

Models to Estimate Volatile Organic Hazardous Air Pollutant Emissions from Municipal Sewer Systems

Donna Lee Jones, Clint E. Burklin, and Joanne C. Seaman
Radian International, Research Triangle Park, North Carolina

Julian W. Jones
U. S. Environmental Protection Agency, Research Triangle Park, North Carolina

Richard L. Corsi
University of Texas, Austin, Texas

ABSTRACT

Emissions from municipal sewers are usually omitted from hazardous air pollutant (HAP) emission inventories. This omission may result from a lack of appreciation for the potential emission impact and/or from inadequate emission estimation procedures. This paper presents an analysis and comparison of the models available to estimate volatile organic HAP (VOHAP) emissions from sewers. Comparisons were made between the different theoretical foundations of the models, as well as between the emissions predicted by the models for a single sewer component. Sewer gas concentrations predicted by the models were also compared to measured sewer gas concentrations reported in the literature. Two of the models were compared in their ability to estimate sewer VOHAP emissions for a large U. S. city using National Pollution Discharge Effluent System data for the influent wastewater to the city's municipal wastewater treatment facilities. This estimate showed that, regardless of the model used, sewer emissions are a potentially significant source of VOHAP emissions in the urban environment. The choice of model, however, is thought to be less critical to sewer emission estimates than the source of sewer wastewater VOHAP concentration data.

IMPLICATIONS

Sewers may be a significant source of emissions of volatile organic hazardous air pollutants (VOHAPs) that are usually overlooked in estimates of municipal pollution. The VOHAP emissions from sewer systems contribute to urban ozone formation and present a potential human health concern, especially since they are emitted at ground level. Several models are available that attempt to predict VOHAP emissions from sewers. This article discusses some of these models and their shortcomings, and should be helpful to APC agencies preparing emissions inventories. The choice of model, however, is less critical than the lack of good sewer influent data.

INTRODUCTION

Wastewater discharges to municipal sewer systems contain many compounds that are among the 189 hazardous air pollutants (HAP) that the U. S. Environmental Protection Agency (EPA) is required to estimate and control if emitted into air, as mandated by the Clean Air Act Amendments of 1990 (CAAA). Based on experience with industrial wastewater treatment and collection systems, the potential exists for emission of large amounts of volatile organic HAP (VOHAP) from municipal sewer systems (sewers) before wastewater enters municipal wastewater treatment facilities (publicly owned treatment works [POTWs]).

Emissions from sewers are usually ignored in VOHAP emission inventories.¹ This omission may result partly from a lack of appreciation for the potential emission impact, but may also be due to inadequate emission estimation procedures. The current models available to estimate emissions from sewers differ in their theoretical bases and have not been sufficiently validated with test data. Many of these models focus on industrial sewers within the fence line of the plant, but not on municipal sewers that receive industrial, commercial, and residential wastewater.

This paper reports on the sewer models that are currently available to estimate VOHAP emissions from municipal sewers. The models were compared on a theoretical basis as well as in terms of their ability to accurately predict emissions. Municipal sewer gas concentration measurements reported in the literature were compared to sewer gas concentrations predicted by each model. One of the models was used to estimate VOHAP emissions from municipal sewers for a large city.

NOMENCLATURE

The following are definitions of the nomenclature typically used to describe components of a municipal sewer system:

- **Manhole:** A covered opening in the ground at surface level that provides access to the sewer lines for maintenance purposes. Manhole covers are usually perforated (one or more holes, typically approximately

1 inch in diameter) so that air exchange between the sewer and the ambient atmosphere can occur.

- **Reach:** A segment of sewer channel which conveys wastewater between two manholes or other sewer components, such as lift stations or junction boxes. Sanitary sewers are naturally ventilated through holes in manhole covers, gooseneck vents (which are sometimes included to enhance ventilation), and vent risers on buildings which are connected to sewers. (Sanitary sewers are sometimes mechanically ventilated; i.e., fans or blowers are used to combat formation of hydrogen sulfide.) Combined sanitary/storm sewers are generally well-ventilated, and include openings associated with street-level storm drains.
- **Drop:** A structure that serves as the junction of two or more sewer lines, where the upstream pipeline enters the chamber at a higher elevation than the exit for the downstream pipeline.
- **Lift station:** A junction of two or more sewer lines where the wastewater is lifted by the use of a pump to a higher elevation.

MODELS AVAILABLE TO ESTIMATE EMISSIONS FROM MUNICIPAL SEWERS

Four models are generally available in the United States and Canada that could be used to predict VOHAP emissions from sewers:

- BACT/LAER-IWW/MRE (manhole regression equation from the Industrial Wastewater—Best Available Control Technology/Lowest Achievable Emission Rate document²);
- BASTE (Bay Area Sewage Toxics Emissions; developed by Dr. R. L. Corsi and available from the Bay Area Air Toxics [BAAT] group, c/o CH2MHill, Inc., Oakland, California 96404);
- CORAL+ (Collection Organic Release Algorithm; developed by Dr. R. L. Corsi and available from Enviromega, Ltd., Hamilton, Ontario, Canada. L9J 1K3), and
- WATER8.³

Of these four models, two (BACT/LAER-IWW/MRE and WATER8) were prepared by the EPA as part of larger studies to address emissions from wastewater from numerous potential emission points, generally from on-site industrial wastewater. In some cases, industrial data were also used to develop the models. Although the authors of WATER8 state that the model can be used with either municipal or industrial sewers, only industrial sewer data were used to develop that model. The other two models, BASTE and CORAL+, were specifically created to address emissions from municipal wastewater.

