ABSTRACT

LI, SONG. Development and Demonstration of a Methodology for Characterizing and Managing Uncertainty and Variability in Emission Inventories. (Under the direction of Dr. H. Christopher Frey.)

Emission factors and emission inventories are subject to both variability and uncertainty. Variability refers to observed differences attributable to true heterogeneity or diversity in emissions. Uncertainty refers to lack of knowledge regarding the true value of emissions. Variability in emissions can be attributed to variations over time, space or across different populations. Uncertainty in emissions typically arises due to limited sample size, lack of accuracy, non-representativeness of data, measurement errors, use of surrogate data, and human errors. This work successfully demonstrated new applications of quantitative methods for characterizing variability and uncertainty in emission estimates. The methods were demonstrated with respect to cases studies on nitrogen oxides (NO_x) and volatile organic compound (VOC) emissions from natural gas-fueled internal combustion engines, and VOC emissions from consumer/commercial product use, gasoline terminal loading, cutback asphalt paving, architectural coatings and wood furniture coatings.

Emission data must be nonnegative, typically are positively skewed and have limited sample size. The restrictive assumption of normality used in analytical methods can lead to biased uncertainty estimates. Therefore, in this work, variability was characterized by fitting parametric distributions and uncertainty due to random sampling errors was quantified based upon numerical bootstrap simulation. Uncertainty in mean emission factors was found as much as minus 90 percent to plus 180 percent in a relative basis. Key methodological issues, including separation of intra- and inter-facility/engine variability, and methods for fitting parametric distributions to unequally weighted data, were addressed. Recommendations include extending these efforts to more emission source categories and for EPA and others to routinely report well-documented emission data to facilitate uncertainty analysis.

DEVELOPMENT AND DEMONSTRATION OF A METHODOLOGY FOR CHARACTERIZING AND MANAGING UNCERTAINTY AND VARIABILITY IN EMISSION INVENTORIES

By

SONG LI

A dissertation submitted to the Graduate Faculty of
North Carolina State University
in partial fulfillment of the
requirements for the Degree of
Doctor of Philosophy

DEPARTMENT OF CIVIL ENGINEERING

ENVIRONMENTAL ENGINEERING AND WATER RESOURCES

Raleigh

2002

APPROVED BY:

Chair of Advisory Committee

BIOGRAPHY

Song Li was born on September 6th, 1973 in the city of Wuxi, China. He earned his B.S. and M.S. degrees in Environmental Engineering from Zhejiang University, China. He joined in the Computational Laboratory for Energy, Air, and Risk of Environmental Engineering at NC State University in 1999. His current research focuses on the quantitative analysis of variability and uncertainty in emission inventories and air quality models.

ACKNOWLEDGEMENTS

First, I want to thank my family, Shengzhen Li, Jing Ping, Jin Li and Feinian Chen, for their love and long-term support. I also want to thank Miss. Jing Chen for her love and understanding.

I am grateful to Dr. H. Christopher. Frey. His advice is invaluable for this work. Also thanks to Mr. Roy Huntley and Mr. Stephen Shedd of U.S. EPA, Dr. Dean H. Judson of U.S. Census Bureau, Dr. Robert P. Anex of University of Oklahoma, Dr. Jay R. Lund of University of California at Davis, and Mr. Adam B. Long at Transcontinental Gas Pipe Line Corporation for their assistance in data collection and analysis.

Finally, I thank my committee members, Dr. Daniel H. Loughlin, Dr. E. Downey Brill, Jr., Dr. Donald Van der Vaart, and the Graduate School Representative, Dr. Marc G. Genton for their inputs to this work.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

1.0 INTRODUCTION

Emission inventories are important supporting tools for air quality modeling, risk assessment, compliance analysis, new source permitting, emission trend analysis and other applications. A major concern in emission inventory development is variability and uncertainty in emission factors. A key question is whether the point estimates of emission factors that are widely used as inputs to develop emission inventories are sufficiently robust with respect to uncertainty.

This research focuses on demonstrating new applications of quantitative methods for characterizing variability and uncertainty in emission factors. The cases studies demonstrated here are for primary emission source categories of nitrogen oxides (NO_x) and volatile organic compounds (VOCs), including natural gas-fueled internal combustion engines, consumer/commercial product use, gasoline terminal loading, cutback asphalt paving, architectural coating, and wood furniture coating. The case studies of these source categories are presented in five chapters in a journal paper format and two of them have been presented at conferences. Except for wood furniture coating, this study is the first known effort to quantify variability and uncertainty in these emission source categories.

The purpose of this study is not to validate or dispute current methodologies to develop emission factors and inventories, but to provide a new perspective and a better understanding of the quality of the emission estimates. Because regulatory or air quality management strategy involve high stakes, such as public health, money, and other impacts, it is important that these decisions are based upon the best information available and are robust to uncertainty.

The key questions addressed in this study include:

- Why should variability and uncertainty be distinguished?
- What methods should be used to quantify uncertainty in emission factors?
- How should intra-engine/facility variability be handled in quantitative analysis for mean emission factors?
- What method can be used for unequally weighted data?
- What is the range of variability in product compositions and emission estimates?
- What is the range of uncertainty in mean emission factors?

1.1 Uncertainty and Variability

Uncertainty refers to lack of knowledge regarding the true value of an unknown quantity (Bogen and Spear, 1987, Frey, 1992). Uncertainty in the statistics of a population can be expressed by either empirical or parametric probability distributions (Morgan and Henrion,1990, Frey and Rhodes, 1996). Another effective way to express uncertainty is a confidence interval. Typically, a 95 percent confidence interval is reported.

