

UNCERTAINTY ANALYSIS OF THE
EMISSION INVENTORY OF AN INDUSTRIAL
WASTEWATER TREATMENT PLANT
A CASE STUDY AT THE IWTP OF
TINKER AIR FORCE BASE, TINKER, OK

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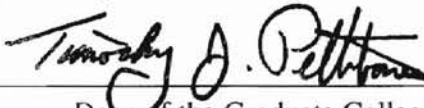
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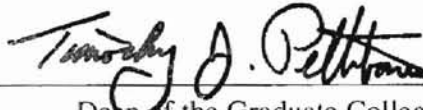
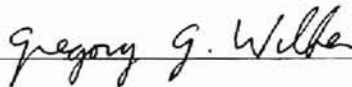
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Dedicated to my grandmother

Mrs. **Suzhen Yang**

with reverence

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Chapter I

Introduction

1.1 Background

The School of Civil and Environmental Engineering at Oklahoma State University is engaged in a project to improve and validate the accuracy, reliability, and repeatability of target pollutant emissions estimates through monitoring, process unit sampling, and computer modeling of the OC-ALC (Oklahoma City Air Logistics Center) / IWTP (Industrial Wastewater Treatment Plant) air emission sources for Tinker Air Force Base. The sources of air emissions include: the primary paint chip clarifier, oil-water separators, aerated equalization basins, storage / stabilization tanks, metals treatment basins, solid contract clarifiers, lift stations, and gravity thickener. In addition, this project will include development of an air emission sampling strategy to improve the accuracy of the air emissions reporting data (Veenstra, et al., 2001).

In production and maintenance processes at the OC-ALC, industrial wastewater streams are generated which contain organic and inorganic compounds. Most of the wastewater is generated from electroplating, chemical cleaning, and chemical depainting operations (Hall, 1999). Before being discharged from the treatment facility to the city of Oklahoma City, these wastewaters are collected and treated in a variety of ways. However, since many of these collection and treatment systems are open to the atmosphere, they allow organic-containing, heavy metal-laden wastewaters to contact ambient air. Based on logs of chemical consumption and field monitoring, benzyl

alcohol, phenol, acetone, 2-butanone, and methylene chloride are the main pollutants emitted via the air phase from this IWTP (Hall, 1999).

The Clean Air Act Amendments of 1990 requires wastewater treatment facilities to identify sources and quantify emissions of volatile organic compounds and hazardous air pollutants. Regulation under 40 CFR Part 63, National Emission Standards for Hazardous Air Pollutants: Publicly Owned Treatment Works, require operations to quantify and report chemical releases to the environment (CFR Title 40: Protection of Environment, US EPA, 1995).

Since residential neighborhoods are located in close proximity to the IWTP, residents are potentially exposed to the chemicals released from the IWTP and could be at risk. To evaluate effects of these chemicals on the environment and residents, measurements of the air contaminants are required.

The overall research project involves three phases. Phase 1 involves the acquisition of facility data and application of various air emission models. Most work for this phase has been accomplished. Two air emission models have been chosen, i.e., WATER9 (USEPA) and TOXCHEM+V3 (Enviromega Inc, Canada). Phase 2 includes the analysis of model output and comparison to field and pilot plant data, while Phase 3 will involve establishing the emission factors from each of the individual industrial wastewater treatment plant process units. The project now is in Phase 2.

Based on the summary of Phase 1, it was found that variability of components in the influent is significant (Veenstra, et al., 2001). For example, benzyl alcohol is not actually measured but estimated, based on the measured concentration of phenol since the consumption of benzyl alcohol is proportional to that of phenol in the chemical consumption logs. It is estimated to have a mean concentration of 15.4 mg/l if the diffusivity of benzyl alcohol and phenol in the liquid phase are considered, and an estimated mean concentration of 52.4 mg/l if the diffusivity of both chemicals are not considered (Veenstra, et al., 2001). The concentrations of the contaminants of concern vary seasonally. Methylene chloride averages range from 18.8 mg/l in winter to 22.75 mg/l in summer. 2-butanone averages 7.97 mg/l in the winter and 8.35 mg/l in the summer, while acetone averages range from 14.75 mg/l to 18.05 mg/l in summer and winter, respectively. Phenol is estimated to have a mean concentration of 14.3 mg/l over 1999-2001, in both summer and winter (Veenstra, et al., 2001).

1.2 The emission uncertainty of the IWTP

WATER9 and TOXCHEM+V3 were used to estimate air emissions from the IWTP based on the concentrations of the five compounds mentioned above. But it is not known which value is more representative and should be selected for use in determining the emission factors. Thus, uncertainty inevitably exists. Generally, uncertainty has three sources: modeling uncertainty, parameter uncertainty and input uncertainty (Monte, 1996). The more that is known about the model, parameter, or input value, the less uncertainty remains. Therefore, exactly modeling the actual units for the treatment facilities is important, and it helps reduce the uncertainty in the estimation of air

emissions from this system. Sensitivity studies can help determine which factor the system is the most sensitive to and potentially has a high contribution to the uncertainty. In this thesis, the uncertainty contributed by the variability of concentrations of compounds in water is the primary focus and will be discussed in detail.

1.3 General Fate Models (GFMs)

Field measurements and general fate models (GFMs) are the two main means to estimate the emissions from IWTPs (Curto and Daly, 1995). GFMs are computational models that perform a mass balance around each specified wastewater unit operation and certain solids handling facilities, as well as the whole wastewater treatment facility. The mass balances are usually performed considering five mechanisms in the treatment system: 1) volatilization across the exposed wastewater-atmosphere interface, 2) stripping to diffused air bubbles, 3) adsorption to solid particles or biomass, 4) absorption to immiscible liquids, and 5) biodegradation (Corsi and Olson, 1998). The development of GFMs for air emissions was prompted by the complexity and high cost of direct air sampling and measurement from wastewater treatment facilities. Using GFMs, it is possible to estimate emissions from complex treatment configurations while considering split flows, liquid streams, quiescent surfaces, weirs, drops, as well as aerated, biological, and covered processes or any single operation or process (Curto and Daly, 1995). Influent wastewater characteristics, physical design characteristics, and operational data are required to set up and run one of these models. Furthermore, GFMs are particularly advantageous when projecting potential emissions under varying flow and design conditions (Curto and Daly, 1995). The comparisons between field measurements and

1.4 Significance of VOCs emissions analysis from IWTPs

Volatile Organic Compounds (VOCs), such as benzyl alcohol, phenol, methylene chloride, 2-butanone and acetone, emitted from Tinker's IWTPs, can cause serious environmental problems due to their odor and toxicities. Some of them are harmful and carcinogenic if they are directly contacted or inhaled. For example, methylene chloride, is carcinogenic and might cause hepatocellular adenomas or carcinomas, hepatocellular cancer and neoplastic nodules with oral exposure (IRIS data base, USEPA, 1986). Potential health problems created by these VOCs would affect not only the workers of the treatment plants, but also the general public and residents in the surrounding area. Before measures are taken to protect the environment from being polluted and people from being at risk, the VOCs emission inventory of the IWTPs and the emission rate should be determined. The emission inventory and emission rate determine what protective actions should be taken. However, the variation and uncertainty of VOCs emissions make it tougher for decision makers, especially in environmental risk assessment. The analysis of variation and uncertainty of VOCs emissions are very important and necessary for an efficient action of protection; however, uncertainty analysis of VOCs emissions from IWTPs was not discussed in literature.

This thesis presented a method for uncertainty analysis of VOCs emissions from IWTPs with a case study.

Chapter II

Literature Review

2.1 Determination of Emission Inventory

The determination of an emission inventory for air phase pollutant-releasing facilities is essential for overall environmental management, environmental risk assessment, and environmental impact assessment. It is required and regulated by the USEPA (United States Environmental Protection Agency) (Curto and Daly, 1995). Methods that are available to estimate air emissions include stack/field testing, published emission factors, engineering equations, and a new and innovative tool/method--general fate modeling (Curto and Daly, 1995). Some authors have also used the input-output table method to predict the emissions from facilities (Jin, 1986; Ni, et al, 2001). USEPA AP-42 (Compilation of Air Pollutant Emission Factors) is widely used in the prediction of air pollutants from mobile sources, coal-fired power plants and other energy facilities, for which published emission factors for the regulated facilities are available. For the prediction of emissions of Volatile Organic Compounds (VOCs) from wastewater treatment facilities, the general fate model is a new and innovative method to estimate the emissions.

GFM's are computational models that perform a mass balance around each specified wastewater unit operation and certain solids handling facilities, as well as the entire wastewater treatment facility. Available GFM's include BASTE (Bay Area Sewage Toxics Emissions) by R.L. Corsi of the University of Texas at Austin, WATER8 (USEPA), CINCI (USEPA Cincinnati model) by Richard Dobbs at the University of

Cincinnati, CORAL (Collection System Organic Release Algorithm) by R.L. Corsi of the University of Texas at Austin while at the University of California-Davis, EPA FATE (Fate and Treatability Estimator) by ABB Environmental, NOCEPM (NCASI Organic Compound Elimination Pathway Model) by D.A. Barton with the National Council of the Paper Industry for Air and Stream Improvement (NCASI), PAVE (Programs to Assess Volatile Emissions) by the U.S. Chemical Manufacture Association, SIMS (Surface Impoundment Modeling Systems-1990) by RADIAN for USEPA Office of Air Quality Planning and Standards, TORONTO (specially for biological wastewater treatment facility) by B. Clark and D. Mackay of the Institute of Environmental Studies, University of TORONTO, and TOXCHEM+V3 (Enviromega, Canada). Among these models, WATER8 and TOXCHEM+V3 were the only two models with temperature correction for Henry's Constant, which is important for volatiles in a wastewater plant (Hall, 1999). Furthermore, WATER8, BASTE, and TOXCHEM were selected by USEPA as appropriate models for wastewater treatment systems (Card, 1995). WATER9 is the newly version of WATER8 developed by USEPA for estimating air emissions from water and wastewater sources.

2.2 Principles of GFMs

Corsi and Olson (1998) discussed the fundamental principles of these emission estimating models or VOC fate models. Under steady-state condition, the mass balance in a treatment system can be expressed as follows:

$$V \frac{dc}{dt} = QC_0 - QC + R_v + R_s + R_{ad} + R_{ab} + R_b \quad (1)$$

where:

V: reactor volume (m^3),

C, C_0 : dissolved contaminant concentration leaving and entering the reactor,
respectively (mg/m^3),

Q : volumetric flow rate entering into the reactor (m^3/s),

R_v , R_s , R_{ad} , R_{ab} , R_b : contaminant removal rate by volatilization, stripping, adsorption,
absorption, and biodegradation, respectively (mg/s).

Since absorption is generally a complex process that is not well understood, absorption is not considered for applications involving municipal wastewater, but may be important in industrial wastewater systems (Corsi and Olson, 1998). The rate of volatilization, stripping, adsorption and biodegradation can be modeled by the following equations:

The rate of volatilization is typically modeled as:

$$R_v = -K_L \left(C - \frac{C_g}{H_c} \right) A \quad (2)$$

where:

K_L is an overall mass transfer coefficient (m/s),

A is the interfacial area over which mass transfer occurs (m^2),

C_g is the contaminant concentration in the gas phase adjacent to the well-mixed liquid
(mg/m^3),

H_c is the Henry's law constant for chemical interested (m_{liq}^3/m_{gas}^3).

The rate of stripping by air bubbles can be modeled as:

$$R_s = -Q_b C_b = -Q_b C H_c \gamma \quad (3)$$

where:

Q_b is the bubble volumetric flow rate (m^3/s),

γ is a variable which represents the degree of saturation.

The adsorption rate can be modeled as:

$$R_{ad} = -Q_w K_p C C_s \quad (4)$$

where:

Q_w is the volumetric sludge wastage rate (m^3/s),

C_s is the solids or biomass concentration (mg/m^3),

K_p is a linear liquid-solid partition coefficient (m^3/mg).

The rate of biodegradation is assumed to follow Monod kinetics and can be modeled as:

$$R_{bio} = -k_b C X V \quad (5)$$

where:

k_b is the first order biodegradation rate constant ($m^3/mg.s$),

X is the active biomass concentration (mg/m^3).

Combining all the above from equations 1 through 5, for a steady-state condition and open process ($C_g = 0$), yields:

$$\frac{C}{C_0} = \frac{1}{1 + K_L A / Q + (Q_b / Q) \gamma H_c + (Q_w / Q) K_p C_s + k_b X / Q} \quad (6)$$

Equation 6 serves to illustrate differences in existing models for estimating VOC emissions from wastewater. For example, some models account for all the terms in the denominator, while others do not. In addition, models differ in how they estimate or prescribe parameters such as K_L , H_c , γ , K_p , and k_b (Corsi and Olson, 1998).

2.3 Uncertainty and Variability in an Emission Inventory

Most emissions inventories are not obtained by field acquisition of data, but predicted based on mass balance and computational models (McKay, et al., 1998). The GFM is based on computational equations to simulate the actual scenarios occurring in a wastewater plant, and as such, variability and uncertainty will inevitably exist. Emission inventory uncertainty and variability analysis is not a new concept and many studies on this topic have been conducted over several decades (McKay, et al., 1998). The U.S. Environmental Protection Agency (EPA) and the State and Territorial Air Pollution Control Officers' Association and Association of Local Air Pollution Control Officers (STAPPA/ALAPCO), published guidelines for evaluating the uncertainty of emission estimates as part of the Emission Inventory Improvement Program in 1997 (Roe and Reisman, 1998). Uncertainty and variability are confusing concepts. A clear understanding of these two terms is required before using these two concepts to express the analysis results when there is uncertainty or variability, or both, in an emission inventory. USEPA (1997) has laid out a detailed definition and description of the two concepts in "Guiding Principles for Monte Carlo Analysis" (USEPA, 1997).

"Uncertainty refers to lack of knowledge about specific factors, parameters, or models. For example, we may be uncertain about the mean concentration of a specific pollutant at a contaminated site or we may be uncertain about a specific measurement of uptake. Uncertainty includes parameter uncertainty (measurement errors, sampling errors, systemic errors), model uncertainty (uncertainty due to simplification of real-world processes, mis-specification of the model structure, model misuse, use of inappropriate surrogate variables), and

scenario uncertainty (descriptive errors, aggregation errors, errors in professional judgment, incomplete analysis), while variability refers to observed differences attributed to true heterogeneity or diversity in a population or exposure parameter. Sources of variability are the result of random processes and stem from environmental, lifestyle, and generic differences among humans. Examples include human physiological variation (e.g., natural variation in bodyweight, height, breathing rates, and drinking water intake rates), weather variability, and variation in soil types and differences in contaminant concentrations in the environment. Variability is usually not reducible by further measurement or study (but can be better characterized) (USEPA, 1997).”

2.4 Methods of Uncertainty Analysis

Many authors also provided commentary and examples to help the non-expert reader have a better understanding of these two concepts using actual applications (Frey, et al., 1995; 1998; 1999). Uncertainty refers to lack of knowledge and measurement error while variability refers to temporal variation. Usually, the uncertainty of the output of an estimating model is the mixture of uncertainty and variability.

Simulation variability, input uncertainty, and structure uncertainty are three sources of uncertainty or variability in the prediction of simulation models (McKay et al., 1999). Many authors have tried different ways to study uncertainty of models. Hanson (1999) presented a framework for assessing uncertainties in simulation predictions. The methods used in the framework included individual experiment analysis, many experiment

analysis, mathematical approximation (i.e. Gaussian approximation), and Markov Chain Monte Carlo simulations. Monte, et al. (1996) used:

$$d^2 = \sum(\ln(M_i) - \ln(O_i))^2/n \quad (7)$$

where:

d^2 is the error term,

M_i is experimental value,

O_i is the predicted value, and

n is the number of couples of experimental and predicted value,

as a measure to perform uncertainty studies and validate environmental models. This method is also called EBUA (empirically based uncertainty analysis). McKay et.al (1999) used:

$$\eta^2 = V(\mathbf{y})/V(y) \quad (8)$$

where:

$V(\mathbf{y})$ is the restricted predicted variance,

$V(y)$ is the predicted variance, and

η^2 is the Pearson relation coefficient,

as a measure to address the uncertainty of predictive models. Wallach and Genard (1998) used mean squared error of prediction (MSEP) with Taylor series expansion to study the effect of uncertainty in input and parameter values on model prediction error. The authors used the following equation:

$$MSEP = E\{[Y^* - f(u,p,q(p))]^2\} \quad (9)$$

where:

Y^* is the value of the output of interest for an individual chosen at random from the population of interest,

$f(u,p,q(p))$ is the corresponding model prediction.

In this paper, Taylor series expansion was used to adjust the effect of parameters. The error propagation was estimated based on the error term of the Taylor series expansion. The Taylor series expansion is shown in the following equation (Chapra and Canale, 2002):

$$Er = \Sigma [f^{(n+1)}(r) * h^{(n+1)} / (n+1)!] \quad (10)$$

where:

$f^{(n+1)}(r)$ represents the $(n+1)^{th}$ derivative of the function $f(x)$ when $x=r$,

$h = x-r$, r is in very close proximity to x .

Their work showed that the uncertainty in model inputs always increases the model variance contribution to MSE. However, one of the properties of these above methods is that while adequate data are required for the uncertainty analysis, sufficient data are usually not present. In addition, these equations (7 through 10) assume that the variables or parameters have normal distribution. This decreases accuracy if the variable does not have a normal distribution. The importance of the input distribution has been proven to be very critical in uncertainty analysis by Frey et al. (1995; 1998; 1999). Roe and Reisman (1998) recently summarized the methods of uncertainty analysis. In their summary, all of the methods typically can be categorized as qualitative, semi-quantitative and quantitative. For the qualitative method, sources of uncertainty are listed and discussed, emission factors are listed and subjectively ranked, and then the uncertainty is estimated in this way. For the semi-quantitative method, some statistical properties of the

data are studied, such as the probability distribution, mean, and standard deviation, and then the error propagation is estimated with standard statistical techniques, i.e. Taylor's series expansion. For the quantitative method, simulation techniques, i.e., Monte Carlo, Latin Hypercube, or Bootstrapping, are used to estimate the confidence intervals of factors of interest. Also, modeling methods based on adequate field measurements are used to achieve high accuracy. A summary table is produced in Table 1 (Roe and Reisman, 1998).

In a general sense, all of the methods used for uncertainty analysis can fit one of the categories discussed above. But to some extent, it is not easy to follow. Hence, if the analysis methods were based on the estimation of emissions from operational units, the uncertainty and variability analysis would be more straightforward. The uncertainty analysis would be conducted based on the variation of the estimation of emissions. The analysis methods then include direct emission analysis, emission factors analysis with simple equations, input-output table analysis, and GFMs (general fate models) uncertainty analysis. Of these methods, the most accurate one is direct emission analysis. However, it requires adequate field emission data, which most facilities do not usually have. Though it is technically feasible, it is not always cost-effective.

Some authors have used the input-output table method to estimate the emissions, i.e. CO₂, natural gas and other air pollutants, from power plants, manufacture factories and wastewater plants (Jin, 1986; Caloghirou, et al., 1996; Ni, et al., 2001). The idea behind this method is application of the principles of mass balance and energy movement. However, based on this method, the uncertainty analysis can be done only when the emissions have a linear and simplified relationship with the input and output. Under such

Table 1. Summary of methods used to estimate emissions uncertainty

Methods	Description	Relative Level of Effort
<i>Qualitative Methods</i>		
Qualitative Discussion	Source of uncertainty are listed and discussed; general direction of bias and relative magnitude of imprecision are given, if known.	Low
Subjective Data Quality Rating	Subjective rankings based on professional judgment are assigned to each emission factor or parameter.	Low
<i>Semi-Quantitative Methods</i>		
Data Attribute Rating System	Numerical values representing relative uncertainty are assigned through objective methods.	Moderate
Expert Estimation Method	Emission distribution parameters (e.g., mean, standard deviation, and distribution type) are estimated by experts. Simple analytical and graphical techniques can then be used to estimate confidence limits from the assumed distributional data.	Moderate
Propagation of Errors Method	Emission parameter means and standard deviations are estimated using expert judgment, measurements, or other methods. Standard statistical techniques of error propagation typically based on Taylor's series expansions are then used to estimate the composite uncertainty.	Moderate
<i>Quantitative Methods</i>		
Direct Simulation Method	Monte Carlo, latin hypercube, bootstrap, and other numerical methods are used to estimate directly the central value and confidence intervals of individual emission estimates.	Moderate to High
Direct or Indirect Measurement (Validation Method)	Direct or indirect field measurements of emissions are used to compute emissions and uncertainty directly.	High
Receptor Modeling Method	Can be used to provide a measure of the relative contribution of each source type but not absolute emission estimates.	High
Inverse Air Quality Modeling Method	Air quality simulation models are used in an inverse, iterative approach to estimate the emissions required to produce observed concentrations.	High

(Roe and Reisman, 1998)

a scenario, the uncertainty of the emission can be expressed with variance. For example, the propagation of errors of input and output-variables contributes to the uncertainty and variability of the emissions.

Suppose:

$$F(x) = \sum a_i x_i \quad (11)$$

where $F(x)$ stands for the emission and is a function of input and output.

It can easily be expressed as:

$$\text{Emission} = \text{Input} - \text{Output} \quad (12)$$

then,

$$\text{Var}(f(x)) = \sum \text{Var}(a_i x_i) + 2 \sum \sum \text{Cov}(x_i, x_j) \quad (i \neq j) \quad (13)$$

where:

$\text{Var}(x)$ represents the variance of x ,

$\text{Cov}(x_i, x_j)$ represents the covariance of x_i and x_j .

If the variance of input and output are independent, then

$$\text{Var}(\text{Emi}) = \text{Var}(\text{Input}) + \text{Var}(\text{Output}) \quad (14)$$

If the appropriate measurement of the statistics of the population is chosen, the uncertainty can then be easily estimated by statistical calculation.

The theoretical treatment of inference is handled in most introductory statistics books such as Ross' (1998) book "A First Course in Probability (5th ed.)". Models are usually simplified when using emission factors and engineering equations to perform uncertainty analysis of an emission inventory, and the models are called engineering equations and comprised of most subjective factors. Roe (1998) provided an example of this method, while he used a Monte Carlo simulation to estimate the emission inventory

uncertainty. As addressed above, GFMs are widely used for estimation of emission inventories. For its uncertainty, simulation techniques, i.e. Monte Carlo simulation, Latin Hypercube simulation and Bootstrapping simulations, etc., are widely used. Frey (1998) presented a paper on uncertainty analysis of air pollutants using the Bootstrapping simulation method, where he also used a two-dimensional approach to probabilistic simulation. When using simulation techniques to estimate the uncertainty, knowledge of the random variables' distributions is very critical. Wrong assumptions concerning the distribution of variables, especially the input distribution, will result in unrealistic outcomes. For the purpose of filling in the gaps due to lacking knowledge of input distributions, Frey and Cullen (1995) published a methodological handbook as practical guidance for uncertainty analysis. Since most of the methods mentioned above are simply based on a single distribution to represent variability and uncertainty in the input of the model, Zheng and Frey (2001) presented another method. They applied mixed distributions to represent the variability in the input of the model. Frey, et al. (1999) summarized the general steps of uncertainty analysis:

1. Assemble and evaluate a database,
2. Visualize data by developing empirical cumulative distribution functions for individual variables and preparing scatter plots to evaluate dependencies among pairs of variables,
3. Select, fit, and critique alternative parametric probability distribution models for representing variability in activity and emissions factors,
4. Characterize uncertainty in the distributions for variability,

5. Evaluate the effect of averaging, over both time and space, on variability and uncertainty, and
6. Propagate uncertainty and variability in activity and emissions factors to estimate uncertainty in emissions.

2.5 Distributions in Uncertainty Analysis

Usually, inputs for models are randomly sampled from specific distributions during a simulation. Normal distribution is the most prevalent, the best known and most widely used distribution in the world (Hahn and Shapiro, 1967). Normal distributions are symmetric with scores more concentrated in the middle than in the tails. They are known to have a bell shape. They are defined by two parameters: the mean (μ) and the standard deviation (σ). Many kinds of behavioral data are approximated well by the normal distribution. Many statistical tests assume a normal distribution. Most of these tests work well even if the distribution is only approximately normal and in many cases as long as it does not deviate greatly from normality. The density function of a normal distribution can be expressed as:

$$f(x) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-(x-\mu)^2/2\sigma^2} \quad (15)$$

where:

μ = the mean of samples

σ = the standard deviation of samples

When $\mu=0$, $\sigma =1$, the normal distribution is called a standard normal distribution as shown in Figure 1.

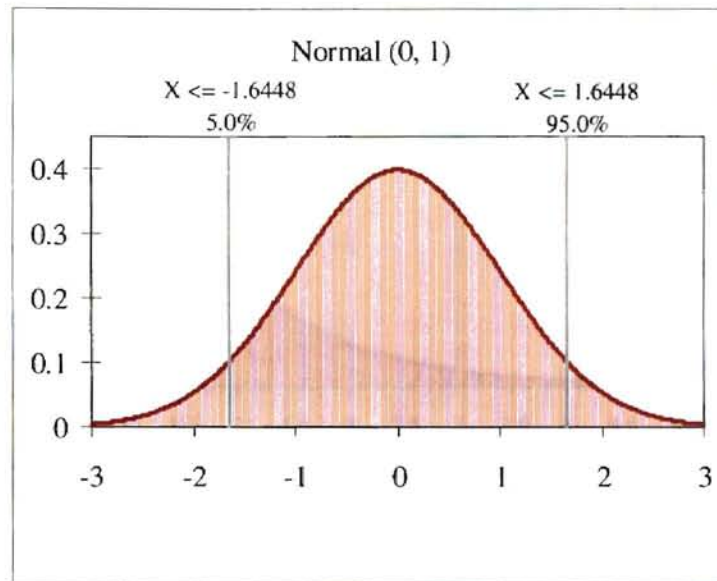


Figure 1. Standard normal distribution

When the scores are not concentrated in the middle, but skewed in the left tail, the distribution will not be symmetric or bell shaped. The distribution will not be a normal distribution, but might be an exponential distribution, Pearson distribution, etc. The following figures are some examples of these skewed distributions.

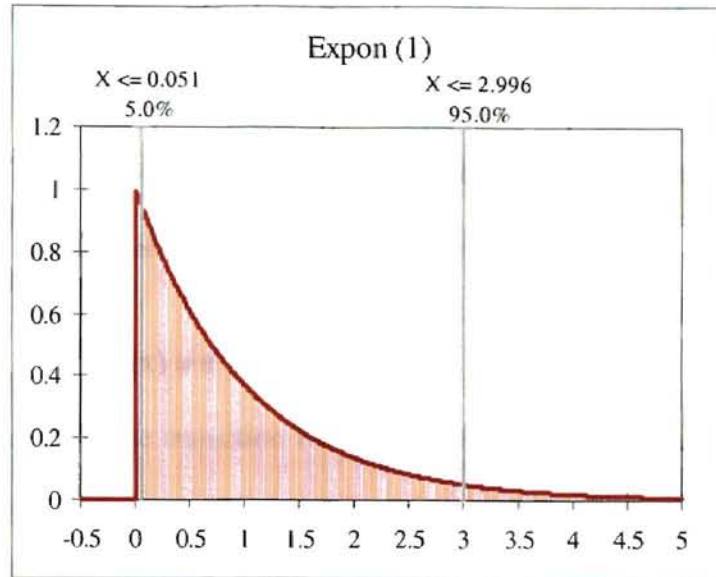


Figure 2. Standard exponential distribution

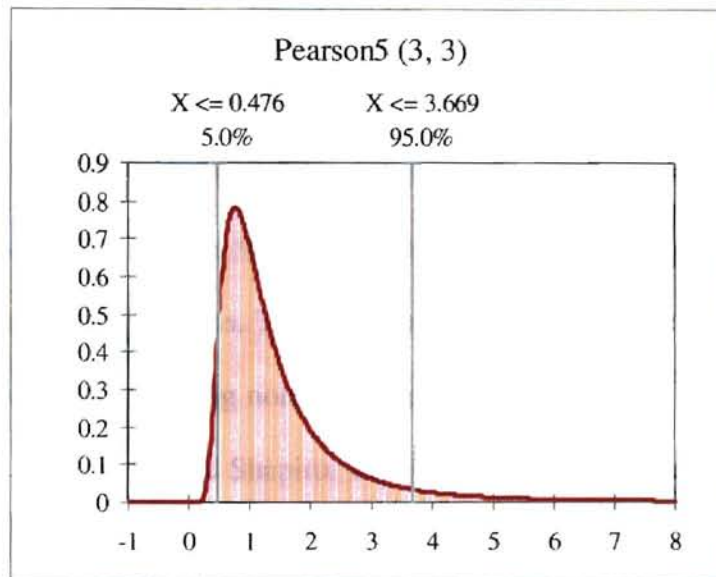


Figure 3. Pearson5 (3,3) distribution

The general formula for the probability density function of the exponential distribution is

$$f(x) = \frac{1}{\beta} e^{-(x-\mu)/\beta}, \quad x \geq \mu; \beta > 0 \quad (16)$$

where μ is the location parameter and β is the scale parameter (the scale parameter is often referred to as λ which equals $1/\beta$ when the scale parameter is expressed as λ). The case where $\mu = 0$ and $\beta = 1$ is called the standard exponential distribution. The equation for the standard exponential distribution is

$$f(x) = e^{-x}, \text{ for } x \geq 0 \quad (17)$$

Pearson5 distribution is the transition form of the Pearson distributions (Jeffreys, 1961). Each family in the Pearson system can be generated as a solution to the differential equation

$$\frac{df(x)}{dx} = \frac{(x - \Phi_3)f(x)}{\Phi_0 + \Phi_1x + \Phi_2x^2} \quad (18)$$

For the random variable x , a probability density function $f(x)$ is determined by proper choice of the four parameters $\Phi_0, \Phi_1, \Phi_2,$ and Φ_3 . Different choices of the four parameters will lead to different distributions. The solution of this equation leads to a large number of distribution families, including normal, Pearson1, and Pearson3 (Pearson distribution families) distributions (Hahn and Shapiro, 1967). Equation 18 can be transformed to

$$\frac{1}{f(x)} \frac{df(x)}{dx} = \frac{(x - \Phi_3)}{\Phi_0 + \Phi_1x + \Phi_2x^2} \quad (19)$$

When the roots of the denominator in Equation 19 are equal, real and finite, then Equation 19 can be written in the form

$$\frac{1}{f(x)} \frac{df(x)}{dx} = -\frac{\alpha}{x-c} + \frac{\beta}{(x-c)^2} \quad (20)$$

whence
$$f(x) = A(x-c)^{-\alpha} \exp[-\beta/(x-c)] \quad (21)$$

where

A will be fixed by the condition that the integral of $f(x)$ is 1,

C is the zero of the denominator in equation (18)

α, β are shape parameter and scale parameter, respectively.

