

The Soap and Detergent Association
Washington, D.C.

**Calculation of Component Chemical
Air Emission Factors
for:**

- **Hand Dishwashing Detergents**
- **Liquid Laundry Detergent**
- **Liquid Fabric Softener**

**Part II – Emissions from Wastewater
Collection and Treatment Systems**

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Abstract

Air emission factors are presented for isopropyl alcohol, ethanol, methanol, ethylene glycol monobutyl ether, propylene glycol, dipropylene glycol methyl ether, and monoethanolamine for losses to atmosphere in wastewater collection and treatment systems. For collection systems an equilibrium approach based on a CARB prototype collection system was used. For wastewater treatment plants, the methodology documented in EPA-453/R-94-080A was used. Emission factors (for the complete collection and treatment system) ranged from 2.27% for isopropyl alcohol to 0.0047% for monoethanolamine. These emission factors represent the percent of the material emitted to atmosphere of the original mass of material entering the wastewater system.

Introduction

This report provides an estimate of air emissions of seven compounds found in consumer fabric and dish care products (i.e., liquid hand dishwashing detergents, liquid laundry detergents, rinse-added liquid fabric softeners) from domestic wastewater collection and treatment systems after the products are disposed of in household drains. These products are isopropyl alcohol, ethanol, methanol, ethylene glycol monobutyl ether, propylene glycol, dipropylene glycol methyl ether, and monoethanolamine. The emission estimates presented were prepared in a systematic and scientific manner using EPA and CARB methodologies. All methodologies provide conservative estimates (overestimation) and should be considered worse case system emissions. The results presented in this report are intended for use in developing regional air emission inventories to establish regulatory priorities.

Summary

Wastewater collection system emissions were estimated using a conservative equilibrium approach based on a prototype collection system developed by CARB (Chang, 1991). The CARB report developed a more refined approach for collection system emissions than was used in this report and produced the SUDS (Sewer Uniform reach with Drop Solutions) computer collection system fate model. Unfortunately, the computational techniques used in SUDS only allowed for the successful calculation of emission factors for highly volatile compounds. The program was numerically unstable and could not calculate emissions for the low volatility compounds that are the subject of this report. Therefore, the more conservative and computationally simple equilibrium approach was used. Based on the CARB report (Chang 1991), and calculations on chloroform using the equilibrium model, the equilibrium model appears to overestimate emissions by a factor of three. Therefore, we can consider the use of this model to represent a 'worse case' emissions scenario.

POTW emissions were estimated based on a methodology developed by CH2M HILL (1994). This methodology was repeated as originally reported, but with the exception that CARB (2006) Henry's Law data was used.

Table 1 presents a summary of the wastewater collection system, wastewater treatment plant, and total wastewater system (collection system plus treatment) emission factors.

Table 1. - Wastewater Collection and Treatment System Emission Factors.

Chemical	Percent of of Total Compound Used by Consumers Entering the Drain that is Emitted to Atmosphere		
	Wastewater	Wastewater	Total
	Collection System	Treatment Plant	Wastewater System
Isopropanol	0.84%	1.44%	2.27%
Ethanol	0.62%	0.60%	1.21%
Methanol	0.42%	0.81%	1.23%
Ethylene glycol monobutyl ether	0.0044%	0.14%	0.15%
Propylene glycol	0.00049%	0.096%	0.097%
Dipropylene glycol methyl ether	0.00025%	0.0086%	0.0089%
Monothanolamine	0.00010%	0.0046%	0.0047%

