-5}$ atm-m$^3$/gmole (Radian, 1990). These values translate to dimensionless Henry’s Law constants of 0.00044 and 0.0010, respectively. Hereinafter, this report will always cite the dimensionless value for Henry’s Law constants. This report uses the 0.00044 value because of the known inconsistencies in the EPA contractor report and an absence of a reference for their use of the 0.001 value.

Volatile from wastewater is a function of the overall mass transfer coefficient for each particular wastewater system component (i.e., pipe, drop, weir, aerator) and compound, as well as the Henry’s Law constant for each different compound. UC Davis found that when compounds have a Henry’s Law constant of greater than 0.1, the overall mass transfer resistance is dominated by liquid phase mass transfer. Therefore, for such compounds, the total mass transfer resistance can be accurately approximated by the liquid phase mass transfer resistance alone (Corsi et al., 1990).

Liquid phase mass transfer resistance is reduced with increasing liquid turbulence, while gas phase mass resistance is reduced by increased, large-scale, gas phase turbulence.

Figure 1 presents these relationships quantitatively. The horizontal axis represents dimensionless Henry’s Law constants. Chloroform and ethanol are located on this axis as reference points. Chloroform has a Henry’s Law constant of 0.14. The other volatile compounds studied in the UC Davis reports, have Henry’s Law constants between 0.1 and 1.0. Ethanol has a Henry’s Law constant of 0.00044. The vertical axis represents the mass transfer coefficient, the inverse of mass transfer resistance. The bold lines, solid and dashed, represent total mass transfer resistance ($K_t$) as a function of Henry’s Law constant. The solid bold line represents total mass transfer resistance ($K_t$) for quiescent conditions. The dashed bold line represents total mass transfer resistance ($K_t$) for conditions of extreme liquid turbulence.

The two horizontal lines represent the liquid phase mass transfer coefficients ($K_l$) for two different levels of liquid turbulence. The lower line represents the liquid phase mass transfer coefficient for quiescent surfaces, the minimum anticipated liquid turbulence in a wastewater facility. The upper line represents the liquid phase mass
Figure 1 - Mass Transfer Coefficients vs. Gas Liquid Partition Constant
transfer coefficient for the maximum expected liquid turbulence in a wastewater facility. These two lines bracket the expected liquid turbulence in wastewater systems. The diagonal line represents the gas phase mass transfer coefficient (HKg) at a surface wind speed of 3 meters per second, a typical annual average wind speed.

Above a Henry’s Law constant of 0.1 (as correctly reported by UC Davis), the total mass transfer coefficient is independent of Henry’s Law and equal to the liquid phase mass transfer coefficient (KL), except for the most extreme liquid turbulence levels. At the most extreme liquid turbulence levels, even chloroform is affected by gas phase resistance. As the Henry’s Law constant decreases below 0.1, gas phase mass transfer (Hkg) becomes first important, in determining total mass transfer resistance, then becomes the dominant controlling mechanism. For compounds like ethanol, with very low Henry’s Law constants, gas phase mass transfer dominates.

According to the reports UC Davis prepared for CARB, volatility (Henry’s Law constant) is generally the controlling mechanism for poorly ventilated systems and mass transfer resistance controls for well ventilated systems. The expected range for mass transfer coefficients for both chloroform and ethanol are shown in Figure 1. For the quiescent surfaces, where only a small fraction of the total emissions occur (Card and Corsi, 1991), the mass transfer for ethanol and chloroform are very similar. For areas of extreme turbulence, where most of the air emissions occur, the mass transfer of ethanol is significantly less than chloroform. In the most extreme turbulence, the total mass transfer coefficient of ethanol is over 100 times less than that of chloroform.

In poorly ventilated systems where Henry’s Law constant controls, the volatilization rate for ethanol will be over three orders of magnitude (1,000 times) less than compounds like chloroform.