For detailed discussions of these distributions the reader is referred to Jeffreys (1961) and Hahn and Shapiro (1967).

Once the distribution is determined, random numbers are sampled from the specific distribution. Models are then run hundreds of times based on the required accuracy of the results. But there is a prerequisite to achieving this goal. The model must be easily mathematically expressed as an equation or the applicable models have the integrated simulation function. All of the methods for uncertainty analysis mentioned above have the same prerequisite, which is the models can be easily entered into Excel or other spreadsheet, and then used with some statistics software, i.e., @RISK (Palisade, Inc.), Crystal Ball (Decisioneering, Inc.), etc. However, estimating software for emission inventories from wastewater treatment facilities such as WATER9, TOXCHEM+V3 focus mostly on air emissions based on mass balances, so that there is no such uncertainty function built into the software. Under such a scenario, there are two alternatives. One is coding the uncertainty function into the software, which is a complicated task. The other is to assume the model is certain based on the expert advice and validation experience,

hence assuming the uncertainty and variability of the input parameters contribute all to the uncertainty of the emissions. Since WATER9 (a newly version of WATER8), and TOXCHEM were selected by USEPA as appropriate models for estimating air emissions from water and wastewater resources (Card, 1995), TOXCHEM+V3 (a newly version of TOXCHEM) and WATER9 were selected for this thesis and assumed to be certain for the process of uncertainty analysis. The operation units were exactly modeled as they are supposed to be in these two programs.

The uncertainty analysis of emissions from wastewater treatment plants has not been adequately studied and discussed in literature. Instead, the uncertainty analysis of air emissions was seen to date mostly to focus on coal-fired power plants. Since GFM were developed as a deterministic tool to estimate the emissions from wastewater treatment systems, it makes the uncertainty analysis of emissions from wastewater plants, or the probabilistic analysis of emissions from wastewater plants, difficult. This thesis strives to present a method to conduct uncertainty analysis of air emissions from wastewater treatment plants.

Chapter III

Methodology

3.1 Emission estimating models

Emission estimating models mainly refer to general fate models (GFMs). Models used to estimate emissions of volatile organic compounds from wastewater plant include TOXCHEM+, WATER8, BASTE, CORAL (Corsi and Olson, 1998). Since TOXCHEM+ and WATER8 are considered as appropriate models for estimating air emissions from water and wastewater resources (Card, 1995), and TOXCHEM+V3 and WATER9 are the newly versions and similar in estimation of emission from process drains (Corsi and Olson, 1998), WATER9 and TOXCHEM+V3 were chosen to be used in this thesis.

3.2 Monte Carlo Simulation

Monte Carlo techniques have been used since the 1940's, when they were first developed by physicists working on the Manhattan project (Hammersley and Handscomb, 1964). Only recently, however, have personal computers become sufficiently powerful and widespread for Monte Carlo techniques to be widely applied for health risk assessments.

Modern spreadsheet programs, such as @RISK (Palisade, Inc.), Crystall Ball (Decisioneering, Inc.), and Xlsim (AnalyCorp, Inc) now provide a range of critical factors to illustrate and order a model, including advanced statistical functions, charting,

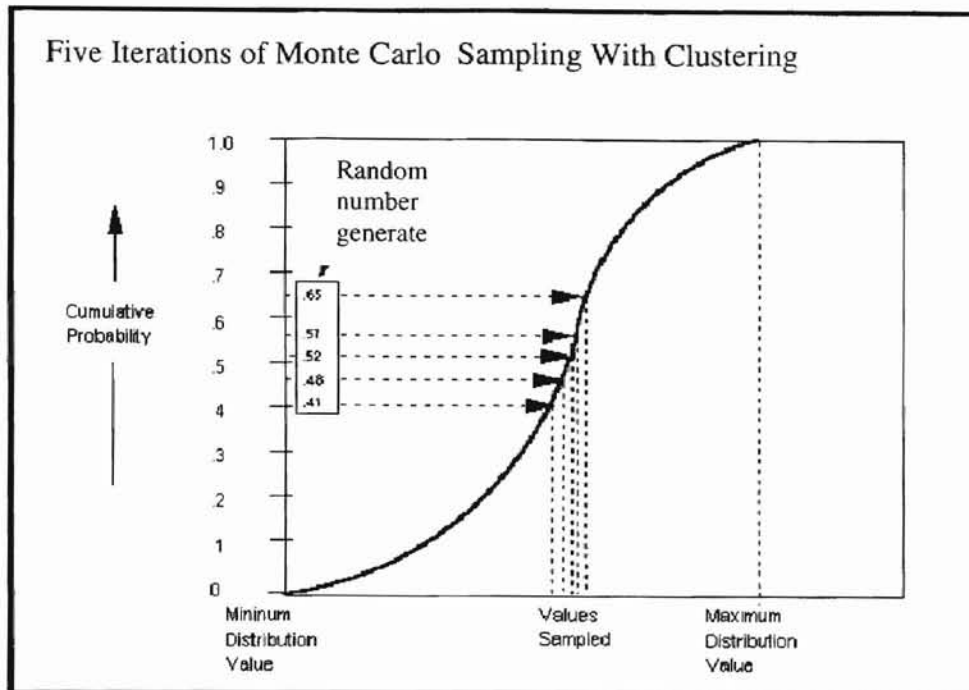


Figure 4. Monte Carlo Sampling. (Palisade Corp., 2001)

3.2.2 Latin Hypercube Sampling

Compared to Monte Carlo sampling, Latin Hypercube sampling is pseudo random (without replacement). Sampling without replacement means that a value might not be sampled twice. Depending on the numbers of samples, the whole range of the distribution is divided into even intervals. Then the values are sampled from these intervals without replacement. Obviously, it reduces time for sampling to achieve a simulated distribution that stands for the input distribution. Figure 2, Latin Hypercube sampling, shows this sampling method (Palisade Corp., 2001).

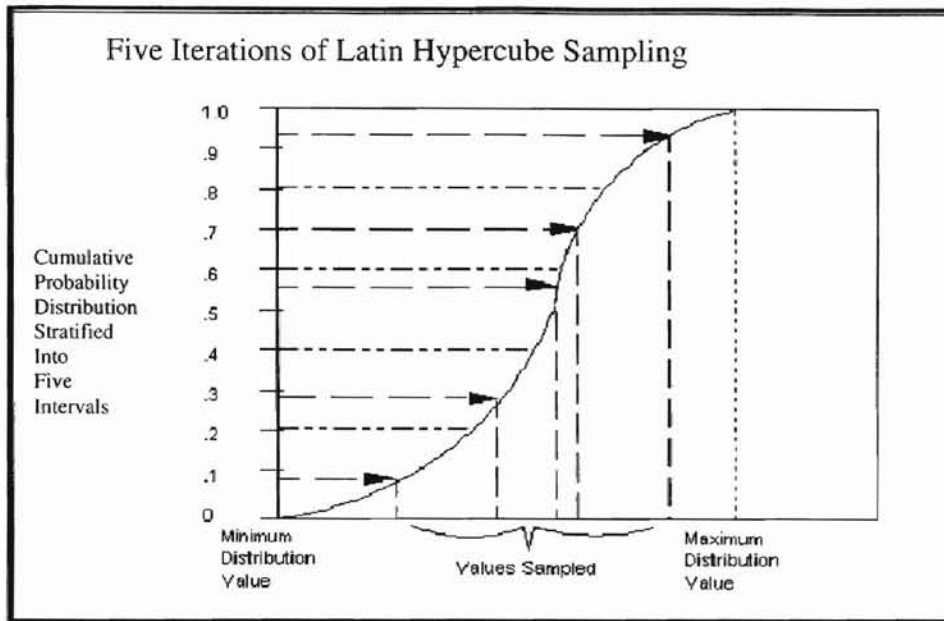


Figure 5. Latin Hypercube Sampling. (Palisade Corp., 2001)

Since Monte Carlo sampling is entirely random, unless sampling is sufficient, it is not even over the distribution. Since Latin Hypercube sampling is pseudo-random, samples are drawn equivalently without replacement. Hence, even a few samples can represent the distribution. Therefore, Latin Hypercube sampling is more effective than Monte Carlo sampling (Palisade, 2001). The common nature of these two sampling techniques is that sampling is based on the known or assumed distribution. If the distribution is not known, acceptable assumptions are then required.

3.3 Bootstrapping

The Bootstrapping technique was introduced by Efron in 1979 for the purpose of estimating confidence intervals for a statistic using numerical methods (Frey and Burmaster, 1999). The key advantage of this technique is that it can provide estimates of confidence intervals in situations for which analytical mathematical solutions may not exist. Therefore, it is used for confirmation of a distribution by fitting the assumed

3. The Anderson-Darling (A-D) Test

The Chi-square statistic is defined as:

$$\chi^2 = \sum (P_i - p_i)^2 / p_i \quad (29)$$

where

P_i = the observed probability value for a given histogram bar,

p_i = the theoretical probability that a value will fall with x range of the histogram bar.

The Kolmogorov-Smirnov statistics is defined as:

$$D_n = \text{Sup}[|F_n(x) - F(x)|] \quad (30)$$

where:

$\text{Sup}(x)$ refers to the maximum value of the function, it equals to $\text{Max}(x)$

n = total number of data,

$F(x)$ = the hypothesized distribution,

$$F_n(x) = \frac{N_x}{n},$$

N_x = the number of x_i 's less than x .

The Anderson-Darling statistic is defined as:

$$A_n^2 = n \int_{-\infty}^{+\infty} [F_n(x) - F(x)]^2 \psi(x) f(x) dx \quad (31)$$

where:

$$\psi^2 = \frac{1}{F(x)[1 - F(x)]},$$

$f(x)$ = the hypothesized density function,

$F(x)$ = the hypothesized distribution,

$$F_n = \frac{N_x}{n},$$

N_x = the number of x_i 's less than x .

Each of these methods has its advantages and weakness. The Chi-Square is the most common goodness of fit test (Palisade, 1997). The weakness is that there are no clear guidelines for selecting intervals. A different conclusion might be reached depending on how the intervals are specified. The Kolmogrov-Smirnov test does not depend on the number of intervals, which makes it more powerful than the Chi-Square test (Palisade, 1997). However, it does not detect tail discrepancies very well. While the Anderson-Darling test is similar to the Kolmogrov-Smirnov test it places more emphasis on tail values, and can only be used with actual sampling data (Law and Kelton, 1993; Walpole and Myers, 1993). In selecting the fitted distribution, the A-D method was used in this work.

3.5 Analysis Tools

Although a proper model for a specific problem is the first step of running a Monte Carlo simulation, the variable distribution used in conjunction with the selected model is the most critical item during a simulation event because all the simulating values will be sampled from the distribution. Analysis software @RISK[®] (Palisade, Inc.) was used for this thesis. @RISK[®] is a professional analysis software for risk assessment that uses the Excel[®] spreadsheet. @RISK[®] uses Monte Carlo simulation techniques to combine all the uncertainties identified in the modeling situation to predict the likelihood of occurrence for each possible value. Minitab[®] (Minitab Inc.) is another professional software used for

statistics. In this thesis, Minitab[®] was used for bootstrapping sampling to produce confidence intervals for chemicals in the influent and the ambient conditions based on the actual data measured.

3.6 Model Setup for IWTP with TOXCHEM+V3 and WATER9

The treatment facility was mainly modeled as units in series and parallel. These units included a primary paint chip clarifier, two covered blending basins, two oil-water separators, two storage tanks, two aerated equalization basins, three mixing basins and a solid contact clarifier, a sand filter and a chlorine contact chamber. Among these units, the blending basins, oil-water separators, equalization basins and aerator basins were in parallel while the others were in series (Veenstra, 2001). The layout of the plant configuration is presented in Appendix A-1.

For the two different estimating softwares, the plant configurations were slightly different. Since there are several parallel units in the plant, the configuration should assure the flow into each of parallel units is exactly half of the total influent. WATER9 and TOXCHEM+V3 have different configurations to set up parallel units. Figures 6 and 7 below are the modeled plant configurations by WATER9 and TOXCHEM+V3, respectively.

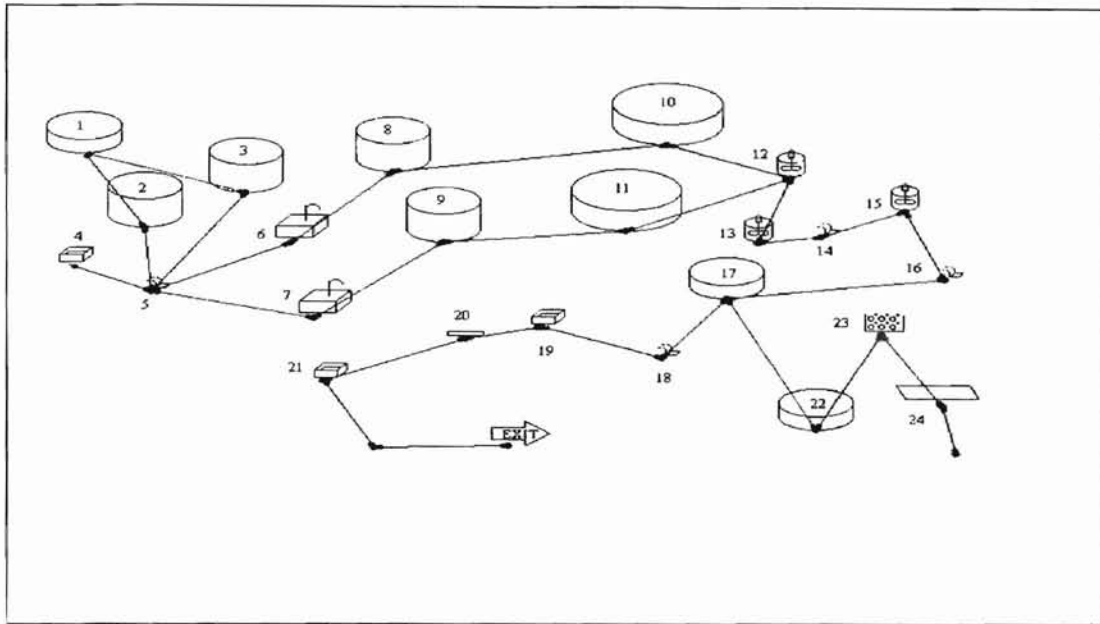


Figure 6. IWTP Configurations with WATER9

Notes:

- 1: Primary municipal clarifier modeling stripping waste clarifier
- 2: Storage tank modeling D1-blending tank
- 3: Storage tank modeling D2-blending tank
- 4: Open sump modeling venturi pipe from Building 3001
- 5: Weir/waterfall modeling the mixing unit of two influents
- 6: Covered separator modeling oil-water separator -1
- 7: Covered separator modeling oil-water separator -2
- 8: Storage tank modeling storage tank-1
- 9: Storage tank modeling storage tank -2
- 10: Equalization basin modeling equalization basin-1
- 11: Equalization basin modeling equalization basin -2
- 12: Mix tank modeling mixing basin-1
- 13: Mix tank modeling mixing basin-2
- 14: Weir/waterfall modeling diversionary structure (DS) between mixing basin 2 and 3
- 15: Mix tank modeling mixing basin-3
- 16: Weir/waterfall modeling diversionary structure (DS) between mixing basin 2 and SCC
- 17: Circular clarifier modeling solid contact clarifier (SCC)
- 18: Weir/waterfall modeling diversionary structure between SCC and wet well
- 19: Open sump modeling wet well
- 20: Hard piped, no space unit modeling sand filter
- 21: Open sump modeling chlorine contact chamber
- 22: Circular clarifier modeling thickener
- 23: Porous solids unit modeling filter press
- 24: Oil film unit modeling the final unit of sludge treatment, plate and frame filter

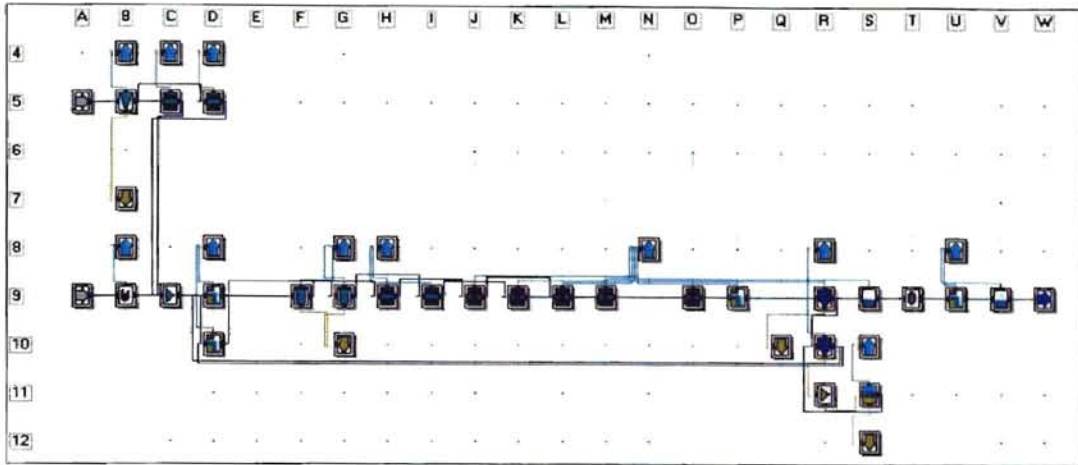


Figure 7. IWTP Configuration with TOXCHEM +V3

Notes:

- B5: Primary clarifier modeling stripping waste clarifier
- C5: Blending tank modeling D1-blending tank
- D5: Blending tank modeling D2-blending tank
- B9: Channel modeling venturi pipe from building 3001
- C9: Wastewater mixer modeling the mixing unit of two influents
- D9: Drop structure-open modeling diversionary structure (DS)
- D10: Drop structure-open modeling diversionary structure (DS)
- F9: Dissolved air-floatation modeling oil-water separator-1
- G9: Dissolved air-floatation modeling oil-water separator-2
- H9: Equalization basin modeling storage basin
- I9: Equalization basin modeling storage basin
- J9: Equalization-mixed/aerated basin modeling aerated equalization basin-1
- K9: Equalization-mixed/aerated basin modeling aerated equalization basin-2
- L9: Equalization-mixed/aerated basin modeling mixing basin-1
- M9: Equalization-mixed/aerated basin modeling mixing basin-2
- O9: Equalization-mixed/aerated basin modeling mixing basin-3
- P9: Drop structure-open modeling weir (diversionary structure) between mixing basin and SCC
- R9: Secondary clarifier/sludge thickener modeling solid contact clarifier (SCC)
- S9: Channel modeling wet well
- T9: Force main modeling sand filter
- U9: Drop structure-open modeling pump station between sand filter and chlorine contact chamber
- V9: Channel modeling chlorine contact chamber

3.7 General procedures

The work steps in this thesis can be summarized as follow:

1. Field data acquisition

There are two potential sources of field data for this thesis. One is from the record logs (consumption of chemicals) over the past several years, from 1999 through 2001. The other source is field sampling and measurement. A flux chamber was used for field sampling of emissions. The flux chamber is one of the most promising technologies for direct measurement of VOCs emissions developed by USEPA (Shen, et al., 1993). SUMMA canisters, where the contents were analyzed by a gas chromatography and mass spectrometer (GC-MS), and an online FTIR (Fourier Transform Infrared Spectroscopy) were used to measure the concentration of chemicals in gas phase samples taken from the flux chamber. The liquid phase constituents were measured by GC-MS. The data used in this thesis is historic data. In addition, methylene chloride, acetone and 2-butanone must be backsolved to the concentration at the front end of the plant since they were sampled at the transfer pit which is in the middle of the plant.

2. Sensitivity study

TOXCHEM+V3 has an integrated subroutine for conducting a sensitivity study. The subroutine was used to determine which variables in the model, such as site parameters, influent characteristics, or chemicals' physiochemical properties, would have significant effect on the air emissions. The results were then applied to WATER9 since WATER9 does not contain such a subroutine.

3. Fit distribution

One of the subroutines in @RISK[®], called “Best Fit”, was used to fit the distribution for the input data. The fitted distributions were ranked using Chi-Square test, Kolmogorov-Smirnov test and Anderson-Darling test based on the least square method. The Anderson-Darling test was used to select the distribution that had best fit. The lower the value of the A-D statistic of a distribution that the test ends up with, the better the distribution fits the actual data. For each distribution fitting, the fitting results were presented by a histogram, Probability-Probability (P-P) plot and Quantile-Quantile (Q-Q) plots. For the best fitted distribution, these two plots would be nearly linear.

4. Distribution confirmation

Since the distributions of most variables used in the model were not known, assumptions concerning these variables had to be made or they must be fitted from actual data. Bootstrapping simulation was used to make the assumed or fitted distribution more appropriate and acceptable. Bootstrapping constructed a confidence interval for each variable of interest based on actual data. If the statistical values of the assumed or fitted distributions fell in the range that the Bootstrapping simulation constructed, the assumption or fitted distribution was then acceptable.

5. Generation of random sample data sets for each model, WATER9 and TOXCHEM+V3

Generating random numbers was an important step in simulation. Since the WATER9 and TOXCHEM+V3 cannot generate random numbers themselves, random numbers were generated externally. At this step, @RISK[®] generated

hundreds of random number sets with the Latin Hypercube sampling method based on the assumed or fitted distributions.

6. Running of models

All of the generated random number sets were substituted into the models manually.

The models were run with these data sets for two hundred times. The number of simulations was determined based on the study of adequacy of simulations.

7. Results analysis and uncertainty estimate

Data analysis had as a focus the construction of a cumulative distribution for each variable, on which uncertainty estimates were based. Furthermore, comparisons of deterministic and probabilistic results helped evaluate the model itself, i.e. applicability. The general procedure is illustrated in Figure 8.

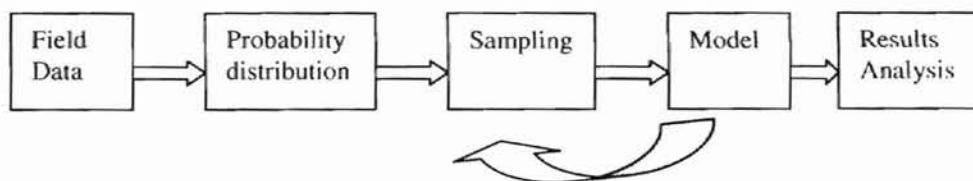


Figure 8. Diagram of simulating procedures

Chapter IV

Results

4.1 Sensitivity study

Sensitivity studies of all of the chemicals in the influent by TOXCHEM+V3 were performed by ranging the values of parameters from 0.2 to 5 times their values. These studies showed that VOCs emissions are mainly sensitive to influent flow rate, concentration and slightly sensitive to influent water temperature, but not sensitive to air temperature, pH, plant elevation, oil/grease concentration in the influent, volatile suspended solid ratio and wind speed. The results are presented in the following figures (Figure 9, Figure 10 and Figure 11). Thus, when the models were run, with the exception of the flow rate and concentration, the averages over years, also called the single value distributions, of the other parameters in the models can be substituted.

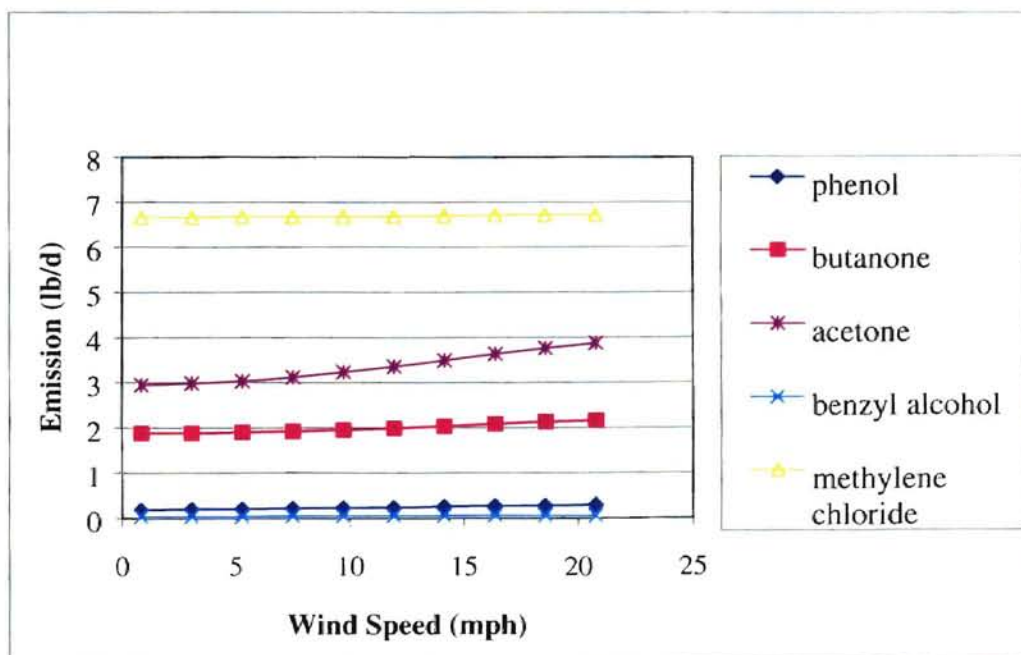


Figure 9. Sensitivity of wind speed on emission rate.

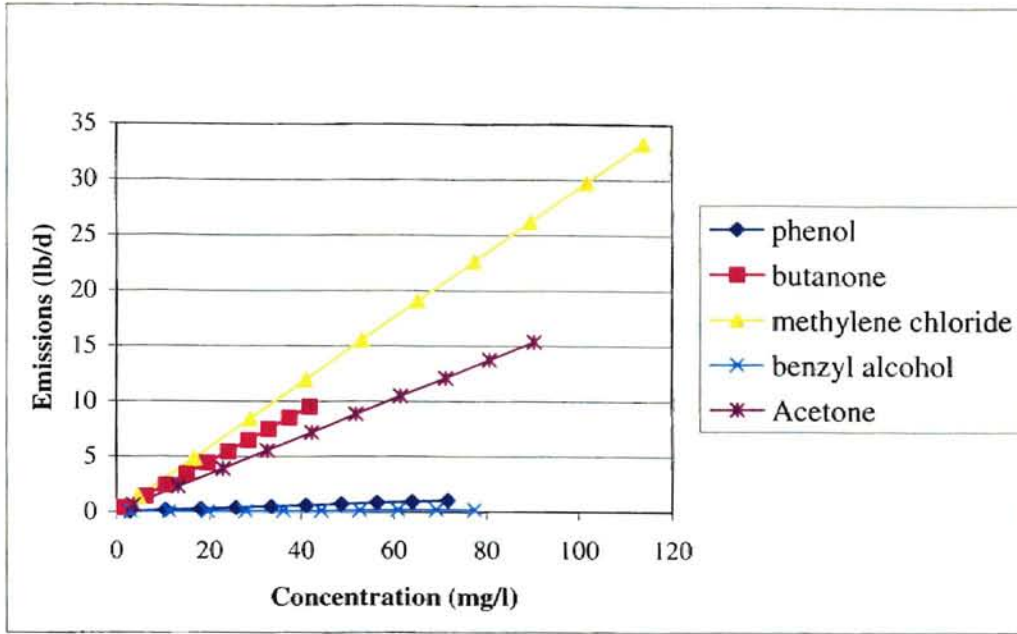


Figure 10. Sensitivity of chemical concentration on emission rate.

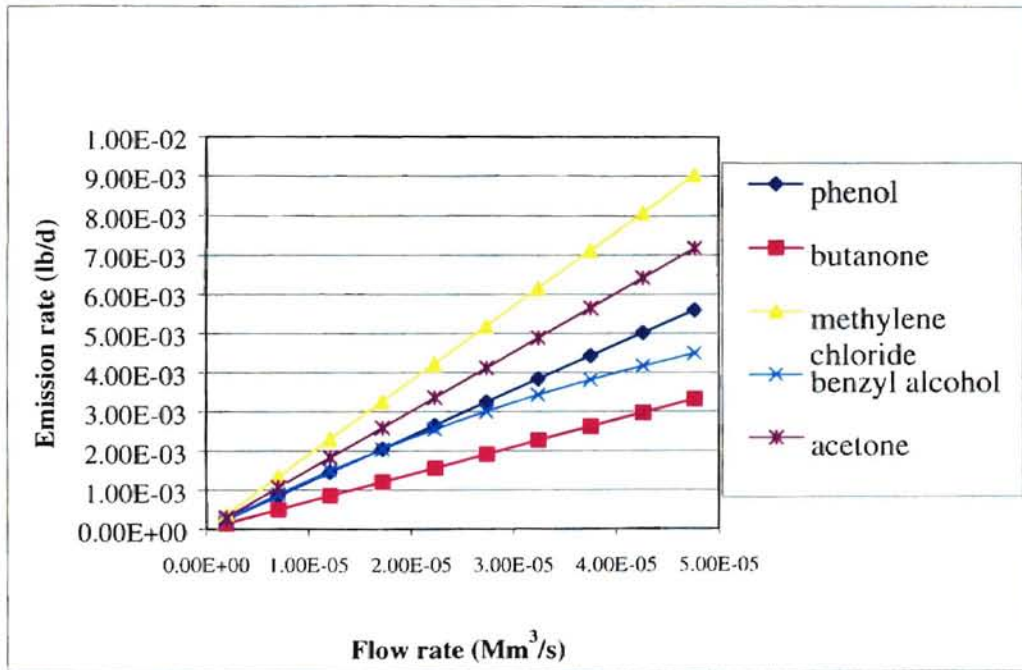


Figure 11. Sensitivity of flow rate on emission rate.