Vents in reach manholes and drop structures, along with building risers, are the most frequently found sewer emission points in sanitary sewers. In municipal sewer systems, most sewer components are enclosed but vented to the atmosphere. Combined sanitary and storm sewers may be found in older U. S. cities (e.g., New York and Boston) and are extremely well ventilated.

The sewer system components addressed by each model are noted in Table 1. Not all of the models address reach manholes and drops, which are the most common components of municipal sewers. The EPA models address some types of sewer components (e.g., process drains) that are more likely to be included in an industrial sewer system rather than in a municipal sewer system. Components likely to be part of a municipal sewer system are also noted in Table 1.

Description of the Models

The following is a description of four models (BACT/LAER-IWW/MRE, BASTE, CORAL+, and WATER8) that can be used to estimate VOHAP emissions from municipal sewer components. Details of the theories on which the models are based can be found elsewhere in the documentation referenced below.

BACT/LAER-IWW/MRE.² The BACT/LAER-IWW/MRE model was developed from an EPA study that addressed emissions for industrial sewers. The only sewer component that is addressed by the model and found in municipal systems is a

Table 1. Sewer components addressed by the models.

| Model | Reach Manholes ^a | | Drops | | Lift Stations | | Junction Boxes | | Drains | | Sumps | | Open Conduits |
|-------------------|--------------------------------|---------------------|-------|---------------------|------------------|---------------------|-------------------|---------------------|--------|--------|-------|--------|------------------|
| | Open | Closed ^a | Open | Closed ^a | Open | Closed ^a | Open | Closed ^a | Open | Closed | Open | Closed | |
| BACT/LAER-IWW/MRE | X | — | — | — | X | — | X | — | X | — | X | — | — |
| BASTE | — | X | X | — | — | — | — | — | — | — | — | — | — |
| CORAL+ | X | X | X | — | — | — | — | — | — | — | — | — | X |
| WATER8 | X | — | — | X | X | X | X | — | — | — | X | X | X |

^a Likely component of a municipal sewer system.

reach manhole. The BACT/LAER-IWW/MRE model was developed from a volatile organic compound (VOC) emission theory that assumes that the pollutants in wastewater reach equilibrium with the vapor phase above the water. The model assumes that volatilization is the only emission mechanism for emissions from manholes. An equation to predict emissions from manholes was developed from a regression of the fraction emitted (estimated using the BACT/LAER-IWW theory) of five pollutants (phenol, 1-butanol, naphthalene, toluene, and 1,3-butadiene) from six model facilities versus Henry's law coefficients of the pollutants. The model facilities were developed from responses to EPA questionnaires sent to facilities in the organic chemicals, plastics, and synthetic fibers industry. The BACT/LAER-IWW/MRE model estimates the fraction of pollutant in the influent wastewater emitted from a reach manhole to the atmosphere as a function of the Henry's law constant of the pollutant.

The primary deficiency of the BACT/LAER-IWW/MRE model is that emissions are a function only of the Henry's law constant of the VOC; no site-specific sewer physical data are used. Therefore, the accuracy of the model depends upon how well the system being modeled matches the sewer physical parameters of the model facilities used to develop the BACT/LAER-IWW/MRE model. The impact of variables such as wastewater flow rate, reach slope, sewer ventilation rate, and chemical properties cannot be addressed by the BACT/LAER-IWW/MRE model. Also, the BACT/LAER-IWW/MRE model is based on an assumption of equilibrium and does not account for mass transfer kinetics or those variables that affect such kinetics.

BASTE.⁴ In response to air toxics legislation in California, a consortium of POTWs pooled their resources to form the San Francisco Bay Area Air Toxics group, and funded the development of a multi-process computer-based model with the flexibility to simulate VOC emissions from liquid processes at any POTW in the consortium. This resulted in the BASTE model. BASTE was intended to serve primarily as a screening model, but it was structured so that it could evolve into a detailed simulation tool as field data became available for model evaluation.

A unit drop structure is the only municipal sewer component covered by BASTE. BASTE estimates air emissions from either open or closed drop structures, and assumes that volatilization is the only fate mechanism. The model provides chemical data, such as Henry's law constant, for a number of compounds. The sewer parameters needed to estimate emissions using the BASTE model are: drop height and width, tailwater depth, wastewater flow rate, VOHAP influent wastewater concentration, headspace ventilation rate, ambient air and wastewater temperature, and wind speed. The user may enter system-specific dissolved oxygen data that have been measured upstream and downstream of the drop. These data are used to obtain oxygen deficit ratios:

$$r_{O_2} = (C_s - C_1) / (C_s - C_2) \quad (1)$$

where: r_{O_2} = oxygen deficit ratio

C_s = saturation oxygen concentration in pure water (mg/m³)

C_1 = upstream wastewater dissolved oxygen concentration (mg/m³)

C_2 = downstream wastewater dissolved oxygen concentration (mg/m³)

The oxygen deficit ratios are then used to estimate the VOC deficit ratios:

$$r_{VOC} = r_{O_2}^{ab} \quad (2)$$

where: r_{VOC} = VOC deficit ratio

a = ratio of mass transfer coefficient of wastewater to that of pure water

b = ratio of liquid molecular diffusion coefficient of wastewater to that of pure water

(Note: a and b are determined from empirical equations in the model).

The VOC deficit ratios are used to determine the differences between the upstream and downstream concentrations of VOCs, and therefore the VOC emissions.

The BASTE model in its current form requires that the sewer (headspace) ventilation rate be known and entered as a parameter. The model, therefore, is limited by the ability to obtain field measurements of the sewer ventilation rate. If this value is estimated the model results may reflect a large uncertainty in the emission estimates.

