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 I – Emissions at Point of Use

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Abstract

The indoor air pollution assessment methodology for consumer appliances/activities developed by the University of Texas for the United States Environmental Protection Agency (USEPA) [Howard-Reed and Corsi, 2000] was extended to calculate the volatilization of the individual organic compounds used in consumer products intended to be used for hand dishwashing and laundry in automatic washing machines. A spreadsheet computational environmental fate model was developed using the USEPA methodology and then calibrated against the results obtained in Howard-Reed and Corsi for toluene emissions in washing machines. The model was then calibrated against laboratory (environmental chamber) data obtained by the University of California [Wooley et al, 1990] for ethanol used in both hand dishwashing and laundry washing machines. After calibration, the model was then used to calculate emission factors for isopropyl alcohol, ethanol, methanol, propylene glycol, and monoethanolamine for hand dishwashing detergent; isopropyl alcohol, ethanol, methanol, ethylene glycol monobutyl ether, propylene glycol, dipropylene glycol methyl ether, and monoethanolamine for laundry detergent; and isopropyl alcohol and ethanol for liquid, rinse-added fabric softener. For all chemicals, a calculation was made for both typical use and a high release scenario. It is intended that this data be used as emission factors to estimate emissions for emission inventories.

Introduction

Historically, in order to determine the air emissions from consumer product use the product was used in the manner desired in an environmental chamber with the system emissions directly measured. This approach has the value of offering close to real world data, but has the burden of both expense and the lack of flexibility to evaluate release mechanisms to learn more about the system in question. An extensive USEPA project completed by the University of Texas bridged the world of environmental chamber testing and environment fate modeling. This project produced and validated a computational environmental fate modeling approach for almost all consumer appliances/activities that use water. This paper will provide a brief overview of that work, but to fully understand and appreciate the scope and depth of this project the USEPA report should be reviewed [Howard-Reed and Corsi, 2000]. In this paper this report will either be referred to by the authors or as the USEPA document identification number, EPA 600/R-00/096.

A spreadsheet computational model was developed based on the USEPA work and calibrated against both the USEPA data set, and environmental chamber data produced by the University of California [Wooley et al., 1990]. The Wooley work is referred to frequently in this report and is usually noted just as the Wooley data set. After calibration, the model was used to calculate emission factors for hand dishwashing products, liquid laundry detergent, and liquid fabric softener.

Summary

Tables 1 through 3 present the emission factor data for hand dishwashing detergent, liquid laundry detergent, and fabric softener, respectively. These tables present the component chemical compounds in the products ranked by emissions potential (highest percentage emitters to lowest percentage emitters). The Wooley et al. [1990] data is presented as a comparison to

past work. The hand dishwashing use parameters were the same in this report as for the Wooley experiment, but the machine laundry parameters are slightly different. These differences had negligible impact on the resulting emission factor values. The last two data columns present the recommended air emission factors to be used for emission inventory purposes. There was no Wooley et al. data for fabric softener. The fabric softener model was calibrated against the USEPA data set for toluene.

Table 1. - Summary of Calculated Emission Factors for Liquid Hand Dishwashing Detergent Component Compounds.

	Calculated Emission Factors (percent of total compound used by consumers that is emitted to atmosphere) Using Two Different Approaches to Estimate Henry's Law Temperature Correction				Previously Reported Factors in Wooley et al		Recommended Value for Emission Inventory		
	CARB Henry's Law/EPA Temperature Correction		Sander Henry's Law Methodology						
Liquid Hand Dishwashing Detergent Component Compound	Typical Use Condition	High Release Condition	Typical Use Condition	High Release Condition	Typical Use Condition	High Release Condition	Typical Use Condition	High Release Condition	**Notes**
Ethanol	2.55%	3.56%	3.92%	6.05%	3.80%	4.90%	3.92%	6.05%	
Methanol	1.65%	2.20%	1.89%	2.62%			1.89%	2.62%	
Propylene glycol	0.419%	0.721%	0.021%	0.034%			0.419%	0.721%	See Note 1
Monoethanolamine	0.0194%	0.0328%	0.00008%	0.0001%			0.0194%	0.0328%	See Note 1

Notes:
1. Sander temperature slope estimated, no compound specific data available
2. No Sanders data available at all for these compounds

Table 2. - Summary of Calculated Emission Factors for Liquid Laundry Detergent Component Compounds.

	Calculated Emission Factors (percent of total compound used by consumers that is emitted to atmosphere) Using Two Different Approaches to Estimate Henry's Law Temperature Correction				Previously Reported Factors in Wooley et al		Recommended Value for Emission Inventory		
	CARB Henry's Law/EPA Temperature Correction		Sander Henry's Law Methodology						
Liquid Laundry Detergent Component Compound	Typical Use Condition	High Release Condition	Typical Use Condition	High Release Condition	Typical Use Condition	High Release Condition	Typical Use Condition	High Release Condition	**Notes**
Isopropanol	0.20%	0.93%	0.24%	1.74%			0.24%	1.74%	
Ethanol	0.13%	0.61%	0.19%	1.19%	0.19%	1.21%	0.19%	1.19%	
Methanol	0.13%	0.54%	0.14%	0.72%			0.14%	0.72%	
Ethylene glycol monobutyl ether	0.041%	0.286%					0.041%	0.286%	See Note 2
Propylene glycol	0.013%	0.126%	0.001%	0.006%			0.013%	0.126%	See Note 1
Dipropylene glycol methyl ether	0.0021%	0.0112%					0.0021%	0.0112%	See Note 2
Monoethanolamine	0.0011%	0.0090%	0.0000%	0.0000%			0.0011%	0.0090%	See Note 1

Notes:
1. Sander temperature slope estimated, no compound specific data available
2. No Sander data available at all for these compounds

Table 3. - Summary of Calculated Emission Factors for Washing Machine Rinse-added, Liquid Fabric Softener Component Compounds.