4.2 Models inputs set-ups

Both models were run two hundred times. Based on the results of the sensitivity studies, the yearly averages were substituted into the models for those insensitive parameters, i.e., total solids, suspended solids, oil/grease concentration, dissolved solids, volatile SS ratio, radius of pipe, air temperature, wind speed, pH, wastewater temperature and plant elevation. The influent wastewater temperature had an average of 68.7 °F with a standard deviation of 8.5 °F. As such, it appears to be relatively stable and uniform. These parameter values mentioned above remained unchanged during the simulations. The inputs of these parameters are listed as follows:

Table 2. Inputs of variables for WATER9 and TOXCHEM+V3 simulation

Parameter	Units	WATER 9	TOXCHEM 3	Note (TOXCHEM)
Total solids	ppm	827	724	Suspended solids
Oil/grease	mg/l	14.04	14.04	
Dissolved solids	ppm	588	24%	Volatile SS ratio
Radius of pipe	cm	15.24	15.24	
Air temperature	F	61.02	61.02	
Wind speed	M/s	3.25	3.25	
pH	SU	7.79	7.79	
Wastewater temp	°F	68.7	68.7	
Elevation	ft	1250	1250	

Note: SU-standard unit

Since benzyl alcohol was not actually sampled and measured, its concentration was estimated from the concentration of phenol according to a proportionality between these two chemicals. The benzyl alcohol and phenol were assumed to follow the same distribution. The equation for calculation of benzyl alcohol by this method could be expressed as follows (Veenstra, et al., 2001):

$$C_{ba} = C_p \times (X_{ba}/X_p) \times (U_{ba}/U_p) \times (H_{ba}/H_p) \times (V_{pba}/V_{pp}) \times (D_{ba}/D_p) \quad (32)$$

where

C_{ba} is the concentration of benzyl alcohol,

C_p is the concentration of phenol,

X_{ba} , X_p is the composition of benzyl alcohol and phenol in water, respectively,

U_{ba} , U_p is the amount of benzyl alcohol and phenol used, respectively,

H_{ba} , H_p is the Henry's constant of benzyl alcohol and phenol, respectively,

V_{pba} , V_{pp} is the vapor pressure of benzyl alcohol and phenol, respectively, and

D_{ba} , D_p is the diffusivity coefficient of benzyl alcohol and phenol, respectively.

Whether the diffusivity of benzyl alcohol and phenol is considered or not, it depends on value of the last item on the right side of equation 32. If the diffusivity is considered, the value of the last item on the right side of equation 32 is 0.29289. If the diffusivity is not considered, the value equals 1 (Veenstra, et al., 2001). In equation 32, the estimated concentration of benzyl alcohol in the influent would be higher if diffusivity of benzyl alcohol and phenol was not considered. Then benzyl alcohol air emission rate would be higher as a result. This scenario can be considered a worse case and was the main approach used in this work. When diffusivity was not considered, the estimated influent concentration of benzyl alcohol is about 3.64 times that of phenol (Veenstra, et al, 2001).

4.3 Fitting Distributions

Distributions were developed for the individual compounds based on the analysis of wastewater constituents in the transfer pit at Tinker's IWTP in 1999 and 2000. Since

these chemicals' probability density curves have a strong tail shape, the Anderson-Darling method, which places more emphases on the tail, was used for data distribution fitting and the results are presented as follows:

1. Benzyl alcohol and phenol

Benzyl alcohol and phenol were assumed to follow the same distribution since the concentration of benzyl alcohol was estimated based on the concentration of phenol. Phenol data was best fitted to be a Pearson5 distribution. Pearson5 (α, β) distribution is defined by the shape factor α and the scale factor β . Its statistics are calculated as follow:

$$\text{Mean} = \beta/(\alpha-1) \quad (33)$$

$$\text{Variance} = \beta^2/(\alpha-1)^2(\alpha-2) \text{ if } \alpha > 2 \quad (34)$$

These calculations are the theoretical values of mean and variance when samples are continuous. The fitting figures are shown as follows:

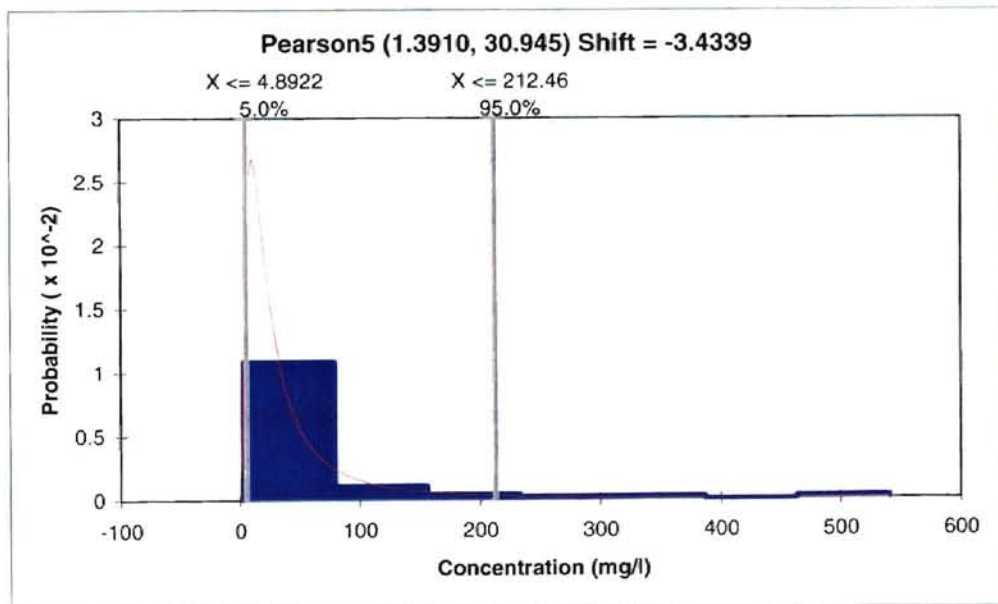


Figure 12. Fitted distribution of phenol

The P-P and Q-Q plots of phenol are shown as Figures 13 and 14.

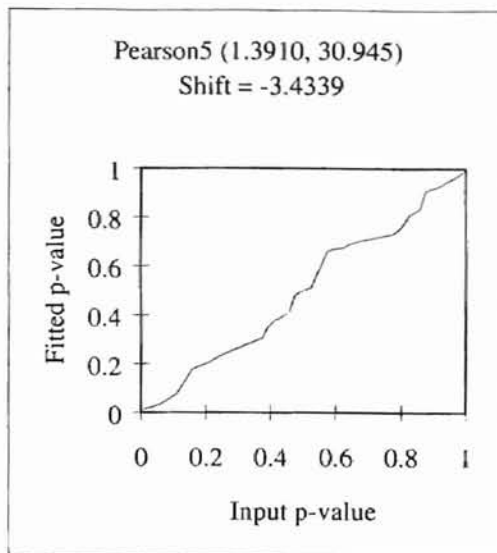


Figure 13. P-P plot of fitted distribution for phenol

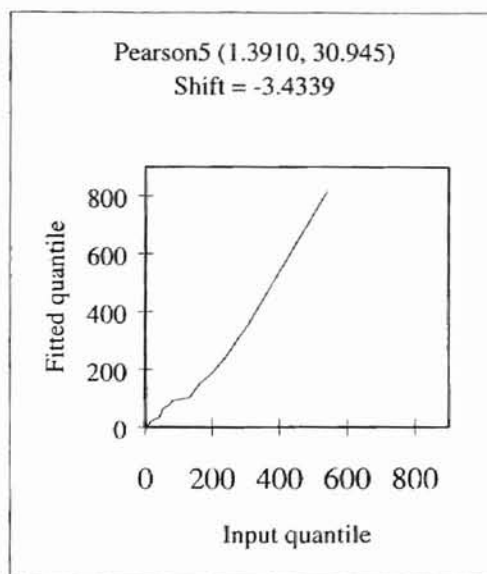


Figure 14. Q-Q plot of fitted distribution for phenol

Probability-Probability (P-P) graphs plot the distribution of the input data vs. the distribution of the result. If the fit is “good”, the plot will be nearly linear. Similarly, Quantile-Quantile (Q-Q) graphs plot the plot percentile values of the input distribution vs. percentile values of the result. If the fit is “good”, the plot will be nearly linear. The linearity of all the P-P and Q-Q plots in this thesis is the

best among all fitted distributions for each compound. The mean calculated with equation (33) is 79.14 mg/l. A summary of the statistics is presented as follows:

Table 3. Summary of statistics for phenol

	Fit	Input
Distribution	Pearson5 (1.3910, 30.945)	N/A
Shift	-3.434	N/A
a	1.391	N/A
b	30.945	N/A
Left X	4.892	4.892
Left P	5.00%	6.67%
Right X	212.457	212.457
Right P	95.00%	95.00%
Diff. X	207.565	207.565
Diff. P	90.00%	88.33%
Minimum	-3.434	2.5
Maximum	Infinity	540
Mean	75.711	55.408
Mode	9.508	15.000 [est]
Median	25.339	25.5
Std. Deviation	Infinity	87.265
Variance	Infinity	7488.25
Skewness	6.240 [est]	3.608
Kurtosis	48.650 [est]	18.239

Note: [est] is the abbreviation of estimate. This note is applicable to all of the tables in this thesis.

The mean of 79.14 mg/l calculated from equation (33) stands for the theoretical value of the Pearson5 distribution with certain α and β values when samples were continuous, while the mean of 75.711 mg/l from Table 3 was obtained from actual data being fitted. Using different test methods, i.e., Chi-Square, Anderson-Darling (A-D) and Kolmogorov-Smirnov (K-S), the fitting will present different statistical results. Table 4 presents different statistics of different test method, i.e. test value, P value, critical value at 0.05 significance level, number of bins and data points. For each distribution fitted, a similar table will be produced.

Table 4. Comparisons of test methods for phenol

	Chi-Sq	A-D	K-S
Test Value	15.6	0.4153	0.1099
P Value	0.0485	N/A	N/A
Critical Value	15.5073	N/A	N/A
# Bins	9	N/A	N/A
Data points	60	60	60

2. Acetone

Acetone data was best fitted to a Pearson5 distribution. The fitting figures are presented as follows:

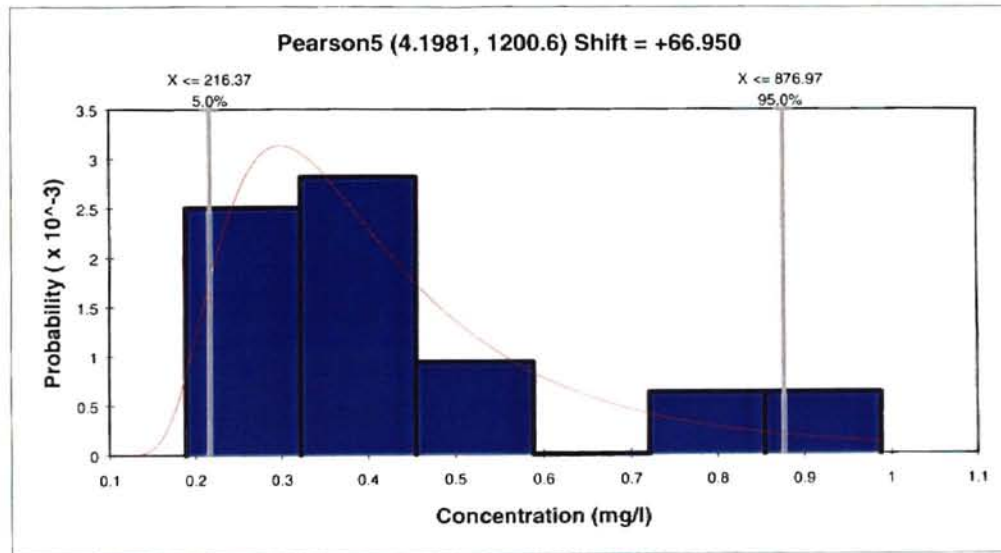


Figure 15. Fitted distribution of acetone

The P-P and Q-Q plots of acetone are shown in Figure 16 and Figure 17.

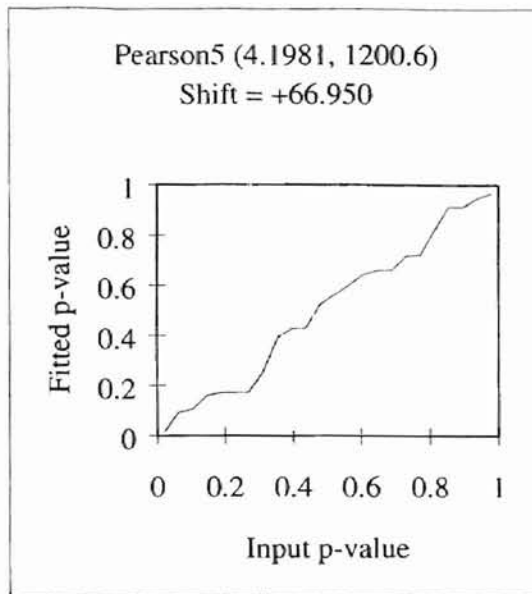


Figure 16. P-P plot of fitted distribution for acetone

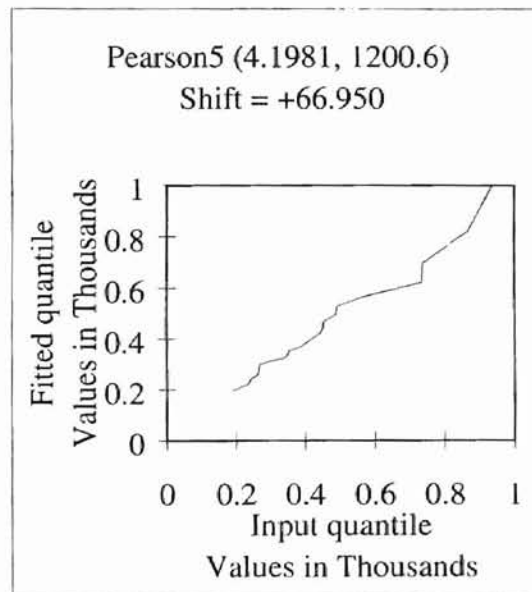


Figure 17. Q-Q plot of fitted distribution for acetone

According to equations (33) and (34), the mean and variance are $375.41 \mu\text{g/l}$ and 64118.8 , respectively. A summary of the statistics is presented as follows:

Table 5. Summary of fitting statistics of acetone

	Fit	Input
Distribution	Pearson5 (4.1981, 1200.6)	N/A
Shift	66.950	N/A
A	4.198	N/A
B	1200.594	N/A
Left X	216.374	216.374
Left P	5.00%	4.17%
Right X	876.970	876.970
Right P	95.00%	95.83%
Diff. X	660.596	660.596
Diff. P	90.00%	91.67%
Minimum	66.95	189
Maximum	Infinity	988
Mean	442.36	437.29
Mode	297.92	267.00 [est]
Median	377.19	395
Std. Deviation	253.22	208.11
Variance	64117.9	41504.29
Skewness	2.371 [est]	1.205
Kurtosis	10.962 [est]	3.690

Table 6 lists the different statistics of different test methods.

Table 6. Comparisons of test methods for acetone

	Chi-Sq	A-D	K-S
Test Value	2.6667	0.2485	0.1173
P Value	0.6151	N/A	N/A
C.Val @ 0.05	9.4877	N/A	N/A
# Bins	5	N/A	N/A
Data points	23	23	23

3. Methylene chloride

Methylene chloride was best fitted to be a Pearson5 distribution. The fitting figures are shown as follows:

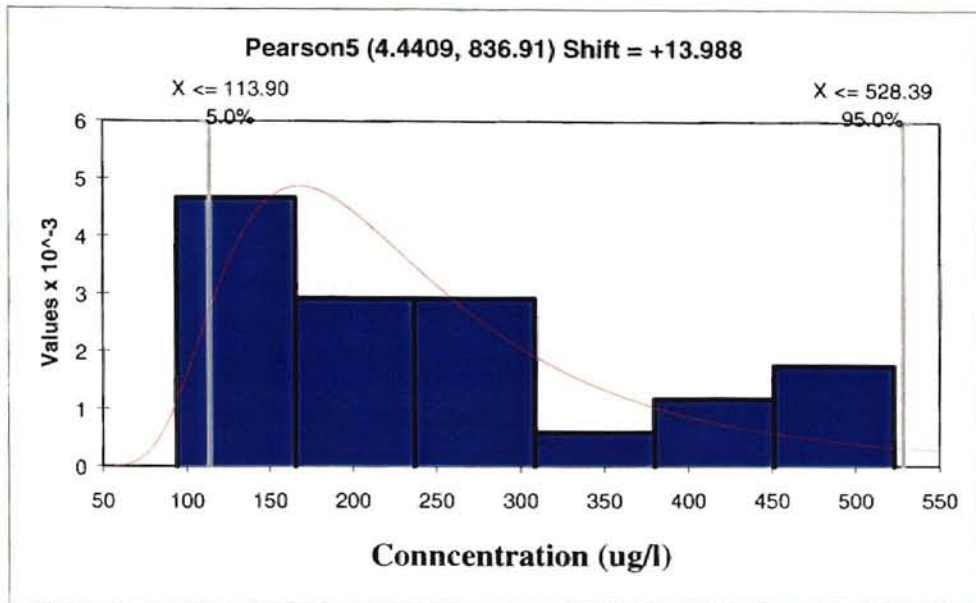


Figure 18. Fitted distribution of methylene chloride

The P-P plot and Q-Q plot are shown in Figures 19 and 20.

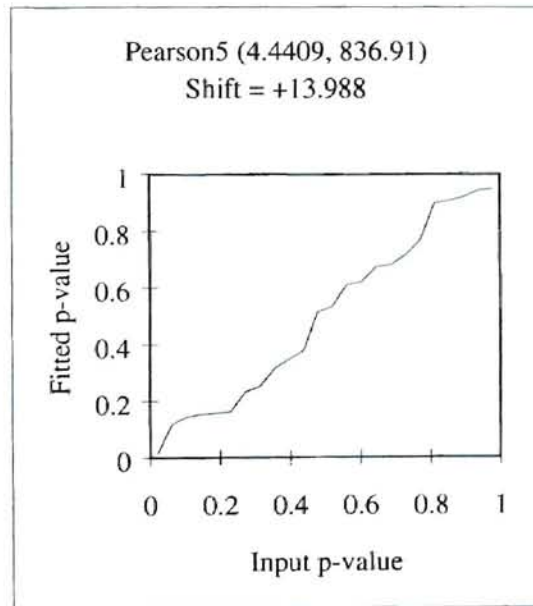


Figure 19. P-P plot of fitted distribution for methylene chloride

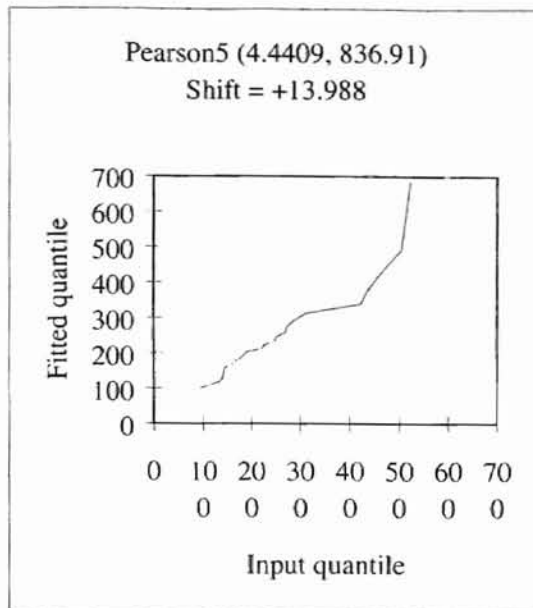


Figure 20. Q-Q plot of fitted distribution for methylene chloride

According to equations (33) and (34), the mean and variance are $243.224 \mu\text{g/l}$ and 24236.14 , respectively. A summary of the statistics is presented as follows:

Table 7. Summary of fitting statistics for methylene chloride

	Fit	Input
Distribution	Pearson5(4.4409, 836.91)	N/A
Shift	13.988	N/A
a	4.441	N/A
b	836.906	N/A
Left X	113.896	113.896
Left P	5.00%	4.17%
Right X	528.394	528.394
Right P	95.00%	100.00%
Diff. X	414.498	414.498
Diff. P	90.00%	95.83%
Minimum	13.988	94.2
Maximum	Infinity	523
Mean	257.21	253.84
Mode	167.8	143.00 [est]
Median	217.49	223.5
Std. Deviation	155.68	126.13
Variance	24234.87	15245.39
Skewness	2.270 [est]	0.891
Kurtosis	10.318[est]	2.592

Table 8 lists the different statistics of different test methods.

Table 8. Comparisons of test methods for methylene chloride

	Chi-Sq	A-D	K-S
Test Value	2.25	0.3379	0.1065
P Value	0.6899	N/A	N/A
C.Val @ 0.05	9.4877	N/A	N/A
# Bins	5	N/A	N/A
Data points	24	24	24

4. 2-Butanone

2-butanone, however, was best fitted by an Exponential distribution. For the Exponential distribution [Expon (β)], β is the only parameter and refers to mean.

Then

$$\text{Mean} = \beta \quad (35)$$

$$\text{Variance} = \beta^2 \quad (36)$$

The fitting plots are presented in the following figures.

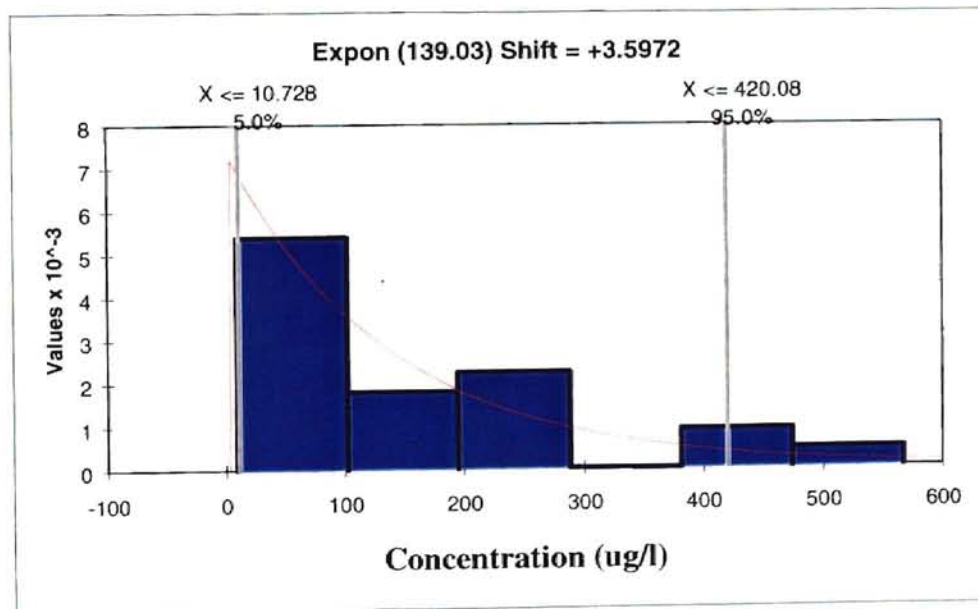


Figure 21. Fitted distribution of 2-butanone

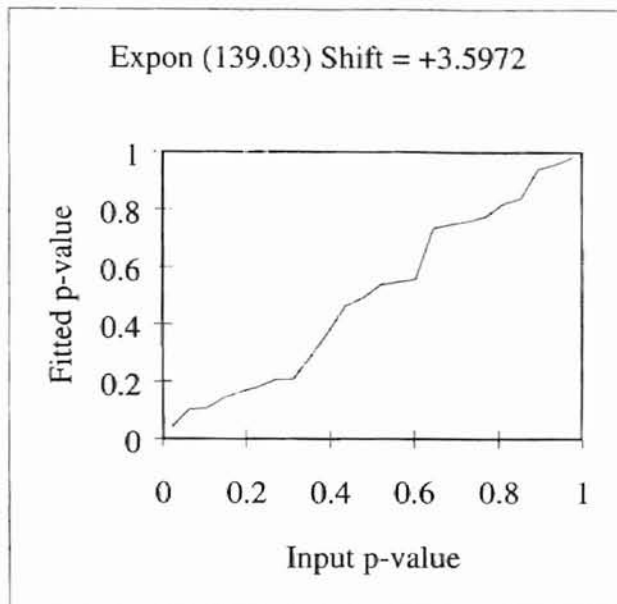


Figure 22. P-P plot of fitted distribution for 2-butanone

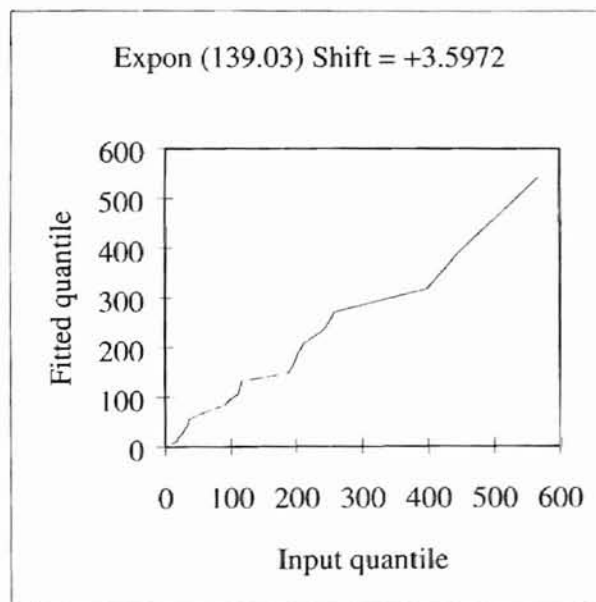


Figure 23. Q-Q plot of fitted distribution for 2-butanone

In term of equations 35 and 36, the fitted mean and variance for 2-butanone are 139.03 $\mu\text{g/l}$ and 19329.34, respectively. A summary of the statistics is presented as follows:

Table 9. Summary of fitting statistics for 2-butanone

	Fit	Input
Distribution	Expon(139.03)	N/A
Shift	3.597	N/A
B	139.026	N/A
Left X	10.728	10.728
Left P	5.00%	4.17%
Right X	420.083	420.083
Right P	95.00%	91.67%
Diff. X	409.354	409.354
Diff. P	90.00%	87.50%
Minimum	3.597	9.39
Maximum	Infinity	567
Mean	142.62	148.42
Mode	3.5972	114.00 [est]
Median	99.963	104.45
Std. Deviation	139.03	147.94
Variance	19328.3	20974.11
Skewness	2	1.378
Kurtosis	9	4.215

Table10 lists the different statistics of different test methods.

Table 10. Comparisons of test methods for 2-butanone

	Chi-Sq	A-D	K-S
Test Value	0.5833	0.3135	0.1243
P Value	0.9649	> 0.25	> 0.25
C.Val @ 0.05	9.4877	0.8572	0.2128
# Bins	5	N/A	N/A
data points	23	23	23

5. Flow rate

Flow rate was best fitted to a Normal distribution. A normal distribution has two parameters; one is the mean (μ), the other is standard deviation (σ). The fitting plots are shown in the following figures.

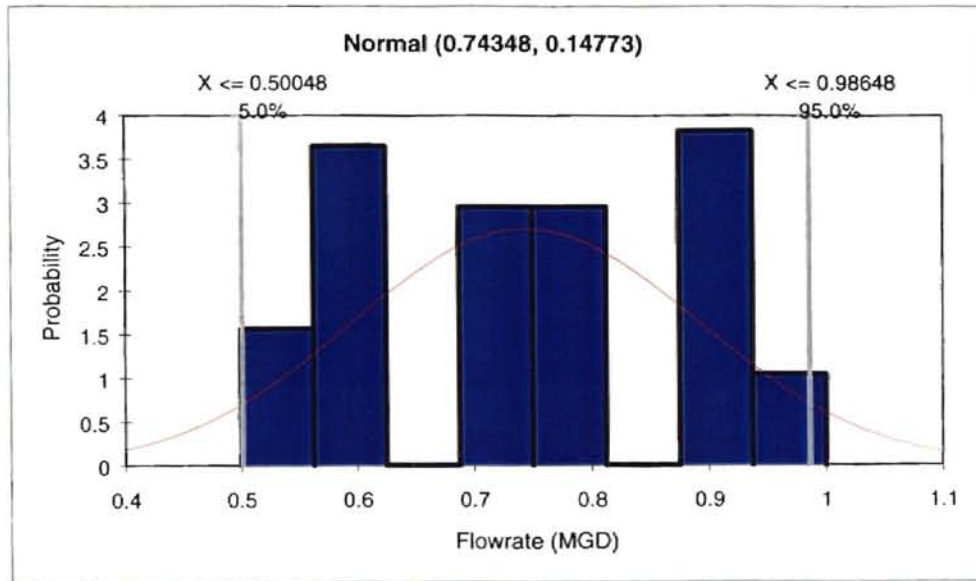


Figure 24. Fitted distribution of flow rate
(Note: MGD-million gallon per day)

The P-P and Q-Q plots of flow rate are shown as Figure 25 and Figure 26.

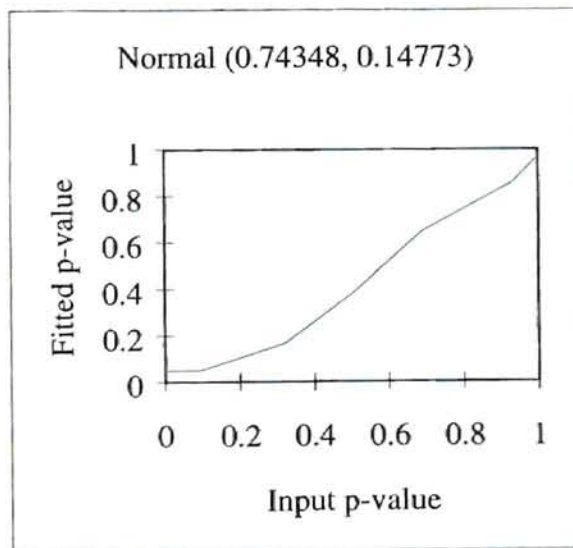


Figure 25. P-P plot of fitted distribution for flow rate

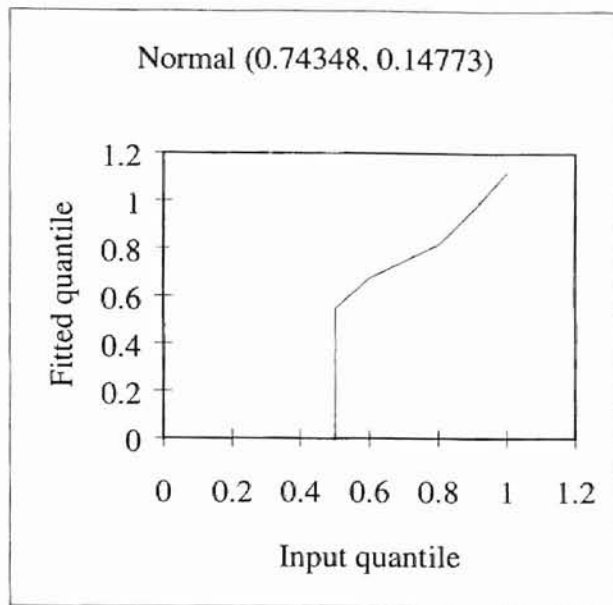


Figure 26. Q-Q plot of fitted distribution for flow rate

The fitted mean and variance are 0.743 million gallons per day (MGD) and 0.148, respectively. A summary of statistics is presented in Table 11.