Calculation Methodology

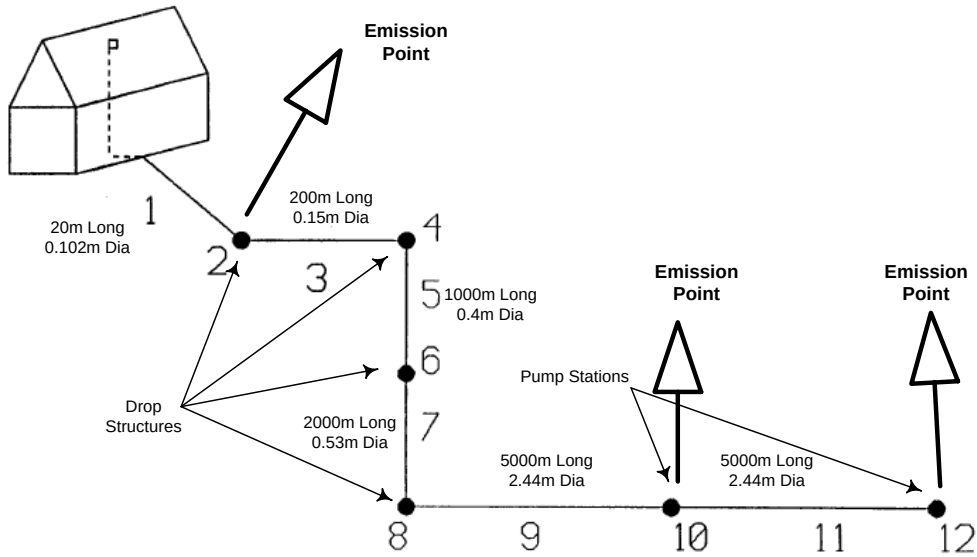
Wastewater Collection Systems

The California Air Resources Board (CARB) completed a project in 1991 that combined collection system measurement and mathematical simulation of VOC emissions (Chang, 1991). As part of that project, the chloroform emissions in a large wastewater collection system were mathematically simulated. This collection system had a radius of about 13 kilometers (8.1 miles) and a flow rate of 3.6 m³/s (82 MGD). This collection system would serve a population of around 300,000 people (assuming a wastewater production of about 300 gallons per capita per day). Using a finite difference model that stepped through both the spatial and time domains, the chloroform emissions from this system were estimated to be 23.4%. That is if 100 grams of chloroform were disposed of in the household down the drain, 76.6 grams would enter the wastewater treatment system. Figure 1 shows the schematic of the simulated collection system.

This system has three emission points. The pump stations at nodes 10 and 12 emit directly into the atmosphere and the junction between segment 1 and segment 3 that emits into the collection system and possibly from there into the atmosphere.

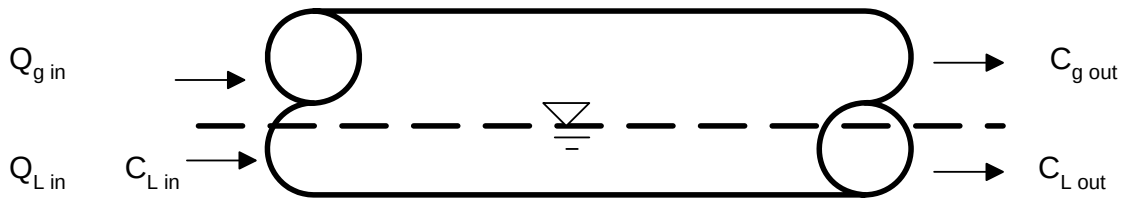
A computer model was produced, called SUDS (Sewer Uniform reach with Drop Solutions) that produced the simulation for chloroform. It was our intent to use SUDS to simulate the rest of the target compounds, but it was found that the SUDS program was numerically unstable when the solution approached equilibrium. A closer inspection of the mathematical approach used for the SUDS model indicated that this methodology would not work for any compounds that had a lower volatility than chloroform. All of our study compounds have volatilities that are order of magnitudes lower than chloroform.

Figure 1 – Schematic of CARB Simulated Collection System.



Therefore, a new approach was developed making the conservative assumption that mass transfer was not limiting and the compounds were always in the equilibrium between liquid phase and gas phase. Figure 2 shows the nomenclature used for the development of the equilibrium model.

Figure 2. Nomenclature for Equilibrium Model



The fundamental assumption for equilibrium is that

$$C_{g\ out} = C_{L\ out} H$$

where $C_{g\ out}$ is the outlet gas phase concentration (g/m^3), $C_{L\ out}$ is the outlet liquid phase concentration (g/m^3), and H is the Henry's Law Coefficient (g/m^3 gas per g/m^3 liquid). By conservation of mass

$$Q_{L\ in} C_{L\ in} = Q_{L\ out} C_{L\ out} + Q_{g\ out} C_{g\ out}$$

Where Q is the liquid/gas flow in m^3/s . This can be solved for the outlet gas concentration as follows

$$C_{g\ out} = \frac{C_{L\ in} Q_L}{Q_g + \frac{Q_L}{H}}$$

The fraction removal is calculated by

$$Fr = \frac{Q_{g\ out} C_{g\ out}}{Q_{L\ in} C_{L\ in}}$$

The total system fraction removed is calculated by

$$Fr_{Total} = Fr_1 + (1 - Fr_1)Fr_2 + (1 - (1 - Fr_1)Fr_2)Fr_3$$

Table 2 presents a summary of the data used to calculate the emissions from the three emission points.