According to the causes, uncertainty can be further categorized as systematic errors and random errors (Morgan and Henrion, 1990). Systematic errors, also referred as inaccuracy or bias, arise due to inaccurate measuring method or non-representativeness of data. Random errors, also referred as imprecision, are introduced by random measurement errors and statistical random sampling errors due to the limited sample size.

Statistically, variability refers to observed differences attributable to true heterogeneity or diversity in a population (ISO, 1993). For example, emissions from fossil combustion may vary from one specific source to another because of variations in design, feedstock compositions, ambient conditions, and other operating conditions. Variability can also be expressed by a probability distribution. Some have suggested the use of the term "frequency distribution" instead of "probability distribution" for variability in order to avoid concept confusion (Morgan and Henrion,1990, Frey and Rhodes, 1996).

1.2 Practice of Quantitative Analysis in the Field of Environmental Protection

Uncertainties in current emission factors and emission inventories are typically not reported. As a surrogate for uncertainty estimates, some emission factors are accompanied by data quality ratings, such as those reported in AP-42 (EPA, 1995). "A" to "E" qualitative ratings are assigned to emission factors as indicators of their quality. A method for qualitatively rating emission inventories, known as the Data Attribute Rating System (DARS), has been developed by EPA (Beck, 1997). Qualitative ratings of emission factors and emission inventories are important. Some sources of uncertainty are difficult to be quantified, such as non-representativeness of a data set. Therefore, there will always be a role for qualitative statements regarding non-quantifiable sources of uncertainty. However, an argument can be made that qualitative rating systems should be used in combination with quantitative approaches.

There is growing recognition of the need for quantitative uncertainty analysis in emission estimations, environmental modeling and decision-making. For example, the National Research Council (NRC) has recommended to EPA that quantitative analysis of uncertainty be included in a variety of applications (NRC, 1994, 2000). The National Council on Radiation Protection and Measurements (NCRP) has published guidance for uncertainty analysis in dose and risk assessments related to environment contaminations (NCRP, 1996). EPA (1997) has developed guidelines for Monte Carlo simulation of uncertainty. The Intergovernmental Panel on Climate Change (IPCC) has proposed "good practices guidance and uncertainty management" on the request from the United Nations Framework Conversion on Climate Change (UNFCCC) for national greenhouse gas inventories (IPCC, 2000). The U.S. Department of Energy (DOE) also recommended using the Monte Carlo simulation of uncertainty in U.S. greenhouse gas emission estimates (U.S. DOE, 2001). A recent NRC report has recommended that the EPA and others "should undertake the necessary measures to conduct quantitative uncertainty analyses of the mobile source emissions models" (NRC, 2000).

As a response to the needs for quantitative uncertainty analysis, researches have been underway to develop and demonstrate methods for quantifying uncertainty in different applications, including emission estimation, climate change and risk assessment.

1.2.1 Uncertainty Analysis in Estimation of Pollutant Emissions

In the area of power plant emissions, Frey *et al.* have quantified uncertainty in emissions of hazardous air pollutants (HAPs) and NO_x from coal-fired power plants (Frey and Rhodes, 1996, Rhodes and Frey, 1997, Frey *et al.*, 1999, Frey and Bharvirkar, 2002, Abdel-Aziz and Frey, 2002, Frey and Zheng, 2002a). Maurice *et al.* (2000) presented a methodological framework to quantitatively evaluate uncertainty in life cycle inventories in coal power plants.

In the area of mobile source emissions, Kini and Frey (1997) developed quantitative estimates of uncertainty associated with the Mobile5b emission factor model estimates of light duty gasoline vehicle base emissions and speed-corrected emissions. Pollack *et al*. (1999) performed a similar study on California's EMFAC7G highway vehicle emission factor model. Frey and Zheng (2002b) revisited the earlier analysis of Mobile5b emission factor estimates to include uncertainties associated with temperature corrections. Frey and Bammi (2002) estimated uncertainty in emission factors for non-road mobile sources.

In the other areas, Frey and Li (2001) estimated uncertainty in NO_x and total organic compounds emissions from stationary natural gas-fueled internal combustion engines. Anex and Lund (1999) conducted a research on quantifying VOC emissions from wood furniture coatings. They applied truncated Gaussian distributions to describe variability and student-t distributions to quantify uncertainty in coating VOC emissions. Li and Frey (2002) estimated uncertainty in VOC emission factors of consumer/commercial product use. Omlin and Reichert (1999) presented practical comparisons of Bayesian techniques and classical statistical techniques to quantify uncertainty in parameters and predictions of ecological models. Bayesian analysis is similar to classical analysis except that a conditional probability density function is used instead of a probability density function. Details of the Bayesian method can be found in Bernarod and Simth (1994). Some researchers also tried to find common statistical properties for a particular emission source. For example, according to the study of Hanssen and Asbjornsen (1996), the COD emission factor of pulp and paper industry tends to be best represented by a binomial distribution.

1.2.2 Uncertainty Analysis in Climate Change

In the field of climate change, simulation models assist policy makers in predicting and understanding the causes and consequences of greenhouse gas emissions. Criticisms have arisen regarding current prediction methods and estimated consequences, as illustrated by the debates on the IPCC Third Assessment Report (TAR) for lack of analysis of uncertainty (Reilly *et al.* 2001, Allen *et al.* 2001). Efforts to establish the magnitude of uncertainty associated with the greenhouse gas emissions and climate change models are encouraged by IPCC (IPCC, 1998).

Carraro and Hourcade (1998) gave a brief review of current economic-environmental quantitative models and pointed out "uncertainty and environmental impacts and feedbacks are largely neglected." Zapert *et al.* (1998) introduced a quantitative method based upon stochastic differential equations (SDEs) and demonstrated its application to assess uncertainty and to rank the contributors of uncertainty on the Integrated Model to Assess the Greenhouse Effect (IMAGE 1.0). Grieb *et al.* (1999) developed a tree-structured density estimation technique that extends the ability of Monte Carlo-based analyses to explore parameter interactions and uncertainty in a global carbon cycling model, GLOCO. Other efforts to quantify uncertainty in climate change decision-making can be found in El-Fadel *et al.* (2001), Pizer (1999) and Guay (1999).