Fabric Softener Component Compound	Calculated Emission Factors (percent of total compound used by consumers that is emitted to atmosphere) Using Two Different Approaches to Estimate Henry's Law Temperature Correction				Recommended Value for Emission Inventory	
	CARB Henry's Law/EPA Temperature Correction		Sander Henry's Law Methodology			
	Typical Use Condition	High Release Condition	Typical Use Condition	High Release Condition	Typical Use Condition	High Release Condition
Isopropanol	0.09%	0.19%	0.09%	0.21%	0.09%	0.21%
Ethanol	0.06%	0.12%	0.08%	0.17%	0.08%	0.17%

Two different approaches to calculate Henry's Law were used for this project. The first set of data columns show the emission factors developed using California Air Resources Board (CARB) Henry's Law values [http://www.arb.ca.gov/db/solvents.htm] with USEPA temperature scaling [EPA 453/R-94-080A]. The temperature range for the analysis in this report was outside of the usual range of environmental temperatures and provided lower Henry's Law values at the higher temperatures than some laboratory data. Therefore, the Henry's Law temperature scaling methodology documented by Sander [1999] was also utilized with separate results provided in these three tables. The Sander values for the top three emitters (isopropyl alcohol ,ethanol, and methanol) are recommended as more representative of actual emissions than the CARB/USEPA values. For the remainder of the compounds, Sander's data is sketchy or non-existent and the CARB/USEPA values are recommended for use. Finally, the CARB Henry's Law values for the low emitting compounds are quite different than either USEPA or literature values and subsequently it is likely that these compound's (propylene glycol and monoethanolamine) emission factors are far in excess of actual emissions, by as much or more as two orders of magnitude.

Calculation Methodology

All these calculations are based on EPA 600/R-00/096 and the reader is referred to that document for derivation and nomenclature.

Fill Cycle

This cycle is used for both washing machine filling and sink filling for the hand dishwashing model.

The fill cycle solution is arrived at by the step-wise calculation of the following (in Euler or first order form):

$$C_L^{n+1} = \left[Q_L C_{L,in} - Q_L C_L^n - K_L A C_L^n + \frac{K_L A C_G^n}{H_c} \right] \frac{\Delta t}{V_L^n} + C_L^n$$

$$V_L^{n+1} = V_L^n + \Delta t Q_L$$

the second order calculation is

$$C_L^{(n+1)s} = C_L^n + \frac{\Delta t}{2}\left[\frac{Q_L C_{L,in} - Q_L C_L^n - K_L A C_L^n + \frac{K_L A C_G^n}{H_c}}{V_L^n} + \frac{Q_L C_{L,in} - Q_L C_L^{n+1} - K_L A C_L^{n+1} + \frac{K_L A C_G^n}{H_c}}{V_L^{n+1}}\right]$$

special consideration has to made for the implementation of this because V_L^n is zero for the first step. In addition, for the readsorption condition (gas phase supersaturated), either or both of the gas phase or liquid phase concentrations can go negative if not controlled.

The first order gas phase solution is

$$C_g^{n+1} = \left[-Q_G C_g^n + Q_L C_g^n + K_L A C_L^n - \frac{K_L A C_g^n}{H_c}\right]\frac{\Delta t}{V_g^n} + C_g^n$$

and the second order gas phase is

$$C_g^{(n+1)s} = C_g^n + \frac{\Delta t}{2}\left[\frac{-Q_G C_g^n + Q_L C_g^n + K_L A C_L^n - \frac{K_L A C_g^n}{H_c}}{V_g^n} + \frac{-Q_G C_g^{n+1} + Q_L C_g^{n+1} + K_L A C_L^n - \frac{K_L A C_g^{n+1}}{H_c}}{V_g^{n+1}}\right]$$

The second order solution was used for analysis in this report for both liquid and gas phases.

Wash/Rinse

The wash/rinse solution is explicit and can be solved for any moment of time in the cycle. However, it is still solved in a step wise manner (15 second steps) to allow for the numerical integration into a total system emission. This was used both for hand dishwashing and laundry.

The liquid phase concentration, $C_L(t)$, is represented by

$$C_L = C_{Lo}\left[\alpha \cosh(\beta t)\right] + \left(\frac{BF}{Z} + \frac{EC_{Lo}}{Z} - \frac{DC_{Lo}}{2}\right)\frac{\alpha \sinh(\beta t)}{\beta}$$

where

$$\alpha = \exp\left(\frac{-Dt}{2}\right)$$

$$\beta = \sqrt{\frac{D^2}{4} - E}$$

$$B = \frac{Z}{H_c}$$

D = Z + Y

E = ZY-BX

$$X = \frac{K_L A}{V_g}$$

$$Y = \frac{Q_g}{V_g} + \frac{X}{H_c}$$

$$Z = \frac{K_L A}{V_L}$$

The gas phase concentration, $C_g(t)$, is represented by

$$C_g = C_{go}\left[\alpha \cosh(\beta t)\right] + \left(F - \frac{DC_{go}}{2}\right)\frac{\alpha \sinh(\beta t)}{\beta}$$

Drain

Drain emissions are again explicit and can be solved for any time. However, since the gas volume continually changes, this is also solved in a step wise manner with the time step equal to 15 seconds.

$$C_g = C_{go} \exp\left(\frac{-Q_g t}{V_g}\right)$$

Soak

The soak cycle for hand dishwashing used the same equations as the wash/rinse cycle, with the exception that the mass transfer values were reduced by two orders of magnitude to account for the reduction in agitation.

Total Emissions

Total emissions are calculated by summing for all the time steps

$$E_T = \sum C_{gi} Q_g \Delta t$$

Chemical Properties

Table 4 lists the chemical properties used for this analysis. They include the compounds that are the subject of this analysis plus additional compounds used to derive the mass transfer values.

Table 4. Summary of Chemical Properties used in this Analysis.