Table 2. – Summary of Data Used to for the Three Emission Points

Parameter	Units	Collection System Element		
		Household Drain	PS 1	PS 2
Diameter	m	0.102	0.533	2.44
Roughness		0.013	0.013	0.013
Slope		0.05	0.002	0.0008
Depth	m	0.025	0.267	1.22
Gas Velocity	m/s	3	0.045	0.75
Radius	m ²	0.051	0.267	1.220
Alpha		1.036	1.573	1.571
Total Area	m ²	0.008	0.223	4.676
Gas Area	m ²	0.007	0.112	2.338
Liquid Area	m ²	0.002	0.112	2.338
Gas Flow	m ³ /s	0.020	0.005	1.753
Wetted Perimeter	m	0.106	0.837	3.833
Hydraulic Radius	m	0.015	0.133	0.610
Liquid Velocity	m/s	1.032	0.897	1.565
Liquid Flow	m ³ /s	0.002	0.100	3.659

Table 3 presents a summary of the calculations for chloroform.

Table 3. – Chloroform Calculations for the Equilibrium Model.

Parameter	Units	Collection System Element		
		Household		
		Drain	PS 1	PS 2
Temperature	0C	35	25	25
H		0.235	0.147	0.147
Co	ug/l	100	100	99.27
Cg	ug/l	6.01	14.62	13.65
Cl	ug/l	25.55	99.27	92.72
Mass Gas	ug	0.12	0.07	23.94
Mass Total	ug	0.16		365.87
Fraction Released		74%		6.5%
Total Removal		79%		

Note:

1. Fraction released and total removal are the percentage of the total mass input to the system

The results of the equilibrium analysis show that, for the equilibrium assumption, the total chloroform emissions would be 79%. This compares to the emissions calculated from SUDS at 23.4%. Therefore we can conclude, at least for the chloroform analysis, that the equilibrium assumption results in emissions that are about 3 times higher than the emissions predicted from the more refined SUDS model.

In summary, the equilibrium model should be substantially more conservative (over estimating emissions) than the SUDS model and, therefore, should represent a worse case scenario for collection system emissions.

This equilibrium model was then used to predict the emissions for the study compounds. The Henry's Law values were the same ones used for the point-of-use study (EMC 2006). The equilibrium model is linear in mass, meaning that influent concentration changes will not affect removal rates. Therefore, all calculations were made using an arbitrary 100 mg/l of compound in the discharge wastewater. Table 4 presents a summary of the results for the collection system emission factors.

Table 4. – Summary of Collection System Emission Factors Based on the Equilibrium Model.

Chemical	Percent of of Total Compound Used by Consumers Entering the Drain that is Emitted to Atmosphere
Isopropanol	0.84%
Ethanol	0.62%
Methanol	0.42%
Ethylene glycol monobutyl ether	0.00%
Propylene glycol	0.000%
Dipropylene glycol methyl ether	0.0003%
Monoethanolamine	0.0001%
Chloroform (For Calibration)	79%

Wastewater Treatment Plants

The fate of compounds from consumer products at Publicly Owned Treatment Works (POTWs) was studied extensively by The Soap and Detergent Association in the early 1990's (CH2M HILL 1994). This methodology used EPA wastewater treatment fate modeling equations, and EPA compound property data to predict emission rates from a proto-typical wastewater treatment plant. This plant included a pump station, inlet screening, grit removal, primary clarifiers, and an activated sludge system.

That methodology was used in the exact manner for this report and the reader is referred to that report (CH2M HILL 1994), or the accompanying spreadsheet model for model for calculation details. This model effort differed only by the following exceptions (ethylene glycol monobutyl ether, propylene glycol, and monoethanolamine were not modeled in 1994):

1. The Henry's Law values used were exclusively CARB (2006)
2. The biological rate constants for the compounds not modeled in 1994 were estimated using the same procedures used in 1994.

A summary of the input chemical data used for the POTW modeling exercise is shown in Attachment 1. The emission factors calculated for the POTW model are shown in Table 5. The detailed unit process emissions are shown in Attachment 2.