1.2.3 Uncertainty Analysis in Risk Assessment

Risk assessment is an important field associated with quantitative analysis. Rai and Krewski (1998) provided a general stochastic framework for uncertainty analysis under a multiplicative risk model. Hattis and Anderson (1999) gave a detailed introduction on the concepts and sources of uncertainty and variability in risk assessment, as well as benefits of uncertainty analysis for risk management decision-making.

Hertwich *et al.* (1999) conducted a research on the potential dose of 236 chemicals and quantitatively analyzed the representative chemicals. Sielken Jr. and Valdez-Flores (1999) suggested a "Distributional Characterization" approach, which assigns probability distributions to the component parameters in an exposure equation, instead of using current approach based upon "Default Characterization." Mowrer (2000) recommend that the Monte Carlo method as the most robust and easily applied to propagate uncertainty. However, in the context of risk assessment, information is often sparse and imprecise, and therefore Guyonnet et al. (1999) questioned the effectiveness of the Monte Carlo method based upon distribution assumptions and proposed a probabilistic approach based upon fuzzy numbers. Some other efforts of uncertainty analysis in risk analysis can be found in Frey and Rhodes (1996, 1998), Fayerweather et al. (1999), Frey and Burmaster (1999) and Wang et al. (2001).

Besides air quality fields, uncertainty analyses are also applied to many other fields of environmental protection, such as water quality (Dilks et al., 1992) and solid waste disposal (Abbaspour et al., 1998).

1.3 Selection of Source Categories

The work associated with this dissertation is a part of a large program sponsored by the U.S. Environment Protection Agency (EPA) to quantify variability and uncertainty in emission factors and emission inventories for a variety of NO_x and VOC source categories. The case study

Table 1.1. Annual Emissions and Rankings for Selected Source Categories

Categories	Annual Emission[a]	SIC ranking		SCC ranking	
		NO_X	VOC	NO_X[b]	VOC[c]
Natural Gas Engine	11437			3rd	
Wood Furniture Coating	36651		1st		1st
Cutback Asphalt Paving	14132				2nd
Consumer Solvents	13347				4th
Architectural Coating	13238				5th
Gasoline Terminal Loading	6594		2nd		

[a] Unit: tons/year

[b] 1st and 2nd largest sources are power plant emissions, different types of boilers

[c] 3rd largest source is open burning, EPA emission factor based 2 data with same value

domain for this program is the Charlotte airshed, in North Carolina. Therefore, this dissertation targets on major emission source categories in the Charlotte airshed.

The Emission Modeling System 95' (EMS-95) emission inventories were used in this work for the identification of major VOC and NO_x sources categories in the Charlotte airshed. Emission source categories were ranked based upon two coding systems, the Standard Industrial Classification (SIC) code and the Source Classification Code (SCC). The SIC is a four-digit code, which classifies a source category according to its economic activity. The SCC is an eight- or ten-digit code, which provides detailed information about an emission point of a source category. Thus, the SIC focuses more on industry classification and the SCC focuses more on emission classification.

A summary of the selected emission source categories is given in Table 1.1. The first and second largest NO_x emission sources in the SCC ranking are power plant emissions, for different types of boilers. NO_x emissions from electric generation are studied in separate work and are not addressed here (Abdel-Aziz and Frey, 2002). The natural gas-fueled reciprocating engine is the third largest NO_x emission source in the SCC ranking, and is included in this work.

Unlike NO_x emissions, there is no dominant source category in VOC emissions. The five VOC emission source categories selected in this work, including consumer/commercial product use, gasoline terminal loading, cutback asphalt paving, architectural coatings and wood furniture coatings, represent approximately 27 percent of total emissions in the Charlotte airshed.

1.4 Overview of This Dissertation

Chapter 2 describes the general methodology used in this study. Chapter 3 is the case study for NOx and VOC emissions from natural gas-fueled internal combustion engines. Chapter 4 is the case study to develop a probabilistic VOC emission factor for consumer/commercial product use. Chapter 5 is the case study for VOC emissions from gasoline terminal loading. Chapter 6 is the case study for VOC emissions from asphalt paving and architecture coatings. Chapter 7 is the case study for VOC emissions from wood furniture coatings. Conclusions and recommendations are discussed in Chapter 8.

1.5 References

Abbaspour, K. C., Schulin, R., van Genuchten, M. Th., Schlappi, E., 1998. Procedures for Uncertainty Analyses Applied to a Landfill Leachate Plume. *Ground Water*, 36, 874-883

Abdel-Aziz, A.; Frey, H. C. 2002. Quantification of Variability and Uncertainty in Hourly NO_x Emissions from Coal-Fired Power Plants. In *Proceedings of the 95th Annual Meeting of the Air & Waste Management Association*, Baltimore, MD

Allen, M., Raper, S., Mitchell, J., 2001. Policy Forum on Climate Change: Uncertainty in the IPCC's Third Assessment Report. *Science (Wash.)*, 293, 430-433

Anex, R. P., Lund, J. R., 1999. Bayesian Estimation of Volatile Organic Emissions From Wood Furniture Coating. *J Environ. Eng.* 125, 92-96

Anex, R. P., Lund, J. R., Grant, R., 1999. A Maximum Entropy Approach to Estimating Emissions. *J. Air & Waste Manage. Assoc*. 49, 943-950