The BASTE model was developed and based on fundamental mass balance and reactor analysis principles. Empirical estimates and/or published partition coefficients and kinetic rate constants were used to close the model calculations. All major components of the BASTE model, as well as a limited comparison between model predictions and measured emissions from several wastewater treatment plants have been presented by the model developers.⁴ The drop structure component of BASTE has not been rigorously evaluated. However, an excellent comparison between predicted and measured ethanol emissions from a drop structure at a large brewery has been found.⁵

CORAL+. The CORAL+ model predicts VOC emissions from open and closed sewer reaches and drops. The model is based on the simultaneous solution of ordinary differential equations that express contaminant transport in a two-phase sewer environment. In CORAL+, mass transfer between the gas and liquid phases, and the ventilation rate between the sewer and ambient environment are assumed to account for VOC emissions. The model incorporates mass transfer kinetics into the emission estimation procedures, as opposed to an assumption of equilibrium. This results in lower estimates of emissions than if equilibrium conditions had been assumed.

In CORAL+, reaches are modeled as a number of continuous-flow stirred-tank reactors in series in both the

gaseous and liquid phases, with each phase assumed to be of equal length. For drop structures, VOC emissions are computed by estimation of the oxygen deficit ratio and theoretical extrapolation of this ratio to a VOC deficit ratio. Unlike the BASTE drop algorithm, CORAL+ accounts for gas-phase resistance to mass transfer, which can be significant for most VOCs if air entrainment serves as the dominant mass transfer mechanism.

The CORAL+ model provides chemical data for a number of compounds. The sewer parameters needed to estimate closed reach emissions using the CORAL+ model are: wastewater flow rate, upstream VOHAP concentration in the wastewater, wastewater temperature, reach length and diameter, reach slope and roughness coefficient, reach air/water flow ratio (reach ventilation rate), and VOC concentration in the ambient air. For closed drops, the additional parameters needed to estimate emissions are: drop height, drop air/water flow ratio (drop ventilation rate), drop tailwater depth, and drop gas volume.

With these inputs, the CORAL+ model provides sewer air emissions (in grams per day), the downstream wastewater concentration of the VOHAP, and the percent air emissions from both the reach and the drop as a function of influent wastewater concentration. As with the other models discussed above, the primary drawback of the model is that it does not include a procedure for estimating sewer ventilation rate.

The CORAL+ model has been rigorously evaluated through controlled releases of volatile tracers under eight separate operating conditions in municipal sewers.^{6,7} The algorithm used to predict mass transfer coefficients along sewer reaches has been shown to predict, within a factor of two, the coefficients observed from field data; the algorithm, however, is typically within $\pm 30\%$.⁷ The drop structure algorithm used in CORAL+ was developed based on a series of field pilot experiments, described in more detail elsewhere.⁸ Model predictions for emissions at drop structures were found to compare very favorably with those measured during independent pilot experiments and field monitoring events, with an average ratio of predicted-to-measured stripping efficiencies of 0.99.⁹

WATER8.³ WATER8 is an EPA model that can be used to estimate air emissions from municipal or industrial sewer collection systems. WATER8 is based on equilibrium gas flow in closed collection elements, and mass transfer for open collection elements. Mass transfer calculations are provided for comparison purposes with both co-current and counter-current gas flow. In WATER8, the primary emission mechanism is assumed to be volatilization. Sewer emissions are estimated based on the flow of air in the sewers relative to the flow of wastewater in the sewers. Emission factors for the sewer components are developed in the model and

expressed in terms of the fraction of material emitted per unit activity in the sewer component.

Unit reach manholes and closed lift stations are the municipal sewer components addressed by WATER8. The WATER8 models are primarily theoretical, with a limited amount of supporting data from industrial sewer systems, wastewater weirs, and laboratory experiments. The WATER8 model provides chemical data for a number of compounds. The sewer parameters needed to estimate emissions using the WATER8 model are: wastewater velocity and flow rate, reach width and length, manhole opening area, air velocity through the manhole openings, upstream VOHAP wastewater concentration, ambient air and wastewater temperature, wind speed, and percent oil present in the wastewater. WATER8 provides default values needed to run the model, but the user can specify site-specific data.

WATER8 estimates the fraction of VOHAP in the wastewater that is emitted into the air from reach manholes for three manhole venting scenarios: venting due to density differences between the ambient and reach air, venting due to wind, and venting due to pressure drop in the reach. WATER8 estimates emissions from lift stations with the assumption of periodic pumping of wastewater from continuously flowing wastewater into an enclosed sump.

The WATER8 model provides default estimates of ventilation velocities based upon theoretical calculations and measured plant data. The combination of the ventilation velocity and the dimension of the opening in the collection system will permit the model to estimate the ventilation rate as the product of the two values. Alternatively, site-specific data may be entered, if available. The WATER8 model can take into account partitioning into oil or biomass by specifying an equivalent oil content. The sewer component of WATER8 (called COLLECT) is being updated.

Comparison of Model Predictions

The predictive abilities of the models were compared using two sets of sewer data. The first data set consisted of sewer physical and operating data for reach manholes and drops that were obtained from a case study of a large U. S. city.¹⁰ The second data set was based on tracer studies performed on various municipal sewers in the United States and Canada.^{6,7} The second data set was used to compare model predictions to actual (measured) sewer gas concentrations. These two comparisons are discussed below.

It should be noted that the comparisons described below do not present a rigorous appraisal of the models, but were performed using available data from only a few sewer systems. The strengths and weaknesses of the models can be determined only by a robust experimental matrix designed to reveal both the similarities and differences of each model for the spectrum of conditions expected in sewer environments. More work is necessary to determine the abilities of the models for all situations.