Table 5. – Summary of POTW Emission Factors

Chemical	Percent of of Total Compound Used by Consumers Entering the Plant that is Emitted to Atmosphere
Isopropanol	1.44%
Ethanol	0.60%
Methanol	0.81%
Ethylene glycol monobutyl ether	0.14%
Propylene glycol	0.096%
Dipropylene glycol methyl ether	0.0086%
Monoethanolamine	0.0046%

Complete Wastewater System Emissions

The complete wastewater system emissions can be calculated using the formula

$$WF = CF + (1 - CF) * TF$$

Where *WF* is the emission factor for the entire wastewater system, *CF* is the emission factor for the collection system, and *TF* is the emission factor for the treatment system. Table 6 presents a summary of the wastewater emissions.

Table 6. – Summary of Wastewater Emission Factors

Chemical	Percent of of Total Compound Used by Consumers Entering the Drain that is Emitted to Atmosphere		
	Wastewater Collection System	Wastewater Treatment Plant	Total Wastewater System
Isopropanol	0.84%	1.44%	2.27%
Ethanol	0.62%	0.60%	1.21%
Methanol	0.42%	0.81%	1.23%
Ethylene glycol monobutyl ether	0.0044%	0.14%	0.15%
Propylene glycol	0.00049%	0.096%	0.097%
Dipropylene glycol methyl ether	0.00025%	0.0086%	0.0089%
Monoethanolamine	0.00010%	0.0046%	0.0047%

References

Chang, D.P.Y. **Emissions of Volatile and Potentially Toxic Organic Compounds from Wastewater Treatment Plants and Collection Systems (Phase II). Volume 2: Wastewater Collection System Study.** State of California Air Resources Board, Research Division. August 1991.

CARB. **Chemical Property Data.** <http://www.arb.ca.gov/db/solvents.htm>. September 2006.

CH2M HILL. **Emissions of Selected VOC Compounds from the use of Laundry and Dishwashing Products.** Prepared for The Soap and Detergent Association. May 1994.

EMC. **Calculation of Component Chemical Air Emission Factors for Hand Dishwashing Detergents, Liquid Laundry Detergent, and Liquid Fabric Softener. Part I Emissions at Point of Use.** Prepared for The Soap and Detergent Association, December 2006.

USEPA. **Air Emissions Models for Waste and Wastewater.** EPA-453/R-94-080A, November 1994.

Attachment 1 – Summary of POTW Model Chemical Property Data.