The compounds that UC Davis studied, have mass transfer resistance that is proportional to liquid phase turbulence. From Figure 1 it can be concluded that ethanol has essentially the same mass transfer resistance, regardless of liquid phase turbulence. This results in essentially a uniform, low level, of ethanol emissions from open wastewater treatment processes, independent of liquid turbulence. The uniform character of ethanol emissions means that the ethanol emissions from open processes can be roughly estimated by either modeling or measuring the chloroform emissions from quiescent surfaces. The ethanol emissions from the entire process will be between 10 and 50 percent (a function of average wind speed) of the quiescent chloroform unit surface area emission rate times the total exposed, plan form, liquid surface area that is upstream of the aeration basins. Ethanol emissions after biological treatment are essentially zero due to the rapid biodegradation of ethanol. The calculations in this report use the EPA biodegradation rate constant for ethanol of 8.8 mg/g biomass-hour and a half saturation constant of 9.78 g/m (Radian, 1990).
Wastewater Flow and Composition

The Hyperion Wastewater Treatment Plant treats an average of 370 mgd of wastewater from approximately 1,000,000 residences, in addition to various industrial sources. Based on data from SDA, the quantity of ethanol entering the wastewater collection system per household from the use of liquid laundry and hand dishwashing detergents is calculated to be 3.372 grams per day. Based on a service area of 1,000,000 homes, this results in an average daily ethanol discharge rate of 3,372,000 grams. At an average wastewater flow of 370 mgd, the average ethanol concentration within the wastewater collection system is 2.41 mg/l.

Emissions from Wastewater Collection Systems

After extensive analysis of collection systems, it was concluded that for the prototype system the ventilation air (sewer gas headspace) would be close to saturated in ethanol. In order to reduce the calculation effort, as well as reduce the amount of variability in each collection system configuration that will effect ethanol emissions, the headspace was conservatively assumed to be saturated. Since it is assumed that the sewer gas headspace is saturated, then mass transfer rates and wastewater turbulence are irrelevant. The important factors are ventilation rate and ventilation configuration. As discussed earlier, it was assumed that the product of ventilation barriers (pump stations and siphons) and the gas headspace velocity (meters per second) was equal to 1.0. Reasons have already been presented why this is extremely conservative. This assumption results in the calculation of an emission factor by the equation (Corsi et al., 1990):

\[
\text{Emission Factor} = H \times \frac{Q_g}{Q_l}
\]

where:

- \( H \) = Henry's Law constant
- \( Q_g \) = gas flow, cubic meters/sec
- \( Q_l \) = liquid flow, cubic meters/sec

Using the assumptions in the prototype system of the pipe being half full and the average liquid velocity of 1 meter per second and the gas flow equals liquid flow, the emission factor is 0.00044 (0.044 percent), equal to the Henry's Law constant.

Headworks

The emissions from headworks were scaled from the emissions from primary clarifiers calculated below. Because the primary emission mechanism for nonaerated headworks is surface losses, the nonaerated headworks were adjusted based on relative
Surface areas. Headworks are about an order of magnitude smaller in exposed liquid surface area than the primary clarifiers, so the emission factor is an order of magnitude less than primary clarifiers. This emission factor is 0.005 percent for covered, nonaerated, headworks and 0.019 percent for uncovered, nonaerated, headworks.

For aerated grit chambers, the normal maximum gas to liquid ratio (volumetric) is 0.5 (CH2M HILL, 1979), leaving an emission factor of 0.022 percent, if the gas is saturated. No downward adjustments in emissions were made to account for covering, another conservative assumption. It was also estimated that one half the treatment capacity in California was aerated grit chambers.

Since the range of emission factors, a minimum of 0.005 percent for covered quiescent, and a maximum of 0.022 percent for aerated grit chambers, is so small, accounting for the exact mix of aerated/quiescent covered/uncovered will not affect the emission factor significantly. In this analysis, it was assumed that one-half of the sewage flow was treated at headworks which were aerated, one-half at quiescent headworks, and that 20 percent of the sewage flow was treated in uncovered processes. The average ethanol emission factor for California wastewater treatment facilities headworks was calculated to be 0.0149 percent.