Bammi, S., Frey, H. C., 2001. Quantification of Variability and Uncertainty in Lawn and Garden Equipment NO_x and Total Hydrocarbon Emission Factors. Proceedings, Annual Meeting of the Air & Waste Management Assoc., Pittsburgh, PA

Beck, L. L., Wilson, D., 1997. EPA's Data Attribute Rating System, Proceedings, Emission Inventory: Planning for the Future, Air & Waste Management Assoc., Pittsburgh, PA

Bernardo, J., Smith, A., 1994. *Bayesian Theory*. Wiley: New York

Bogen, K. T., Spear, R. C., 1987. Integrating Uncertainty and Interindividual Variability in Environmental Risk Assessment. *Risk Anal.* 7, 427-436

Carraro, C., Hourcade, J. C., 1998. Climate Modelling and Policy Strategies. The Role of Technical Change and Uncertainty. *Energy Econ*. 20, 463-471

Cullen, A. C., Frey, H. C., 1999. *Probabilistic Techniques in Exposure Assessment: A Handbook for Dealing with Variability and Uncertainty in Risk Analysis*; Plenum Press: New York

Dilks, D. W., Canale, R. P., Meier, P.G., 1992. Development of Bayesian Monte Carlo Techniques for Water Quality Model Uncertainty. *Ecol. Model*. 62, 149-162

El-Fadel, M., Massoud, M., Semerjian, L., 2001. Energy Related GHG Emissions: Assessment of Emission Factor Uncertainty. *World Resour. Rev*. 13, 61-73

Fayerweather, W. E., Collins, J. J., Schnatter, A. R., Hearne, F. T., Menning, R. A., Reyner, D. P., 1999. Quantifying Uncertainty in a Risk Assessment Using Human Data. *Risk Anal*. 19, 1077-1090

Frey, H. C., 1992. Quantitative Analysis of Uncertainty and Variability in Environmental Policy Making, Directorate for Science and Policy Programs. American Association for the Advancement of Science, Washington, DC

Frey, H. C., Rhodes, D. S., 1996. Characterizing, Simulating, and Analyzing Variability and Uncertainty: An Illustration of Methods Using an Air Toxics Emissions Example. *Hum. Ecol. Risk Assess.* 2, 762-797

Frey, H.C., Rhodes, D.S., 1998. Characterization and Simulation of Uncertain Frequency Distributions: Effects of Distribution Choice, Variability, Uncertainty, and Parameter Dependence. *Hum. Ecol. Risk Assess.* 4, 423-468

Frey, H. C., Burmaster, D. E., 1999. Methods for Characterizing Variability and Uncertainty: Comparison of bootstrap Simulation and Likelihood-Based Approaches. *Risk Anal.* 19, 109-129

Frey, H. C., Bharvirkar, R., Zheng, J., 1999. Quantitative Analysis of Variability and Uncertainty in Emissions Estimation, Prepared by North Carolina State University for the U.S. Environmental Protection Agency, Research Triangle Park, NC

Frey, H. C., Li, S., 2001. Quantification of Variability and Uncertainty in Stationary Natural Gas-fueled Internal Combustion Engine NOx and Total Organic Compounds Emission Factor. Proceedings, Annual Meeting of the Air & Waste Management Association, Pittsburgh, PA

Frey, H.C.; Bammi, S. 2002. Quantification of Variability and Uncertainty in Lawn and Garden Equipment NO_x and Total Hydrocarbon Emission Factors. *J. of Air & Waste Manage. Assoc*., 52, 435-448.

Frey, H.C., Bharvirkar, R., 2002. Quantification of Variability and Uncertainty: A Case Study of Power Plant Hazardous Air Pollutant Emissions. Chapter 10 in *The Risk Assessment of Environmental and Human Health Hazards: A Textbook of Case Studies*. Paustenbach, D., Ed., John Wiley and Sons: New York

Frey, H.C.; Bammi, S. 2002. Probabilistic Nonroad Mobile Source Emission Factors. *ASCE Journal of Environ. Eng*. accepted

Frey, H.C.; Zheng, J. 2002a. Quantification of Variability and Uncertainty in Utility NOx Emission Inventories; *J. of Air & Waste Manage. Assoc.* accepted

Frey, H. C.; Zheng, J. 2002b. Probabilistic Analysis of Driving Cycle-Based Highway Vehicle Emission Factors. *Environmental Science and Technology.* accepted

Grieb, T. M., Hudson, R. J. M., Shang, N., Spear, R. C., Gherini, S. A., Goldstein, R. A., 1999. Examination of Model Uncertainty and Parameter Interaction in a Global Carbon Cycling Model (GLOCO). *Environ. Int*. 25, 787-803

Guay, L., 1999. Constructing a Response to Ecological Problems Under Scientific Uncertainty: A Comparison of Acid Rain and Climate Change Policy in Canada. *Energy Environ*. 10, 597-616

Guyonnet, D., Come, B., Perrochet, P., Parriaux, A., 1999. Comparing Two Methods for Addressing Uncertainty in Risk Assessments. *J Environ. Eng.* 125, 660-665

Hanssen, O. J., Asbjornsen, O. A., 1996. Statistical Properties of Emission Data in Life Cycle Assessments. *J. Cleaner Prod*. 4, 149-157

Hattis, D., Anderson, E. L., 1999. What Should Be the Implications of Uncertainty, Variability, and Inherent "Biases"/"Conservatism" for Risk Management Decision-Making?. *Risk Anal.*, 19, 95-107

Hattis, D., Burmaster, D. E., 1994. Assessment of Variability and Uncertainty Distributions for Practical Risk Analyses. *Risk Anal.*, 14, 713-730

Hertwich, E. G., McKone, T. E., Pease, W. S., 1999. Parameter Uncertainty and Variability in Evaluate Fate and Exposure Models. *Risk Anal.*, 19, 1193-1204