Table 11. Summary of fitting statistics for flow rate

	Fit	Input
Distribution	Normal (0.74348, 0.14773)	N/A
m	0.743	N/A
s	0.148	N/A
Left X	0.500	0.500
Left P	5.00%	9.78%
Right X	0.986	0.986
Right P	95.00%	93.48%
Diff. X	0.486	0.486
Diff. P	90.00%	83.70%
Minimum	-Infinity	0.5
Maximum	+Infinity	1
Mean	0.743	0.743
Mode	0.743	0.900 [est]
Median	0.743	0.7
Std. Deviation	0.148	0.148
Variance	0.022	0.022
Skewness	0	-0.0158
Kurtosis	3	1.865

Table 12 lists the different statistics of different test methods.

Table 12. Comparisons of test methods for flow rate

	Chi-Sq	A-D	K-S
Test Value	101.696	2.76	0.160
P Value	0	< 0.005	< 0.01
C.Val @ 0.05	18.307	0.746	0.093
# Bins	11	N/A	N/A
data points	92	92	92

As an alternative to using concentration, the mass of each contaminant in the influent was used to generate the best-fitted distribution. The results showed that the same distribution was arrived at for each contaminant using either mass or concentration. This result is detailed in the discussion section that follows.

4.4 Bootstrapping simulation

To confirm these fitting distributions, the Bootstrapping simulation was also applied. Samples were bootstrapped from the actual field data (historic concentration data from Tinker's IWTP) with replacement, and the mean and standard deviation of each bootstrapped sample were calculated and then the cumulative distribution function was plotted for all bootstrapped samples. A bootstrapping sample consisted of 20 samples taken from field data. In total, 100 bootstrapping samples were developed. The results are presented in the following section.

The bootstrapping results for flow rate are presented in Figure 27. The mean of each bootstrapping sample was calculated. Figure 27 shows the cumulative distribution of the means of 100 bootstrapping samples for flow rate.

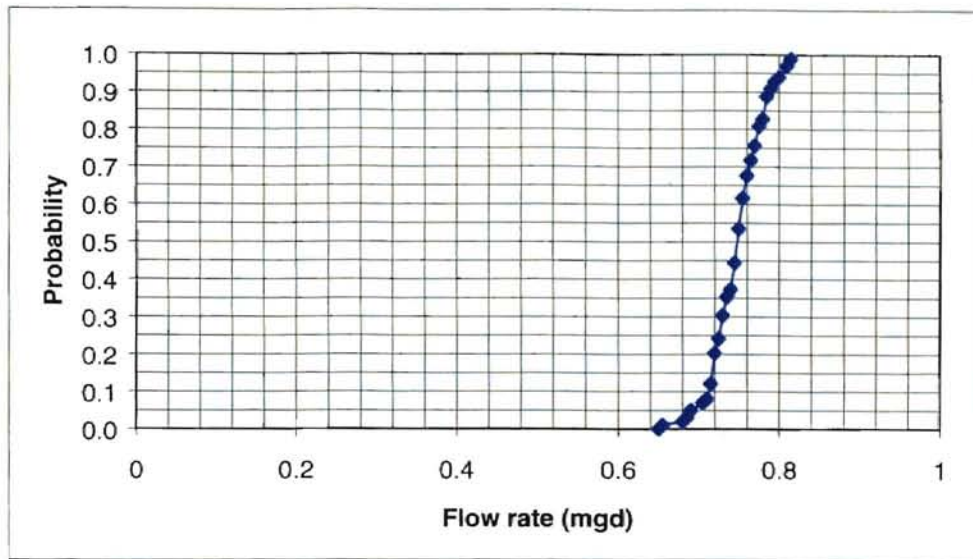


Figure 27. Cumulative distribution of flow rate with bootstrapping

The standard deviation of each bootstrapping sample was calculated and the cumulative distribution of the standard deviation is presented in Figure 28.

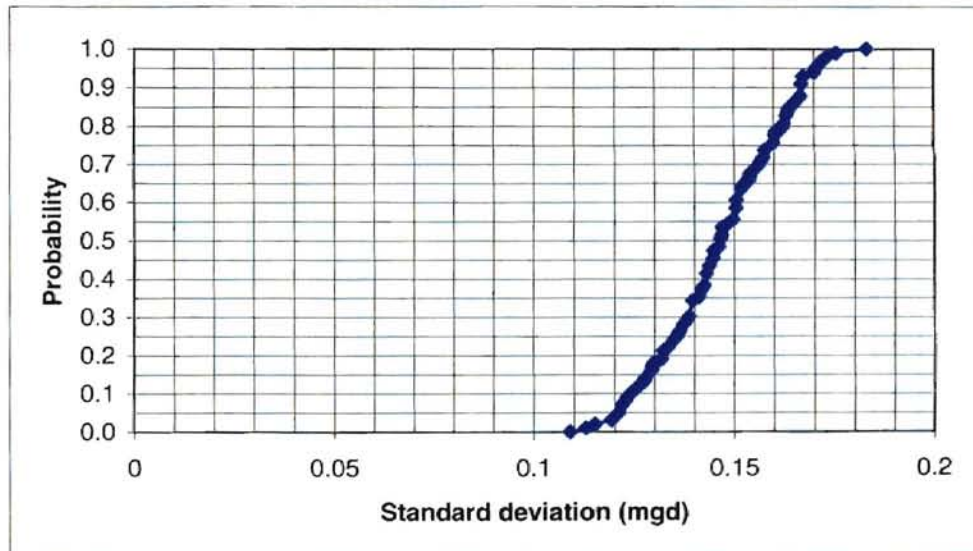


Figure 28. Cumulative distribution of the standard deviation of flow rate with bootstrapping

The bootstrapping results for acetone are presented in Figure 29. The mean of each bootstrapping sample was calculated. Figure 29 shows the cumulative distribution of means of all bootstrapping samples for acetone. In Figure 30, the

standard deviation of each bootstrapping sample was calculated and the cumulative distribution of the standard deviation is presented.

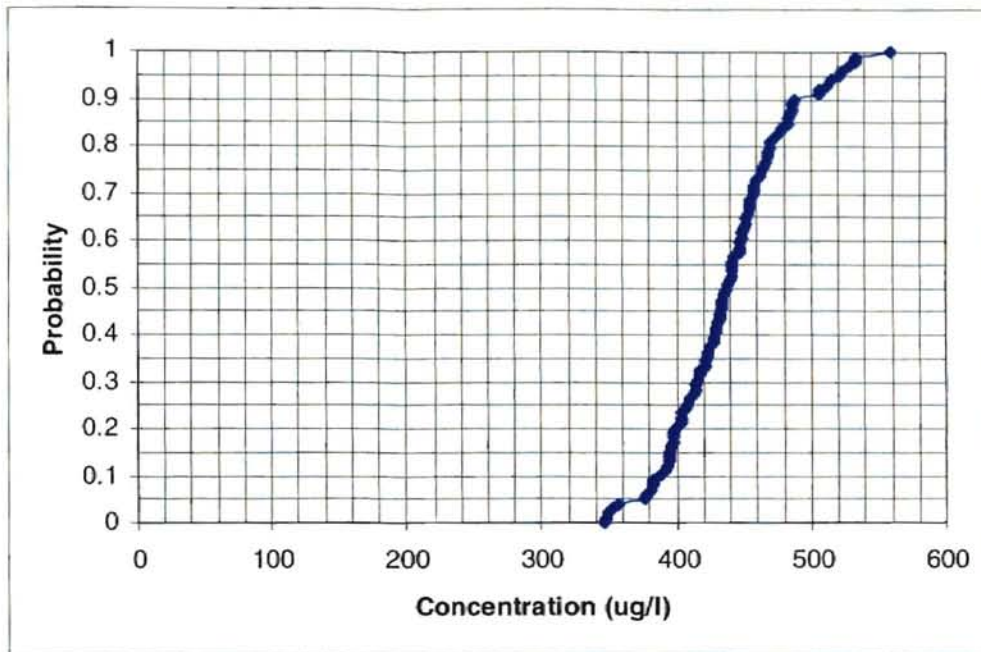


Figure 29. Cumulative distribution of acetone with bootstrapping

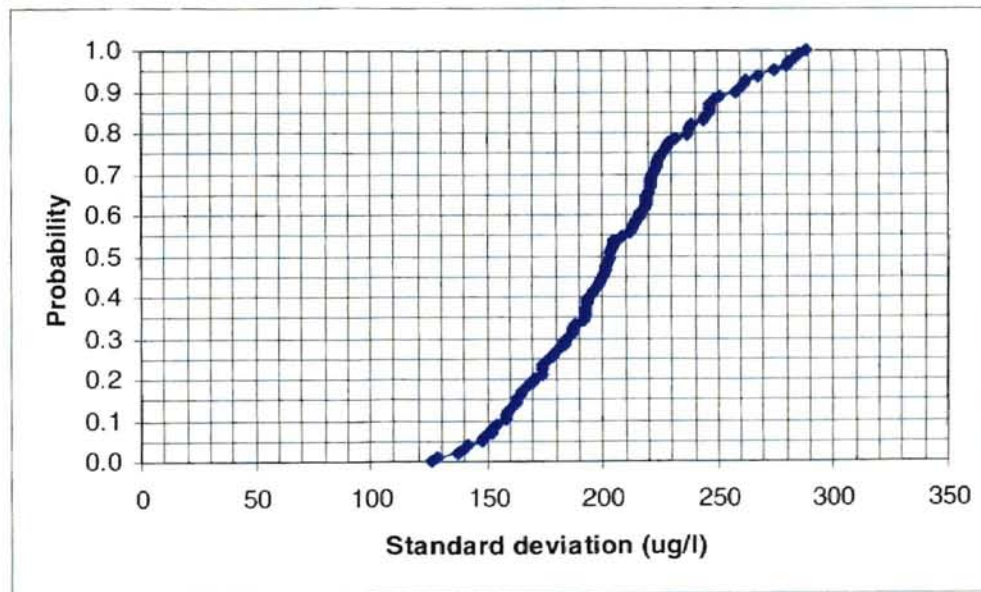


Figure 30. Cumulative distribution of standard deviation of acetone with bootstrapping

The bootstrapping results for methylene chloride are presented in Figure 31. The mean of each bootstrapping sample was calculated. Figure 31 shows the cumulative distribution of means of all bootstrapping samples of methylene chloride.

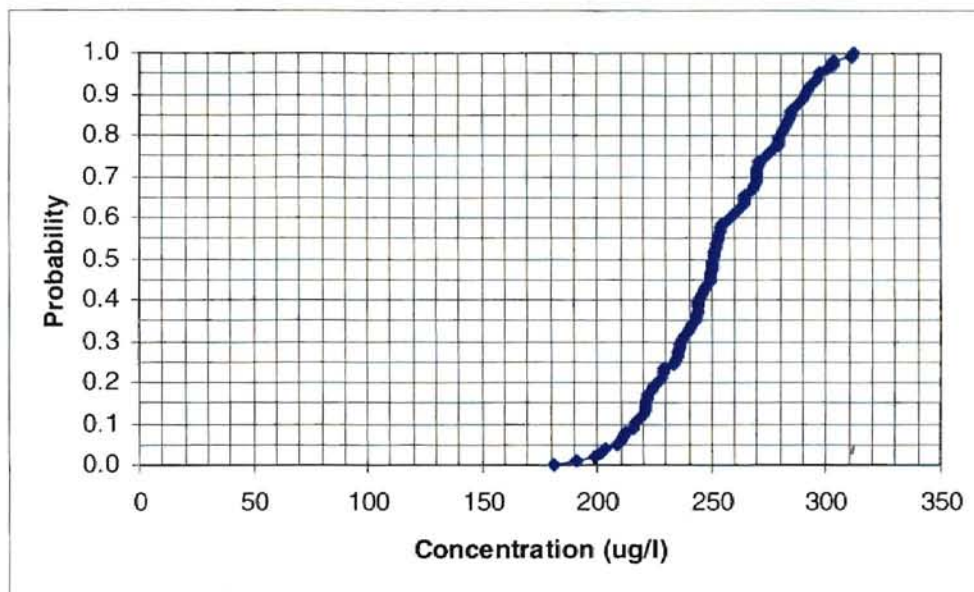


Figure 31. Cumulative distribution of methylene chloride with bootstrapping

The standard deviation of each bootstrapping sample was calculated and the cumulative distribution of the standard deviation is presented in Figure 32.

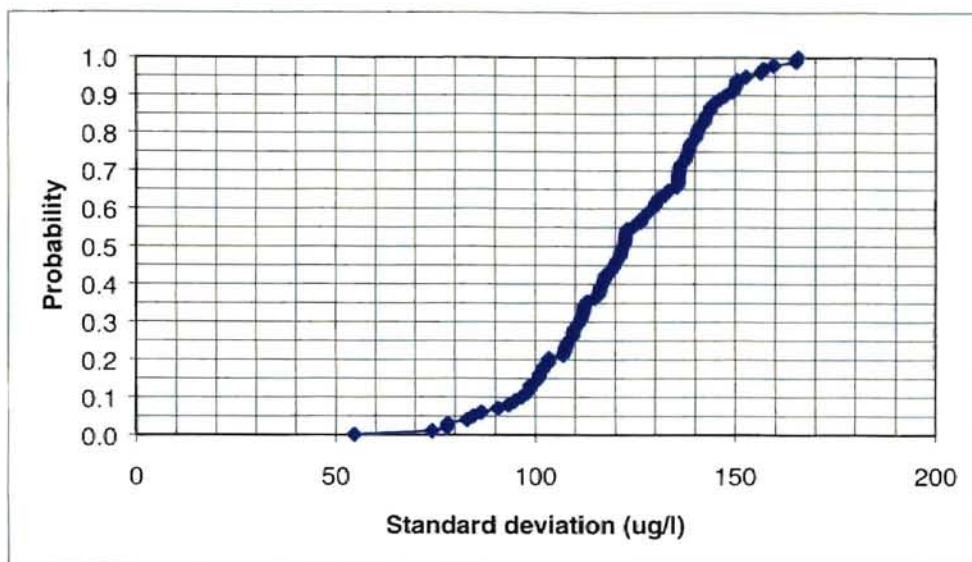


Figure 32. Cumulative distribution of standard deviation of methylene chloride with bootstrapping

The Bootstrapping results for 2-butanone are presented in Figure 33. The mean of each bootstrapping sample was calculated. Figure 33 showed the cumulative distribution of means of all bootstrapping samples of 2-butanone.

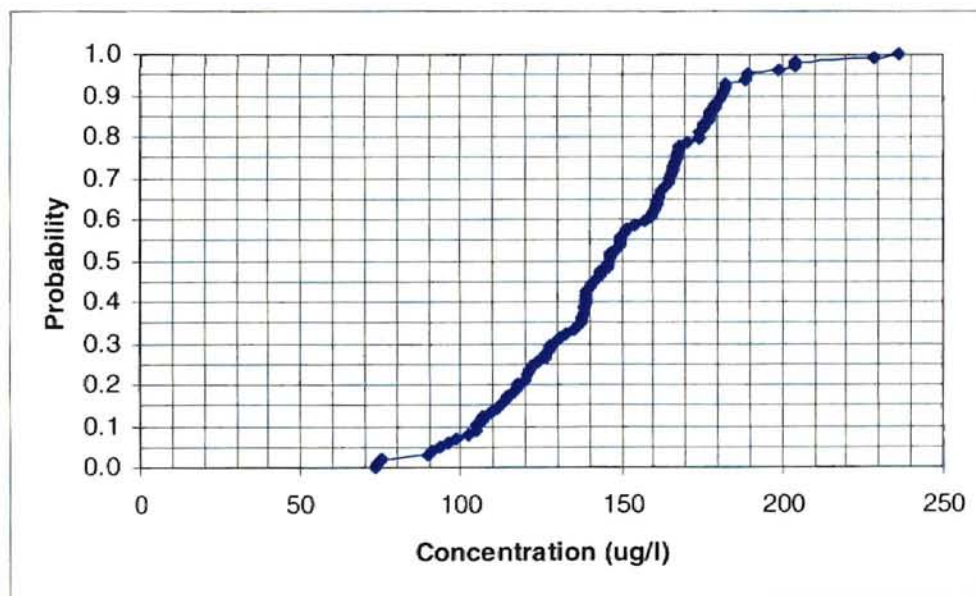


Figure 33. Cumulative distribution of 2-butanone with bootstrapping

The standard deviation of each bootstrapping sample was calculated and the cumulative distribution of the standard deviation is plotted in Figure 34.

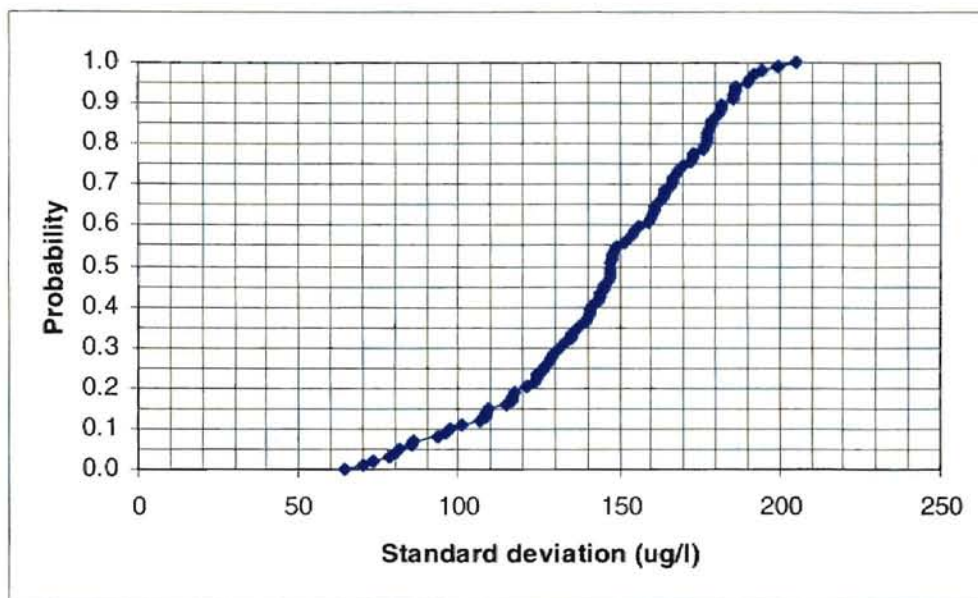


Figure 34. Cumulative distribution of standard deviation of 2-butanone with bootstrapping

The bootstrapping results for phenol are presented in Figure 35. The mean of each bootstrapping sample was determined.

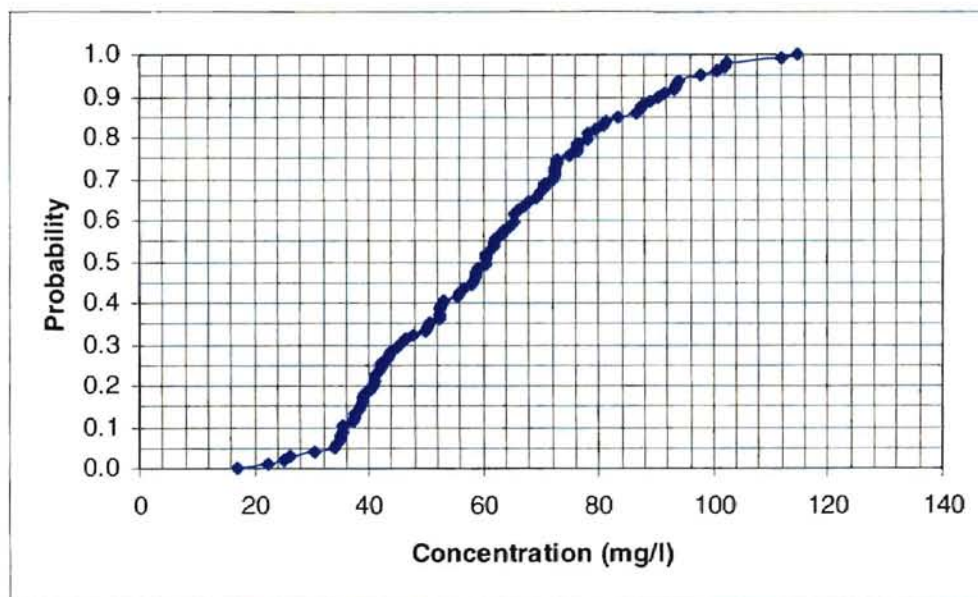


Figure 35. Cumulative distribution of phenol with bootstrapping.

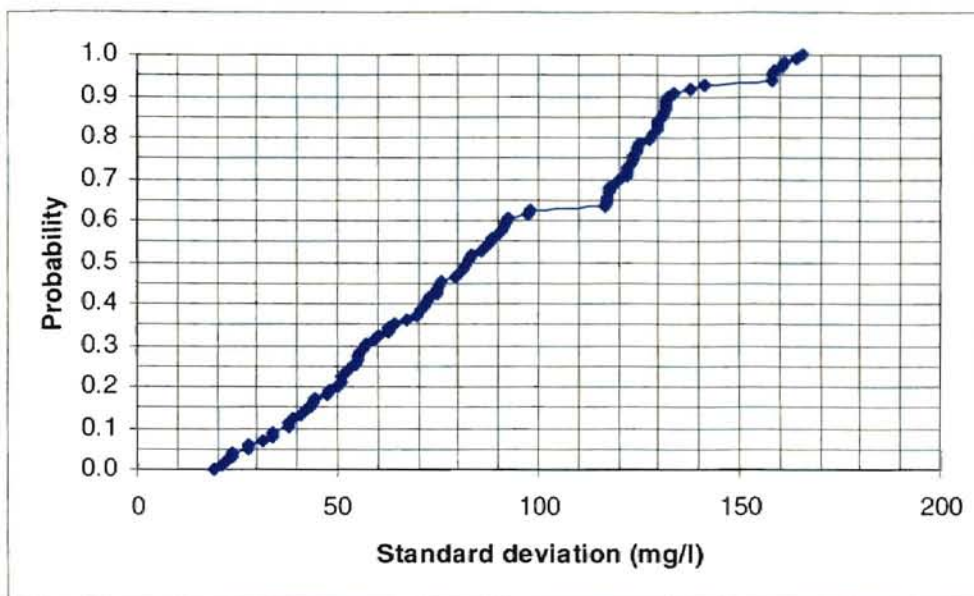


Figure 36. Cumulative distribution of standard deviation of phenol with bootstrapping.

The standard deviation of each bootstrapping sample was calculated and the cumulative distribution of the standard deviation is presented in Figure 36.

The results of fitting distributions and bootstrapping simulation are presented in the tables below (Tables 13 and 14):

Table 13. Comparisons of fitted and bootstrapped means

Parameters	Fitted distribution		Bootstrapping Mean		
	Distributions	Mean	5%	50%	95%
Phenol/Benzyl Alcohol	PEARSON5 (α, β)	79.14	34.02	60.58	97.8
Acetone	PEARSON5 (α, β)	375.41	376.04	438.75	521.35
Methylene Chloride	PEARSON5 (α, β)	243.22	208.97	250.82	297.35
2-Butanone	EXPON (β)	139.03	93.14	146.53	189.50
Flow rate	NORMAL (μ, σ)	0.74	0.69	0.75	0.8

Table 14. Comparisons of fitted and bootstrapped standard deviation

Parameters	Fitted distribution		Bootstrapping standard deviation		
	Distributions	SD	5%	50%	95%
Phenol/Benzyl Alcohol	PEARSON5 (α, β)	N/A	27.7	82.7	157.9
Acetone	PEARSON5 (α, β)	253.2	147.2	203.4	274.6
Methylene Chloride	PEARSON5 (α, β)	155.7	84.5	122.4	152.8
2-Butanone	EXPON (β)	139.03	81.6	147.2	189.7
Flow rate	NORMAL (μ, σ)	0.15	0.12	0.15	0.17

Note: the standard deviation of Pearson5 distribution for phenol is not available because α is less than 2 in equation 34.

In summary, the distributions of all the chemicals and the flow rate are listed in Table 15.

Table 15. Summary of fitted distributions for compounds and flow rate

Parameters	Fitted distribution
Phenol	PEARSON5 (1.3910, 30.945)
Benzyl Alcohol	PEARSON5 (1.3910, 30.945)
Methylene Chloride	PEARSON5 (4.4409, 836.91)
Acetone	PEARSON5 (4.1981, 1200.6)
2-Butanone	EXPON (139.03)
Flow rate	NORMAL (0.74348, 0.14773)

Note: Benzyl alcohol follows the same distribution as phenol, but the values are 3.64 times more.

4.5 Backsolver study

Since acetone, methylene chloride, and 2-butanone were sampled in the transfer pit, which is almost in the middle of the treatment plant, these values are not representative of the influent concentrations to the plant. Therefore, the backsolver routine inside TOXCHEM+V3 was used to project the influent concentrations of methylene chloride, 2-butanone, and acetone. This method was applied and backsolving was done during phase 1 of the Tinker project (Veenstra, et al, 2001). The influent concentrations of acetone, methylene chloride and 2-butanone were backsolved again during this work. Sampling of

the transfer pit was performed during October and November in 1999. For phenol, the concentration was obtained based on samples taken from D1/D2, which are mixing basins following the primary clarifier. These phenol concentrations were regarded as the influent concentration. The backsolver showed the concentrations in the influent were proportional to those in the transfer pit. The results are shown in Figure 37. The fitted distributions were determined based on the field data in the transfer pit. The influent concentrations have a linear relationship with the concentrations in the transfer pit. As a result the compounds' distributions in both locations are the same because the concentrations in both locations are simply related linearly. Random numbers generated from the fitted distribution stood for the random concentration of compound in the transfer pit. But what was needed is the influent concentrations of compounds. Therefore, random number sets for the influent concentrations of compounds were produced by multiplying generated random numbers by the slope of each compound's curve in Figure 37. These random number sets were used for the simulations.

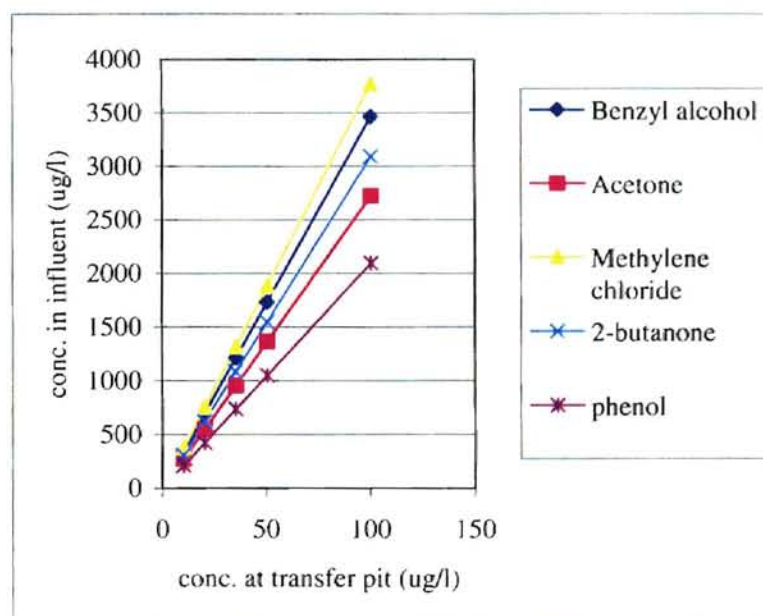


Figure 37. Linearity of backsolver for chemicals of concern

Table 16 presents the details of the backsolving studies and the slope of each compound. The slope of each compound will be used for estimating the influent concentrations.

Table 16. Backsolving studies of all the compounds

Chemicals	Concentration (µg/l)					Slope
	10	20	35	50	100	
Benzyl alcohol	346.1	692.13	1211.31	1730.32	3460.96	34.61
Acetone	272.03	544.11	952.19	1360.14	2720.32	27.20
Methylene chloride	376.46	752.98	1317.67	1882.35	3764.28	37.64
2-butanone	308.63	617.23	1080.19	1543.12	3086.28	30.86

Note: In the tabular area of concentration, the top numerical row stands for the concentrations of compounds in the transfer pit. The rest are the backsolved influent concentrations of compounds.

Then, the influent concentration for each compound was calculated using the following equation:

$$C_{in} = C_{ip} \times \text{Slope} \quad (37)$$

where:

C_{in} = concentration in the influent

C_{ip} = concentration in the transfer pit.

4.6 Simulation adequacy study

The adequacy of the number of simulations was studied to determine whether more simulations are needed. The results are presented in the following figures (Figures 38, 39, 40, 41 and 42). Due to the different scales of the y-axis, the adequacy studies are presented in Figures 38 and 39 for TOXCHEM+V3; the adequacy studies are presented in Figures 40, 41 and 42 for WATER9. These results showed that running 200

simulations was adequate, because the results began to converge at a constant value for each compound.

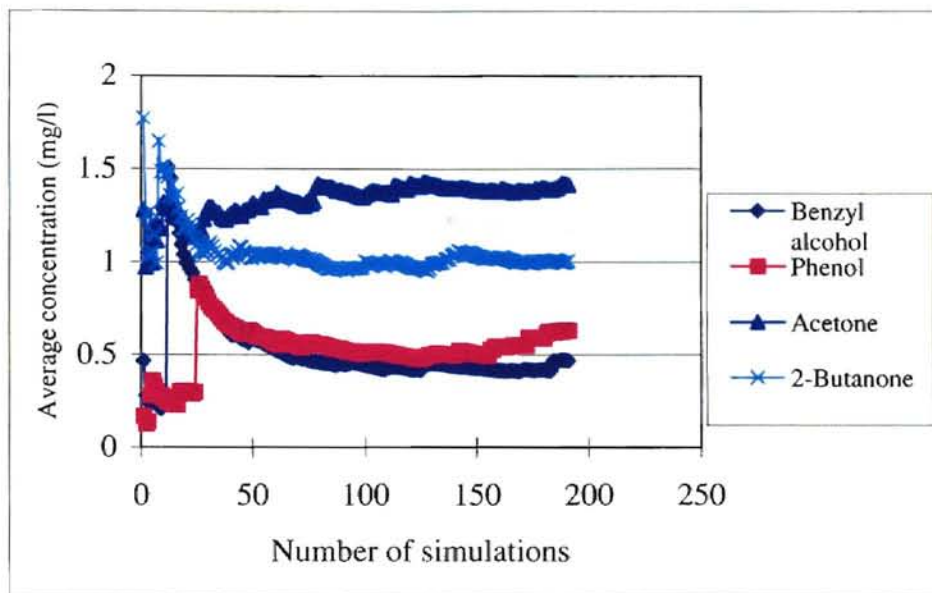


Figure 38. Adequacy of simulation using TOXCHEM+V3 for benzyl alcohol, phenol, acetone and 2-butanone.