**Primary Clarification**

Previously (ESI, 1990) emissions were estimated from primary clarifiers by applying EPA models (EPA 1990) to the Hyperion Wastewater Treatment Plant. The methodology and calculations used in this previous report are believed to be as representative as currently known for the primary treatment process, when the process is uncovered. The emission factor calculated for uncovered primary clarifiers in the ESI report is 0.19 percent. This is in excellent agreement with the UC Davis developed theory and other literature as well. The emission factor reported for chloroform for primary clarifiers is about 20 percent (Card and Corsi, 1991). This is two orders of magnitude greater than the 0.19 percent reported above, and correlates well with the UC Davis hypothesis that, based on its Henry's Law constant, ethanol should have an emission factor between two and three orders of magnitude less than volatile compounds (Corsi et al., 1990).

However, the majority of the primary clarifiers in California, on a flow basis, are covered. Covered primary clarifiers are normally vented at 12 air changes per hour (NFPA, 1990). Using this value, and the covered Hyperion primary clarifiers as the prototype system, the emission factor for covered primary clarifiers is 0.05 percent (see Appendix A for calculations).

**Secondary Biological Treatment Systems**

**Diffused Air-Activated Sludge.** Approximately 87 percent of all wastewater treated by the surveyed POTWs in the state of California is treated by the diffused air-activated
sludge process, where the aeration air is introduced into the bottom of the aeration tank through an air distributor called a diffuser. Ethanol emissions from activated sludge processes can be modelled using the Programs to Assess Volatile Emissions (PAVE) developed by the Chemical Manufacturers Association (CMA, 1990). PAVE is a set of models for determining volatile emissions from certain secondary emission sources. It contains a model that can be used to simulate aerated activated sludge treatment processes. Since PAVE is unique in the fact that it does not use oxygen-based mass transfer models, it can be used for semivolatiles, like ethanol. However, even though the PAVE model calculates an accurate emissions value internally for ethanol, the prediction of air emissions from the PAVE model are only output to two decimal places. Thus any value less than 0.005 percent is printed as a zero value. Based on this it was conservatively assumed that the emission factor for diffused air secondary activated sludge secondary treatment systems was 0.01 percent. The "zero" PAVE output value assures that it actually must be lower. In addition, it was conservatively assumed that the emissions from covered systems would be the same for open systems.

The PAVE model results indicate that virtually 100 percent of the ethanol present in the wastewater is biodegraded by activated sludge treatment. The aeration basin effluent ethanol concentration is estimated at 0.00223 mg/l (2.23 micrograms per liter).

Mechanically Aerated Activated Sludge Systems. Approximately 4 percent of the secondary treatment systems in California are mechanically aerated, where surface mixing devices disperse the liquid on the surface into the atmosphere to aid in oxygen mass transfer. All of these systems are probably uncovered. Because mechanically aerated systems are typically completely mixed systems, chemicals treated in these systems should have the same biodegradation rate as the completely mixed activated sludge systems. It was assumed that all ethanol that was not degraded was volatilized, leaving zero ethanol in the effluent. This resulted in an emission factor of 0.175 percent.

Trickling Filters. Enclosed trickling filters are designed so that 1,000 percent of the required oxygen demand is supplied from the mechanical (fan) ventilation system (CH2M HILL, 1985). Assuming that this air is saturated with ethanol, another conservative assumption, the resulting emission factor is 0.00176. It was conservatively estimated that open trickling filters could have as high as one order of magnitude more air flow than the enclosed systems, resulting in an emission factor of 0.0176 for open systems. About 6 percent of the secondary systems in California are trickling filters. Although no formal survey was taken, it was conservatively assumed that 80 percent of the trickling filter capacity was uncovered.