IPCC, 1998. Meeting Report: Managing Uncertainty in National Greenhouse Gas Inventories, Report of the meeting held in Paris, Intergovernmental Panel on Climate Change (IPCC)

IPCC National Greenhouse Gas Inventories Program, 2000. Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories. Intergovernmental Panel on Climate Change (IPCC)

ISO, 1993. Guide to the Expression of Uncertainty in Measurement. ISBN 92-67-10188-9. International Organization for Standardardization (ISO), Geneva, Switzerland

Kini, M. D., Frey, H. C., 1997. Probabilistic Evaluation of Mobile Source Air Pollution: Volume 1, Probabilistic Modeling of Exhaust Emissions from Light Duty Gasoline Vehicles, Prepared by North Carolina State University for Center for Transportation and the Environment, Raleigh

Lemons, J., 1996. Scientific Uncertainty and Environmental Problem Solving, Blackwell Science, Cambridge, Mass.

Li, S.; Frey, H. C. Methods and Example for Development of a Probabilistic Per-Capita Emission Factor for VOC Emissions from Consumer/Commercial Product Use. In *proceedings of the 95th Annual Meeting of the Air & Waste Management Association*, Baltimore, MD, June, 2002.

Maurice, B., Frischknecht, R., Coelho-Schwirtz, V., Hungerbuhler, K., 2000. Uncertainty Analysis in Life Cycle Inventory. Application to the Production of Electricity with French Coal Power Plants. *J. Cleaner. Prod.* 8, 95-108

Morgan, M. G., Henrion, M., 1990. *Uncertainty: A Guide to Dealing with Uncertainty in Quantitative Risk and Policy Analysis*. Cambridge University Press: Cambridge, Mass.

Mowrer, H. T., 2000. Uncertainty in Natural Resource Decision Support System: Sources, Interpretation, and Importance. *Computers & Electronics in Agriculture*, 27, 139-154

NCRP, 1996. A Guide for Uncertainty Analysis in Dose and Risk Assessments Related to Environment Contamination. National Council on Radiation Protection and Measurements (NCRP)

National Research Council (NRC), 1994. *Science and Judgement in Risk Assessment*. National Academy Press: Washington, DC

National Research Council (NRC), 2000. *Modeling Mobile-Source Emissions*. National Academy Press: Washington, DC

Omlin, M., Reichert, P., 1999. A Comparison of Techniques for the Estimation of Model Prediction Uncertainty. *Ecolo. Model.*, 115, 45-59

Pollack, A. K., Bhave, P., Heiken, J., Lee, K., Shepard, S., Tran, C., Yarwood, G., Sawyer, R. F., Joy, B. A., 1999. Investigation of Emission Factors in the California EMFAC7G Model. PB99-149718INZ, Prepared by ENVIRON International Corp, Novato, CA, for Coordinating Research Council, Atlanta, GA

Pukkala, T., Kanagas, J., 1995. A Method for Integrating Risk and Attitude toward Risk into Forest Planning. *Forest Science*. 42, 198-205

Pizer, W. A., 1999. Optimal Choice of Climate Change Policy in the Presence of Uncertainty. *Resour Energy Econ*. 21, 255-287

Rai, S. N., Krewski, D., 1998. Uncertainty and Variability Analysis in Multiplicative Risk Models. *Risk Anal.* 18, 37-45

Reilly, J., Stone, P. H., Forest, C., Webster, M. D., Jacoby, H. D., Prinn, R. G., 2001. Policy Forum on Climate Change: Uncertainty and Climate Change Assessments. *Science (Wash.)*, 293, 430-433

Rhodes, D. S., Frey, H. C., 1997. Quantification of Variability and Uncertainty in AP-42 Emission Factors Using Bootstrap Simulation. Emission Inventory: Planning for the Future (held October 28-30 in Research Triangle Park, NC), Air and Waste Management Association, Pittsburgh, PA

Sielken Jr., R. L., Valdez-Flores, C., 1999. Probabilistic Risk Assessment's Use of Trees and Distributions to Reflect Uncertainty and Variability and to Overcome the Limitations of Default Assumptions. *Environ. Int.* 25, 755-722

U.S. DOE, 2001. Monte Carlo Simulations of Uncertainty in U.S. Greenhouse Gas Emissions Estimates and Related Support Work, prepared by Science Applications International Corporation for U.S. Department of Energy (DOE)

US EPA, 1995. Compilation of Air Pollutant Emission Factors, AP-42, Fifth Edition. US Environmental Protection Agency

US EPA, 1997. Guiding Principles for Monte Carlo Analysis, EPA/630R-97/001, US Environmental Protection Agency (EPA)

Wang, G., Edge, W. D., Wolff, J. O., 2001. Demographic Uncertainty in Ecological Risk Assessments. *Ecol. Model*. 136, 95-102

Zapert, R., Gaertner, P. S., Filar, J. A., 1998. Uncertainty Propagation within an Integrated Model of Climate Change. *Energy Econ.* 20, 571-598

2.0 METHODOLOGY

Variability refers to observed differences attributable to heterogeneity or diversity in a population. In general, only a finite number of samples are available to approximate the true value of an unknown quantity. Thus, uncertainty arises due to limited sample size. Statistical techniques presented in this chapter for quantitative analysis include (1) plotting position methods to visualize the data, (2) fitting parametric distributions, (3) estimating parameters of parametric distributions, (4) random sampling techniques and bootstrap simulation and (5) propagation of distributions through a model.