	Product Additives							Mass Transfer Surrogates			
Property	Ethanol	Mono-ethanol-amine	Iso- propanol	Ethylene glycol monobutyl ether	Methanol	Dipropylene glycol methyl ether	Propylene glycol	**Acetone**	**Methyl Ethyl Ketone**	**Dibromo-chloro-methane**	**Toluene**
NIST Name	Ethanol	Ethanol-amine	Isopropyl alcohol	2-n-Butoxy-1-ethanol	Methyl alcohol						
Structure	CH3- CH2OH	NH2-CH2CH2OH	CH3-CH2OHCH3	CH3CH2CH2-CH2O-CH2CH2OH	CH3OH	CH3-(OCH2CHCH3)2- OH	CH3CH-(CH2OH)-CH2CH2OH				
CAS	64-17-5	141-43-5	67-63-0	111-76-2	67-56-1	34590-94-8	57-55-6				
Mw (gm/gmole)	46.1	61.09	60.09	118.18	32	148.2	76.11				
Henry's Law											
CARB H											
(atm-m3/mol)	5.000E-06	3.300E-08	7.900E-06	1.600E-06	4.550E-06	1.070E-07	1.700E-07				
(mg/l / mg/l)	2.045E-04	1.350E-06	3.231E-04	6.544E-05	1.861E-04	4.376E-06	6.953E-06				
USEPA H											
(atm-m3/mol)	5.263E-06	1.161E-10	7.692E-06	5.197E-07	7.143E-06	NA	3.288E-10				
(mg/l / mg/l)	2.200E-04	6.597E-09	3.100E-04	2.125E-05	2.900E-04	NA	1.345E-08	0.0015	0.006	0.048	0.27
CARB/USEPA Ratio	0.95	284.17	1.03	3.08	0.64	NA	517.02				
Diffusion Coefficients											
Dl (cm2/s)	1.300E-05	1.140E-05	1.040E-05	8.150E-06	1.640E-05	*7.998E-06*	1.020E-05	1.10E-05	9.80E-06	1.00E-05	9.10E-06
Dg (cm2/s)	0.123	0.107	0.098	0.06253	0.15	*0.0470722*	0.93	0.11	0.097	0.086	0.085
Antoine Coefficients											
A	8.321	7.456	8.117	8.1986	7.897	NA	8.2082				
B	1718.21	1577.67	1580.92	2008.895	1474.08	NA	2085.9				
C	237.52	173.37	219.61	206.77	229.13	NA	203.54				
Sander Coefficients											
Reference (25 oC) Value	160	6,200,000	130	NA	210	NA	100,000				
Slope	6,500	NA	7,500	NA	5,400	NA	NA				
Mass Fraction in Product											
Hand Dish Washing											
Current Value	0.07	0.05	Not Used	Not Used	***0.1***	Not Used	0.08				
Wooley	0.054										
Laundry											
Current Value	0.09	0.04	***0.1***	***0.1***	***0.1***	***0.1***	0.13				
Wooley	0.085										
Fabric Softeners	0.03	Not Used	0.10	Not Used	Not Used	Not Used	Not Used				

Notes:
1. USEPA data is from USEPA WATER9 Chemical Database.
2. CARB Henry's Law Data from CARB Consumer Products Solvents Database (http://www.arb.ca.gov/db/solvents.htm)
3. DPGME estimated Dg=22.335(Mw)^-1.2328, Dl=8e-5(Mw)^-0.4607
4. Sander coefficients are from Sander [1999], see text for units and use.
5. NA = Not Available
6. Numbers in ***Bold/Italics*** are conservatively high estimates as detailed company information is not available.

Henry's Law Values

The gas/liquid partition coefficient is the most important chemical property parameter for calculating emissions for these compounds. The original intent of the analysis was to use CARB reference (25 ^{o}C) values and scale them for temperature using the methodology and data USEPA uses for the WATER9 wastewater treatment fate model [EPA-454/R-94-080A]. This methodology consists of multiplying the reference Henry's Law value times the ratio of the vapor pressure at the target temperature to vapor pressure at the reference temperature. The vapor pressure was estimated using Antoine's equation with USEPA Antoine coefficients. The USEPA's version of the Antoine equation is:

$$P_v(T) = A - \frac{B}{T + C}$$

where $P_v(T)$ is the vapor of the compound in mm of Hg; A, B, and C are the Antoine coefficients and T is the temperature in ^{o}C.

This approach was not chosen based on scientific validity rather it was chosen based on regulatory acceptance. During model calibration it became apparent that this temperature scaling was dramatically under-predicting the higher temperature Henry's Law values.
Sander [1999] completed a fairly comprehensive compilation of Henry's Law values along with a temperature scaling factor for most compounds. Figure 1 shows the Henry's Law values for all the compounds in this analysis and Figure 2 shows a more detailed look at the higher emitting compounds. These figures show that the Sander data has significantly higher Henry's Law values at the higher temperatures.

Figure 1. Henry's Law Value as a Function of Temperature (All compounds).