Rotating Biological Contactors (RBCs). All RBC processes in California are enclosed because of poor performance of open systems. It was assumed that (worst
case) the emissions would be the same for enclosed trickling filters. RBCs represent about 1 percent of the California wastewater flow.

**Lagoons.** Because lagoons often have surface aerators, a worst-case assumption was that they would have the same emission factors as surface aerated activated sludge systems. No lagoons are covered. About 2 percent of the wastewater in California is treated in lagoons.

**Secondary Clarifiers**

The ethanol emission factor for secondary clarifiers is calculated to be 0.45 percent (Appendix C). As in the previous cases, this emission factor is based on the quantity of ethanol entering the clarifier. The methodology used was identical to that of primary clarifiers. Calculations for estimating ethanol emissions from secondary clarifiers are summarized in Appendix C. The 0.45 percent ethanol emission factor applies only for uncovered secondary clarifiers. It is highly unusual for secondary clarifiers to be covered. However, the concentration of ethanol is so low by the time it reaches this process, due to biodegradation in preceding biological units, the total emissions here are negligible.

**Estimation of Statewide Ethanol Emission Factors**

The emissions factors developed based on the prototype collection and treatment systems are shown in Table 1. The first column in Table 1 are the processes and process configurations evaluated. The second column represents the portion of flow that is treated in each process configuration in the State. The third column is the portion of the processes that are covered or uncovered. The fourth column is the emission factor for each process and process configuration, as described in the above text. This factor represents the mass of ethanol that is emitted, divided by the influent mass of ethanol entering into the specific process. The fifth column represents the flow proportioned emission factor where emission factors for process groups are adjusted based on the portion of total California wastewater flow that the process treats. The sixth column is the assumed or calculated biological oxidation removal factor. It was assumed that only the secondary processes biologically decomposed ethanol.

The cumulative emission factor column shows the ethanol volatilized in each process as a percentage of total ethanol that enters the collection system. The percent remaining in solution, shown in the far right column, shows the fraction of total ethanol entering the system that is in solution at each process.

This table shows that the overwhelming portion of ethanol entering the wastewater system is biodegraded in wastewater treatment systems and is not volatilized into the atmosphere.
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References


Appendix A
Covered Primary Clarifier Emissions Calculations

Prototype Primary Clarifier

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Chemical Properties

- Diffusivity of Ethanol in Water (D_w): 1.30 x 10^{-5} cm²/sec
- Diffusivity of Ether in Water (D_ether): 8.5 x 10^{-6} cm²/sec
- Henry's Law Constant of Ethanol (H): 1.07 x 10^{-5} atm·m³/mol
- Density of Air (p_a): 1.2 x 10^{-3} g/cm³
- Viscosity of Air (u_a): 1.81 x 10^{-4} g/cm·sec
- Diffusivity of Ethanol in Air (D_a): 0.123 cm²/sec

1. Calculate Liquid-Phase Mass Transfer Coefficient k_L

\[ k_L = 2.78 \times 10^{-6} (D_w/D_{ether})^{0.67} \]

\[ k_L = 2.78 \times 10^{-6} (1.3 \times 10^{-5}/8.5 \times 10^{-6})^{0.67} \]

\[ k_L = 3.70 \times 10^{-6} \text{ m/sec} \]

2. Calculate Gas-Phase Mass Transfer Coefficient k_G

\[ k_G = 4.82 \times 10^{-3} U^{0.78} S_c G^{-0.67} d_e^{-0.11} \]

\[ d_e = (\text{Area}/3.14)^{0.5} \times 2 \]