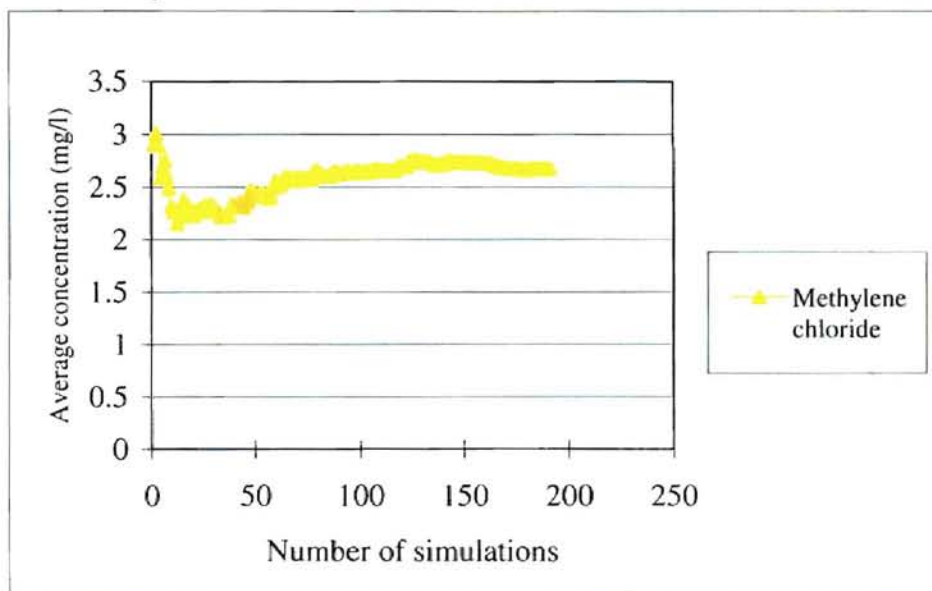


Figure 39. Adequacy of simulations using TOXCHEM+V3 for methylene chloride

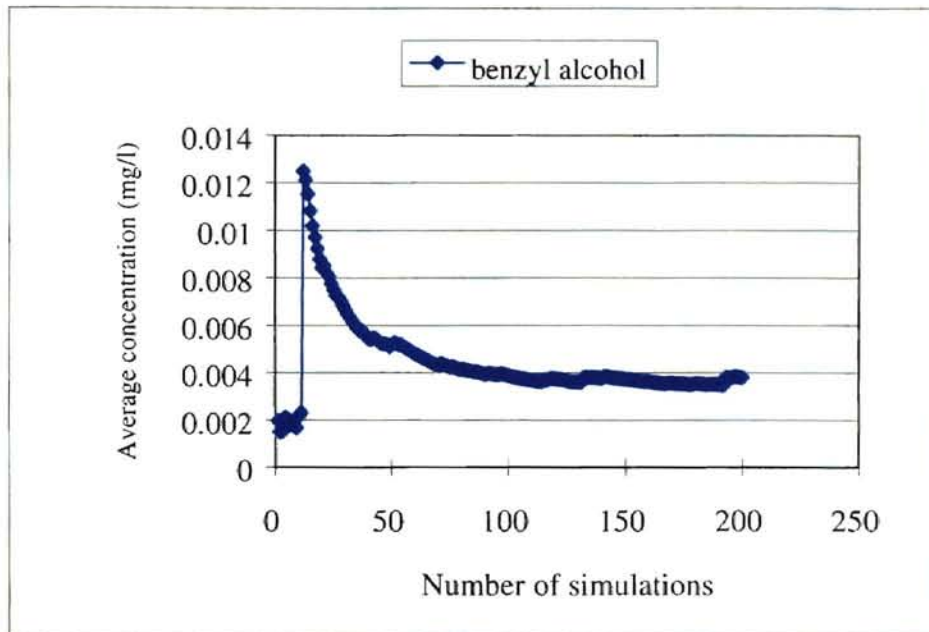


Figure 40. Adequacy of simulations using WATER9 for benzyl alcohol

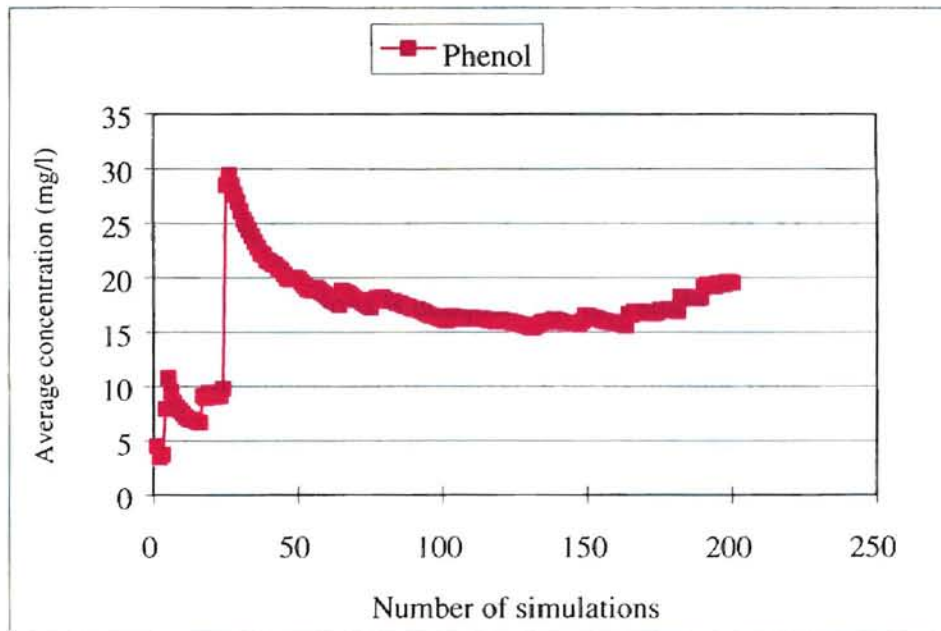


Figure 41. Adequacy of simulations using WATER9 for phenol

The curve in Figure 41 starts to tail up at the end is probably due to the variation of the average concentration of phenol substituted into the model.

However, it tends to flat again after 200 simulations. The tendency is clearer in Figure 45 where the standard deviation is used.

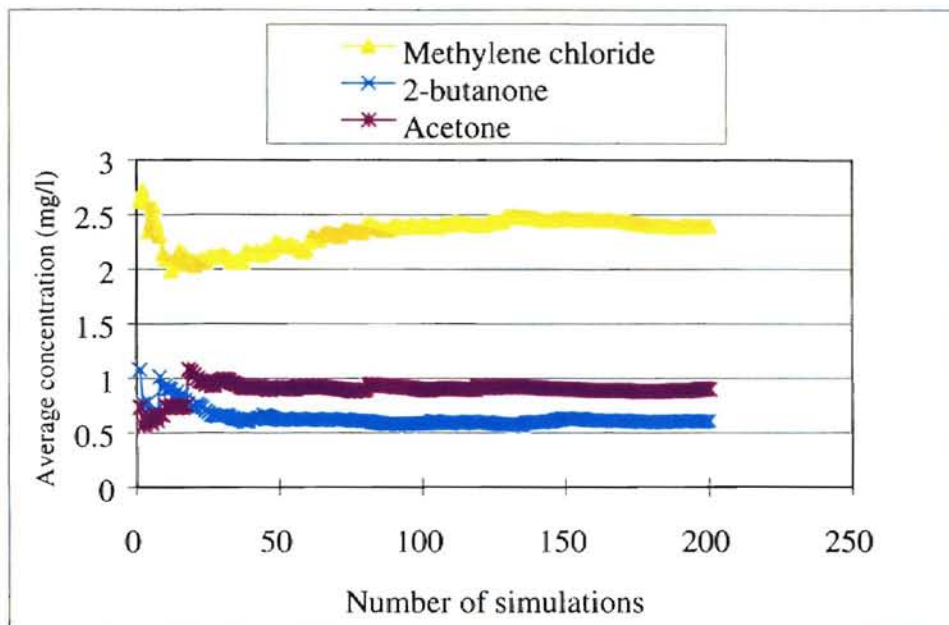


Figure 42. Adequacy of simulations using WATER9 for methylene chloride, 2-butanone and acetone

Simulation adequacy studies were also performed on the standard deviation of all the simulated results. These results are shown in Figures 43, 44 and 45. These results show that 200 simulations is adequate for this study because the standard deviation of these compounds start to converge on a constant value.

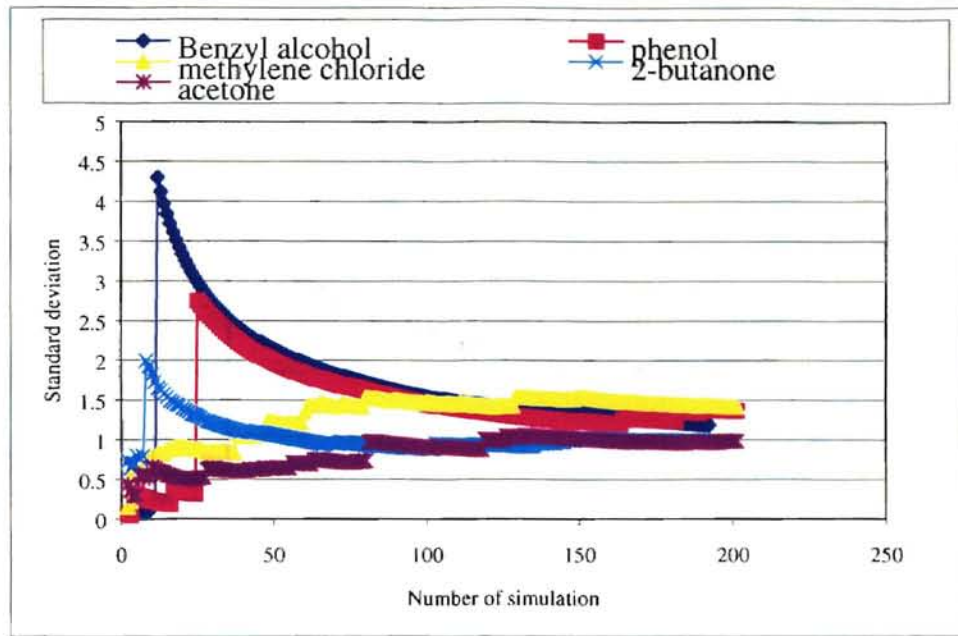


Figure 43. Adequacy of simulations using TOXCHEM+V3 with standard deviation

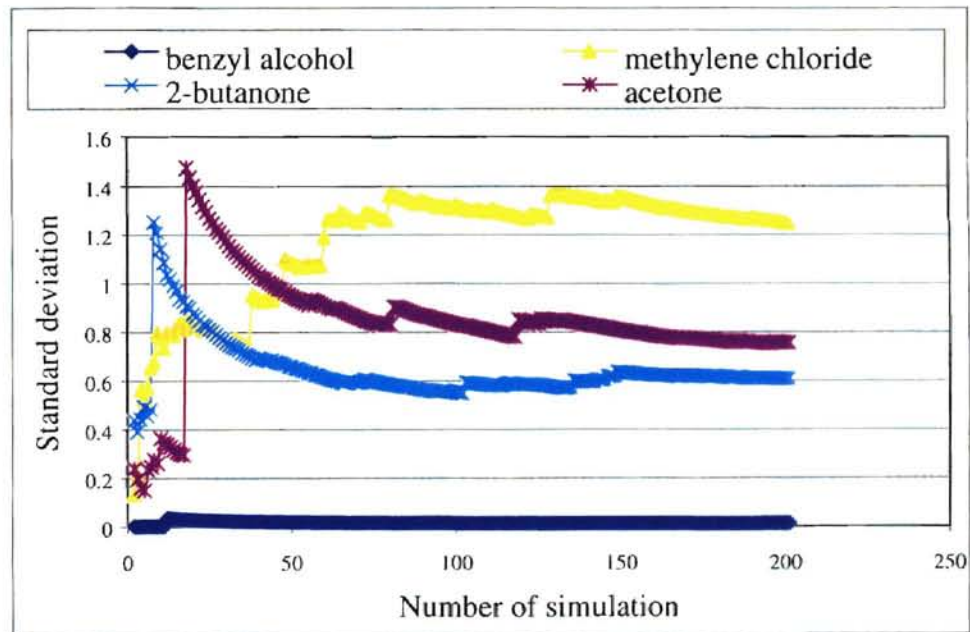


Figure 44. Adequacy of simulations using WATER9 with standard deviation

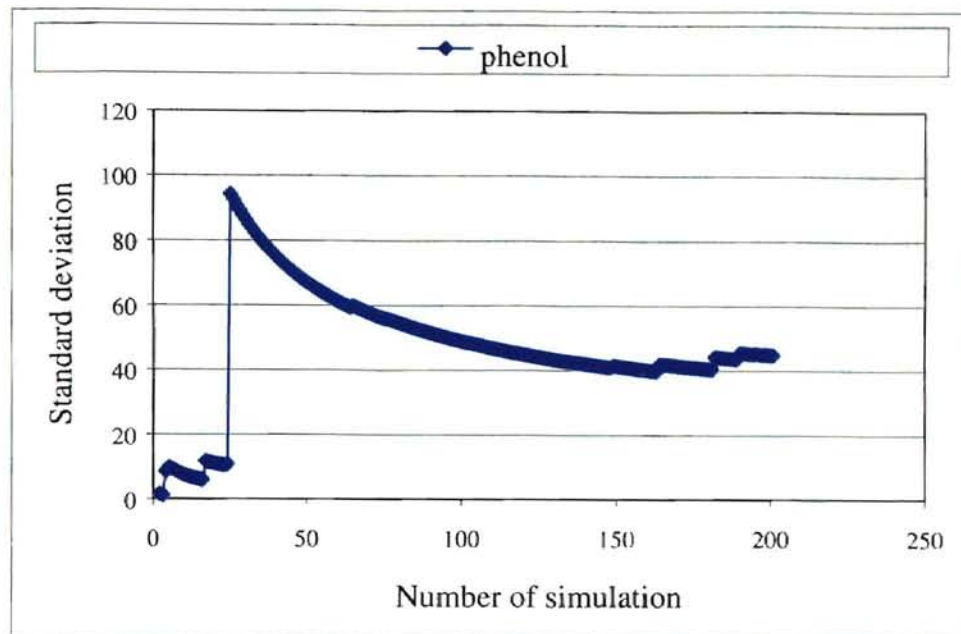


Figure 45. Adequacy of simulation using WATER9 with standard deviation for phenol

4.7 Model simulation results

Two hundred random number sets were generated from the fitted distributions. Each set included flow rate, as well as benzyl alcohol, phenol, methylene chloride, 2-butanone and acetone concentrations. The concentrations of these compounds were backsolved and then each random number set was substituted into TOXCHEM+V3 and WATER9 to serve as model input. The two models were then run. The pooled results from these simulations are called probabilistic results. In addition, the deterministic runnings of these models were also performed. The actual field data for flow rate from logs of record and the compounds concentrations from the transfer pit were also averaged and the averaged concentrations were backsolved. The backsolved concentrations were then substituted into the models and the models were run. Then, the deterministic results were obtained. Since the Henry's constants in both models were different, simulations using TOXCHEM+V3 were run four hundred times, two hundred times with the Henry's

constants in its library, the other two hundred times with the same Henry's constants as WATER9. TOXCHEM+V3 does not have a Henry's constant for benzyl alcohol in its library, the Henry's constant of 1.60E-5 for benzyl alcohol was derived from the Michigan Environmental Response Division website. These results are presented below.

- a. TOXCHEM+V3 simulation results with Henry's constants from its library (except benzyl alcohol)

Simulation results are presented in Figures 46, 47, 48, 49 and 50.

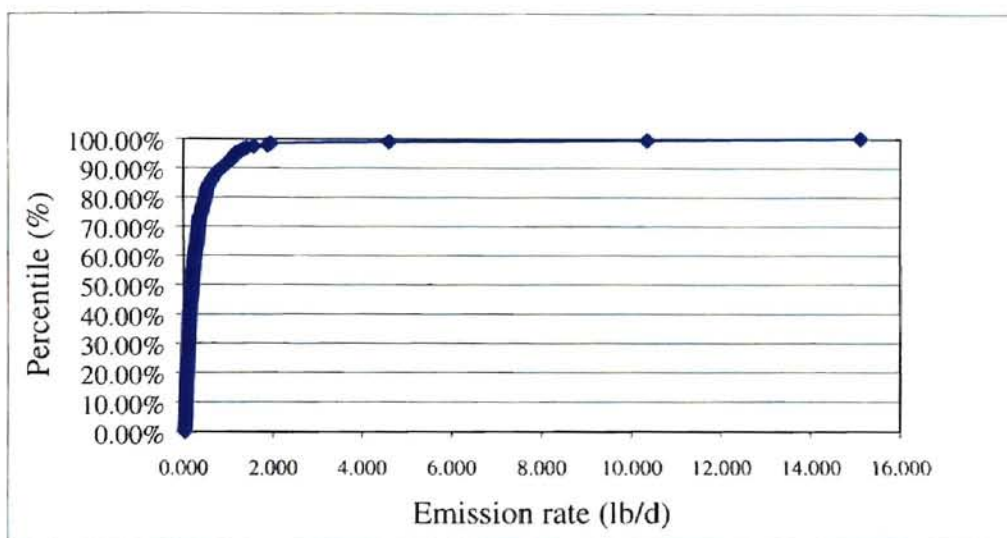


Figure 46. Simulation results of benzyl alcohol by using TOXCHEM+V3.

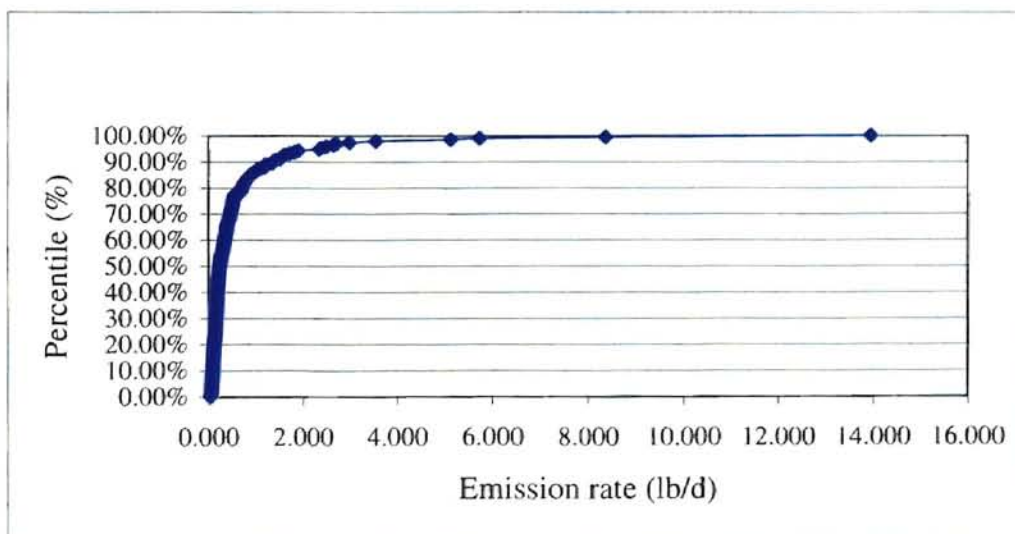


Figure 47. Simulation results of phenol by using TOXCHEM+V3.

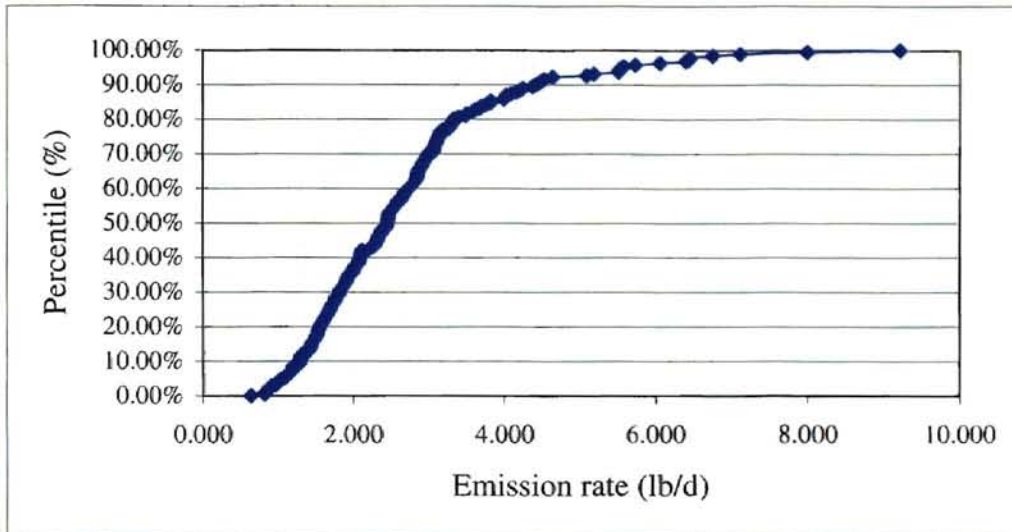


Figure 48. Simulation results of methylene chloride by using TOXCHEM+V3.

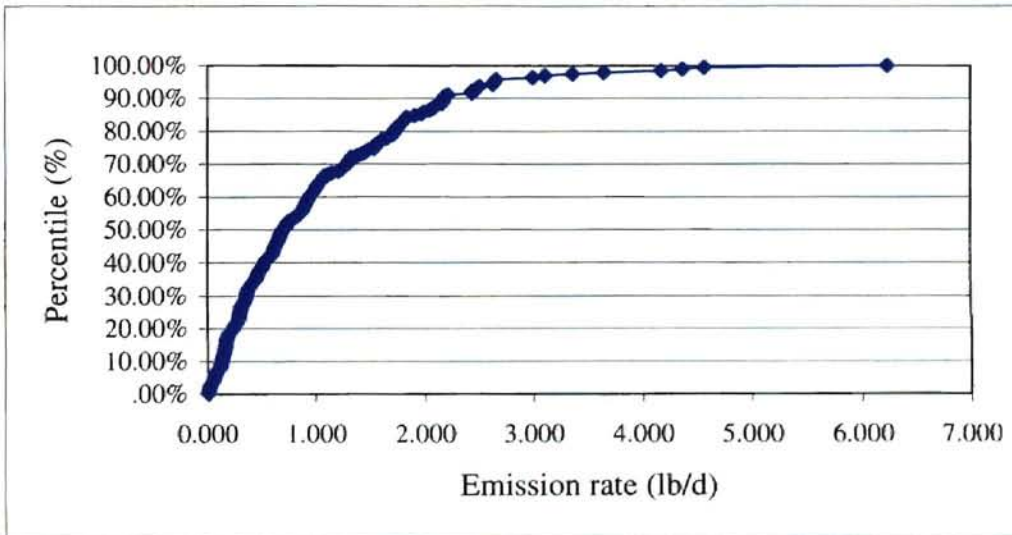


Figure 49. Simulation results of 2-butanone by using TOXCHEM+V3.

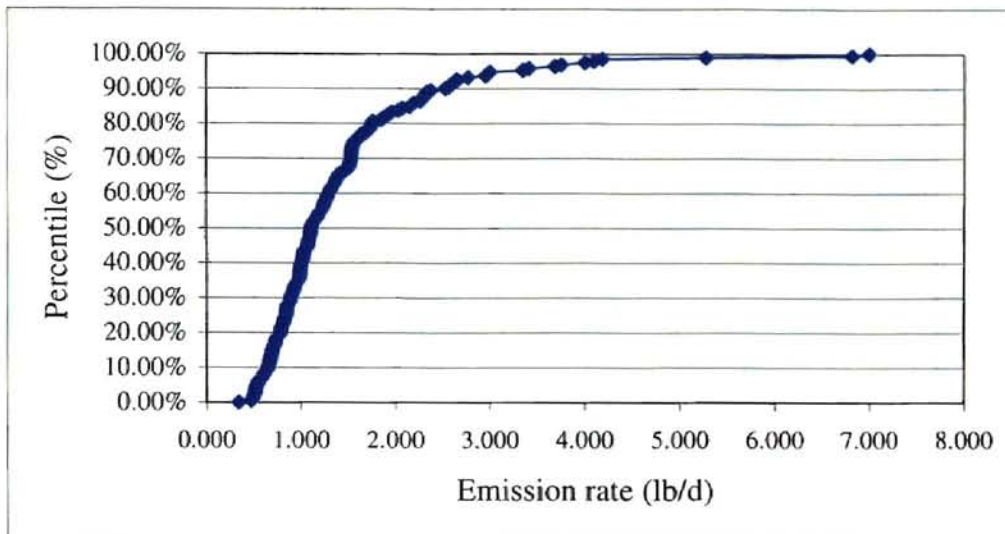


Figure 50. Simulation results of acetone by using TOXCHEM+V3.

b. WATER9 simulation results using Henry's constants contained in its database

Simulation results are shown in Figures 51, 52, 53, 54 and 55.

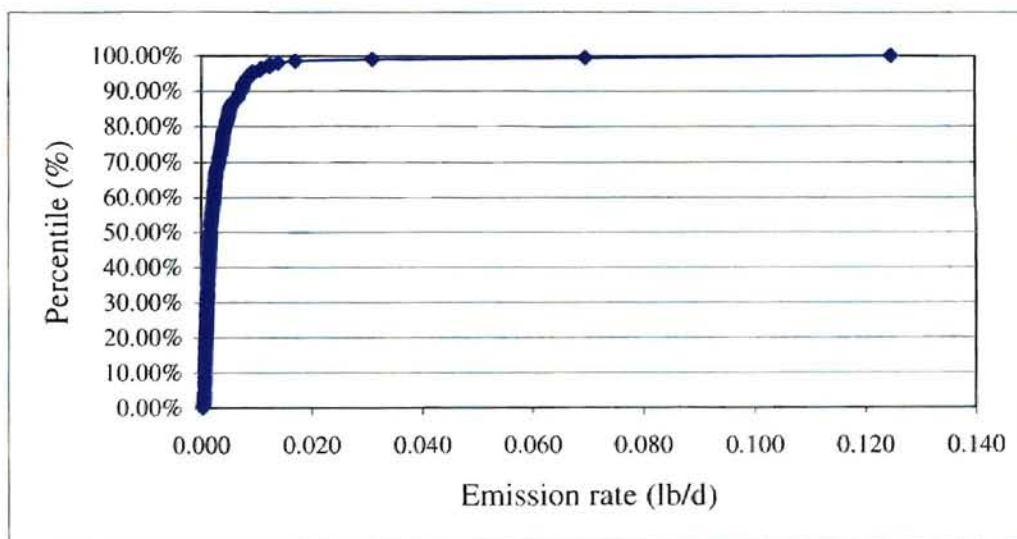


Figure 51. Simulation results of benzyl alcohol by using WATER9.

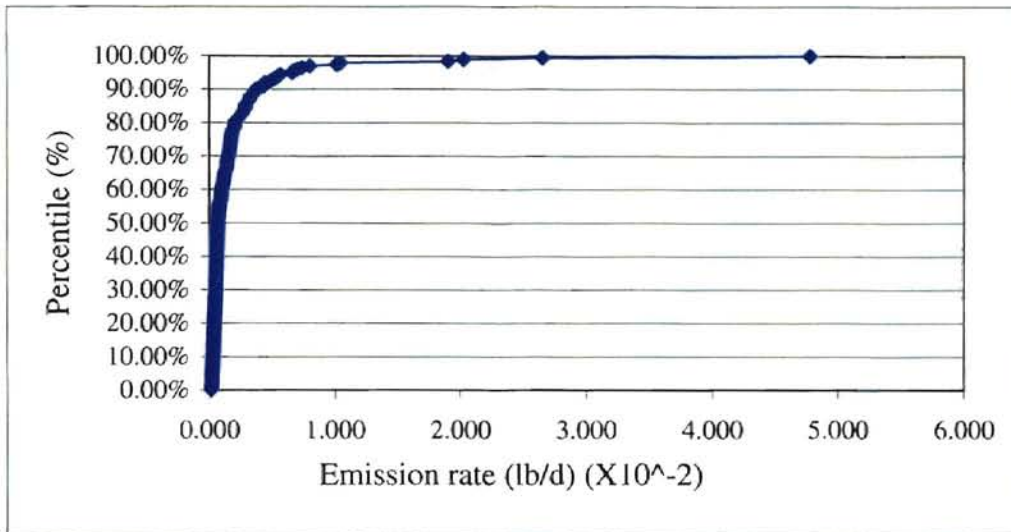


Figure 52. Simulation results of phenol by using WATER9.

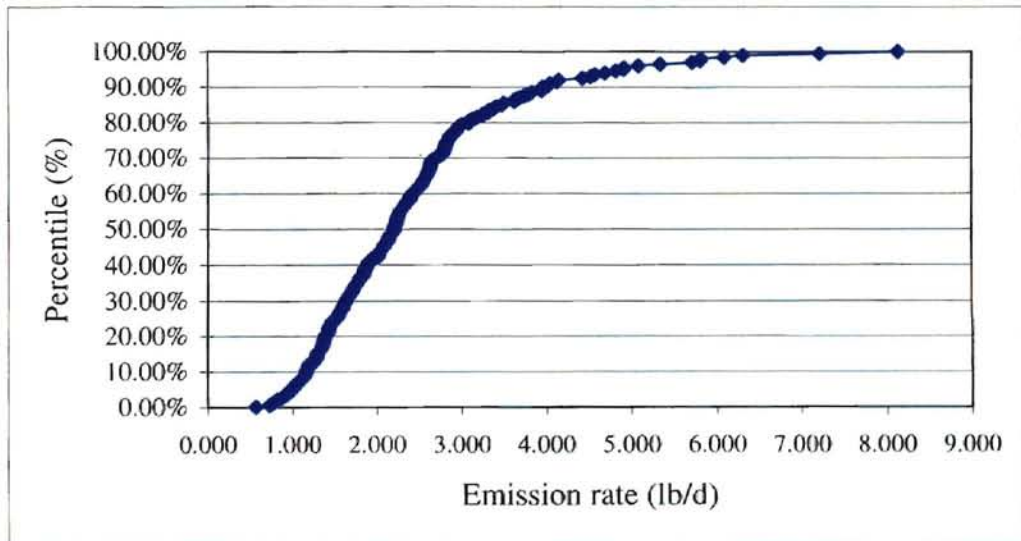


Figure 53. Simulation results of methylene chloride by using WATER9.