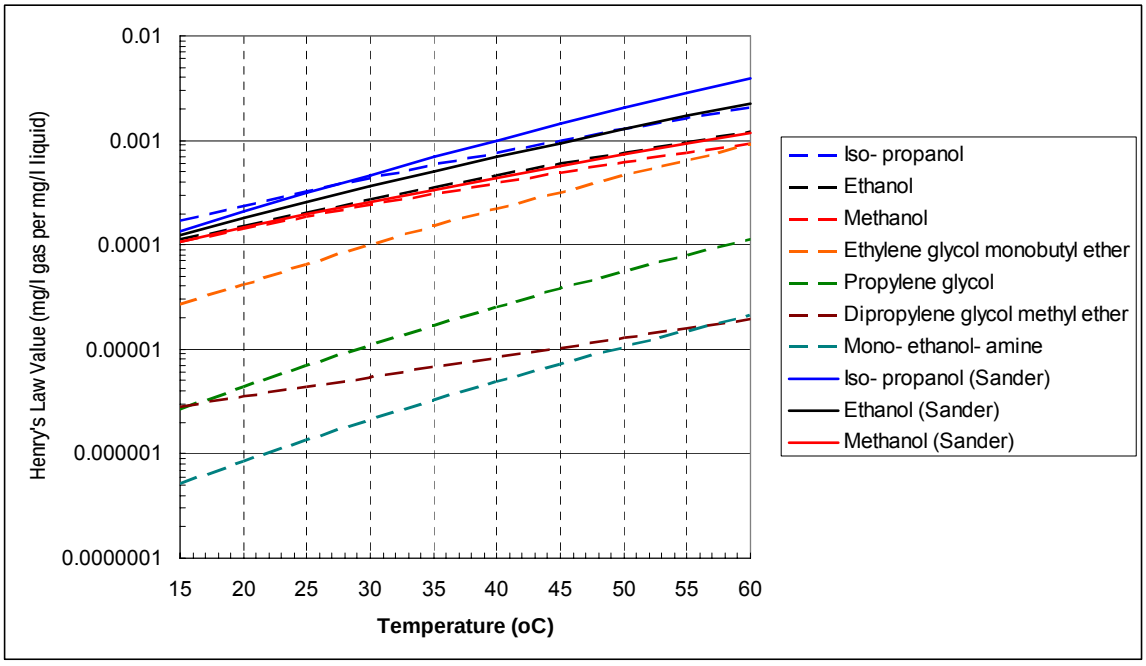
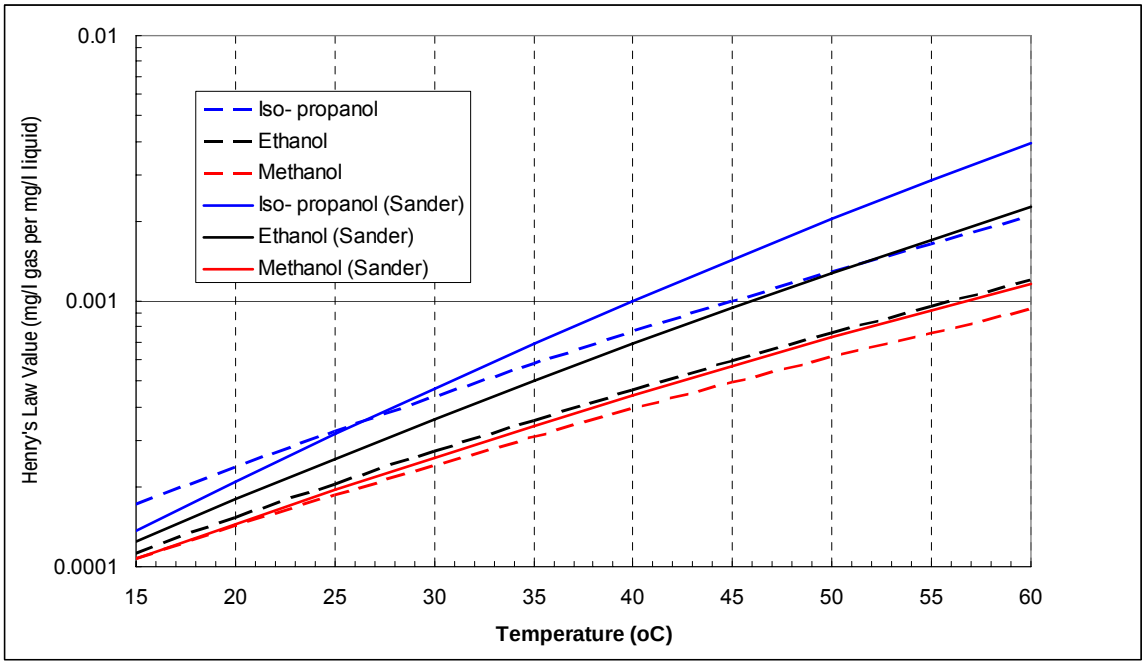


Figure 2. Henry's Law Value as a Function of Temperature (Highest emitting compounds).



The Sander database consists of a reference value k^{o}_{H}, the liquid/gas partition coefficient in mole/m^3 liquid per atm gas at 298.15 ^{o}K (25 ^{o}C). The temperature slope value, that in this analysis is called α, is represented by

$$\alpha = \frac{-d\ln(k_H)}{d\left(\frac{1}{T}\right)}$$

This can be converted to the units mg/l gas per mg/l liquid by the following equation.

$$H\left(\frac{mg/l}{mg/l}\right) = \frac{1}{K_H^{\Theta} 1{,}000 RT \exp\left[\alpha\left(\frac{1}{T} - \frac{1}{T^{\Theta}}\right)\right]}$$

where T is the temperature in ^{o}K, R is the universal gas constant [8.2057(10^{-5}) m^3-atm/gmole-^{o}K], and T^{o} is equal to 298.15 ^{o}K.

Ethanol

Sander offers several literature values for ethanol. The value that came the closest in calibration against the Wooley *et al* data set was the reference value from Timmermans [1960] which was 160 mole/m^3 per atm. The Timmermans value did not have temperature data, so the values from the two literature references with temperature data were averaged. The two slope values were 6,600 and 6,400 with average equal to 6,500.

Isopropyl Alcohol

The Sander database had one source that contained both a reference value and temperature source [Snider and Dawson, 1985] so that value was used. This was a reference value of 130 mole/m^3 per atm with a slope of 7,500.

Methanol

Methanol had value from Timmermans as well so that was used. As with ethanol, the slope was the average of the reported values. This resulted in a reference value of 210 mole/m^3 per atm with a slope of 5,400.

Ethylene glycol monobutyl ether

This compound had no Sander data so the CARB value was used with the USEPA temperature correction methodology. The CARB reference value was close to the USEPA reference value for this compound.

Propylene glycol

Sander had a reference value range for this compound and no slope data. Therefore this compound used the CARB value with the USEPA temperature correction methodology. The CARB reference value is the highest value found in the literature by far for this compound. It is over 500 times the USEPA value. Based on this, it is likely that using the CARB value will overestimate emissions substantially.

Dipropylene glycol methyl ether

This compound had no Sander data so the CARB value was used with the USEPA temperature correction methodology. This compound is not in the USEPA database so no comparison was made.

Monoethanolamine

Sander had a reference value range for this compound and no slope data. Therefore this compound used the CARB value with the USEPA temperature correction methodology. The CARB reference value is the highest value found in the literature by far for this compound. It is about 300 times the USEPA value. Based on this, it is likely that using the CARB value will overestimate emissions substantially.

Mass Transfer Values

Mass transfer values for the individual compounds were estimated based on toluene mass transfer data from the USEPA data set. The original intent of the analysis was to use the acetone dataset, because acetone is chemically closer than toluene for the study compounds. However, the acetone data set had a combination of some questionable data points and very low mass transfer values. The toluene data set, matched the Wooley data quite closely and no calibration at all was required for the hand dishwashing simulation.

Mass transfer values were calculated by the following equation based on the methodology used in EPA 600/R-00/096.

$$K_{xy} = K_{xToluene}\left(\frac{D_{xy}}{D_{xToluene}}\right)^{2/3}$$

where K_{xy} is the mass transfer coefficient for x phase (liquid or gas) and y chemical, D_{xy} is the diffusion coefficient for x phase and y chemical. The ratio of the mass transfer coefficients is referred to by the character Ψ.

The overall mass transfer coefficient for each chemical was calculated by

$$K_T = \frac{1}{\frac{1}{K_L} + \frac{1}{HK_g}}$$

where K_T is the overall mass transfer coefficient, K_L is the liquid phase mass transfer coefficient, H is the Henry's Law value (mg/l liquid per mg/l gas) and K_g is the gas phase mass transfer value. Table 5 presents a summary of the mass transfer values used.