Model 1 Primary Clarifier - Area = 16,950 ft² = 1575 m²

\[ d_e = (1575m/3.14)^{0.5} \times 2 = 44.8 \text{ m} \]

\[ Sc_G = u_a/p_a D_a \]
\[ Sc_G = 1.81 \times 10^4 / (0.123 \times 1.2 \times 10^{-3}) = 1.226 \]

\[ U = \text{vent rate (AC/hr) x volume of enclosed space/cross sectional area} \]

\[ U = \text{vent rate (AC/hr) x length} \]

\[ U = 12 \text{ AC/hr} \times 300 \text{ ft} \times (0.3048 \text{ m/ft} / 3600 \text{ sec/hr}) = 0.3 \text{ m/s} \]

\[ k_G = 4.82 \times 10^{-3} (0.3)^{0.78} (1.226)^{-0.67} (44.8)^{-0.11} \]

\[ k_G = 1.09 \times 10^{-3} \text{ m/sec} \]

3. Calculate Overall Mass Transfer Coefficient \( K \)

\[ 1/K = 1/k_L + 1/K_eqk_G \]

\[ K_eq = H/RT \quad R = 8.21 \times 10^{-5} \text{ atm-m}^3/\text{gmole}^\circ\text{K} \]

\[ T = 298^\circ\text{K} \]

\[ K_eq = 1.07 \times 10^{-5} / (8.21 \times 10^{-5} \times 298) \]

\[ K_eq = 4.37 \times 10^{-4} \]

\[ 1/K = 1/(3.70 \times 10^{-6}) + [1/(4.37 \times 10^{-4}) \times (1.09 \times 10^{-3})] \]

\[ K = 4.26 \times 10^{-7} \text{ m/sec} \]

4. Calculate Ethanol Emissions

\[ E = KC_iA \]

\[ C_i = 2.41 \text{ mg/l} = 2.41 \text{ g/m}^3 \]

\[ E = (4.26 \times 10^{-7} \text{ m/sec})(2.41 \text{ g/m}^3)(1575 \text{ m}^2) \]

\[ E = 0.00162 \text{ g/sec per primary clarifier} \]

\[ \text{Emissions from 12 clarifiers} = 0.0194 \text{ g/sec} \]

\[ \text{Daily Emissions} = (0.0194 \text{ g/sec})(86,400 \text{ sec/day}) = 1,676 \text{ g/day} \]

\[ \text{Percent Emitted} \ P_e = (E/QC_i) \times 100 \]
Q = 370 mgd = 1,400,450 m³/day

\[ P_e = \frac{1676}{(1,400,450 \times 2.41)} \times 100 = 0.05\% \]
Appendix B

PAVE MODEL OUTPUT

Note: For explanation of PAVE output see CMA, 1990.

AERATED ACTIVATED SLUDGE

HYPERION WASTEWATER TREATMENT PLANT

SUMMARY OF ITEMS 1 THROUGH 200 EXCLUDING ZEROS

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AERATED ACTIVATED SLUDGE

HYPERION WASTEWATER TREATMENT PLANT

DIFFUSED AERATION MODEL

MATERIAL BALANCE SUMMARY

FEED STREAM TO SYSTEM

FLOW = 26058.80 FT**3/HR
ORGANIC CONCENTRATION = 2.40E+00 PPM BY WT
OXYGEN CONCENTRATION = .00 PPM BY WT
MICROORGANISM LEVEL = .00 PPM BY WT
ORGANIC FLOWRATE = 3.91 LB/HR
WINDSPEED = 7.00 MPH

BASIN EFFLUENT

FLOW = 31665.21 FT**3/HR
ORGANIC CONCENTRATION = 2.23E-03 PPM BY WT
OXYGEN CONCENTRATION = 7.14 PPM BY WT
MICROORGANISM LEVEL = 2516.32 PPM BY WT

EFFLUENT FROM CLARIFIER

FLOW = 23697.21 FT**3/HR
ORGANIC CONCENTRATION = 2.23E-03 PPM BY WT
ORGANIC FLOWRATE = .00 LB/HR
OXYGEN CONCENTRATION = 7.14 PPM BY WT
MICROORGANISM LEVEL = .00 PPM BY WT