		Ethanol		Isopropanol		Methanol		Ethylene glycol monobutyl ether		Propylene glycol		Dipropylene Glycol Methyl Ether		Mono- ethanol- amine	
Process	Variable	Value	Ref #	Value	Ref #	Value	Ref #	Value	Ref #	Value	Ref #	Value	Ref #	Value	Ref #
Basic Physical/Chemical Constants															
	Dw, Diffusivity in Water, cm^2/sec	1.30E-05	8	9.90E-06	13	1.64E-05	8	8.15E-06	6	1.02E-05	8	8.00E-06	Estimate	1.14E-05	8
	Da, Diffusivity in Air, cm^2/sec	0.123	8	0.12	13	0.15	8	0.06	6	0.93	8	0.047072178	Estimate	0.11	8
	Do2w, Diffusivity in Water of Oxygen, cm^2/sec	2.40E-05	7	2.40E-05	7	2.40E-05	7	2.40E-05	7	2.40E-05	7	2.40E-05	7	2.40E-05	7
	Dether, Diffusivity in Water of Ether, cm^2/sec	8.50E-06	7	8.50E-06	7	8.50E-06	7	8.50E-06	7	8.50E-06	7	8.50E-06	7	8.50E-06	7
	H, Henry's Law Constant, atm-m^3/gmol	5.00E-06	21	7.90E-06	21	4.55E-06	21	1.60E-06	21	1.70E-07	21	1.07E-07	21	3.30E-08	21
	R, Universal Gas Constant, atm-m^3/gmol-K	8.21E-05	7	8.21E-05	7	8.21E-05	7	8.21E-05	7	8.21E-05	7	8.21E-05	7	8.21E-05	7
	pl, Density (liquid), g/cm^3	1		1		1		1		1		1		1	
	ul, Viscosity (liquid), g/cm-s	8.93E-03	10	8.93E-03	10	8.93E-03	10	8.93E-03	10	8.93E-03	10	8.93E-03	10	8.93E-03	10
	pa, Density (air), g/cm^3	1.20E-03	10	1.20E-03	10	1.20E-03	10	1.20E-03	10	1.20E-03	10	1.20E-03	10	1.20E-03	10
	ua, Viscosity (air), g/cm-s	1.81E-04	10	1.81E-04	10	1.81E-04	10	1.81E-04	10	1.81E-04	10	1.81E-04	10	1.81E-04	10
	T, Temperature (liquid), K	298	10	298	10	298	10	298	10	298	10	298	10	298	10
	T, Temperature (liquid), C	25	10	25	10	25	10	25	10	25	10	25	10	25	10
	MW, Molecular Weight, g/gmol	46.07	8	60.1	15	32	8	118.18	19	76.11	19	148.23	18	61.09	8
	Scg, Schmidt Number (gas) (Scg=ua/(pa*Da)	1.23	3	1.26	3	1.01	3	2.41	3	0.16	3	3.20	3	1.41	3
	Scl, Schmidt Number (liquid) (Scl=ul/(pl*Dw)	686.92	3	902.02	3	544.51	3	1095.71	3	875.49	3	1116.53	3	783.33	3
	Q, Total Flow Rate, mgd	32	1	32	1	32	1	32	1	32	1	32	1	32	1
	Q, Total Flow Rate, m^3/sec	1.40	1	1.40	1	1.40	1	1.40	1	1.40	1	1.40	1	1.40	1
	bi, Biomass Concentration, g/m^3	4000	2	4000	2	4000	2	4000	2	4000	2	4000	2	4000	2
	Ks, Half Saturation Biorate Concentration, g/m^3	9.78	8	200.00	8	90.00	8	9.78	Calc'd	9.78	Calc'd	9.78	Calc'd	9.78	Calc'd
	Kmax, Maximum Biorate Constant, g/g-s	2.44E-06	8	4.17E-06	20	5.00E-06	20	2.44E-06	Calc'd	2.44E-06	Calc'd	2.44E-06	Calc'd	2.44E-06	Calc'd
References															
No.	Source	Item													
1	Draft Report to Congress	Table 5-2													
2	SIMS Documentation	Table 5-9													
3	SIMS Documentation	Table 4-2													
4	Draft Report to Congress	Page F-50													
5	Draft Report to Congress	Table E-2													
6	Draft Report to Congress	Table 5-4													
7	SIMS Documentation	Table 4-4													
8	SIMS Documentation	Appendix B													
9	Metcalf and Eddy														
10	SIMS Documentation	Tables 6-3 to 6-8													
11	Draft Report to Congress	Table E-3													
12	SIMS Documentation	Page 4-10													
13	Simulation Sciences PROII and ENPRO Models														
14	Mookerjee and Hine, 1975														
15	Verschueren, K., 1983														
16	Howard, P., 1989 (Vols. 2 and 4)														
17	Dow Glycol Ether Bulletin, Dec. 1993														
18	Sax's Dangerous Properties of Industrial Materials														
19	Perry's Chemical Engineers Handbook, 5th Ed.														
20	EPA WATER7 User's Guide for Wastewater Treatment Compound Property Processor and Air Emissions Estimator, November 1990														
21	CARB														

Attachment 2 – Summary of POTW Unit Process Emission Factors.

				Primary	Primary	Activated	Activated	Secondary	Secondary	
	Lift	Bar-	Aerated	Clarifier	Clarifier	Sludge	Sludge	Clarifier	Clarifier	
Chemical	Station	Screens	Grit	Quiescent	Weir	Surface	Weir	Quiescent	Weir	Total
Ethanol	0.0023%	0.0001%	0.0542%	0.4940%	0.0003%	0.0338%	0.0000%	0.0152%	0.0000%	0.60%
Isopropanol	0.0036%	0.0002%	0.0729%	0.6465%	0.0002%	0.4969%	0.0002%	0.2198%	0.0000%	1.44%
Methanol	0.0024%	0.0001%	0.0569%	0.5258%	0.0003%	0.1570%	0.0001%	0.0705%	0.0000%	0.81%
Ethylene glycol monobutyl ether	0.0005%	0.0000%	0.0133%	0.1193%	0.0002%	0.0077%	0.0000%	0.0035%	0.0000%	0.14%
Propylene glycol	0.0003%	0.0000%	0.0086%	0.0799%	0.0002%	0.0051%	0.0000%	0.0023%	0.0000%	0.096%
Dipropylene Glycol Methyl Ether	0.0000%	0.0000%	0.0008%	0.0071%	0.0001%	0.0005%	0.0000%	0.0002%	0.0000%	0.009%
Mono- ethanol- amine	0.0000%	0.0000%	0.0004%	0.0038%	0.0001%	0.0002%	0.0000%	0.0001%	0.0000%	0.005%