Table 2. Case study sewer physical and operating data for a unit sewer reach in a large U.S. city.^a

| Parameters | Data | Source of Information |
|----------------------------------|--|---|
| Drop height | 4.6 meters 15 feet | City-supplied data |
| Drop diameter | 1.8 meters 6 feet | City-supplied data |
| Drop tailwater depth | 0.91 meters 3 feet | Assumed as 40 percent of reach height/diameter |
| Reach air/water volume fraction | 0.015 dimensionless | Calculated from reach ventilation rate and wastewater flowrate |
| Reach diameter | 2.3 meters 7.5 feet | City-supplied data |
| Reach length | 183 meters 600 feet | City-supplied data: typical length between manhole covers |
| Reach manhole gas volume | 15.6 cubic meters 551 cubic feet | Calculated from manhole diameter and reach height, as a cylinder |
| Reach slope | 0.1 percent | Assumed, based on literature |
| Reach type | closed | Assumed, based on municipal scenario |
| Reach ventilation rate | 10 turnovers per day (TO/D) | Assumed, based on literature |
| Roughness coefficient | 0.015 dimensionless | Based on concrete pipes |
| VOC concentration in ambient air | 0 ppm | Assumed, based on literature |
| Wastewater depth/height | 1.1 meters 3.6 feet | From reach diameter and assumption that reach is half-full; consistent with Manning's equation and hydraulic parameters |
| Wastewater flowrate | 243,381 cubic meters per day 8,591,349 cubic feet per day | Calculated from wastewater velocity provided; assumed half-full reach |
| Wastewater temperature | 20 °C | Assumed, based on literature |

^a The city contains approximately 5 million people and covers 2,259 square kilometers (872 square miles).

Case Study Data. The four models capable of predicting sewer emissions from reach manholes or closed drops (discussed above) were used with sewer physical and operating data obtained or estimated for a large U. S. city. The sewer design data for the city are shown in Table 2. The method and assumptions used to obtain these data are discussed in detail elsewhere.¹⁰

Table 3 shows the results of using the sewer physical and operating data shown in Table 2 with the four models for five VOHAPs (benzene, carbon disulfide, dichloromethane (methylene chloride), 1,1,1-trichloroethane, and o-xylene) to predict emissions for a single reach and drop. These VOHAPs were chosen because in the case study they were predicted to have relatively high emissions and were also likely to be the most hazardous, when toxicity was taken into account. Note that only three models (BACT/LAER-IWW/MRE, CORAL+, and WATER8) can be used to predict

reach manhole emissions and only two models (BASTE and CORAL+) can be used for closed drop emissions.

The case study comparison shows that for reaches, CORAL+ and WATER8 produced similar emissions estimates, while the BACT/LAER-IWW/MRE model produced emissions estimates that were approximately five times higher than that predicted by the other two models. Although the CORAL+ and WATER8 model predictions are close for the five VOHAPs, agreement between CORAL+ and WATER8 is expected for lower volatility VOHAPs than for higher volatility VOHAPs, since lower volatility VOHAPs will be closer to equilibrium in the reach environment (a key assumption in WATER8). Also, because the sewer gas flowrate was relatively low for the case study (2 centimeters per second [cm/s]), the conditions were favorable for the establishment of equilibrium and, hence, for better agreement between the CORAL+ and WATER8 emissions estimates.

Table 3. Model predictions with case study data.

| Compound | Influent Wastewater Discharge g/day (lb/day) | Reach Emissions, g/day (lb/day) | | | Drop Emissions, g/day (lb/day) | |
|-----------------------|--|---------------------------------|---------------|---------------|--------------------------------|--------------|
| | | BACT/LAER-IWW/MRE | CORAL+ | WATER8 | BASTE | CORAL+ |
| Benzene | 1,097 (2.4) | 6.8 (0.015) | 1.1 (0.002) | 1.5 (0.003) | 3.3 (0.007) | 2.1 (0.005) |
| Carbon disulfide | 1,430 (3.2) | 28.9 (0.064) | 2.5 (0.006) | 6.5 (0.014) | 12.9 (0.028) | 8.8 (0.019) |
| Dichloromethane | 55 (0.1) | 0.2 (0.0004) | 0.04 (0.0001) | 0.04 (0.0001) | 0.1 (0.0001) | 0.1 (0.0002) |
| 1,1,1-Trichloroethane | 1,037 (2.3) | 19.2 (0.042) | 1.6 (0.004) | 4.0 (0.009) | 8.3 (0.018) | 6.1 (0.013) |
| o-Xylene | 956 (2.1) | 7.7 (0.017) | 1.0 (0.002) | 1.1 (0.002) | 2.9 (0.006) | 2.4 (0.005) |

Note: Predicted emissions shown in this table are for a single reach and single drop.

For drops, the emissions predicted with the BASTE model were on the average 30% higher than the sewer drop emissions predicted by CORAL+. The CORAL+ model incorporates estimates of gas-phase resistance associated with entrained air bubbles. Such resistance leads to emissions suppression.

Measurement Data. Four sets of sewer measurement data were obtained from tracer studies performed at sewer reaches in:

- Davis, California;⁶
- Sacramento, California;⁶ and
- Guelph, Canada (two locations).⁷

At two locations, Davis and Guelph (Site No. 1), triplicate tests were performed. Deuterated chloroform (chloroform-d) was used as the tracer compound at all locations, and 1,1,1-trichloroethane was used as a tracer in addition to chloroform-d at the Guelph sites. These tracers were selected based on their low octanol/water partition coefficients and, therefore, low affinities for adsorption to solid particles in wastewater. Furthermore, they are generally of low biodegradability. These characteristics were required, as the intent of the field experiments was to isolate the effects of gas-liquid mass transfer, so that the overall mass transfer coefficients could be measured.