2.1 Plotting Position Methods

It is often useful to graphically visualize sample data in uncertainty analysis. The typical approaches to visualize data are assigning certain fractiles to data and expressing them as an empirical cumulative distribution function (CDF). There are several possible "plotting position" functions to estimate the fractiles from sample data. The typical way is to sort the data in an ascending order. Then, equal probability, $\frac{1}{n}$, is assigned to each data in a sample data set of size n. Therefore an empirical CDF can be expressed as a step function:

$$F(x_i) = P[x \leq x_i] = \frac{i}{n} \tag{2.1}$$

Where:

$F(x_i)$, empirical CDF of sample x_i, $x_1 < x_2 < \ldots < x_n$

n, total number of samples

This function will give x_n 100% fractile, which might be biased for continuous variables because it is not possible to observe the true maximum value of a population. In order to avoid giving 100% to the largest observed value in sample data set, some alternative formulas are proposed:

$$\text{Mean plotting position: } F(x_i) = P[x \le x_i] = \frac{i}{n+1} \quad (2.2)$$

$$\text{Hazen plotting position: } F(x_i) = P[x \le x_i] = \frac{i-0.5}{n} \quad (2.3)$$

Where:

$F(x_i)$, empirical CDF of sample x_i, $x_1 < x_2 < \ldots < x_n$

n, total number of samples

Some other plotting position functions are also available, but involve minor adjustments to the above functions (Morgan and Henrion, 1990). In this study, the Hazen plotting position function was used.

2.2 Fitting Parametric Distributions and Estimating Parameters

One limitation of empirical CDF is that there is no extrapolation beyond the range of observed data. Thus, for small data sets, the real range of variability may be underestimated because variation in a sample observed may be much narrower than that in the population. Fitting parametric probability distributions has benefits in that they can provide a plausible means for extrapolating to the unobserved part of the unknown population distribution. Parametric distributions also may have underlying theoretical basis. For examples, quantities formed from adding many uncertain quantities tend to be normally distributed, and quantities formed from multiplying uncertain quantities tend to be lognormally distributed. Physical quantities, such as pollutant concentrations, can be represented by the lognormal distribution (Morgan and Henrion, 1990).

2.2.1 Samples and Statistics

Statistics are functions defined on samples and to describe the characteristics of samples (Cullen and Frey, 1999). The sample mean and sample variance used in this study are specified here. The sample mean for a sample data set (x_1, x_2, …, x_n) is:

$$\bar{x} = \frac{\sum_{i=1}^{n} x_i}{n} \tag{2.4}$$

The sample variance is a measure of spread or dispersion. For a sample data set (x_1, x_2, …, x_n), sample variance can be calculated as:

$$S_*^2 = \frac{1}{n}\sum_{i=1}^{n}(x_i - \bar{x})^2 \tag{2.5}$$

For small sample size, S_*^2 is called the biased estimate of the sample variance. The unbiased estimate of the sample variance is:

$$S^2 = \frac{1}{n-1}\sum_{i=1}^{n}(x_i - \bar{x})^2 \tag{2.6}$$

2.2.2 Normal Distribution

The normal distribution, also referred as Gaussian distribution, plays a central role in classical statistics mainly because of the Central Limit Theorem, which shows that the normal distribution can be used to approximate the mean of large samples, typically with sample sizes n>30 or 40 in practice (Morgan and Henrion, 1990).

The normal distribution, usually denoted as n(μ, σ^2), has two parameters, arithmetic mean μ and variance σ^2. The probability density function (PDF) of normal distribution is:

$$f(x) = \frac{1}{\sqrt{2\pi}\,\sigma} e^{\frac{-(x-\mu)^2}{2\sigma^2}} \qquad -\infty < x < \infty \tag{2.7}$$

There is no closed-form representation of CDF. If x ~ n(μ, σ^2), then the random variable $z = \frac{x-\mu}{\sigma}$ has a n(0, 1) distribution, which is known as standard normal distribution:

$$f(z) = \frac{1}{\sqrt{2\pi}} e^{\frac{-z^2}{2}} \qquad -\infty < x < \infty \tag{2.8}$$

The parameters of normal distribution can be estimated from sample mean $\bar{x}$ and unbiased sample variance S^2.

$$\hat{\mu} = \bar{x} \tag{2.9}$$

$$\hat{\sigma}^2 = S^2 \tag{2.10}$$

The above parameter estimation method based upon central moments (mean and variance are the first and second central moments) is referred as the method of matching moments (MoMM). Another commonly used parameter estimation method is the maximum likelihood estimation (MLE). MLE estimates the parameters θ_k of a distribution based upon maximizing the likelihood function given in Eq. 2.11.

$$L(q_1, q_2 .. q_k) = \prod_{i=1}^{n} f(x_i | q_1, q_2 .. q_k) \tag{2.11}$$

The analytical solutions for maximizing the normal likelihood function are

$$\hat{m} = \overline{x} \tag{2.12}$$

$$\hat{s}^2 = S_*^2 \tag{2.13}$$

2.2.3 Lognormal Distribution

If the logarithm of a random variable is normally distributed, then the random variable has a lognormal distribution. The PDF of the lognormal distribution given in Eq. 2.14 can be obtained by transforming the PDF of the normal distribution

$$f(x) = \frac{1}{\sqrt{2p}\, f} \frac{1}{x} e^{\frac{-(\ln x - x)^2}{2f^2}} \qquad 0 < x < \infty \tag{2.14}$$

The parameters of the lognormal distribution are x and f, which can be estimated from sample data by the MoMM:

$$\hat{x} = \ln\left(\frac{\overline{x}^2}{\sqrt{S^2 + \overline{x}^2}}\right) \tag{2.15}$$

$$\hat{f}^2 = \sqrt{\ln\left(\frac{S^2 + \overline{x}^2}{\overline{x}^2}\right)} \tag{2.16}$$

The MLE estimates are:

$$\hat{x} = \frac{\sum_{i=1}^{n} \ln x_i}{n} \tag{2.17}$$

$$\hat{f}^2 = \frac{1}{n}\sum_{i=1}^{n}(\ln x_i - \hat{x})^2 \tag{2.18}$$

It is worthy to mention that some investigators also use $e^{\hat{x}}$ and $e^{\hat{f}}$ as the parameters of the lognormal distribution (Frey and Rhodes in BootSim program, 1999). The lognormal distribution often provides good representation for no-negative and positively skewed physical quantities, such as pollutant concentrations.