Table 5. – Summary of Mass Transfer Values.

Property	Toluene	Ethanol	Mono-ethanol-amine	Iso-propanol	Ethylene glycol monobutyl ether	Methanol	Dipropylene glycol methyl ether	Propylene glycol	Methyl Ethyl Ketone	Dibromo-chloro-methane
H (mg/l / mg/l)	0.27	0.0002	1.35E-06	0.000323	0.00006544	0.000186	4.3763E-06	6.953E-06	0.006	0.048
Dl (cm2/s)	9.10E-06	1.30E-05	1.14E-05	1.04E-05	8.15E-06	1.64E-05	8.00E-06	1.02E-05	9.80E-06	1.00E-05
Dg (cm2/s)	0.085	0.123	0.107	0.098	0.063	0.150	0.047	0.930	0.097	0.086
ΨL		1.27	1.16	1.09	0.93	1.48	0.92	1.08	1.05	1.06
ΨG		1.28	1.17	1.10	0.81	1.46	0.67	4.93	1.09	1.01
Fill Cycle										
Kg/KL	**9.5**									
KL	**4**	5.07	4.65	4.37	3.72	5.92	3.67	4.32	4.20	4.26
Kg	**38**	48.62	44.30	41.78	30.97	55.49	25.63	187.28	41.50	38.30
KT (25 oC)	2.878	0.010	0.000	0.013	0.002	0.010	0.00011	0.001	0.235	1.284
Wash										
Kg/KL	**2.3**									
KL	**1.5**	1.90	1.74	1.64	1.39	2.22	1.38	1.62	1.58	1.60
Kg	**3.45**	4.41	4.02	3.79	2.81	5.04	2.33	17.00	3.77	3.48
KT (25 oC)	0.575	0.001	0.000	0.001	0.000	0.001	0.000010	0.000	0.022	0.151
Rinse										
Kg/KL	**2.3**									
KL	**2.2**	2.79	2.56	2.40	2.04	3.26	2.02	2.37	2.31	2.34
Kg	**5.06**	6.47	5.90	5.56	4.12	7.39	3.41	24.94	5.53	5.10
KT (25 oC)	0.843	0.001	0.000	0.002	0.000	0.001	0.000015	0.000	0.033	0.222

Cycle/Activity Parameters

The following paragraphs present the operating parameters used for the model for each cycle/activity for each operation.

Hand Dishwashing

Table 6 provides a summary of cycle/activity parameters for the hand dishwashing analysis for both the typical use and high release conditions. EPA 600/R-00/096 presented a methodology for simulating hand dishwashing, which was used for this analysis, but presented no calibration

data. The hand dishwashing was calibrated against the Wooley data set and no specific parameter adjustment was needed to match the Wooley data. Some of the modeling parameters had to be assumed as they were not reported in Wooley. These include liquid flow rate, liquid depth, and liquid surface area. In addition, the temperature loss during soaking had to be estimated. Of these parameters, the liquid flow rate was the emissions were the strongest function of liquid flow rate. The other factors had only minor effects on emissions even for extreme assumptions. Since the model calibrated well against the Wooley data, it appeared that the above estimates were accurate. The data used to calculate emission factors for this activity were supplied by the Soap and Detergent Association [Sedlak 2006]. The data not provided by SDA was estimated based on the Wooley calibration.

Table 6. Summary of Cycle/Activity Parameters for the Hand Dishwashing Analysis.

Typical Use Condition

Wooley et al Simulation Parameters

Activity Data						Other Parameters		
	Product Use (ml)	Duration (minutes)	Liquid Flow Rate (l/m)	Temp. (oC)	Vent Rate (l/m)	Parameter	Value	Units
Fill	**15**	3.3	2.3	**45**	**833**	Room Volume	**20,000**	liters
Soak		**0.1**		**45**	**833**	Room Vent Rate	**2.5**	Ach/hr
Wash		**10**		**45**	**833**	Room Vent Rate	**833**	l/m
Rinse		3.3	2.3	**40**	**833**	Liquid Volume	**7.6**	liters
						Liquid Depth	10	cm
						Liquid Area	0.076	m2

Simulation Parameters Used for This Analysis

Activity Data						Other Parameters		
	Product Use (ml)	Duration (minutes)	Liquid Flow Rate (l/m)	Temp. (oC)	Vent Rate (l/m)	Parameter	Value	Units
Fill	**15**	3.3	2.3	**45**	**833**	Room Volume	**20,000**	liters
Soak		**0.1**		**45**	**833**	Room Vent Rate	**2.5**	Ach/hr
Wash		**10**		**45**	**833**	Room Vent Rate	**833**	l/m
Rinse		3.3	2.3	**40**	**833**	Liquid Volume	**7.6**	liters
						Liquid Depth	10	cm
						Liquid Area	0.076	m2

High Release Condition

Wooley et al Simulation Parameters

Activity Data						Other Parameters		
	Product Use (ml)	Duration (minutes)	Liquid Flow Rate (l/m)	Temp. (oC)	Vent Rate (l/m)	Parameter	Value	Units
Fill	**37.5**	3.3	2.3	**55**	**833**	Room Volume	**20,000**	liters
Soak		**60**		**40**	**833**	Room Vent Rate	**2.5**	Ach/hr
Wash		**10**		**35**	**833**	Room Vent Rate	**833**	l/m
Rinse		3.3	2.3	**55**	**833**	Liquid Volume	**7.59**	liters
						Liquid Depth	10	cm
						Liquid Area	0.0759	m2

Simulation Parameters Used for This Analysis

Activity Data						Other Parameters		
	Product Use (ml)	Duration (minutes)	Liquid Flow Rate (l/m)	Temp. (oC)	Vent Rate (l/m)	Parameter	Value	Units
Fill	**37.5**	3.3	2.3	**55**	**833**	Room Volume	**20,000**	liters
Soak		**60**		**40**	**833**	Room Vent Rate	**2.5**	Ach/hr
Wash		**10**		**35**	**833**	Room Vent Rate	**833**	l/m
Rinse		3.3	2.3	**55**	**833**	Liquid Volume	**7.59**	liters
						Liquid Depth	10	cm
						Liquid Area	0.0759	m2

Notes:
1. Bold values explicity provided in literature source, other values are estimated.