B-1
CLARIFIER UNDERFLOW TO THICKENER

FLOW = 2361.58 ft³/hr
ORGANIC CONCENTRATION = 2.23E-03 ppm by wt
ORGANIC FLOW RATE = .00 lb/hr
OXYGEN CONCENTRATION = .00 ppm by wt
MICROORGANISM LEVEL = 10000.00 ppm by wt or 1.00 wt %

RECYCLE STREAM

FLOW = 5606.41 ft³/hr
ORGANIC CONCENTRATION = 2.23E-03 ppm by wt
OXYGEN CONCENTRATION = .00 ppm by wt
MICROORGANISM LEVEL = 10000.00 ppm by wt

SUMMARY OF ORGANIC DISTRIBUTION

ORGANIC EATEN BY MICROORGANISM = 3.91 lb/hr or 100.00 % OF FEED
ORGANIC STRIPPED TO ATMOSPHERE = .00 lb/hr or .00 % OF FEED
ORGANIC WASTED TO THICKENER = .00 lb/hr or .01 % OF FEED
ORGANIC IN CLARIFIER EFFLUENT = .00 lb/hr or .00 % OF FEED

AERATED ACTIVATED SLUDGE
HYPERION WASTEWATER TREATMENT PLANT

DIFFUSED AERATION MODEL

MASS TRANSFER COEFFICIENTS

LIQUID FILM AROUND BUBBLE (lb mole/hr-ft²)
KL ORGANIC = 13.27
KL OXYGEN = 18.06

LIQUID FILM AT BASIN (lb mole/hr-ft²)
KL ORGANIC = 13.27
KL OXYGEN = 18.06

GAS FILM IN BUBBLE (lb mole/hr-ft²)
KG ORGANIC = INFINITE
KG OXYGEN = INFINITE

GAS FILM AT BASIN SURFACE (lb mole/hr-ft²)
KG ORGANIC = .2335
KG OXYGEN = .2991

OVERALL MASS TRANSFER COEFFICIENTS (lb mole/hr-ft²)
KL ORGANIC - BUBBLE = 13.268
KL OXYGEN - BUBBLE = 18.065
KL ORGANIC - SURFACE = .126
KL OXYGEN - SURFACE = 18.040
RATES OF REACTION

RATE OF OXYGEN USE = 12.05 LB/HR
RATE OF ORGANIC USE = 3.91 LB/HR
RATE OF MICROORGANISM GROWTH = 26.76 LB/HR

AERATED ACTIVATED SLUDGE
HYPERION WASTEWATER TREATMENT PLANT

DIFFUSED AERATION MODEL

COMPONENT PHYSICAL PROPERTIES

ORGANIC COMPONENT IS ETHANOL

MW = 46.10
DIFFUSIVITY IN AIR = .12 CM**2/SEC
DIFFUSIVITY IN WATER = .000013 CM**2/SEC
VAPOR PRESSURE = 50.00 MM HG
SATURATION CONC IN WATER = 500000.00 PPM BY WT
INFINITE DILUTION ACTIVITY COEFFICIENT IN WATER = 8.27E+00
INFINITE DILUTION ACTIVITY COEFFICIENT-WATER IN ORGANIC = 2.46E+00
BOD5 = 1.34
COD = 1.89
DISTRIBUTION COEFFICIENT = .54

OXYGEN

MW = 32.00
DIFFUSIVITY IN AIR = .18 CM**2/SEC
DIFFUSIVITY IN WATER = .000024 CM**2/SEC
SATURATION CONC IN WATER = 8.38 PPM BY WT
DISTRIBUTION COEFFICIENT = 44550.56