The sewer physical, operating, and chemical data for the four studies are shown in Table 4. The tracer studies were unique in the fact that forced ventilation through open manholes was used during the measurements instead of natural sewer ventilation.

The sewer data from the tracer studies were used with the three models available to predict reach gas concentrations

(BACT/LAER-IWW/MRE, CORAL+, and WATER8). The concentrations predicted by each of the models were compared to actual measurement data to assess the predictive ability of the model. Table 5 shows the measured sewer gas concentrations (MC) and the concentrations predicted (PC) with the three models. Standard errors (SE) were calculated according to the equation:

$$SE = (PC - MC)^2 / MC \quad (3)$$

A least squares index (LSI) was calculated for each data set using the calculated SE for each data point, according to the equation:

$$LSI = \text{Sum SE} / \text{number of data points} \quad (4)$$

The LSI is the value that is minimized when a regression line is fit to the data by the least squares method. A model that predicted emissions perfectly would have an LSI of zero.

These results show that the CORAL+ model, with an LSI of 0.24, predicted emissions better than the BACT/LAER-IWW/MRE and WATER8 models, with LSI values of 0.70 and 244, respectively. (The high LSI for the WATER8 model was a reflection of three data points: Guelph Site No. 1, Run C, and Guelph Site No. 2 for both chloroform-d and 1,1,1-trichloroethane. If these four data points are disregarded, the LSI for the WATER8 predictions is only 3.7. This LSI value, however, is still higher than the LSI values for the other two models.)

It is likely that the difference in LSI between the CORAL+ and WATER8 models would be greater at higher ventilation rates, i.e., further from equilibrium conditions. WATER8 also tends to predict much larger air emissions in the early sections of industrial collection systems (e.g., drains, trenches,

Table 4. Sewer physical and operating data for tracer studies in municipal sewers.

| Parameter | Units | Tracer Study Site | | | | | | | |
|---------------------------|-------------------|--------------------|---------|-------------------------|-----------|--------------------------------|---------|--------------------------------|--------|
| | | Davis ^a | | Sacramento ^a | | Guelph Site No. 1 ^b | | Guelph Site No. 2 ^b | |
| | | A | B | C | | A | B | C | |
| Reach | | | | | | | | | |
| Reach length | meters | 131 | 131 | 131 | 291 | 122 | 122 | 122 | 64 |
| | feet | 430 | 430 | 430 | 954 | 400 | 400 | 400 | 210 |
| Type of reach | dimensionless | closed | closed | closed | closed | closed | closed | closed | closed |
| Reach flowrate | cubic meters/day | 5,010 | 4,840 | 2,851 | 201,000 | 14,700 | 6,100 | 8,600 | 1,730 |
| | cubic feet/day | 176,853 | 170,852 | 100,640 | 7,095,300 | 518,910 | 215,330 | 303,580 | 61,069 |
| Wastewater temperature | centigrade | 20.8 | 20.8 | 22.2 | 24.4 | 15.6 | 16.3 | 17.0 | 18.9 |
| Reach diameter | meters | 0.53 | 0.53 | 0.53 | 2.6 | 1.2 | 1.2 | 1.2 | 0.52 |
| | feet | 1.7 | 1.7 | 1.7 | 8.5 | 3.9 | 3.9 | 3.9 | 1.7 |
| Wastewater depth/height | meters | 0.19 | 0.19 | 0.15 | 0.98 | 0.3 | 0.2 | 0.23 | 0.06 |
| | feet | 0.62 | 0.62 | 0.49 | 3.21 | 0.98 | 0.66 | 0.75 | 0.19 |
| Roughness coefficient | dimensionless | 0.014 | 0.014 | 0.014 | 0.014 | 0.014 | 0.014 | 0.014 | 0.014 |
| Reach slope | percent | 0.24 | 0.24 | 0.24 | 0.063 | 0.1 | 0.1 | 0.1 | 3.5 |
| Reach ventilation rate | TO/D | 31.2 | 37.1 | 35.4 | 100 | — | — | — | — |
| VOC conc in ambient air | ppm | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Air/water volume fraction | dimensionless | 0.36 | 0.46 | 0.73 | 0.77 | 0.245 | 0.49 | 1.83 | 1.5 |
| Wastewater Tracers | | | | | | | | | |
| 1,1,1-Trichloroethane | mg/m ³ | — | — | — | — | 8.4 | 5 | 42 | 99 |
| Chloroform-d | mg/m ³ | 40 | 48 | 58 | 4.1 | 18 | 13 | 49 | 94 |

^a Reference 6.

^b Reference 7.

Table 5. Comparison of model predictions with measured sewer gas concentration from tracer studies in municipal sewers.