Laundry

Table 7 provides a summary of cycle/activity parameters for the laundry analysis for both the typical use and high release conditions. The USEPA report explicitly defined all the required values. For the Wooley data set, the values not provided in the Wooley report were estimated based on the USEPA parameters. The model was calibrated to the Wooley data set by adjusting the water flow rate for the fill cycle. This parameter is both a likely variable and strongly effects emissions. It also makes sense in that in normal situations, hot water has a lower flow rate because it has a longer travel path in the residential plumbing. The data used to calculate emission factors for this activity were supplied by the Soap and Detergent Association [Sedlak 2006]. The data not provided by SDA was estimated based on the Wooley calibration.

Table 7. Summary of Cycle/Activity Parameters for the Laundry Analysis.

Typcial Use Condition	High Release Condition

USEPA Simulation Parameters

Cycle Data						Volume Data	
	Product Use (ml)	Duration (minutes)	Liquid Flow Rate (l/m)	Temp. (oC)	Vent Rate (l/m)	Parameter	Volume (liters)
Fill		**3.3**	**13.8**	**35**	**55**	Total	**150**
Wash		**10**		**35**	**53**	Fill	**45.6**
Drain		**4**			**53**	Clothes	**11**
Fill		**3.3**	**13.8**	**22**	**55**	Headspace	**93.4**
Rinse		**4**		**22**	**53**		
Drain		**6**			**53**		

Wooley et al Simulation Parameters

Cycle Data						Volume Data	
	Product Use (ml)	Duration (minutes)	Liquid Flow Rate (l/m)	Temp. (oC)	Vent Rate (l/m)	Parameter	Volume (liters)
Fill	**110**	4.95	10.1	**35**	55	Total	150
Wash		**9**		**35**	53	Fill	**50**
Drain		4			53	Clothes	11
Fill		3.3	15.15	**22**	55	Headspace	89
Rinse		4		**22**	53		
Drain		6			53		

Wooley et al Simulation Parameters

Cycle Data						Volume Data	
	Product Use (ml)	Duration (minutes)	Liquid Flow Rate (l/m)	Temp. (oC)	Vent Rate (l/m)	Parameter	Volume (liters)
Fill	**110**	8.20	6.1	**55**	160	Total	150
Wash		**9**		**55**	160	Fill	**50**
Drain		4			160	Clothes	11
Fill		3.3	15.15	**35**	160	Headspace	89
Rinse		4		**35**	160		
Drain		6			160		

Simulation Parameters Used for This Analysis

Cycle Data						Volume Data	
	Product Use (ml)	Duration (minutes)	Liquid Flow Rate (l/m)	Temp. (oC)	Vent Rate (l/m)	Parameter	Volume (liters)
Fill	**110**	6.34	10.1	**35**	55	Total	150
Wash		**15**		**35**	53	Fill	**64**
Drain		4			53	Clothes	11
Fill		4.2	15.15	**21**	55	Headspace	75
Rinse		10		**21**	53		
Drain		6			53		

Simulation Parameters Used for This Analysis

Cycle Data						Volume Data	
	Product Use (ml)	Duration (minutes)	Liquid Flow Rate (l/m)	Temp. (oC)	Vent Rate (l/m)	Parameter	Volume (liters)
Fill	**110**	13.61	6.1	**55**	160	Total	150
Wash		**15**		**55**	160	Fill	**83**
Drain		4			160	Clothes	11
Fill		5.5	15.15	**21**	160	Headspace	56
Rinse		10		**21**	160		
Drain		6			160		

Notes:
1. Screened values were calculated based on calibration.
2. Bold values explicity provided in literature source, other values are estimated.

Fabric Softener

Table 8 provides a summary of cycle/activity parameters for the fabric softener analysis for both the typical use and high release conditions. Fabric softener is used in the rinse cycle of the machine laundry cycle. There is no explicit calibration data for fabric softener, but the machine rinse cycle was calibrated against the EPA data set. The data used to calculate emission factors for this activity were supplied by the Soap and Detergent Association [Sedlak 2006]. The data not provided by SDA was estimated based on the Wooley calibration.

Table 8. Summary of Cycle/Activity Parameters for the Fabric Softener Analysis.

Typcial Use Condition	High Release Condition

Simulation Parameters Used for This Analysis

Cycle Data						Volume Data	
	Product Use (ml)	Duration (minutes)	Liquid Flow Rate (l/m)	Temp. (oC)	Vent Rate (l/m)	Parameter	Volume (liters)
Fill		6.34	10.1	**35**	55	Total	150
Wash		**15**		**35**	53	Fill	**64**
Drain		4			53	Clothes	11
Fill	**56**	4.2	15.15	**21**	55	Headspace	75
Rinse		10		**21**	53		
Drain		6			53		

Simulation Parameters Used for This Analysis

Cycle Data						Volume Data	
	Product Use (ml)	Duration (minutes)	Liquid Flow Rate (l/m)	Temp. (oC)	Vent Rate (l/m)	Parameter	Volume (liters)
Fill		13.61	6.1	**55**	160	Total	150
Wash		**15**		**55**	160	Fill	**83**
Drain		4			160	Clothes	11
Fill	**56**	5.5	15.15	**21**	160	Headspace	56
Rinse		10		**21**	160		
Drain		6			160		

Notes:
1. Screened values were calculated based on calibration.
2. Bold values explicity provided in literature source, other values are estimated.

Model Calibration

The following paragraphs present the results of the model calibration efforts. There was no explicit calibration of fabric softener use, but the calibration against the USEPA data set includes the rinse cycle that the fabric softener is used in.

USEPA Data Set

The model was initially calibrated against the USEPA data set [EPA 600/R-00/096] for toluene. This calibration was for emissions from the complete cycle (wash and rinse) with toluene present in both the wash and rinse water. Table 9 presents the results of this calibration. The discrepancies are likely due more to mathematics than physical modeling. The model simulates emissions based on very small steps and the total emissions are the sum of the emissions from the small steps. With this model great care was taken not have accumulated errors in this addition process which resulted in a slightly different values than the USEPA's values.

Table 9. Comparison of this Model's Results to USEPA results (% emitted is the percent compound used that is emitted).