2.2.4 Gamma Distribution

The gamma family of distributions is a flexible family of distributions on [0, ∞]. One parameter, r, of the gamma distribution is called the shape parameter since it most influences the peakedness of the distribution. Another parameter of the gamma distribution is scale parameter, λ, which influences the spread of the distribution. The PDF of the gamma distribution is:

$$f(x) = \frac{l^r x^{r-1} e^{-lx}}{\Gamma(r)} \qquad \Gamma(r) = \int_0^\infty x^{r-1} e^{-x} dx \qquad 0 \le x < \infty \tag{2.19}$$

It is worthy to mention that some researchers use $\frac{1}{l}$ as the scale parameter (Casella and Berger, 1990, Cullen and Frey, 1999). There is no closed-form representation of the gamma CDF. The parameters of the gamma distribution can be estimated from sample mean $\bar{x}$ and sample variance S^2 by the MoMM:

$$\hat{r} = \frac{\bar{x}^2}{S^2} \tag{2.20}$$

$$\hat{l} = \frac{\bar{x}}{S^2} \qquad (2.21)$$

As discussed above, the MLE actually is an optimization process. The likelihood function is defined in terms of a product of probabilities of random sample data. The log-likelihood function is to take logarithmic transformation on the likelihood function so that it can be written in terms of a sum of logarithms of the probabilities of random sample data. Since most PDFs have "e^x" terms, taking logarithmic transformation will simplify the optimization process. Thus the log-likelihood functions are more widely used in practice. The log-likelihood function of the gamma distribution is given by:

$$Jgamma(r, l) = -n[r \ln \frac{1}{l} + \ln \Gamma(r)] + \sum_{i=1}^{n} [(r-1) \ln x_i - l x_i] \qquad (2.22)$$

No parameter estimation method is always ideal for all circumstance. MLE is considered to be statistically efficient for large sample size. However, for small sample size, MLE do not always yield unbiased estimates (Holland and Fitz-Simons, 1982).

The gamma distribution is similar to the lognormal distribution, but is less positively skewed and less "tail-heavy" in that it prescribes a lower probability to extreme values than does the lognormal (Morgan and Henrion, 1990). The gamma distribution is widely applicable to many physical quantities, such as precipitation quantity and pollutant concentration.

2.2.5 Weibull Distribution

The Weibull distribution is another distribution related to the gamma family. However, it is less skewed and "tail heavy" than the gamma distribution, and exhibits negative skewness when the shape parameter becomes large (greater than 3.6, Morgan and Henrion, 1990). The parameters of the Weibull distribution are shape parameter *k* and scale parameter *c*. The PDF and CDF of the Weibull distribution are given by:

$$f(x) = \frac{k}{c^k} x^{k-1} e^{-(\frac{x}{c})^k} \qquad 0 \le x < \infty \qquad (2.23)$$

$$F(x) = 1 - e^{-(\frac{x}{c})^k} \qquad 0 \le x < \infty \qquad (2.24)$$

There is no simple equation to calculate the Weibull parameters and both MoMM and MLE require numerical iterations. The MoMM estimates of the Weibull parameters can be obtained by iteratively solving Eq. 2.25 and 2.26 using the Newton's method.

$$\bar{x} = \hat{c}\Gamma(1 + \frac{1}{\hat{k}}) \qquad (2.25)$$

$$S^2 = \hat{c}^2[\Gamma(1 + \frac{2}{\hat{k}}) - \Gamma^2(1 + \frac{1}{\hat{k}})] \qquad (2.26)$$

The log-likelihood function of the Weibull distribution is given by:

$$J_{weibull}(k, c) = n \ln \frac{k}{c} + \sum_{i=1}^{n}[(k-1)\ln \frac{x_i}{c} - (\frac{x_i}{c})^k] \qquad (2.27)$$

Morgan and Henrion (1990) provide an alternative way to calculate the Weibull parameters based upon regression techniques. First, rearrange CDF as:

$$Z = mY + b \tag{2.28}$$

where:

$Z = \ln\{-\ln[1 - F(x)]\}$ and $Y = \ln x$. Then:

$$\hat{k} = m \text{ and } \hat{c} = e^{\frac{-b}{m}} \tag{2.29}$$

Plot and regress *Z* vs. *Y*. The slope *m* and the intercept *b* are used to estimate *k* and *c*.

2.2.6 Beta Distribution

The beta distribution is defined on the fixed range (0, 1). The PDF of the beta distribution is:

$$f(x) = \frac{1}{B(a,b)} x^{a-1}(1-x)^{b-1} \qquad B(a,b) = \frac{\Gamma(a)\Gamma(b)}{\Gamma(a+b)} \tag{2.30}$$

There is no closed-form representation of the beta CDF. The MoMM is commonly used to estimate the beta parameters:

$$\hat{a} = \frac{(\bar{x}^2 - \bar{x}^3 - S^2\bar{x})}{S^2} \tag{2.31}$$

$$b = \frac{\bar{x}(1-\bar{x})^2 - S^2(1-\bar{x})}{S^2} \tag{2.32}$$

The log-likelihood function of the beta distribution is given by:

$$J_{beta}(a,b) = n \ln \frac{1}{B(a,b)} + \sum_{i=1}^{n} [(a-1)\ln x_i + (b-1)\ln(1-x_i)] \tag{2.33}$$

The beta distribution can take many shapes as the parameters a and b vary. The PDF of the beta distribution can be strictly increasing ($a > 1$, $b = 1$), strictly decreasing ($a = 1$, $b > 1$), U-shaped ($a < 1$, $b < 1$) or unimodal ($a > 1$, $b > 1$). The PDF becomes more concentrated as a increases (Casella and Berger, 1990).