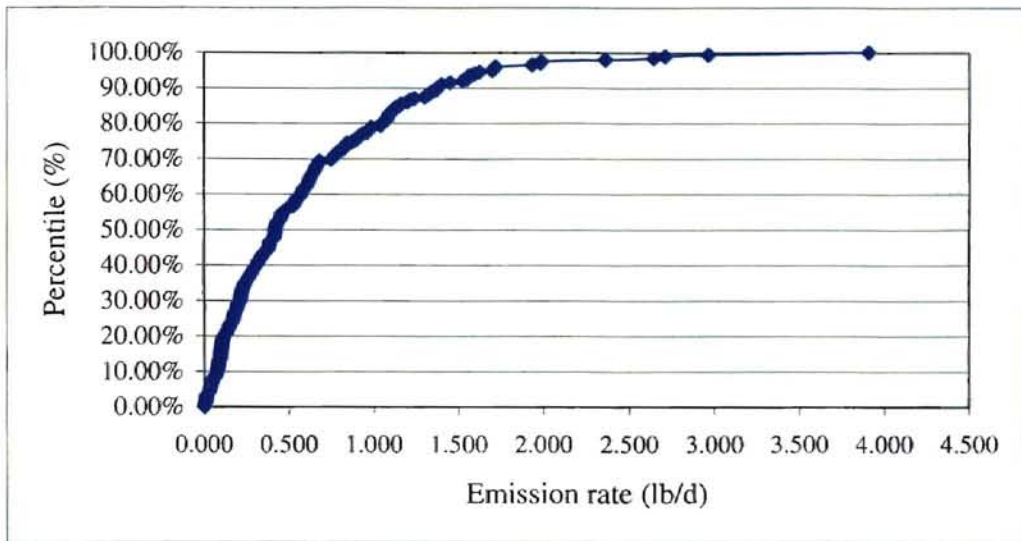


Figure 54. Simulation results of 2-butanone by using WATER9.

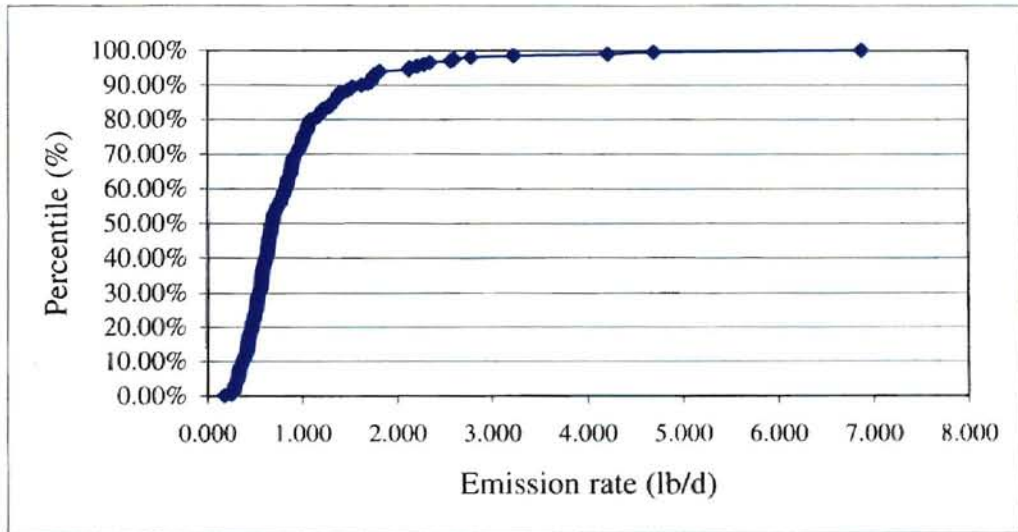


Figure 55. Simulation results of acetone by using WATER9.

c. TOXCHEM+V3 simulation results with Henry's constants from WATER9 library

Simulation results are presented in Figures 56, 57, 58, 59 and 60.

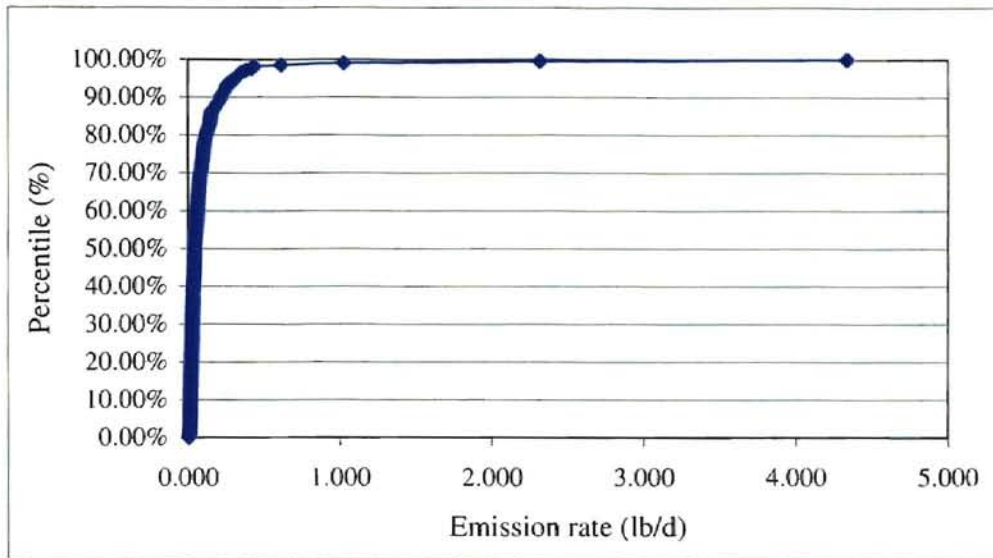


Figure 56. Simulation results of benzyl alcohol with WATER9 Henry's constant using TOXCHEM+V3

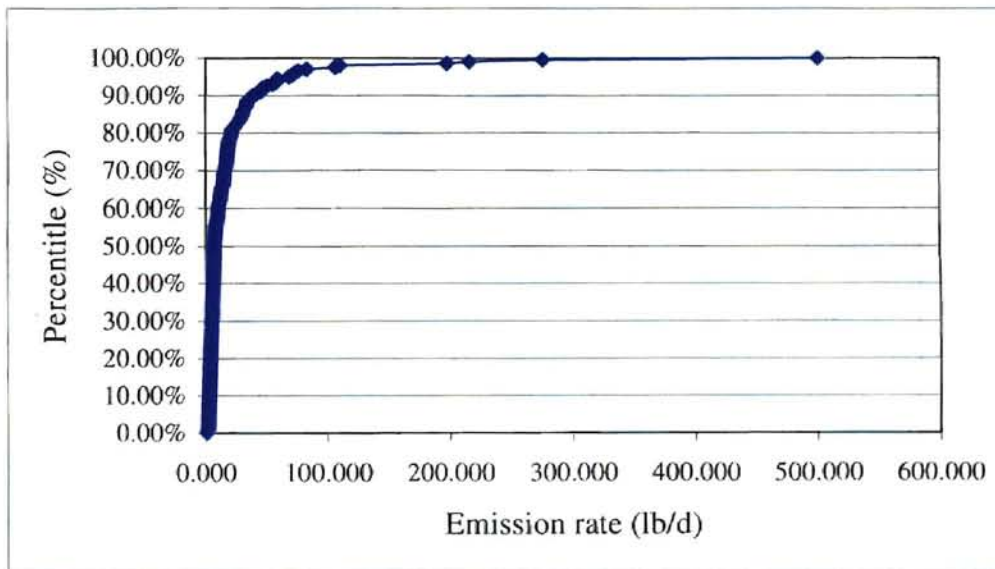


Figure 57. Simulation results of phenol with WATER9 Henry's constant using TOXCHEM+V3

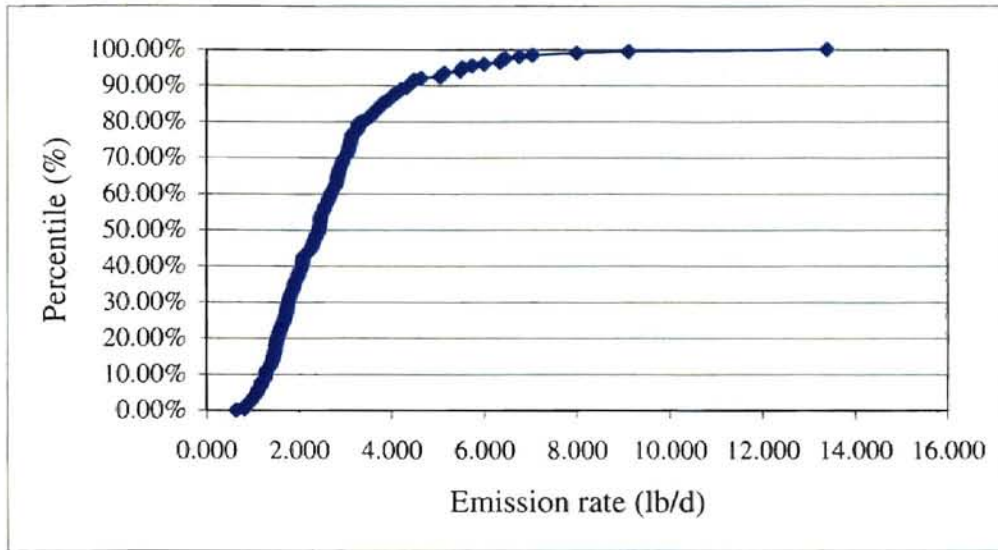


Figure 58. Simulation results of methylene chloride with WATER9 Henry's constant using TOXCHEM+V3

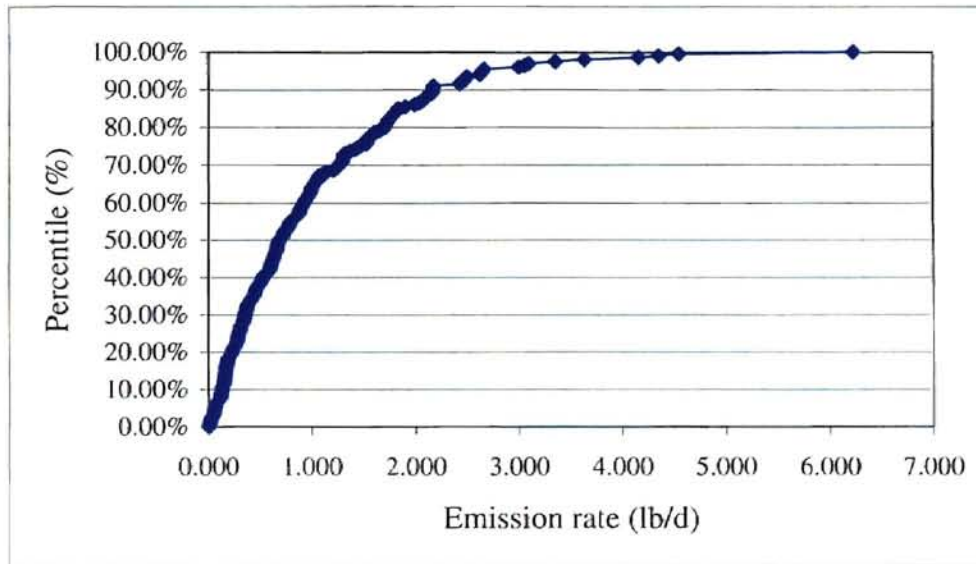


Figure 59. Simulation results of 2-butanone with WATER9 Henry's constant using TOXCHEM+V3

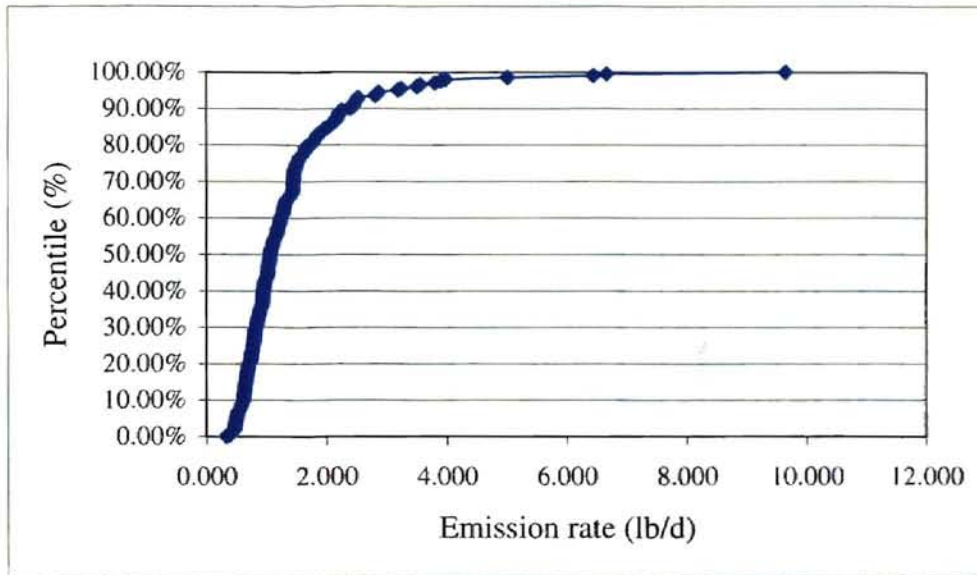


Figure 60. Simulation results of acetone with WATER9 Henry's constant using TOXCHEM+V3

With different Henry's constants, the simulations produced different results. The detailed discussions are presented in the Discussion chapter. The Henry's constants used during the simulations and a summary of these results is presented in Tables 17, 18, 19, 20 and 21.

Table 17. Summary of probabilistic and deterministic simulations of emission rates (TOXCHEM+V3 and WATER9 using their own Henry's constants)

Simulation	Models		Emission rate (lb/d)				
			Benzyl alcohol	Phenol	Methylene chloride	2-Butanone	Acetone
TOXCHEM+V3	Probabilistic	5%	0.048	0.070	1.087	0.061	0.540
		50%	0.196	0.236	2.445	0.685	1.108
		95%	1.171	2.365	5.577	2.648	3.348
TOXCHEM+V3	Deterministic		0.38	0.538	2.873	1.044	1.648
WATER9	Probabilistic	5%	0.001	1.904	0.995	0.035	0.317
		50%	0.002	6.723	2.194	0.419	0.679
		95%	0.009	66.199	4.906	1.695	2.122
WATER9	Deterministic		0.003	16.352	2.590	0.629	1.029

Table 18. Summary of probabilistic and deterministic simulations of emission rates (TOXCHEM+V3 and WATER9 using same Henry's constants)

Simulation	Models		Emission rate (lb/d)				
			Benzyl alcohol	Phenol	Methylene chloride	2-Butanone	Acetone
TOXCHEM+V3	Probabilistic	5%	0.012	1.979	1.079	0.060	0.495
		50%	0.045	6.904	2.429	0.682	0.682
		95%	0.314	68.020	5.519	2.644	2.644
TOXCHEM+V3	Deterministic		0.074	16.362	2.822	0.999	1.570
WATER9	Probabilistic	5%	0.001	1.904	0.995	0.035	0.317
		50%	0.002	6.723	2.194	0.419	0.679
		95%	0.009	66.199	4.906	1.695	2.122
WATER9	Deterministic		0.003	16.352	2.590	0.629	1.029

Table 19. Cumulative frequency of deterministic results on the simulated cumulative distribution (TOXCHEM+V3 and WATER9 using their own Henry's constants)

	Benzyl alcohol	Phenol	Methylene chloride	2-Butanone	Acetone
TOXCHEM+V3	74.0%	76.5%	65.7%	65.0%	77.0%
WATER9	72.8%	72.1%	65.8%	65.0%	76.3%

Table 20. Henry's constants used in both models (dimensionless)

	Benzyl alcohol	Phenol	Methylene chloride	2-Butanone	Acetone
TOXCHEM+V3	1.60E-05	5.32E-05	1.21E-01	5.32E-03	1.50E-03
WATER9	4.54E-06	0.522	1.02E-01	9.80E-03	1.36E-03

Note: the Henry's constant for benzyl alcohol in TOXCHEM+V3 is obtained from Michigan Environmental Response Division.

Table 21. Cumulative frequency of deterministic results on the simulated cumulative distribution (TOXCHEM+V3 and WATER9 using same Henry's constants)

	Benzyl alcohol	Phenol	Methylene chloride	2-Butanone	Acetone
TOXCHEM+V3	66.6%	71.3%	64.1%	64.3%	77.8%
WATER9	72.8%	72.1%	65.8%	65.0%	76.3%

Chapter V

Discussion

5.1 Distributions fitting

As discussed in the section on Monte Carlo simulation, a proper model for a specific problem is the first step of running a Monte Carlo simulation. Variables distributions used in conjunction with the selected model are the most critical elements during a simulation event because all the simulating values will be sampled from the distribution.

Based on the principle of mass balance, the emission rate of VOCs is proportional to the concentration in the influent. If the exact amount of these chemicals is known in the influent, the emission rates can be determined with few uncertainties. However, the chemicals in the influent follow specific distributions. It is critical for accurate simulations to know the chemical's distribution. If there were adequate concentration data available to fit a distribution for these chemicals, the fitted distribution would match the actual distribution better. The fitted results would be more accurate. As the shapes of the fitted distributions for the chemicals of interest were generally skewed, the Anderson-Darling test method, which places more emphases on the tail, was utilized to select the proper fitted distribution. Distribution fitting of these chemicals was performed using the sampled concentrations and calculated masses. The selection of the best-fit distributions was based on the concentration data. The distribution developed using masses was used for reference, or to confirm the distribution that was selected based on concentration, and to try to help limit scatter in the data. The results were consistent except that there was a slightly different ranking of the fitted distribution for 2-butanone. An Exponential (EXPON (β)) distribution was ranked best and a LOGNORM2 (μ , σ^2) distribution ranked

second using the A-D test with concentration, while the ranking were reversed when they were fitted with mass. The mass was calculated by multiplying the flow rate and the concentration of each compound on the same day at the sample unit. The sample unit is the transfer pit for acetone, 2-butanone, and methylene chloride. It is D1/D2 for phenol and benzyl alcohol. The flow rate used for fitting distribution was obtained from the effluent record of the first quarter 2001 of the treatment plant. Since the flow measurement is at the tail end of the plant and there is a lag time within the plant, the EXPON (β) distribution was still considered to be the best fit for 2-butanone in the influent. For phenol, the fitted distribution using both concentration and mass were the same. Both data sets were best fit by the PEARSON5 (α , β) distribution. For acetone, the top three fitted distributions were INVGAUSS (μ, λ), LOGNORM2 (μ , σ^2) and PEARSON5 (α , β) based on mass and concentration. For methylene chloride, the top three fitted distributions were INVGAUSS (μ, λ), LOGLOISTIC (γ , β , α) and PEARSON5 (α , β) based on mass and concentration. To pick a distribution thought to be the best among these fitted ones, Bootstrapping simulation was used to provide a range of the mean and standard deviation of the actual field data of chemicals. The theoretical values of the mean and standard deviation of each distribution were calculated and compared to the Bootstrapping results. The closer the mean and standard deviation of the fitted distribution were to the mode of the bootstrapped values, the better the fitted distribution would represent the true distribution. The theory behind this procedure was discussed in detail in the Methodology section. On the other hand, the more data that is used for fitting, the more accurate the result would be (Palisade, 1997). Since the quantity of the fitting data is so limited, it is not possible to select an absolutely representative

distribution for each compound. Among the four chemicals for which data exist, phenol had the most data so that the fitted distribution could be considered to be the most representative. Therefore, among the distributions that fit the input data well, the one that was similar to that of phenol was preferentially selected. Benzyl alcohol, phenol, methylene chloride, and acetone all followed the PEARSON5 (α , β) distribution. However, 2-butanone followed the EXPON (β) distribution.

Tables 3, 5, 7, 9, and 11 present summaries of the statistics of the fitted distributions for all compounds. It was found that the mean and standard deviation calculated from Equations 33, 34, 35 and 36, are slightly different from those listed in these tables for each compound. For example, the mean phenol concentration calculated from Equation 33 was 79.14 mg/l while Table 3 lists a mean of 75.71 mg/l. The difference exists because 79.14 mg/l calculated from Equation 33 stands for the theoretical value of the Pearson5 distribution with certain α , β values ($\alpha = 1.3910$; $\beta = 30.945$), while 75.71 mg/l was obtained from samples being fitted. The theoretical equations assume that the samples are continuous. However, as a matter of fact, samples being fitted are discrete. When the bootstrapping results were used to confirm the fitted distribution, the theoretical values of each statistics for each distribution were used.

5.2 Interpretations of probabilistic results

Simulations provided cumulative distributions for each compound. When using TOXCHEM+V3, with 90% confidence interval (5% to 95%), the OC-ALC/IWTP was estimated to release benzyl alcohol ranging from 0.048 lb/d to 1.171 lb/d (i.e., 5% and 95% values, respectively), phenol ranging from 0.070 lb/d to 2.365 lb/d, methylene

chloride ranging from 1.087 lb/d to 5.577 lb/d, 2-butanone ranging from 0.061 lb/d to 2.648 lb/d, and acetone ranging from 0.54 lb/d to 3.348 lb/d. From WATER9, with a 90% confidence interval (from 5% to 95%), the OC-ALC/IWTP was estimated to release benzyl alcohol ranging from 0.001 lb/d to 0.009 lb/d (i.e., 5% and 95% values, respectively), phenol ranging from 1.904 lb/d to 66.199 lb/d, methylene chloride ranging from 0.995 lb/d to 4.906 lb/d, 2-butanone ranging from 0.035 lb/d to 1.695 lb/d, and acetone ranging from 0.317 lb/d to 2.122 lb/d.

Table 17 also presents the simulation results using average concentrations and flow rate, which is the deterministic mode of the models. By using TOXCHEM+V3, the estimated annual VOCs emission is 2366 lb/yr (6.48 lb/d), while WATER9 predicts an annual VOCs (five compounds discussed in this thesis) emission of 7520 lb/yr (20.60 lb/d). If the Henry's constants used in TOXCHEM+V3 were adjusted to the same as those used in WATER9, the annual estimated emissions of VOCs would be 7966 lb/yr (21.83 lb/d). Card (1995) conducted a study on comparisons of mass transfer models with direct measurement for free liquid surfaces at municipal wastewater plants and found that WATER7 over estimated by a factor of five and TOXCHEM over estimated by a factor of two compared to the actually measured results. In Card's study it was shown that the average measured emission rate for those IWTPs was about 70 pounds per year per MGD of the influent flow. Compared to Card's (1995) results, TOXCHEM+V3 and WATER9 both predicted significantly larger emissions from the IWTP for this study, which was 7000-8000 lb/yr with an average flow rate of 1MGD. The huge difference between these two estimations of VOC emissions might be due to the different industrial processes in the plants of Card's study and this thesis. Different industrial processes

would use different chemicals with different amount. Hence, more attention should be paid to reduce the emissions from Tinker's IWTP and protect the residents from exposure. However, these deterministic simulation results only represent a point on the cumulative distribution curve of each compound. Information consisting of one-point is not enough to make a good decision relative to protective action. To make a better decision, not only the emission rate is needed, but also the probability of the emission rate is needed. The cumulative frequency of these values corresponding to the cumulative distribution curve are shown in Tables 19 and 21. Comparing to probabilistic results, the deterministic results could only tell there is about a 70% probability that the VOC emissions rate from the IWTP would be or less as Tables 19 and 20 both indicate, or tell that there is still 30% probability that the emission rate would be more. In this study for the OC-ALC/IWTP, the total emissions simulated by WATER9 are significantly higher than that by TOXCHEM+V3 if each model uses Henry's constants contained in its library. Henry's constants for all compounds in each model are different from each other. These Henry's constants are listed in Table 20. If the Henry's constants in TOXCHEM+V3 are adjusted to be the same as those used in WATER9, it was found that both models have very similar estimations of emission rates. The simulation results are presented in Table 18. The total estimated emission rate with TOXCHEM+V3 is 21.83 lb/d (3.98 ton/yr) while it is 20.60 lb/d (3.76 ton/yr) with WATER9. TOXCHEM+V3 has slightly higher estimation of emission rate than WATER9.

Table 17 showed that the deterministic results predicted by WATER9 and TOXCHEM+V3 are very different for benzyl alcohol and phenol. For benzyl alcohol, the prediction derived from TOXCHEM+V3 is about 100 times greater than that predicted by

WATER9. But for phenol, the simulation result from WATER9 is about 30 times greater than that from TOXCHEM+V3. One of the reasons for these differences is the different Henry's constant used in these two models, especially for phenol where there is four orders of magnitude of difference in the dimensionless Henry's constant. These Henry's constants are listed in Table 20. These Henry's constants are integrated in each model's data library, with the exception of benzyl alcohol for TOXCHEM+V3. The data library in TOXCHEM+V3 does not have Henry's constant for benzyl alcohol. The Henry's constant was obtained from the Michigan Environmental Response Division website, (website source, 2002). More work is needed to figure out why different Henry's constants are used in WATER9 and TOXCHEM+V3. This area of research is partly beyond the scope of this thesis.

When the Henry's constant for phenol in TOXCHEM+V3 was greatly increased after it was adjusted to be the same as in WATER9, the emission rate increased. The emission rate of phenol ranged from 1.079 lb/d to 68.020 lb/d with 90% confidence interval (from 5% to 95%) with TOXCHEM+V3. The prediction range of emission rates for benzyl alcohol was changed to 0.012 lb/d to 0.314 lb/d with 90% confidence interval (from 5% to 95%). While for the other compounds the emission rates were almost the same as those using their own Henry's constants in the library of TOXCHEM+V3. For methylene chloride, it ranged from 1.079 lb/d to 5.519 lb/d, for 2-butanone, it ranged from 0.060 lb/d to 2.644 lb/d, and for acetone it ranged from 0.495 lb/d to 2.644 lb/d. The percentage of the deterministic estimation on the cumulative distribution curve is presented in Table 21. The simulated cumulative distribution curves are presented in Figures 53, 54, 55, 56

and 57. The deterministic simulations were done by using the same Henry's constants in both models. Furthermore, only the Henry's constants in the library of TOXCHEM+V3 were changed is because the database in WATER9 was not editable.

Due to different unit's definition in TOXCHEM+V3 and WATER9, the actual units were modeled differently in each model. The emissions were different for each unit in both models, though the total emissions for the whole plant were close. For example, the diversionary structure ahead of the oil/water separator was modeled as an open drop-structure in TOXCHEM+V3, while it was modeled as weir/waterfall in WATER9. Thus, the emissions from both units were different. The emissions were 206 lb/yr from the open drop-structure in TOXCHEM+V3 and 48.7 lb/yr from weir/waterfall in WATER9 with the same model's setups for deterministic simulations. The detailed comparisons of these units with different models are listed in Table 22, Figure 61, and Figure 62.

Table 22. Comparisons of unit emissions in TOXCHEM+V3 and WATER9 (deterministic simulation with same Henry's constants)

Units	TOXCHEM+V3						WATER 9					
	Benzyl alcohol	Phenol	Methylene chloride	2-Butanone	Acetone	Cpds Sum	Benzyl alcohol	Phenol	Methylene chloride	2-Butanone	Acetone	Cpds Sum
	lb/d	lb/d	lb/d	lb/d	lb/d	lb/d	lb/d	lb/d	lb/d	lb/d	lb/d	lb/d
Primary Clarifier	0.01	2.68	0.47	0.16	0.24	3.560	0.003	2.000	0.400	0.152	0.362	2.917
Blending Tank D1/D2	0.04	3.48	0.6	0.24	0.46	4.820	0.000	3.162	0.571	0.229	0.533	4.495
Diversionary Structure	1.23E-05	0.26	0.02	7.19E-04	5.11E-04	0.281	0.000	0.133	0.000	0.000	0.000	0.133
Oil Water Separators	8.64E-04	0.26	0.04	1.42E-02	0.02	0.335	0.000	9.905	0.914	0.076	0.038	10.933
Storage Tanks	2.50E-11	1.08E-06	4.55E-08	1.39E-09	9.28E-10	0.000	0.000	0.610	0.076	0.000	0.000	0.686
Equalization Basins	0.02	9.2	1.64	0.56	0.8	12.220	0.000	0.514	0.495	0.076	0.038	1.124
Mixing Basin-1	2.97E-04	0.03	4.95E-03	3.34E-03	6.23E-03	0.045	0.000	0.000	0.038	0.019	0.000	0.057
Mixing Basin-2	2.97E-04	0.03	4.75E-03	3.31E-03	6.21E-03	0.045	0.000	0.000	0.038	0.019	0.000	0.057
Mixing Basin-3	5.26E-04	0.06	0.01	8.48E-03	0.01	0.089	0.000	0.019	0.038	0.019	0.000	0.076
Weir from the Mixing Basin	6.07E-05	0.06	5.53E-03	1.29E-03	1.84E-03	0.069	0.000	0.000	0.000	0.000	0.000	0.000
SCC-N	1.88E-03	0.01	3.15E-03	5.69E-03	0.02	0.041	0.000	0.010	0.019	0.038	0.038	0.105
Wet Well	9.71E-05	2.43E-04	5.35E-05	1.76E-04	9.26E-04	0.001	0.000	0.000	0.000	0.000	0.000	0.000
Sand Filter	0	0	0	0	0	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Pump station	3.36E-05	0.03	2.86E-03	7.08E-04	1.02E-03	0.035	0.000	0.000	0.000	0.000	0.000	0.000
Chlorine Contact Chamber	2.28E-04	5.24E-04	1.21E-04	4.12E-04	2.17E-03	0.003	0.000	0.000	0.000	0.000	0.000	0.000
Diversionary Structure	1.23E-05	0.26	0.02	7.19E-04	5.11E-04	0.281	0.000	0.000	0.000	0.000	0.000	0.000
Thickener	1.17E-05	9.54E-04	1.86E-04	1.76E-04	2.96E-04	0.002	0.000	0.000	0.000	0.000	0.019	0.019
Belt Filter	0	0	0	0	0	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sum	0.074	16.362	2.822	0.999	1.570		0.003	16.352	2.590	0.629	1.029	
Total	21.827						20.603					

Note: For blending tanks D1/D2, oil/water separators, storage tanks and equalization basins, the emissions are a combination of two parallel units.