		Chemical		
Item	**Units**	**Toluene**	**Dibromo chloro methane**	**Methyl ethyl ketone**
Mass In	mg	0.911	0.911	0.911
This Analysis				
Total Emitted	mg	0.217	0.059	0.017
% Emitted		23.8%	6.5%	1.9%
USEPA				
Total Emitted	mg	0.210	0.067	0.018
% Emitted		22.0%	7.1%	1.9%
Relative Percent Difference		-3%	11%	4%

In order to illustrate the emissions rate as a function of cycle sequence Figure 3 is presented showing this analysis. This can be compared to Figure 4, which is the reproduced Figure 8-4 for the USEPA report.

Figure 3. Emissions as Function of Cycle Time for This Analysis (EPA conditions).

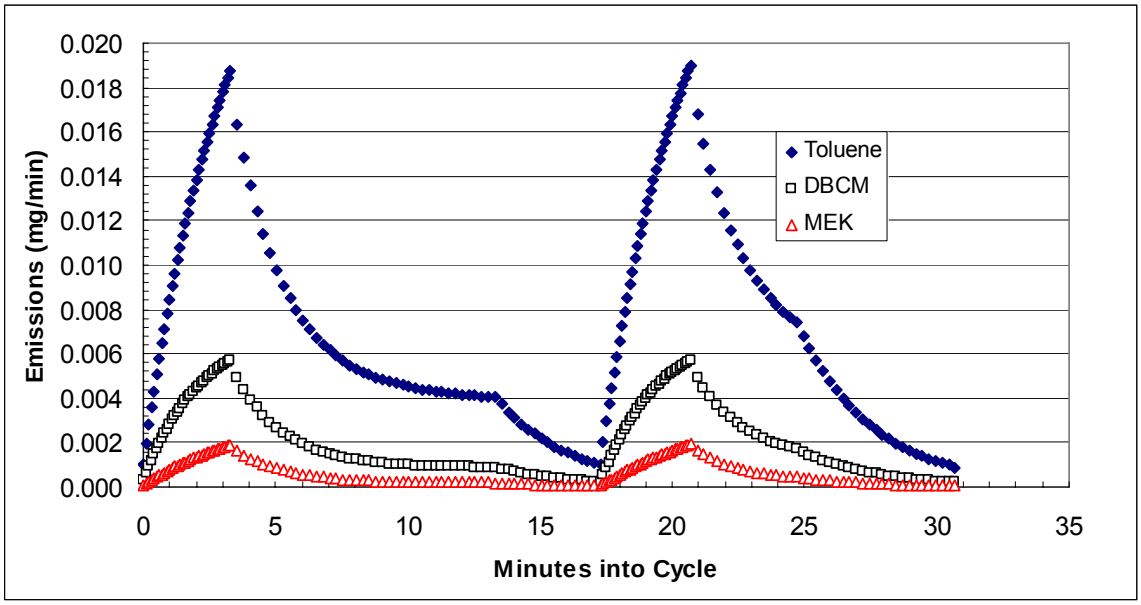
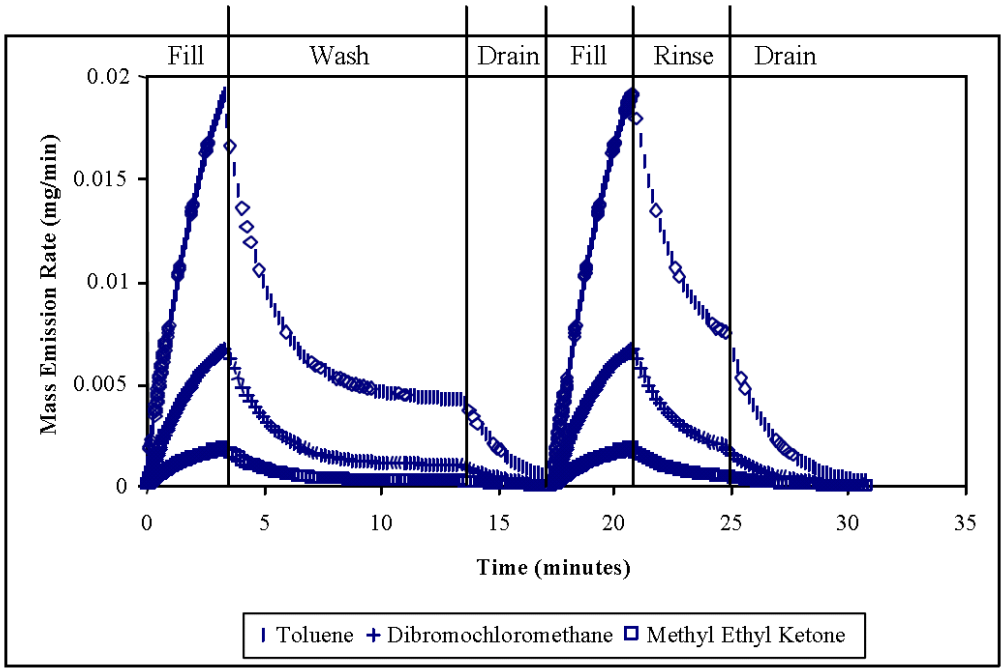


Figure 4. Reproduction of Figure 8-4 from EPA 600/R-00/096.



Wooley et al [1990] Data Set

Wooley et al. completed experiments in an environmental chamber at the University of California in 1990. Table 10 compares the results of the Wooley research to this analysis. Note that the water fill rate was adjusted to calibrate to Wooley for this analysis. No specific adjustments were made to the hand dishwashing analysis to calibrate to the Wooley data.

Table 10. – This Analysis Compared to Wooley *et al* [1990] Experimental Data Set (all results in ethanol fraction emitted as percent of ethanol used in the cleaning task).

Product Use	Typical Use	High Release
Hand Dishwashing		
Wooley et al [1990]	3.8%	4.9%
This analysis	3.92%	6.05%
Machine Laundry		
Wooley et al [1990]	0.19%	1.21%
This analysis	0.19%	1.21%

Model Implementation

The model was implemented using Microsoft Excel® spreadsheets with each compound for each operating condition of each product use as separate calculation sheet. Each operation was modeled with around 150 time steps of an average duration of about 20 seconds each. For each time step the differential equation was either solved explicitly or using numerical analysis (2^{nd} Order Runge-Kutta). The total emissions were calculated by summing the individual time step emissions and then adding the residual compound mass that was in the gas phase at the end of the simulation.