AERATED BASIN GEOMETRY AND CHARACTERISTICS

VOLUME = 1.3806E+05 FT**3 OR 1.0327E+06 GALLONS
DEPTH = 15.10 FT
AERATION RATE = 5000.00 SCFM
BUBBLE DIAMETER = .66 CM
TOTAL SURFACE AREA = 3.30542E+05 FT**2
EFFECTIVE SURFACE AREAS
BUBBLE INTERFACE = 3.21488E+05 FT**2
BASIN SURFACE AREA = 9.05384E+03 FT**2
Appendix C
Secondary Clarifier Emissions Calculations

Prototype Secondary Clarifier

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Chemical Properties

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1. Calculate Liquid-Phase Mass Transfer Coefficient k_L

\[ k_L = 2.78 \times 10^{-9} (D_w/D_ether)^{0.67} \]

2. Calculate Gas-Phase Mass Transfer Coefficient k_G

\[ k_G = 4.82 \times 10^{-3} U^{0.78} Sc_G^{-0.67} d_e^{-0.11} \]

\[ d_e = (\text{Area}/3.14)^{0.5} \times 2 \]

Model 1 Primary Clarifier - Area = 9,500 ft² = 883 m²

\[ d_e = (883 \text{ m}/3.14)^{0.5} \times 2 = 33.5 \text{ m} \]

\[ Sc_G = \frac{u_a}{p_a D_a} \]

\[ Sc_G = 1.81 \times 10^{-4}/(0.123 \times 1.2 \times 10^{-3}) = 1.226 \]
U = 7 mph = 3.13 m/sec

\[ k_G = 4.82 \times 10^{-3}(3.13)^{0.78}(1.226)^{-0.67}(33.5)^{-0.11} \]

\[ k_G = 6.96 \times 10^{-3} \text{ m/sec} \]

3. **Calculate Overall Mass Transfer Coefficient K**

\[ 1/K = 1/k_L + 1/K_{eq}k_G \]

\[ K_{eq} = H/RT \quad R = 8.21 \times 10^{-5} \text{ atm-m}^3/\text{gmole}^9\text{K} \]

\[ T = 298^\circ\text{K} \]

\[ K_{eq} = 1.07 \times 10^{-5}/(8.21 \times 10^{-5} \times 298) \]

\[ K_{eq} = 4.37 \times 10^{-4} \]

\[ 1/K = 1/(3.70 \times 10^{-6}) + [1/(4.37 \times 10^{-4}) \times (6.96 \times 10^{-3})] \]

\[ K = 1.67 \times 10^{-6} \text{ m/sec} \]

4. **Calculate Ethanol Emissions**

\[ E = KC_iA \]

\[ C_i = 0.00223 \text{ mg/l} = 0.00223 \text{ g/m}^3 \]

\[ E = (1.67 \times 10^{-6} \text{ m/sec})(0.00223 \text{ g/m}^3)(883 \text{ m}^2) \]

\[ E = 3.29 \times 10^{-6} \text{ g/sec per secondary clarifier} \]

Emissions from 49 secondary clarifiers = 0.000161 g/sec

Daily Emissions = 13.92 g/day

5. **Percent Emitted**

\[ \text{Percent Emitted } P_e = (E/QC_i) \times 100 \]

\[ Q = 370 \text{ mgd} = 1,400,450 \text{ m}^3/\text{day} \]

\[ P_e = [13.92/(1,400,450 \times 0.00223)] \times 100 = 0.45\% \]
## Appendix D
### CHARACTERISTICS OF CALIFORNIA POTWs

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Notes

- mgd = million gallons per day
- D = Design Flow

Total influent flow is the total flow for which data on covered/not-covered processes is presented in this table and does not include the flow for plants for which only the flow is listed.

Total flow to POTWs in California is approximately 3 billion gallons per day.
(Takashi Asano, State Water Resources Control Board.)

References

- AB2555 Air Toxics Report - Data obtained from individual plant's AB2555 Air Toxics Report filed with the local AQMD
- Individual Name - Data obtained from CH2M HILL staff or other contact identified
- Phone Number - Data obtained by contacting named plant at referenced phone number