When the Henry's constants were adjusted to be the same, TOXCHEM+V3 has higher estimation of emission rates than that of WATER9. Figure 61 shows the deterministic results with same Henry's constants from WATER9.

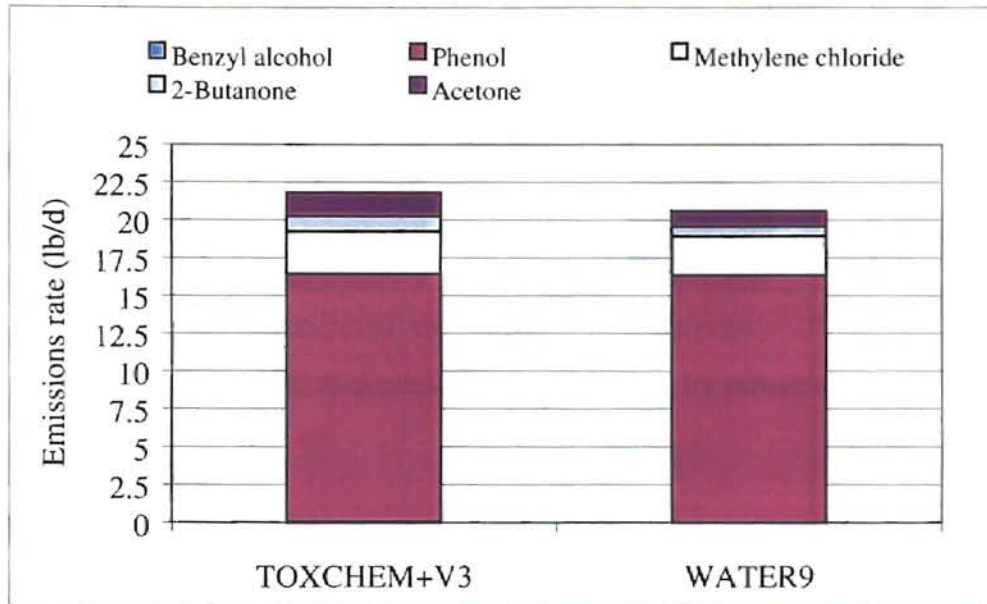


Figure 61. Prediction of VOC emissions with GFMs

From Table 22, it is obvious that the top four units that have the most emissions are the equalization basins, blending tanks, primary clarifier, and oil water separators for TOXCHEM+V3, while the sequence for WATER9 is the oil-water separators, blending tanks, primary clarifier, and equalization basins. It is also clearly found that phenol is the major VOC emitted from the Tinker's IWTP and mainly controls which unit is the major emitter for WATER9 and TOXCHEM+V3. For TOXCHEM+V3, the equalization basin has the most emission of 9.2 lb/d while the oil-water separator has the most emission of 9.9 lb/d for WATER9. More work is needed to figure out the reason for the big difference in the future. A comparison of emission rates from major emitter for both models is presented in Figure 62. The comparison is based on the deterministic simulation with the same Henry's constants from WATER9.

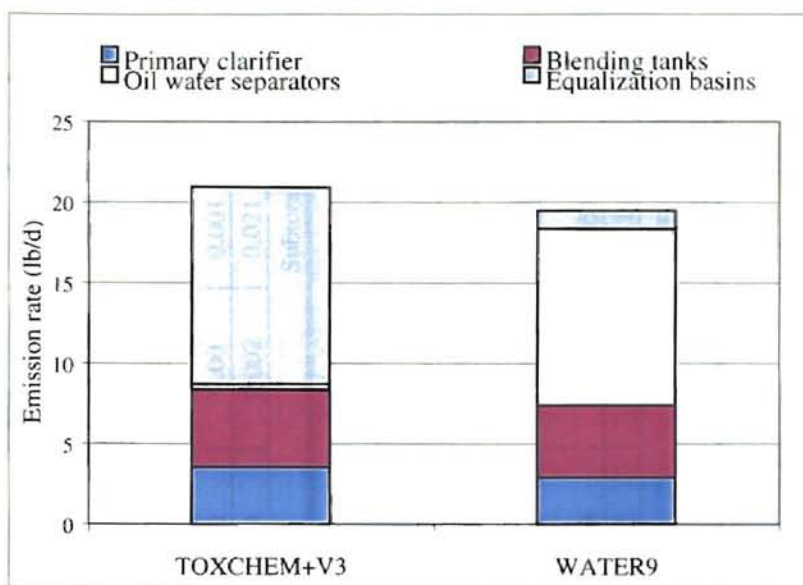


Figure 62. Estimated VOCs emissions by process.

During the Phase 2 of this project, field sampling (March 8, 2002) was performed by the Department of Civil and Environmental Engineering of Oklahoma State University and Southwest Lab of Oklahoma. Three covered units (primary clarifier, blending tanks and oil water separator) and two uncovered units (storage tanks and equalization basins) were sampled and the total emission rate was estimated. The results of liquid phase samples analyzed were not received in time to be used in this thesis; only the gas phase data was available. Moreover, benzyl alcohol and phenol was not measured. The field measurements showed that the emissions of methylene chloride, acetone and 2-butanone were relatively low compared with the predicted emissions. The predicted emission rate of all five compounds with TOXCHEM+V3 and WATER9 was around 20 lb/d based on the historic liquid phase concentration data, while the actual estimation of the emission rate was only 0.885 lb/d. The field test results are listed in Table 23. The compounds concentrations were analyzed and determined by GC/MS.

Table 23. Emission rate of compounds based on field measurement

Covered units	Sampling velocity	Opening Area	Flow Rate	Compounds concentration ($\mu\text{g}/\text{m}^3$)			Emission rate (lb/d)			
	at vents			Methylene chloride	2-Butanone	Acetone	Methylene chloride	2-Butanone	Acetone	
	(fpm)	(ft ²)	(m ³ /d)	($\mu\text{g}/\text{m}^3$)	($\mu\text{g}/\text{m}^3$)	($\mu\text{g}/\text{m}^3$)	lb/d	lb/d	lb/d	
D1/D2	50	7.8	15905	5630	47.85	594.3	0.197	0.002	0.021	
Primary clarifier	10	2.56	1044	799.5	11.4	54.1	0.002	0.00	0.00	
Oil water separator	15	2.56	1566	5590	24.5	217.2	0.019	0.00	0.001	
SUM							0.219	0.002	0.021	
									Subtotal	0.242
Uncovered units	Surface area of uncovered unit	Flux chamber X-cross area	Flow Rate	Compounds concentration ($\mu\text{g}/\text{m}^3$)			Emission rate (lb/d)			
				Methylene chloride	2-Butanone	Acetone	Methylene chloride	2-Butanone	Acetone	
	(ft ²)	(ft ²)	l/min	($\mu\text{g}/\text{m}^3$)	($\mu\text{g}/\text{m}^3$)	($\mu\text{g}/\text{m}^3$)	lb/d	lb/d	lb/d	
Storage tanks	4570	3.043	22	3,025.00	161.75	607.00	0.317	0.017	0.064	
Equalization basins	5005	3.043	22	1425	271.75	440	0.164	0.031	0.051	
SUM							0.481	0.048	0.114	
									Subtotal	0.643
									Total	0.885

Note:

The calculation equations of emission rate are:

For Covered units, Emission rate (mass/d) = Velocity (m/d) * Opening Area (m²) * Concentration (ug/m³)

For uncovered units, Emission rate (mass/d) = Flow rate (m³/d) * Concentration (ug/m³) * Surface area (ft²) / Flux chamber area (ft²)

Chapter VI

Conclusion and suggestions

Uncertainty analysis of an emission inventory from an IWTP is a new issue, though uncertainty analysis is widely applied in risk assessment. This thesis has presented a method to perform this type of uncertainty analysis and its application in a case study. Model uncertainty, parameter uncertainty and input uncertainty are three important sources of uncertainty. Once the source of uncertainty is to be studied, the distribution of the variables of interest becomes the most critical factor in the study. This thesis used simulation techniques to fit the distribution for the variables of interest. Since the source of uncertainty in this study was categorized as input uncertainty, all of the input variables were discussed. The distributions for the influent flow rate and chemicals concentrations were fitted and selected. The emissions rate of each compound was simulated using TOXCHEM+V3 and WATER9. The simulation results presented a range of VOCs emissions from the IWTP. When the same Henry's constants (from WATER9 library) are used, with WATER9, emission rate of benzyl alcohol ranged from 0.001 lb/d to 0.009 lb/d with 90% confidence interval (5%-95%); phenol ranged from 1.904 lb/d to 66.199 lb/d; methylene chloride ranged from 0.995 lb/d to 4.906 lb/d; 2-butanone ranged from 0.035 lb/d to 1.695 lb/d, and acetone ranged from 0.317 lb/d to 2.122 lb/d; with TOXCHEM+V3, benzyl alcohol ranged from 0.012 lb/d to 0.314 lb/d, phenol ranged from 1.979 lb/d to 68.020; methylene chloride ranged from 1.079 lb/d to 5.519 lb/d, 2-butanone ranged from 0.060 lb/d to 2.644 lb/d, and acetone ranged from 0.495 lb/d to 2.644 lb/d. The average emission rate of Tinker's IWTP was 21.83 lb/d (3.98 ton/yr) with

TOXCHEM+V3 and 20.60 lb/d (3.76 ton/yr) with WATER9. However, there is only about a 70% probability for both models to tell that the emission rate would be or less based on these deterministic simulation results.

Uncertainty analysis of the emission inventory of the industrial wastewater treatment plant can provide a range of VOC emission rates with confidence intervals. Monte Carlo simulation was used to analyze the emission uncertainty. Based on the simulation results, the emission rate and its probability can be easily read from the cumulative distribution. This idea would be very useful for uncertainty analysis of environmental systems and would be of great significance in environmental risk assessment.

The emission estimating models, TOXCHEM+V3 and WATER9, do not have a simulation subroutine, i.e., Monte Carlo simulation; this makes it extremely difficult to take other sources of uncertainty into consideration. More work is needed to solve this problem, i.e. coding a simulation subroutine. In addition, more study is needed in finding other possible reasons for the differences between these two estimating models, with the exception of Henry's constants, such as the fundamentals of how the individual process units are modeled in both models. Further exploration on these differences would be very useful in the application of these two models.

Due to the limited time of study, the liquid phase concentrations of compounds of interest sampling on March 8, 2002 are not analyzed yet, and thus those concentrations are not substituted into models for deterministic simulation. The deterministic simulation results with the field samples liquid phase concentrations might provide useful information for comparisons between field measurement and models estimates.

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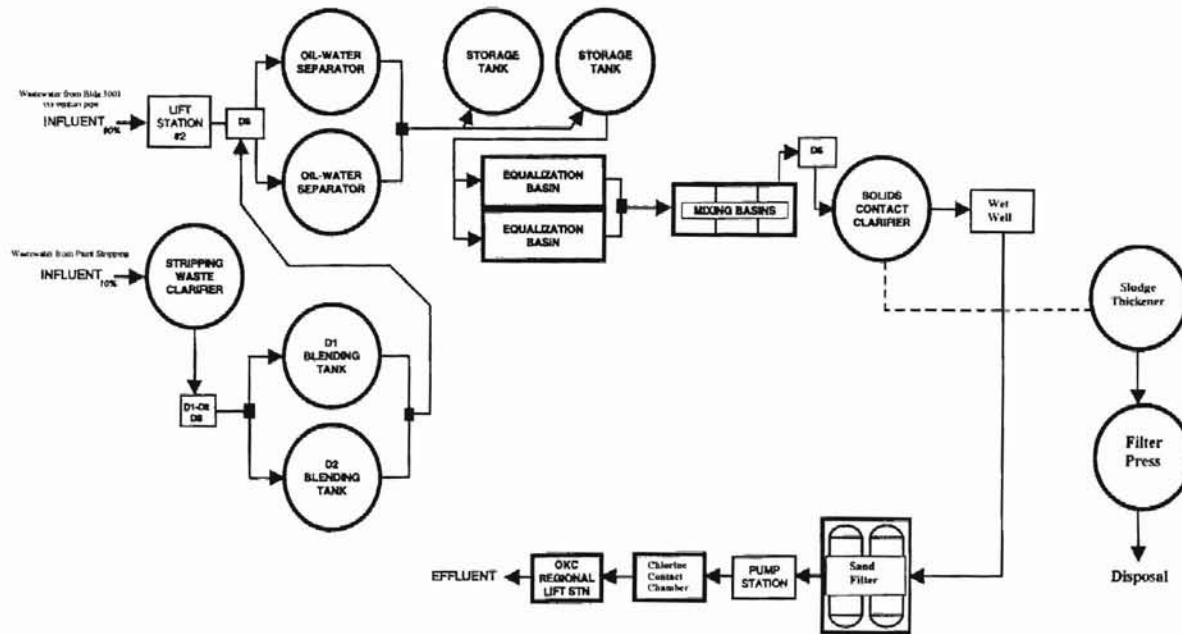
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Appendix

Appendix A-1. The unit process diagram of the IWTP used in case study



IWTP PROCESS FLOW DIAGRAM



Note:

Oil separators, Blending Tanks, Storage Tanks, and Equalization Basin are parallel units. The rests are in series when they are put in operation.

Sludge from all units in the plant was directed to the sludge thickener for further treatment.

This figure was modified based on the actual information provided by Dr. Freddie Hall from the IWTP of OC-ALC at Tinker, OK.

Appendix A-2. The units dimensions of the IWTP in case study

Unit No	Unit Name and Parameters Measured	Field Data
1	Oil Water Separators	
	Weirs	18 sections with 15 plates per section and a length of 12 ft per section. Height = 0.3 ft. Top of polygon = 0.5 ft.
	headspace (ft)	2.2
	inside measured circumference (ft)	203.9
	depth (ft)	9.1
	wall thickness (ft)	0.7
	outside measured circumference (ft)	207
	inside radius (ft)	31
	outside radius (ft)	32 ft (note that the wall thickness was measured to be 0.7 ft, therefore one of the measurements may be inaccurate)
	measured inside diameter (ft)	64.8
	distance from outside of inlet to inside of wall (ft)	27.7
	raker arm speed	Travels 12 ft in 1 min 25 sec (12 ft is the length of one weir section)
	outlet dimensions (ft)	Length = 1.8, width = 1.4, depth = 9
	capacity (gal)	
2	Oil Water Diversionary Structure	
	outside dimensions (ft)	10 x 7.7 measured on the outside of the concrete tower
	inside dimensions for entire diversion structure (ft)	8.5 x 6.2 (this measurement includes the concrete partitions in the structure)
	sluice gate width (ft)	2
	wall and partition thickness (ft)	2
	side well length (ft)	6.2
	side well width (ft)	1.9
	side well depth to top of waterfall (ft)	1.9
	side well depth to top of water surface (ft)	3.9
	side well depth to bottom (ft)	5.1
	center well length (ft)	6.2
	center well width (ft)	2.6
	center well depth to water surface (ft)	1.7
	center well depth to water bottom (ft)	11.1
	dimensions (ft)	
	capacity (gal)	
3	Blending Tanks	
	diameter (ft)	60
	depth (ft)	12
4	Paint Stripper	
	inside radius (ft)	31.6
	measured diameter (ft)	60
	headspace (ft)	2.7

	depth (ft)	15.1
	waterfall drop height (ft)	2
	weir length(ft)	29.6
5	Oil Water Separators	
	inside radius (ft)	32.6
	inside diameter calculated from measured inside radius (ft)	65.2
	measured inside diameter (ft)	63
	depth (ft)	10
	raker arm speed	Travels 12 ft in 1min 25 sec (12 ft is the length of one weir section)
	outlet dimensions (ft)	Length = 1.8, width = 1.4, depth = 9
	capacity (gal)	
6	EQ Basins	
	outside length (ft)	102
	inside length (ft)	100.1
	inside width (ft)	50
	outside width (ft)	52
	sidewalk width (ft)	4
	sidewalk overhang (ft)	1.5 (on both sides)
	backwash recycle influent pipe circumference (ft)	1.7
	depth to water surface (ft)	6.35
	depth to basin bottom (ft)	11.6
	spray pattern diameter from field estimation (ft)	16
	spray pattern diameter from photo estimation (ft)	18.5
7	Storage Tanks	
	diameter (ft)	76.3
	specified total height (ft) (taken of label on tank)	32
	measured total height (ft)	32.4
	depth to water (ft)	9.7
	measured tank circumference (ft)	240.1
	capacity (gal)	
8	Mixing Basin 1	
	inside length (ft)	13.2
	inside width (ft)	16
	depth to water surface (ft)	2.5
	depth to basin bottom (ft)	15.8
	mixing impeller rev. speed (rpm)	64
9	Mixing Basin 2	
	inside length (ft)	13.2
	inside width (ft)	16
	depth to water surface (ft)	2.5
	depth to basin bottom (ft)	15.8
	mixing impeller rev. speed (rpm)	64
10	Mixing Basin 3	
	inside length (ft)	9
	inside width (ft)	9

	depth to water surface (ft)	2.5
	depth to basin bottom (ft)	11.7
	mixing impeller rev. speed (rpm)	48
11	Mixing Basin Weir	
	Type	broad crested weir
	change in water height across weir (ft)	0.25
	length of wier (ft)	9
	tailwater depth (ft)	10
12	Diversiory Structure between the mixing basins and the SCC	
	drop height (ft)	2.8
	outside dimensions (ft)	
	sluice gate width (ft)	3.1
	wall and partition thickness (ft)	1
	side well 1 length (ft)	6.3
	side well 1 width (ft)	1.8
	side well 2 length (ft)	6.2
	side well 2 width (ft)	1.8
	side well 2 depth to top of waterfall (ft)	2.8
	side well 2 depth to top of water surface (ft)	3.8
	side well 2 depth to bottom (ft)	5.8
	center well length (ft)	6.2
	center well width (ft)	2.7
	center well depth to water surface (ft)	2.8
	center well depth to water bottom (ft)	10
13	North SCC	
	weir information	18 sections, 17 plates per section, top of polygon = 0.3ft, bottom = 0.5ft, length = 12 ft.
	raker arm speed	50 sec per 6 feet of arc length (6ft*25 six foot sections + 1*6.4ft section = 156.4 feet total in one complete revolution.
	headspace (ft)	na
	inside measured circumference (ft)	not measured
	depth from top of water to bottom of sludge blanket (ft)	16.6
	wall thickness (ft)	1
	outside measured circumference (ft)	not measured
	inside radius (ft)	30
	outside radius (ft)	31
	diameter of outer inlet baffle (ft)	18
	diameter of inner inlet baffle (ft)	14.1
	outlet dimensions (ft)	Length = 1.4, width = 1.3 (trough is 1.3 ft in width)
	sludge blanket depth (ft)	2
	depth from top of wall to bottom of trough (ft)	4.2
	distance from inside of wall to weir ring (ft)	1.6
	distance from weir ring to weir baffle (ft)	0.5

	capacity (gal)	
	diameter (ft)	
	Depth	
14	Chlorine Contact Chamber	
	distance from inlet pipe discharge to water surface (ft)	2
	basin length (ft)	24.7
	basin width (ft)	15.4
	distance from top of wall to water surface (ft)	8.1
	distance from top of wall to bottom of basin (ft)	12.6
	waterfall height (ft)	2
	capacity (gal)	
	basin height (ft)	
15	Thickener	
	depth (ft)	9.1
	diameter (ft)	30.2

Appendix A-3. Raw flow rate data for distribution fitting in case study

The recorded flow rate into the plant is in units of MGD. The following data were not consecutive and recorded in calendar year 2001.

Flow rate (MGD)	0.90	0.60	0.70
	0.80	0.60	0.70
	0.90	0.60	0.80
	0.90	0.60	0.80
	1.00	0.60	0.90
	1.00	0.60	0.90
	0.90	0.60	0.80
	0.90	0.60	0.70
	0.90	0.60	0.80
	0.90	0.60	0.90
	0.90	0.60	0.90
	0.90	0.60	0.90
	0.80	0.60	0.90
	0.70	0.60	0.80
	0.70	0.50	0.70
	0.90	0.50	0.60
	0.90	0.60	0.60
	1.00	0.70	0.60
	1.00	0.60	0.70
	0.70	0.50	0.80
	0.70	0.50	0.90
	0.80	0.50	0.90
	0.80	0.50	0.80
	0.80	0.60	0.80
	0.70	1.00	0.80
0.70	1.00	0.80	
0.70	0.70	0.80	
0.70	0.60	0.90	
0.70	0.50	0.90	
0.80	0.50	0.90	
0.70	0.50		
Mean		0.74	
SD		0.15	

Note: SD-standard deviation

Appendix A-4. Raw compounds data for distribution fitting in case study

In 1999 all of the chemicals listed here, except phenol, were sampled at the transfer pit in unit of $\mu\text{g/l}$. Phenol was sampled at D1-D2, toward the very front end of the plant and was reported in units of mg/l . There were 3 shifts a day. For each shift, one sample was analyzed.

Note: SD-standard deviation

Sample Date	Acetone	Methylene chloride	2-Butanone
10/19-10/20	267.00	433.00	567.00
10/19-10/20	452.00	221.00	444.00
10/19-10/20	442.00	251.00	398.00
10/22-10/26	189.00	287.00	68.50
10/22-10/26	262.00	421.00	18.60
10/22-10/26	487.00	457.00	19.30
10/26-10/27	267.00	311.00	188.00
10/26-10/27	387.00	270.00	243.00
10/26-10/27	351.00	226.00	97.90
10/29-10/30	242.00	144.00	9.39
10/29-10/30	266.00	189.00	25.00
10/29-10/30	350.00	272.00	31.60
11/02-11/03	237.00	505.00	90.60
11/02-11/03	294.00	523.00	202.00
11/02-11/03	420.00	140.00	114.00
11/05-11/06	403.00	176.00	212.00
11/05-11/06	577.00	143.00	111.00
11/05-11/06	736.00	142.00	196.00
11/09-11/10	338.00	163.00	117.00
11/09-11/10	490.00	159.00	28.50
11/09-11/10	451.00	248.00	35.80
11/12-11/13	734.00	94.20	50.60
11/12-11/13	988.00	134.00	36.20
11/12-11/13	865.00		
Mean	437.29	256.92	143.65
SD	208.11	128.04	149.37

Sample date	Phenol (mg/l)	Sample date	Phenol (mg/l)	Sample date	Phenol (mg/l)
1-Jun-99	130.0	29-Jan-00	51.0	10-Dec-00	15.0
2-Jun-99	140.0	6-Dec-99	45.0	30-Dec-00	18.0
8-Jun-99	10.0	7-Dec-99	42.0	1-Jan-01	15.0
9-Jun-99	46.0	8-Dec-99	44.0	2-Jan-01	17.0
10-Jun-99	30.0	9-Dec-99	70.0	3-Jan-01	15.0
1-Jul-99	165.0	10-Dec-99	40.0	29-Jan-01	6.0
2-Jul-99	150.0	1-Jun-00	20.0	30-Jan-01	6.0
14-Jul-99	240.0	2-Jun-00	10.0	1-Feb-01	3.0
15-Jul-99	540.0	8-Jun-00	15.0	2-Feb-01	4.0
30-Jul-99	24.0	9-Jun-00	15.0	3-Feb-01	6.0
1-Aug-99	310.0	27-Jun-00	26.0	27-Feb-01	4.0
2-Aug-99	200.0	1-Jul-00	15.0	28-Feb-01	11.0
28-Aug-99	42.0	2-Jul-00	20.0		
29-Aug-99	41.0	3-Jul-00	10.0		
30-Aug-99	50.0	26-Jul-00	20.0		
1-Dec-99	60.0	27-Jul-00	26.0		
2-Dec-99	54.0	5-Aug-00	12.0		
21-Dec-99	50.0	6-Aug-00	11.0		
22-Dec-99	50.0	7-Aug-00	12.0		
23-Dec-99	50.0	29-Aug-00	15.0		
25-Jan-00	40.0	30-Aug-00	25.0		
26-Jan-00	80.0	7-Dec-00	11.0		
27-Jan-00	80.0	8-Dec-00	2.5		
28-Jan-00	50.0	9-Dec-00	15.0		
Mean					55.41
SD					87.26

Appendix B-1. Units' parameters set-up for TOXCHEM+V3

Units of IWTP	Primary Clarifier	Blending Basin	Venturi pipe	D.-S.	Oil Separator	Storage tank	Equalization Basin	Mixing Basin (1,2)	Mixing Basin (3)	D.-S.	Solid contact Clarifier	Wet well	Pump Station	chlorine contact chamber
Mark in the Layout	B5	C5, D5	B9	D9, D10	F9, G9	H9, I9	J9, K9	L9, M9	O9	P9	R9	S9	U9	V9
Depth (ft)	12.4	12	N/A	N/A	6.9	9.7	5.25	13.3	9.2	N/A	16.6	7.6	N/A	4.5
Surface area (ft ²)	3135.5	2826	N/A	N/A	3017.5	4570	5005	211.2	81	N/A	2826	N/A	N/A	N/A
Weir length (ft)	29.6	N/A	N/A	N/A	216	N/A	N/A	N/A	N/A	N/A	216	N/A	N/A	N/A
waterfall height (ft)	2	N/A	N/A	N/A	2.2	N/A	N/A	N/A	N/A	N/A	1	N/A	N/A	N/A
Diameter (ft)	N/A	N/A	2.8	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Slope (%)	N/A	N/A	0.05%	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
length (ft)	N/A	N/A	12.5	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	16.7	N/A	24.7
roughness	N/A	N/A	0.013	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
No. of CSTRs	N/A	N/A	1	N/A	N/A	N/A	2	1	1	N/A	N/A	N/A	N/A	N/A
tailwater depth (ft)	N/A	N/A	N/A	9.4	N/A	N/A	N/A	N/A	N/A	7.2	N/A	N/A	2	N/A
Drop height (ft)	N/A	N/A	N/A	1.7	N/A	N/A	N/A	N/A	N/A	2.8	N/A	N/A	2	N/A
Stream width (ft)	N/A	N/A	N/A	2	N/A	N/A	N/A	N/A	N/A	3.1	N/A	9.7	2	15.4
Oxygen Transfer (OT) eff. (%)	N/A	N/A	N/A	N/A	N/A	N/A	6%	6%	6%	N/A	N/A	N/A	N/A	N/A
Std. O.T. rate (lb O ₂ /hp.hr)	N/A	N/A	N/A	N/A	N/A	N/A	0.25	2	2.8	N/A	N/A	N/A	N/A	N/A
Dirty/clean water correction	N/A	N/A	N/A	N/A	N/A	N/A	0.8	0.8	0.8	N/A	N/A	N/A	N/A	N/A
Total mixer power (hp)	N/A	N/A	N/A	N/A	N/A	N/A	15	0.25	0.5	N/A	N/A	N/A	N/A	N/A
SS removal eff. (%)	N/A	N/A	N/A	N/A	50%	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Oil removal eff. (%)	N/A	N/A	N/A	N/A	95%	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Effluent SS conc. (mg/l)	724	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	19	N/A	N/A	N/A
Sludge SS conc. (mg/l)	61	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	6429	N/A	N/A	N/A
Air flow rate (cfm)	N/A	N/A	N/A	N/A	0	N/A	0	0	0	N/A	N/A	0	N/A	0
Flow rate of float stream (MGD)	N/A	N/A	N/A	N/A	0.0048	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Covered (Yes/No)	Y	Y	N/A	N/A	Y	Y	N	N	N	N/A	N	N	N/A	N
Ventilation (cfm)	763.14	2325.2	N/A	N/A	763.14	1.E-05	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A

Note: D.-S.: Diversionary structure

Appendix B-2. Units' parameters set-ups for WATER 9

The following is a list of input specifications for each unit with WATER 9

Type of unit is primary municipal clarifier

1 Description of unit	1 Primary Clarifier	
2 Wastewater temperature (C)		25.83
3 primary clarifier diameter (m)		9.632
4 primary clarifier depth (m)		3.7795
5 clarifier solids removal efficiency		0.7
6 waterfall drop height (cm)		20
7 clarifier weir/circumference		0.5
8 Center well present, =1		0
10 Number of identical units in parallel		0
15 vent air emission control factor		0.03601
16 Cover vent rate (m ³ /s per m ² surface)		0.01
17 If covered, then enter 1		0

Type of unit is storage tank

1 Description of unit	2 Blending Basin-1	
2 Wastewater temperature (C)		25.83
3 Open surface area of tank (m ²)		216.011
4 Density of liquid in tank (g/cc)		1
5 tank waste Mwt, water=18		18
6 tank storage time (days)		2
7 tank paint factor		1.2
8 tank diameter (m)		9.9
9 tank vapor space height (m)		1
10 diurnal temp. change (deg.C)		5.3
11 tank height (m)		4.72
12 oil in composite wastewater (wt. %)		0.2

Type of unit is storage tank

1 Description of unit	3 Blending Basin -2	
2 Wastewater temperature (C)		25.83
3 Open surface area of tank (m ²)		216.011
4 Density of liquid in tank (g/cm ³)		1
5 tank waste Mwt, water=18		18
6 tank storage time (days)		2
7 tank paint factor		1.2
8 tank diameter (m)		9.9
9 tank vapor space height (m)		1

10 diurnal temp. change (deg.C)	5.3
11 tank height (m)	4.72
12 oil in composite wastewater (wt. %)	0.2

Type of unit is open sump

1 Description of unit	4 Influent from Bldg.3001
2 Underflow T (C)	25.83
3 Total water added at the unit (l/s)	30
4 Area of openings at unit (cm ²)	50
5 Radius of drop pipe (cm)	5
6 Drop length to conduit (cm)	61
7 Open surface=1	1
8 Subsurface entrance=1	0
9 subsurface exit =1	0
10 radius of underflow conduit (cm)	12
11 distance to next unit (cm)	2374.4
12 slope of underflow conduit	0.015
13 area of surface (cm ²)	10000
14 flow entrance depth under surface (cm)	10
15 depth of liquid in sump (cm)	50
16 velocity air at opening (ft/min)	88
17 municipal waste in conduit =1	0
18 Assume equilibrium in unit, =1	0