| Tracer Study | | | Model Results | | | | | |
|-----------------------------------|---------------------------|--|---|-------------------|--|-------------------|--|-------------------|
| Site | VOHAP/Run | Measured Concentration mg/m ³ | BACT/LAER-IWW/MRE | | CORAL+ | | WATER8 | |
| | | | Predicted Concentration mg/m ³ | Standard Error | Predicted Concentration, mg/m ³ | Standard Error | Predicted Concentration, mg/m ³ | Standard Error |
| Davis ^a | Chloroform-d | | | | | | | |
| | Run A | 1.3 | 0.18 | 0.96 | 1.7 | 0.12 | 1.8 | 0.21 |
| | Run B | 2.1 | 0.22 | 1.68 | 1.7 | 0.08 | 2.9 | 0.30 |
| | Run C | 2.6 | 0.26 | 2.11 | 2.1 | 0.10 | 5.6 | 3.4 |
| Sacramento ^a | Chloroform-d | 0.02 | 0.02 | 0.00 | 0.02 | 0.00 | 0.45 | 9.3 |
| Guelph Site No. 1 ^b | 1,1,1- Trichloroethane | | | | | | | |
| | Run A | 0.20 | 0.16 | 0.01 | 0.23 | 0.00 | 0.89 | 2.4 |
| | Run B | 0.06 | 0.09 | 0.02 | 0.13 | 0.08 | 0.96 | 14 |
| | Run C | 0.23 | 0.78 | 1.32 | 0.25 | 0.00 | 20.1 | 1717 |
| | Chloroform-d | | | | | | | |
| | Run A | 0.38 | 0.08 | 0.24 | 0.44 | 0.01 | 0.48 | 0.03 |
| | Run B | 0.25 | 0.06 | 0.14 | 0.31 | 0.01 | 0.67 | 0.71 |
| | Run C | 0.15 | 0.22 | 0.03 | 0.29 | 0.13 | 8.6 | 476 |
| Guelph Site No. 2 ^b | 1,1,1- Trichloroethane | 2.8 | 1.83 | 0.34 | 0.83 | 1.39 | 45 | 636 |
| | Chloroform-d | 2.3 | 0.42 | 1.54 | 0.79 | 0.99 | 15.1 | 71 |
| Least Squares Performance Index | | — | — | 0.70 | — | 0.24 | — | 244 |

^a Reference 6.^b Reference 7.

or laterals) than in reaches. The mass transfer calculations of WATER8 may be more appropriate than equilibrium assumptions for well-mixed, highly ventilated reaches, such as in municipal sewers.

The tracer studies used for this comparison of the model predictions are based upon the subsurface addition of tracer. Actual waste addition to a collection system may involve splashing and surface stratification not accounted for either in the tracer test or in some of the models. This potential stratification would result in air emissions greater than predicted. Additional research may identify the significance of this effect.

USE OF MODELS TO ESTIMATE VOHAP EMISSIONS FROM MUNICIPAL SEWERS

The most accurate means of estimating VOHAP emissions from sewers would be, of course, to obtain air measurement data on a continuous basis. In a previous study, aromatic VOHAP emissions were estimated from a small section of municipal sewer in Toronto, Canada.¹¹ Emissions were calculated as the product of measured headspace concentrations and exhaust air flowrates. The latter were determined by the metered introduction of sulfur hexafluoride (SF₆) in the sewer headspace, and subsequent analysis of SF₆ dilution in naturally-ventilated air flows. However, because of the extensive area over which most sewers are located, this approach is impractical for determining emissions from entire sewer networks. Even the continuous measurement of wastewater concentration data, the second-best approach to providing sewer emissions estimates, would also be difficult to implement on a large scale.

In the absence of measured data, an alternative method is needed that can be used to estimate sewer VOHAP emissions.

To be practical and relatively easy to implement on a large scale, the method should address three necessary components to estimate sewer emissions:

- Sewer wastewater VOHAP concentration data;
- Sewer physical and operating data; and
- A model that relates the above two data components to emissions.

A method was developed that used influent POTW wastewater measurements performed for the National Pollutant Discharge Effluent System (NPDES) to estimate the VOHAP wastewater concentration, as well as information concerning sewer physical and operating data that are generally available from municipal sewer engineers.¹⁰ The sewer physical and operating data needed to estimate VOHAP emissions could also be estimated from literature values.

Influent POTW wastewater concentration data are required to be reported annually to the NPDES for 111 priority pollutants as defined by the Clean Water Act. Frequently, data for other pollutants in the wastewater are also provided by the methods used to test the priority pollutants. Of the 111 priority pollutants, only 46 are HAPs; therefore, the VOHAP coverage of the NPDES data is expected to be low as compared to the universe of 189 potential HAPs. However, within the 46+ HAP coverage, the NPDES data are expected to be fairly representative of the actual wastewater pollutants in a municipal sewer system, since measurements are taken from wastewater that is composed of industrial, commercial, and residential sewer inputs. Because NPDES data are usually obtained from one to four annual wastewater samples, the data may or may not represent the annual

average wastewater concentration entering a POTW. Nevertheless, the NPDES data represent the VOHAP wastewater concentrations *after* sewer emissions occur, since the POTWs are downstream of the sewer emission points. If NPDES data are used to predict sewer emissions, the estimate may be much lower than if wastewater samples could be taken at the influent points in the sewer system.

In fact, many large industrial wastewater sources are required to report discharges to public sewers to meet the requirements of NPDES permits. Furthermore, the EPA maintains a Toxic Release Inventory System (TRIS) which serves as a compilation of industrial releases to the environment, including municipal sewer releases, derived, in part, from NPDES permits. However, the use of such databases would still lead to underestimates of VOHAP discharges as these databases generally omit small sources, e.g. dry cleaners and other solvent users, which collectively account for a large fraction of some VOHAPs, such as tetrachloroethene.

Comparison of Model Estimates of Sewer Emissions for a Large U. S. City

The method described above was used to estimate sewer emissions for a large U. S. city with a population of approximately 5 million and an area of 2,259 square kilometers (872 square miles).¹⁰ The sewer physical and operating data for

the city are shown in Table 2. In order to scale up the unit reach emissions to the city level, information on the number of reach manholes (4,000) and drops (2,000) was also obtained from city sewer engineers. This information was used with unit reach and drop emissions predictions to provide a city-wide sewer VOHAP emissions estimate.