Results

The following paragraphs present the results of this analysis. All results are shown as the percentage of product chemical component used that is volatilized to the atmosphere during the proscribed activity.

Hand Dishwashing

The hand dishwashing use conditions for this analysis were the same as were used for the Wooley experiment. For emission inventory use, the emission factors developed using the Sander Henry's Law approach are recommended for ethanol and methanol. Since complete Sander data is not available for propylene glycol and monoethanolamine, the emission factors developed using the CARB/USEPA data are recommended to be used.

Table 11. - Calculated Emission Factors for Liquid Hand Dishwashing Detergent Component Compounds

Liquid Hand Dishwashing Detergent Component Compound	Calculated Emission Factors (percent of total compound used by consumers that is emitted to atmosphere) Using Two Different Approaches to Estimate Henry's Law Temperature Correction				Previously Reported Factors in Wooley et al		Recommended Value for Emission Inventory		Notes
	CARB Henry's Law/EPA Temperature Correction		Sander Henry's Law Methodology						
	Typical Use Condition	High Release Condition	Typical Use Condition	High Release Condition	Typical Use Condition	High Release Condition	Typical Use Condition	High Release Condition	
Ethanol	2.55%	3.56%	3.92%	6.05%	3.80%	4.90%	3.92%	6.05%	
Methanol	1.65%	2.20%	1.89%	2.62%			1.89%	2.62%	
Propylene glycol	0.419%	0.721%	0.021%	0.034%			0.419%	0.721%	See Note 1
Monoethanolamine	0.0194%	0.0328%	0.00008%	0.0001%			0.0194%	0.0328%	See Note 1

Notes:
1. Sander temperature slope estimated, no compound specific data available
2. No Sanders data available at all for these compounds

Laundry

Table 12 presents the results of this analysis for the liquid laundry detergent component compounds. For the top three emitting compounds; isopropanol, ethanol, and methanol; the emission factors calculated using the Sander data are recommended for emission inventory purposes. For the remaining compounds, the Sander data is incomplete and the emission factors calculated using the CARB/USEPA Henry's Law values are recommended to be used as emission inventory values. These values were calculated based on slightly different use parameters than the Wooley experiments. However, the impact of the different use parameters on the results was negligible.

Table 12. - Calculated Emission Factors for Liquid Laundry Detergent Component Compounds

Liquid Laundry Detergent Component Compound	Calculated Emission Factors (percent of total compound used by consumers that is emitted to atmosphere) Using Two Different Approaches to Estimate Henry's Law Temperature Correction				Previously Reported Factors in Wooley et al		Recommended Value for Emission Inventory		Notes
	CARB Henry's Law/EPA Temperature Correction		Sander Henry's Law Methodology						
	Typical Use Condition	High Release Condition	Typical Use Condition	High Release Condition	Typical Use Condition	High Release Condition	Typical Use Condition	High Release Condition	
Isopropanol	0.20%	0.93%	0.24%	1.74%			0.24%	1.74%	
Ethanol	0.13%	0.61%	0.19%	1.19%	0.19%	1.21%	0.19%	1.19%	
Methanol	0.13%	0.54%	0.14%	0.72%			0.14%	0.72%	
Ethylene glycol monobutyl ether	0.041%	0.286%					0.041%	0.286%	See Note 2
Propylene glycol	0.013%	0.126%	0.001%	0.006%			0.013%	0.126%	See Note 1
Dipropylene glycol methyl ether	0.0021%	0.0112%					0.0021%	0.0112%	See Note 2
Monoethanolamine	0.0011%	0.0090%	0.0000%	0.0000%			0.0011%	0.0090%	See Note 1

Notes:
1. Sander temperature slope estimated, no compound specific data available
2. No Sander data available at all for these compounds

Fabric Softener

Table 13 presents the results of the fabric softener analysis. The only volatile compounds in rinse-added liquid fabric softener are isopropanol and ethanol. Based on the results of the hand dishwashing and liquid laundry detergent analysis, it is recommended the emission factor calculated using the Sander Henry's Law data be used as the emission inventory value.

Table 13. - Calculated Emission Factors for Rinse-added Liquid Fabric Softener Component Compounds

	Calculated Emission Factors (percent of total compound used by consumers that is emitted to atmosphere) Using Two Different Approaches to Estimate Henry's Law Temperature Correction				Recommended Value for Emission Inventory	
	CARB Henry's Law/EPA Temperature Correction		Sander Henry's Law Methodology			
Fabric Softener Component Compound	Typical Use Condition	High Release Condition	Typical Use Condition	High Release Condition	Typical Use Condition	High Release Condition
Isopropanol	0.09%	0.19%	0.09%	0.21%	0.09%	0.21%
Ethanol	0.06%	0.12%	0.08%	0.17%	0.08%	0.17%

Note that these calculations have been conservative in estimating the amounts of VOC that partition down the drain for the rinse-added liquid fabric softener calculations. They have not taken into account the effect of monolayer formation by the quaternary active on the surface of the rinse water in the washing machine nor the formation of micelles in the rinse water. Both of these phenomenon will have the effect of retarding the evaporation of VOCs into the atmosphere. When a monolayer forms on the water surface, it acts as a mechanical barrier to molecules from beneath being able to reach the surface and then evaporate. Thus, the monolayer acts to shift the equilibrium of potential evaporating materials back towards solution. When micelles form in solution, the hydrophobic interior of the micelles can act as solubility domains for hydrophobic components solubilized in solution such as many components of the perfumes. This solubilization shifts the equilibrium toward the micelle interior and away from solution for these solutes. This, in turn, leaves less of these potentially VOC solutes in solution to find their way to the rinse water surface and evaporate.

Conclusions

Using the methodology developed by the USEPA, emission factors for liquid hand dishwashing, liquid laundry detergent, and rinse-added liquid fabric softener can accurately be calculated using environmental fate modeling techniques. Using these methods, an emission factor can be developed for any compound that has known chemical properties.

The emission rates for the compounds modeled ranged from low to very low with the majority of the compound leaving the appliance in the liquid phase down the drain. Isopropanol had the largest fraction emitted and monoethanolamine had the lowest. Hand dishwashing was the highest emitting process. For typical use conditions, the VOCs had emission factors ranging

from about 4% (isopropanol for hand dishwashing) to around 0.001% (monoethanolamine for liquid laundry detergent).

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