Type of unit is weir, waterfall

1 Description of unit	5 lift station
2 Underflow T (C)	25.83
3 Total water added at the unit (l/s)	0
4 waterfall width at surface (m)	0.7925
5 waterfall drop height (cm)	0.5182
6 tailwater depth (m)	2.8651
7 Open surface=1	0
8 Subsurface entrance=1	0
9 subsurface exit =1	0
10 radius of underflow conduit (cm)	30.48
11 distance to next unit (cm)	500
12 slope of underflow conduit	0.015

Type of unit is covered separator

1 Description of unit	6 Oil-water separator-1
2 Wastewater temperature (C)	25.83
3 area of run vent or opening (cm ² /unit)	3000
4 velocity air at opening (ft/min)	88

5 length of unit (m)	19.873
6 width of unit (m)	19.873
7 depth of unit (m)	3.048
8 cover vent rate (m ³ /s per m ² surface)	0.0005
9 headspace depth (cm)	67.06
11 fraction of oil recovered from water	0.8
12 oil in composite wastewater (wt. %)	0.2

Type of unit is covered separator

1 Description of unit	7 Oil-water separator-2
2 Wastewater temperature (C)	25.83
3 area of run vent or opening (cm ² /unit)	3000
4 velocity air at opening (ft/min)	88
5 length of unit (m)	19.873
6 width of unit (m)	19.873
7 depth of unit (m)	3.048
8 cover vent rate (m ³ /s per m ² surface)	0.0005
9 headspace depth (cm)	67.06
11 fraction of oil recovered from water	0.8
12 oil in composite wastewater (wt. %)	0.2

Type of unit is storage tank

1 Description of unit	8 Storage Tank-1
2 Wastewater temperature (C)	25.83
3 Open surface area of tank (m ²)	0
4 Density of liquid in tank (g/cc)	1
5 tank waste Mwt, water=18	18
6 tank storage time (days)	2.79
7 tank paint factor	1
8 tank diameter (m)	23.256
9 tank vapor space height (m)	2.9566
10 diurnal temp. change (deg.C)	5.3
11 tank height (m)	9.876
12 oil in composite wastewater (wt. %)	0.2

Type of unit is storage tank

1 Description of unit	9 Storage Tank-2
2 Wastewater temperature (C)	25.83
3 Open surface area of tank (m ²)	0
4 Density of liquid in tank (g/cm ³)	1
5 tank waste Mwt, water=18	18
6 tank storage time (days)	2.79
7 tank paint factor	1

8 tank diameter (m)	23.256
9 tank vapor space height (m)	2.9566
10 diurnal temp. change (deg.C)	5.3
11 tank height (m)	9.876
12 oil in composite wastewater (wt. %)	0.2

Type of unit is equalization

1 Description of unit	10 Equalization Basin-1
2 Wastewater temperature (C)	25.83
3 length of unit (m)	31.09
4 width of unit (m)	15.85
5 depth of unit (m)	3.5357
6 Area of agitation (each aerator, m ²)	47
7 Total number of agitators in the unit	1
8 Power of agitation (each aerator, HP)	15
9 Impeller diameter (cm)	60
10 Impeller rotation (RPM)	1200
11 Agitator mechanical efficiency	0.83
12 aerator effectiveness, alpha	0.83
13 if there is plug flow, enter 1	0
14 Overall biorate (mg/g bio-hr)	19
15 Aeration air flow (m ³ /s)	0
16 active biomass, (g/l)	0.05
17 vent factor (covered=1)	0.0005

Type of unit is equalization

1 Description of unit	11 Equalization Basin-2
2 Wastewater temperature (C)	25.83
3 length of unit (m)	31.09
4 width of unit (m)	15.85
5 depth of unit (m)	3.5357
6 Area of agitation (each aerator, m ²)	47
7 Total number of agitators in the unit	1
8 Power of agitation (each aerator, HP)	15
9 Impeller diameter (cm)	60
10 Impeller rotation (RPM)	1200
11 Agitator mechanical efficiency	0.83
12 aerator effectiveness, alpha	0.83
13 if there is plug flow, enter 1	0
14 Overall biorate (mg/g bio-hr)	19
15 Aeration air flow (m ³ /s)	0
16 active biomass, (g/l)	0.05

17 vent factor (covered=1) 0.0005

Type of unit is mix tank

1 Description of unit	12 Mixing Basin-1
2 Wastewater temperature (C)	25.83
3 length of unit (m)	4.0234
4 width of unit (m)	4.8768
5 depth of unit (m)	4.8158
6 Area of agitation (each aerator, m ²)	47
7 Total number of agitators in the unit	1
8 Power of agitation (each aerator, HP)	0.25
9 Impeller diameter (cm)	60
10 Impeller rotation (RPM)	1200
13 if there is plug flow, enter 1	0
15 Aeration air flow (m ³ /s)	0
16 vent air emission control factor	0
17 If covered, then enter 1	0

Type of unit is mix tank

1 Description of unit	13 Mixing Basin-2
2 Wastewater temperature (C)	25.83
3 length of unit (m)	4.0234
4 width of unit (m)	4.8768
5 depth of unit (m)	4.8158
6 Area of agitation (each aerator, m ²)	47
7 Total number of agitators in the unit	1
8 Power of agitation (each aerator, HP)	0.25
9 Impeller diameter (cm)	60
10 Impeller rotation (RPM)	1200
13 if there is plug flow, enter 1	0
15 Aeration air flow (m ³ /s)	0
16 vent air emission control factor	0
17 If covered, then enter 1	0

Type of unit is weir, waterfall

1 Description of unit	14 Weir/Water drop
2 Underflow T (C)	25.83
3 Total water added at the unit (l/s)	0
4 waterfall width at surface (m)	0.7925
5 waterfall drop height (cm)	0.5182
6 tailwater depth (m)	2.8651
7 Open surface=1	0
8 Subsurface entrance=1	0
9 subsurface exit =1	0
10 radius of underflow conduit (cm)	30.48

11 distance to next unit (cm)	500
12 slope of underflow conduit	0.015

Type of unit is mix tank

1 Description of unit	15	Mixing Basin-3
2 Wastewater temperature (C)	25.83	
3 length of unit (m)	2.7432	
4 width of unit (m)	2.7432	
5 depth of unit (m)	3.5662	
6 Area of agitation (each aerator, m ²)	47	
7 Total number of agitators in the unit	1	
8 Power of agitation (each aerator, HP)	0.5	
9 Impeller diameter (cm)	60	
10 Impeller rotation (RPM)	1200	
13 if there is plug flow, enter 1	0	
15 Aeration air flow (m ³ /s)	0	
16 vent air emission control factor	0	
17 If covered, then enter 1	0	

Type of unit is weir, waterfall

1 Description of unit	16	Weir/Water drop
2 Underflow T (C)	25.83	
3 Total water added at the unit (l/s)	0	
4 waterfall width at surface (m)	0.7925	
5 waterfall drop height (cm)	0.5182	
6 tailwater depth (m)	2.8651	
7 Open surface=1	0	
8 Subsurface entrance=1	0	
9 subsurface exit =1	0	
10 radius of underflow conduit (cm)	30.48	
11 distance to next unit (cm)	500	
12 slope of underflow conduit	0.015	

Type of unit is circular clarifier

1 Description of unit	17	Solids Contact Clarifier
2 Wastewater temperature (C)	25.83	
3 secondary clarifier diameter (m)	18.288	
4 secondary clarifier depth (m)	5.0597	
5 clarifier solids removal efficiency	0.7	
6 waterfall drop height (cm)	20	
7 clarifier weir/circumference	0.57	

Type of unit is weir, waterfall

1 Description of unit	18 Weir/water drop
2 Underflow T (C)	25.83
3 Total water added at the unit (l/s)	0
4 waterfall width at surface (m)	0.7925
5 waterfall drop height (cm)	0.5182
6 tailwater depth (m)	2.8651
7 Open surface=1	0
8 Subsurface entrance=1	0
9 subsurface exit =1	0
10 radius of underflow conduit (cm)	30.48
11 distance to next unit (cm)	500
12 slope of underflow conduit	0.015

Type of unit is open sump

1 Description of unit	19 Wet Well
2 Underflow T (C)	25
3 Total water added at the unit (l/s)	0
4 Area of openings at unit (cm ²)	50
5 Radius of drop pipe (cm)	5
6 Drop length to conduit (cm)	61
7 Open surface=1	0
8 Subsurface entrance=1	0
9 subsurface exit =1	0
10 radius of underflow conduit (cm)	12
11 distance to next unit (cm)	500
12 slope of underflow conduit	0.015
13 area of surface(cm ²)	10000
14 flow entrance depth under surface (cm)	10
15 depth of liquid in sump (cm)	137.2
16 velocity air at opening (ft/min)	88
17 municipal waste in conduit =1	0
18 Assume equilibrium in unit, =1	0

Type of unit is hard piped, no headspace

1 Description of unit	20 Sand Filter
2 Underflow T (C)	25.83
3 Total water added at the unit (l/s)	0
7 Open surface=1	0
8 Subsurface entrance=1	1
9 subsurface exit =1	1
10 radius of underflow conduit (cm)	12
11 distance to next unit (cm)	500
12 slope of underflow conduit	0.015

Type of unit is open sump

1 Description of unit	21 Chlorine Contact chamber	25
2 Underflow T (C)		0
3 Total water added at the unit (l/s)		50
4 Area of openings at unit (cm ²)		5
5 Radius of drop pipe (cm)		61
6 Drop length to conduit (cm)		0
7 Open surface=1		0
8 Subsurface entrance=1		0
9 subsurface exit =1		0
10 radius of underflow conduit (cm)		12
11 distance to next unit (cm)		500
12 slope of underflow conduit		0.015
13 area of surface(cm ²)		10000
14 flow entrance depth under surface (cm)		10
15 depth of liquid in sump (cm)		137.2
16 velocity air at opening (ft/min)		88
17 municipal waste in conduit =1		0
18 Assume equilibrium in unit, =1		0

Type of unit is circular clarifier

1 Description of unit	22 Thickener	25.83
2 Wastewater temperature (C)		60
3 secondary clarifier diameter (m)		5.0597
4 secondary clarifier depth (m)		0.7
5 clarifier solids removal efficiency		20
6 waterfall drop height (cm)		0.57
7 clarifier weir/circumference		

Type of unit is porous solids unit

1 Description of unit	23 Filter Press	0
2 temperature in porous solids (C)		0
3 depth of waste layer (cm)		0
4 total porosity		0
5 air porosity		0
6 mwt oil		0
7 time of calculations (days)		0
8 active biomass (g/cc)		0
9 loading g/cc soil		0
10 Wind velocity (cm/s at 10 m)		0
11 area of land treatment (m ²)		0

Type of unit is oil film unit

1 Description of unit	24 Sludge Treatment Unit
2 Wastewater temperature (C)	25.83
3 oil in composite wastewater (wt. %)	0
4 oil film impoundment length (m)	50
5 oil film impoundment width (m)	50
6 oil film impoundment depth (m)	4
8 Density of oil (g/cc)	0.7
9 Months for disposal (0 flow through)	0
10 Oil molecular weight	180

Appendix C. An Example of Bootstrapping Simulation

The following is an example of the steps utilized in performing a bootstrapping simulation. The original data set for acetone was used in this example. This data set consisted of only 24 data points and has a very wide range from 189 $\mu\text{g/l}$ to 988 $\mu\text{g/l}$. The data set is listed as follows:

{267, 452, 442, 189, 262, 487, 267, 387, 351, 242, 266, 350, 237, 294, 420, 403, 577, 736, 338, 490, 451, 734, 988, 865}

As discussed in the chapter on Methodology in this thesis, the bootstrapping sample is drawn from the sample set equivalently with the same probability of $1/n$. Minitab[®] was used to generate random numbers from the original data set mentioned above with replacement. Actually, all of the data in the original data set has the same probability being sampled. The probability is $1/24 = 0.041$. From the main menu of Minitab[®], go to Calc to Random Data to Discrete, follow the prompt windows and input the desire values. For example,

{988, 577, 350, 403, 351, 577, 577, 403, 490, 189, 490, 442, 189, 403, 736, 189, 452, 736, 865, 189}

is just a bootstrapping sample from the original data. The mean and standard deviation of the bootstrapping sample were then calculated, which were 479.8 and 224.55, respectively.

In this thesis, for each compound, a bootstrapping sample consists of 20 data points and the bootstrapping was repeated 100 times. Then, there were 100 means and standard deviations of the bootstrapping samples. These statistics were then analyzed to provide confidence intervals. These data are listed in the following Table C1.

Table C1. Bootstrapping samples of acetone

No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	Mean	SD
1	988	577	350	403	351	577	577	403	490	189	490	442	189	403	736	189	452	736	865	189	479.8	224.554
2	237	490	403	487	294	865	242	734	736	338	242	350	403	338	267	865	734	387	338	242	449.6	215.153
3	487	452	451	189	267	420	420	242	487	734	267	865	262	294	736	262	487	237	267	351	408.9	187.612
4	577	262	452	237	351	242	988	734	442	734	988	865	350	267	487	403	490	403	403	988	533.2	258.197
5	420	189	988	350	865	338	237	350	865	351	420	267	736	442	351	988	189	351	865	865	521.4	283.463
6	237	442	242	487	262	865	267	351	237	237	865	237	490	420	451	189	350	338	734	189	394.5	208.957
7	988	294	736	865	338	577	487	262	734	865	865	189	237	442	237	266	988	262	242	266	507	289.1
8	452	736	262	387	267	442	189	734	734	242	452	490	267	338	734	577	451	490	294	237	438.8	183.613
9	267	988	267	237	350	442	242	736	988	988	420	487	865	189	350	451	237	294	420	189	470.4	280.869
10	736	267	267	387	736	403	266	387	294	351	242	988	387	237	403	242	266	451	577	350	411.9	200.933
11	736	267	267	420	487	294	865	487	734	403	736	577	403	865	242	338	189	734	237	451	486.6	220.926
12	242	338	490	338	237	189	387	577	451	577	865	577	189	420	262	351	487	451	420	451	415	162.204
13	420	242	242	338	420	338	262	734	189	267	736	487	350	237	865	387	451	266	351	577	408	187.81
14	242	420	420	387	988	490	734	420	350	487	266	420	403	189	420	988	442	736	451	865	505.9	231.701
15	262	403	736	237	237	267	350	452	266	577	242	577	242	490	189	338	420	577	442	267	378.6	151.652
16	734	267	267	487	988	350	267	351	420	490	387	237	865	294	262	351	262	237	351	487	417.7	212.293
17	387	736	338	487	338	403	420	451	237	442	736	988	242	490	351	294	403	237	490	988	472.9	222.325
18	242	267	577	442	242	267	865	988	988	350	237	403	487	338	490	734	242	262	242	487	457.5	250.964
19	350	242	267	988	451	577	403	865	452	338	262	266	350	988	387	350	487	451	267	420	458.1	229.001
20	451	237	351	242	387	736	420	487	351	988	387	403	350	266	487	487	237	442	865	242	440.8	204.902
21	189	487	577	865	420	577	577	350	420	865	267	387	351	387	242	262	403	267	350	189	421.6	192.169
22	237	442	189	420	262	487	452	452	294	387	490	490	387	262	487	442	403	387	242	734	397.3	125.232
23	262	350	734	452	237	487	262	988	266	451	452	403	736	577	487	487	237	487	294	189	441.9	201.592
24	988	442	403	734	294	338	338	451	487	387	267	452	237	237	338	338	387	267	350	403	406.9	176.064
25	350	242	237	387	350	988	294	267	294	266	490	189	266	294	267	387	267	487	294	294	345.5	169.916
26	451	403	262	577	988	237	266	487	189	338	294	351	267	420	267	736	242	267	350	452	392.2	193.055
27	267	988	189	338	736	736	988	487	442	452	294	387	988	736	242	237	267	266	420	242	485.1	274.64
28	267	266	294	865	189	387	577	350	490	452	452	452	242	442	734	442	736	350	267	442	434.8	178.961
29	387	267	988	351	267	988	338	442	351	387	734	294	351	865	267	734	351	442	452	988	512.2	262.489
30	490	294	736	262	267	442	267	487	189	267	734	442	350	294	490	262	338	487	988	487	428.7	200.093
31	451	338	577	487	338	865	262	736	338	351	487	442	267	736	237	351	420	266	189	403	427.1	180.749
32	189	351	267	487	267	262	490	734	350	452	988	242	451	266	577	189	452	736	451	736	446.9	216.198
33	237	338	189	267	451	734	577	577	351	351	865	442	988	451	267	734	294	266	442	577	469.9	221.761
34	266	237	350	242	988	452	487	403	736	420	262	294	262	452	338	267	338	403	487	267	397.6	184.086
35	189	242	338	242	350	865	294	267	403	487	338	442	451	734	267	338	452	387	442	442	398.5	162.412
36	387	420	267	338	577	490	420	387	338	387	452	267	403	338	237	267	189	736	487	267	382.7	128.002
37	267	351	736	387	451	351	267	387	577	452	242	865	451	267	267	267	490	262	451	294	404.1	166.631
38	262	237	338	267	266	988	490	734	577	865	338	267	577	294	350	734	338	403	189	420	446.7	227.268
39	338	451	267	736	736	577	442	452	237	387	420	577	577	387	988	736	452	351	403	237	487.6	193.678
40	736	267	338	487	351	338	267	242	988	420	338	865	294	736	350	387	294	403	294	988	469.2	246.715
41	420	350	189	452	237	736	490	577	490	442	294	338	487	865	487	442	350	262	490	442	442	159.476
42	351	387	452	736	267	294	351	237	734	351	242	237	452	262	267	338	350	266	237	242	352.7	147.253
43	351	338	237	403	294	266	451	242	267	577	736	451	266	403	865	387	865	237	451	351	421.9	195.564
44	387	577	490	442	242	351	189	865	338	451	420	237	351	420	351	351	736	734	865	242	452	202.894
45	487	420	988	988	420	988	442	865	487	420	242	262	736	734	403	267	242	266	351	452	523	261.892
46	351	988	338	267	350	420	350	865	350	442	189	490	865	266	490	451	338	266	294	266	431.8	220.506
47	442	736	266	338	988	487	262	242	734	452	237	734	189	350	350	865	350	487	242	242	449.7	236.488

48	736	736	351	387	403	577	988	420	242	403	266	490	442	350	266	242	262	294	403	420	433.9	193.549
49	452	577	267	351	294	350	734	736	452	577	487	442	451	351	237	387	442	490	452	294	441.2	137.143
50	350	351	451	490	865	242	451	189	736	338	452	267	189	490	736	736	237	452	403	262	434.4	197.908
51	266	403	350	451	988	577	262	267	242	490	267	451	237	267	988	577	237	350	452	452	428.7	221.188
52	338	294	242	262	387	338	338	451	442	420	451	420	262	487	387	266	452	988	338	734	414.9	174.55
53	267	267	294	487	242	266	350	338	865	451	387	577	487	420	262	577	242	577	267	338	398.1	160.569
54	451	442	266	267	351	338	387	420	266	267	988	577	237	490	262	487	266	734	267	865	431.4	213.311
55	267	988	350	262	266	351	487	403	988	865	577	452	988	736	451	294	266	338	988	350	533.4	280.581
56	267	267	266	262	487	490	577	442	734	351	865	442	387	267	262	865	338	267	338	294	423.4	196.264
57	242	734	736	189	237	988	267	267	242	451	442	420	865	490	338	294	865	387	267	262	449.2	248.742
58	452	420	242	267	294	734	262	988	189	734	242	266	736	267	266	242	736	736	237	487	439.9	244.304
59	294	734	577	734	420	338	736	350	338	262	487	451	442	266	387	865	403	338	420	452	464.7	174.375
60	237	338	262	189	490	237	262	736	267	734	403	451	387	865	351	403	988	865	267	577	465.5	244.579
61	237	242	338	351	736	189	420	338	452	442	442	267	865	452	267	487	442	736	266	387	417.8	179.765
62	865	403	294	734	266	403	294	351	988	734	294	736	338	351	294	865	387	267	242	262	468.4	246.455
63	734	490	403	420	988	577	734	865	487	988	452	452	487	420	442	267	237	387	266	490	529.3	221.179
64	451	267	487	736	387	452	736	350	267	451	189	267	294	350	189	403	294	452	487	403	395.6	148.841
65	267	734	451	350	262	351	420	736	451	736	387	577	865	452	387	267	736	865	262	189	487.3	216.832
66	865	350	294	577	420	988	490	865	189	189	350	736	734	403	403	387	351	490	242	242	478.3	239.067
67	189	734	338	736	865	734	266	350	267	420	865	294	420	266	338	487	262	242	338	242	432.7	223.356
68	490	865	266	420	451	988	242	577	242	267	387	442	988	350	577	237	387	736	351	403	483.3	237.835
69	452	189	452	451	451	487	452	242	490	736	865	351	387	351	351	237	403	267	452	487	427.7	157.982
70	237	294	267	387	189	988	237	487	267	452	487	420	351	734	267	338	577	338	294	267	393.9	192.937
71	865	865	865	267	294	262	577	338	420	242	237	420	262	736	189	267	267	338	734	734	459	246.389
72	267	420	351	490	267	267	242	490	242	242	387	577	267	403	267	487	734	736	577	189	395.1	165.631
73	189	262	338	242	403	452	266	294	865	237	420	189	350	451	988	387	237	350	351	350	381.1	203.883
74	351	267	267	267	338	734	487	262	242	266	387	294	267	267	490	189	387	237	734	242	348.8	153.988
75	237	451	294	403	338	242	237	350	294	262	865	420	442	403	267	736	242	267	734	988	423.6	225.525
76	267	351	577	487	403	267	490	577	420	736	442	420	490	242	403	577	267	262	736	266	434	152.254
77	189	577	267	865	267	189	350	338	267	338	350	452	442	420	451	242	988	237	237	189	382.8	214.26
78	387	451	490	267	294	351	189	734	487	189	490	262	420	294	451	420	442	865	451	351	414.3	164.008
79	189	350	442	237	266	387	189	420	490	451	865	267	350	338	189	734	266	865	451	338	404.2	203.355
80	387	577	242	266	266	451	189	865	294	451	267	988	294	988	267	267	189	266	736	490	437	259.7
81	267	266	266	242	487	267	420	262	387	490	351	865	988	403	487	734	451	490	577	403	455.2	204.714
82	189	237	266	338	865	736	267	736	577	734	988	734	734	387	267	736	988	267	403	734	559.2	267.888
83	487	988	350	452	267	865	267	487	403	351	350	294	338	267	262	734	442	487	451	487	451.5	199.015
84	487	988	267	242	736	487	451	387	351	351	262	403	294	487	351	865	237	351	451	490	446.9	202.116
85	487	350	189	387	734	189	403	451	266	189	266	338	242	351	442	734	242	387	242	237	356.3	158.427
86	351	262	237	338	403	487	387	189	266	189	865	490	865	267	865	452	350	237	736	267	425.2	228.355
87	350	294	189	267	736	734	865	420	865	237	577	420	420	403	242	490	237	577	294	736	467.7	219.511
88	420	387	267	266	403	237	734	452	350	734	420	403	266	189	351	294	351	267	387	350	376.4	141.282
89	451	452	403	189	242	420	420	865	490	577	451	442	338	442	452	267	487	420	267	988	453.2	188.697
90	865	262	262	266	487	242	487	734	237	189	577	736	338	267	865	734	487	267	487	451	462	223.266
91	490	267	442	865	294	577	403	338	734	262	267	736	338	294	490	351	487	736	451	865	484.4	201.828
92	403	262	487	451	988	338	490	988	451	351	267	350	577	242	387	451	262	351	266	734	454.8	218.585
93	734	267	267	988	387	237	865	237	452	403	294	451	294	266	262	294	242	350	350	189	391.5	219
94	189	262	451	865	736	350	451	736	350	487	387	350	487	350	403	294	577	420	294	420	443	170.727
95	420	420	267	387	387	338	237	237	294	490	736	452	262	262	988	267	442	237	338	294	387.8	185.341

96	452	262	487	734	237	338	734	403	734	420	442	736	442	988	267	577	577	442	577	452	515.1	193.09
97	338	442	451	988	267	262	294	451	442	266	988	294	734	452	242	442	452	442	267	577	454.6	219.591
98	490	403	420	403	403	242	189	490	734	442	267	294	577	242	351	403	189	442	237	865	404.2	174.083
99	262	267	734	451	189	988	267	294	189	267	988	338	266	865	442	988	351	294	237	490	458.4	285.046
100	294	487	189	351	487	189	237	267	266	350	490	338	189	577	577	189	237	577	403	262	347.8	139.289

Note: SD - standard deviation

An EXCEL[®] integrated tool “Data Analysis” was used to analyze the standard deviation of these bootstrapping samples. From EXCEL[®] main menu, go to Tool to Data Analysis, choose Rank and Percentile, specify the data set, a report of rank and percentile was then generated. Using the chart wizard, a cumulative distribution curve of the statistics of interest was then produced. A report is listed in the following Table C2.

Table C2. Ranking and percentiles of the bootstrapping samples of acetone

<i>Point</i>	<i>Column1</i>	<i>Rank</i>	<i>Percent</i>	<i>Point</i>	<i>Column1</i>	<i>Rank</i>	<i>Percent</i>
7	289.1	1	100.00%	44	202.894	51	49.40%
99	285.046	2	98.90%	84	202.116	52	48.40%
5	283.463	3	97.90%	91	201.828	53	47.40%
9	280.869	4	96.90%	23	201.592	54	46.40%
55	280.581	5	95.90%	10	200.933	55	45.40%
27	274.64	6	94.90%	30	200.093	56	44.40%
82	267.888	7	93.90%	83	199.015	57	43.40%
29	262.489	8	92.90%	50	197.908	58	42.40%
45	261.892	9	91.90%	56	196.264	59	41.40%
80	259.7	10	90.90%	43	195.564	60	40.40%
4	258.197	11	89.80%	39	193.678	61	39.30%
18	250.964	12	88.80%	48	193.549	62	38.30%
57	248.742	13	87.80%	96	193.09	63	37.30%
40	246.715	14	86.80%	26	193.055	64	36.30%
62	246.455	15	85.80%	70	192.937	65	35.30%
71	246.389	16	84.80%	21	192.169	66	34.30%
60	244.579	17	83.80%	89	188.697	67	33.30%
58	244.304	18	82.80%	13	187.81	68	32.30%
66	239.067	19	81.80%	3	187.612	69	31.30%
68	237.835	20	80.80%	95	185.341	70	30.30%
47	236.488	21	79.70%	34	184.086	71	29.20%
14	231.701	22	78.70%	8	183.613	72	28.20%
19	229.001	23	77.70%	31	180.749	73	27.20%

86	228.355	24	76.70%	61	179.765	74	26.20%
38	227.268	25	75.70%	28	178.961	75	25.20%
75	225.525	26	74.70%	24	176.064	76	24.20%
1	224.554	27	73.70%	52	174.55	77	23.20%
67	223.356	28	72.70%	59	174.375	78	22.20%
90	223.266	29	71.70%	98	174.083	79	21.20%
17	222.325	30	70.70%	94	170.727	80	20.20%
33	221.761	31	69.60%	25	169.916	81	19.10%
51	221.188	32	68.60%	37	166.631	82	18.10%
63	221.179	33	67.60%	72	165.631	83	17.10%
11	220.926	34	66.60%	78	164.008	84	16.10%
46	220.506	35	65.60%	35	162.412	85	15.10%
97	219.591	36	64.60%	12	162.204	86	14.10%
87	219.511	37	63.60%	53	160.569	87	13.10%
93	219	38	62.60%	41	159.476	88	12.10%
92	218.585	39	61.60%	85	158.427	89	11.10%
65	216.832	40	60.60%	69	157.982	90	10.10%
32	216.198	41	59.50%	74	153.988	91	9.00%
2	215.153	42	58.50%	76	152.254	92	8.00%
77	214.26	43	57.50%	15	151.652	93	7.00%
54	213.311	44	56.50%	64	148.841	94	6.00%
16	212.293	45	55.50%	42	147.253	95	5.00%
6	208.957	46	54.50%	88	141.282	96	4.00%
20	204.902	47	53.50%	100	139.289	97	3.00%
81	204.714	48	52.50%	49	137.143	98	2.00%
73	203.883	49	51.50%	36	128.002	99	1.00%
79	203.355	50	50.50%	22	125.232	100	.00%

Based on the above table, the following plot (Figure C3) for acetone was then generated.

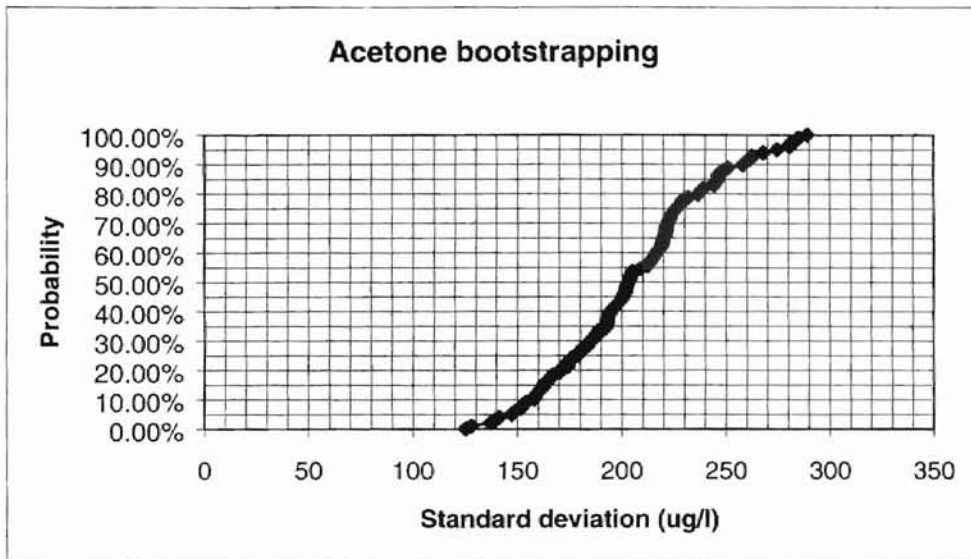


Figure C3. Bootstrapping of acetone on standard deviation

VITA 2

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Master of Science

Thesis: UNCERTAINTY ANALYSIS OF THE EMISSION INVENTORY OF AN
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A CASE STUDY AT THE IWTP OF THE TINKER AIR FORCE BASE,
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