The CORAL+ model was chosen in this study to estimate sewer VOHAP emissions, since this model was developed from municipal sewer studies and provided emissions estimates for both reach manholes and drops. For these two sources, the estimated VOHAP emissions from the city were 278 megagrams (Mg) per year (306 tons per year [tpy]). Reach emissions, at 145 Mg per year (160 tpy), comprised 52% of the total estimated emissions; drop emissions comprised 48%.¹⁰ It is important to recognize that these estimates are only for VOHAPs and not for total VOCs or hydrogen sulfide. Furthermore, emissions were estimated only for reaches and drop structures (e.g., lift station wet wells), and did not include other sewer components, such as storm drains in combined sanitary/stormwater systems. Thus, total VOC emissions would likely be significantly greater than 278 Mg/yr and may be of concern as precursors to ozone formation in nonattainment areas.

The city-wide sewer reach emissions estimated with the CORAL+ model were compared to sewer reach emissions estimates using the BACT/LAER-IWW/MRE model. The sewer reach VOHAP emissions predicted with the BACT/LAER-IWW/MRE model were 971 Mg per year (1,070 tpy). This estimate is approximately a factor of 7 greater than the CORAL+ estimate. The CORAL+ and BACT/LAER-IWW/MRE estimates for reach emissions of the 14 VOHAPs reported to NPDES for the city are shown in Table 6. Also shown are the drop and total emissions estimated by the CORAL+ model. If the same proportion between reach and drop emissions that was found with the CORAL+ model (52% versus 48%) is assumed for the BACT/LAER-IWW/MRE reach estimate, then the city-wide sewer emissions based on the BACT/LAER-IWW/MRE model results for reach emissions would be 1,867 Mg per year (2,057 tpy).

Sources of Uncertainty in the Sewer Emissions Estimate

The analysis described above is intended only as a screening exercise to provide "order of magnitude" estimates of VOHAP emissions from a large U.S. city. The authors acknowledge that there are significant uncertainties associated with these estimates. The major sources of uncertainty are described below.

VOHAP Concentrations. For this study, average VOHAP concentrations in wastewater within sewers were estimated based on NPDES data for POTWs, i.e., "end of pipe" data. However, it has been reported that a significant fraction of VOHAPs may be removed from wastewater and emitted to the ambient atmosphere before reaching a treatment

Table 6. Estimates of sewer VOHAP emissions for the city using the CORAL+ and BACT/LAER-IWW/MRE models.

| VOHAPs | Calculated Wastewater Concentration, ^a µg/L | Estimated Emissions, Mg per year (tpy) | |
|----------------------------|---|---|-------------------|
| | | CORAL+ | BACT/LAER-IWW/MRE |
| Aniline | 91 | 0.018 (0.019) | 12.5 (13.7) |
| Benzene | 8 | 2.92 (3.22) | 18.8 (20.7) |
| Bis(2-ethylhexyl)phthalate | 26 | 0.001 (0.001) | 3.6 (3.9) |
| Carbon disulfide | 4 | 2.48 (2.74) | 26.7 (29.4) |
| Cresol | 270 | 0.049 (0.054) | 36.7 (40.5) |
| Dibutylphthalate | 7 | 0.0002 (0.0002) | 1.0 (1.1) |
| Dichloromethane | 381 | 89.1 (98.2) | 465 (513) |
| Ethylbenzene | 17 | 6.57 (7.24) | 53.7 (59.2) |
| Methyl ethyl ketone | 13 | 0.292 (0.322) | 2.4 (2.7) |
| Naphthalene | 14 | 0.730 (0.805) | 4.3 (4.8) |
| Phenol | 83 | 0.012 (0.013) | 11.3 (12.4) |
| Toluene | 35 | 13.4 (14.8) | 90.1 (99.3) |
| Trichloroethane (1,1,1) | 11 | 6.13 (6.76) | 73.3 (80.8) |
| o-Xylene | 60 | 23.7 (26.1) | 171 (189) |
| Total for Reaches | | 145 (160) | 971 (1070) |
| Total for Drops | | 133 (146) | — ^b |
| Total for City Sewers | | 278 (306) | — ^b |

^a From NPDES reports of measured POTW influent wastewater concentrations, weighted by individual POTW wastewater volume.

^b BACT/LAER-IWW/MRE model does not estimate drop emissions (see text).

facility.¹¹ Thus, the concentrations used in this study may have led to significant underestimation of VOHAP discharges to (and subsequent emissions from) sewer systems. For example, a 90% reduction in VOHAP concentrations in the system would translate to an approximate tenfold increase in VOHAP emission estimates, i.e., approaching 3,000 tpy. The use of TRIS data could be used to supplement VOHAP discharge information, but would still lead to underestimates based on the exclusion of smaller industries, commercial establishments, and consumer products.

Sewer Ventilation. The high sensitivity of VOHAP emissions to sewer headspace ventilation has been illustrated previously.⁷ For poorly ventilated sewers, small increases in ventilation rates can lead to order-of-magnitude or greater increases in VOC emissions. The ventilation rate used for this assessment was very low, leading to an air flowrate of only 2 cm/s—that is two orders of magnitude lower than the air flowrate reported for a naturally ventilated sewer.¹¹ The ventilation assumption used in the analysis presented here also contributed to the likely underestimation of VOHAP emissions. Improvements in future VOHAP emission estimates for municipal sewers will depend in a large part on improved estimates of sewer ventilation, including the role of building rises and other locations for air exchange between sewer and ambient atmospheres.

Scaling. The analysis described above was based on average reach and drop operating conditions, with subsequent extrapolation to all reaches and drops in the target sewer network. The results of several million model simulations have been used to illustrate the sensitivity of VOHAP stripping in sewers to several parameters.¹² Relative depth of flow was determined to be a very important parameter that influences VOC stripping in the model simulations. Also, the simulations implied that a significant fraction of VOC stripping occurs along reaches characterized by low wastewater depths. For the data presented in this paper, all sewer reaches were assumed to flow half-full, a condition which is likely to lead to high chemical stripping efficiencies. If a significant fraction of sewer reaches in the target city flows less than half-full, the emissions (and model predictions) would be increased.

Chemical Formation. The estimates provided above did not account for VOHAP formation in sewers. Although this is not believed to be a major source of VOHAP occurrence in sewers, some chloroform can form following the discharge of residual chlorine to public sewers.¹³ It is conceivable that some VOHAPs may also form via biotransformation reactions in sewers. Such formation has been widely documented for an inorganic compound (hydrogen sulfide) but has not been documented for any VOHAPs.

Sorption. Untreated wastewater is a complex matrix containing treated drinking water contaminated with dissolved

and suspended solids, dissolved liquids, and possibly other free-phase liquids. It is possible that VOHAP emissions could be reduced by absorption into oils present in wastewater, or by adsorption to the surfaces of solids suspended in wastewater. The former has not been documented in the published literature. Adsorption has been previously addressed.¹² Given typical suspended solids concentrations in municipal sewers, the estimated adsorption losses for municipal sewers ranged from 2% (for methylene chloride) to 16% (for tetrachloroethene).¹²

Biodegradation. A previous study¹⁴ used bioluminescence techniques to quantify the concentration of active biomass suspended in untreated wastewater. Based on several analyses, it was determined that suspended biomass concentrations are typically less than 1 mg/l in sewer reaches far upstream of wastewater treatment facilities, but may exceed 10 mg/l at plant headworks. These values were determined to be too low to compete with volatilization as a fate pathway. Additional experiments were performed to ascertain the importance of attached biofilms as a mechanism for VOHAP degradation. Fabricated "tags" were suspended in operating sewers for several weeks, allowing for biofilm growth. These were then returned to the laboratory and placed in specially-designed reactors containing toluene and tetrachloroethene. Both compounds were found to be taken up by and degraded within the biofilm. However, the rate of uptake and degradation was again determined to be small, relative to the rate of volatilization within sewers.

Exfiltration/Infiltration. Infiltration and inflow should effectively increase wastewater flows in sewers, while exfiltration would decrease wastewater flows. However, these phenomena were effectively accounted for by using reported flowrates within the target city. While infiltration and inflow would act to reduce VOHAP concentrations by dilution, they should not affect total VOHAP mass flows within the system. Exfiltration would not affect VOHAP concentrations, but would reduce total mass flow within the system. The effects of these phenomena are likely to be negligible relative to other uncertainties described above.

In summary, adsorption to solids and biodegradation are competing fate mechanisms that can act to reduce VOHAP emissions from sewers. However, their impact on VOHAP emission estimates is likely to be negligible in comparison to the emissions associated with assumed aqueous-phase HAP concentrations and headspace ventilation rates, which are both believed to have been underestimated in this study. The net result is that the VOHAP emissions estimates described in this paper should serve as a lower-bound; actual VOHAP emissions may be an order-of-magnitude or more higher, and may still be small relative to total VOC emissions.

CONCLUSIONS AND RECOMMENDATIONS

A number of models are available to predict municipal sewer emissions. These models all lack at least one critical sewer parameter that must be estimated or measured through the use of difficult-to-implement field measurements. The CORAL+ model appears to predict sewer reach manhole emissions better than the BACT/LAER-IWW/MRE and WATER8 models; the CORAL+ model can also be used to predict emissions from drops, a common emission point in municipal sewer systems. A new version of WATER8 for sewer systems (called COLLECT) that calculates the sewer ventilation rate from other known parameters may improve the current ability of the model. It is desirable that more work be done to compare the models and to determine which model(s) gives the most accurate emissions estimates for all situations.

The CORAL+ model has been used to estimate sewer VOHAP emissions from a large U.S. city.¹⁰ Using data from NPDES and city sewer design engineers, the estimated sewer VOHAP emissions for the city with the CORAL+ model were 278 Mg per year (306 tpy). The CORAL+ estimates were compared to city sewer reach emissions predicted using the BACT/LAER-IWW/MRE model. The comparison showed that the BACT/LAER-IWW/MRE model predicted approximately seven times higher emissions than the CORAL+ model. Both model emission estimates were believed to be lower than actual emissions, since NPDES data are POTW influent (sewer effluent) measurements. Because relatively low ventilation rates were used, the BACT/LAER-IWW/MRE model emission estimates may be even lower.

A significant source of variability in sewer VOHAP emission estimates is the sewer wastewater VOHAP concentration data. No single source of these data is currently available that can be readily used to determine true sewer VOHAP emissions. It would be helpful if more work were done to obtain a readily available source of these data, which could then be used with the available models to determine true sewer VOHAP emissions. Also, it would be helpful if additional work were done to improve understanding of the natural ventilation of sewers.

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About the Authors

Dr. Donna Lee Jones (corresponding author) is a Senior Environmental Scientist for EC/R, Inc., 3721-D University Drive, Durham, North Carolina 27707. Mr. Julian W. Jones is a Senior Chemical Engineer for the Environmental Protection Agency's National Risk Management Research Laboratory, Air Pollution Prevention and Control Division, Emissions Characterization and Prevention Branch (MD-61), in Research Triangle Park, North Carolina. Ms. Joanne C. Seaman is a Chemical Engineer for EC/R, Inc. in Durham, North Carolina. Dr. Richard Corsi is a Professor in the Department of Civil/Environmental Engineering at the University of Texas at Austin. Mr. Clinton E. Burklin, P.E. is a Principal Engineer for ERG, Inc. in Research Triangle Park, North Carolina.