2.3 Kolmogorov-Smirnov Goodness of Fit Test

Kolmogorov-Smirnov (K-S) test is a commonly used goodness-of-fit test for continuous distributions. K-S test calculates the maximum discrepancy between the step-wise empirical CDF and the CDF of a fitted distribution. If the discrepancy is larger than the K-S test critical value at certain significance level, the hypothesized distribution is rejected. The step-wise empirical CDF is:

$$S_n(x_k) = \frac{k}{n} \tag{2.34}$$

Maximum discrepancy therefore is

$$D_n = \max |F(x) - S_n(x)| \tag{2.35}$$

The K-S test critical values at different significance levels can be found in Ang and Tang (1975).

There are debates on the validness of K-S test when parameters of an assumed distribution are unspecified and are estimated from sample data. Chakavarti *et al.* (1967) remarked that the K-S test "cannot be used if parameters involved in the distribution function are unspecified." The Engineering Statistics Internet Handbook indicates "Perhaps the most serious limitation is that the distribution must be fully specified. That is, if location, scale, and shape parameters are estimated from the data, the critical region of the K-S test is no longer valid." Stephens (1974) pointed out that a disadvantage of using empirical distribution function (EDF) statistics in goodness of fit test is that they are not adapted for "the case when parameters must be estimated from sample". However, a modified critical value at the 0.05 significance level for sample size, n, larger than 30 has been proposed to be $\frac{0.886}{\sqrt{n}}$ for unspecified distributions (Mage, 1988).

Although it is often quoted that goodness of fit tests are "objective", they are actually not. At best, they are empirical based (Cullen and Frey, 1999). As Cullen and Frey (1999) pointed out, fitting a distribution to sample data is something a little subjective. Therefore, goodness-of-fit tests only provide means to help to select parametric distributions, but not necessarily to designate a distribution to sample data.

2.4 Monte Carlo Sampling Method

The Monte Carlo sampling method provides approximate solutions to a variety of mathematical models by conducting statistical sampling experiments on a computer. The origin of the Monte Carlo method can date from Buffon's needle experiment conducted by a French scientist, Georges Louis Leclerc Comte de Buffon in 1777 to estimate the value of Pi. The modern Monte Carlo method was systematically developed by John von Newuann and Stanislaw Ulam in the simulation of random neutron diffusion during the Second World War.

There are many ways of sampling from a space, of which the best known and simplest is the Monte Carlo sampling (Morgan and Henrion, 1990). The Monte Carlo sampling basically is drawing values at random from a distribution. During the Monte Carlo sampling process, random numbers are inputted into an inverse CDF of the assumed population distribution, and then a group of random sample data is obtained for that population. For distributions that have no closed-form CDF, numerical methods are typically available. The following methods of generating random sample for different distributions are given by Morgan and Henrion (1990). X_i denotes the random sample and U_i denotes the random number.

(a) Normal random variates:

$$X_i = X_s s + m \qquad \text{Where: } X_s = (\sum_{i=1}^{12} U_i) - 6 \tag{2.36}$$

(b) Lognormal random variates:

$$X_i = \exp(X_s f + x) \qquad \text{Where: } X_s = (\sum_{i=1}^{12} U_i) - 6 \tag{2.37}$$

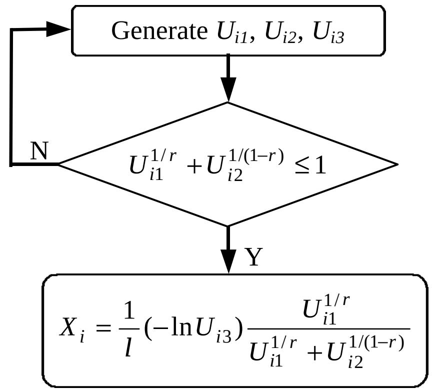
(c) Gamma random variates:

For integer r:

$$X_i = -\frac{1}{l} \sum_{i=1}^{r} \ln U_i \tag{2.38}$$

For noninteger r<1, sampling process is shown in Figure 2.1:

Figure 2.1 Gamma Random Variates Generation Process When Shape Parameter r<1



For noninteger r>1:

$$r_1 = FLOOR(r) \qquad \text{then, } r_2 = r - r_1 \tag{2.39}$$

Generate X_{i1} from i. Based upon l and r_1. Generate X_{i2} from ii. Based upon l and r_2. Then:

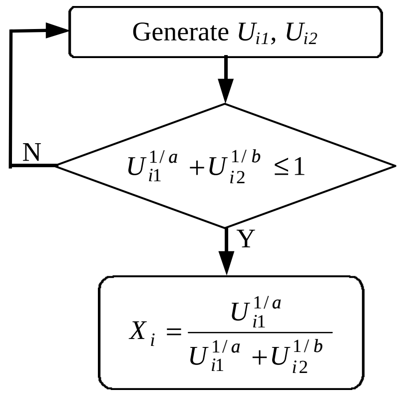
$$X_i = X_{i1} + X_{i2} \tag{2.40}$$

(d) Weibull random variates:

$$X_i = c(-\ln U_i)^{\frac{1}{k}} \tag{2.41}$$

(e) Beta random variates, sampling process is shown in Figure 2.2:

Figure 2.2. Beta Random Variates Generation Process

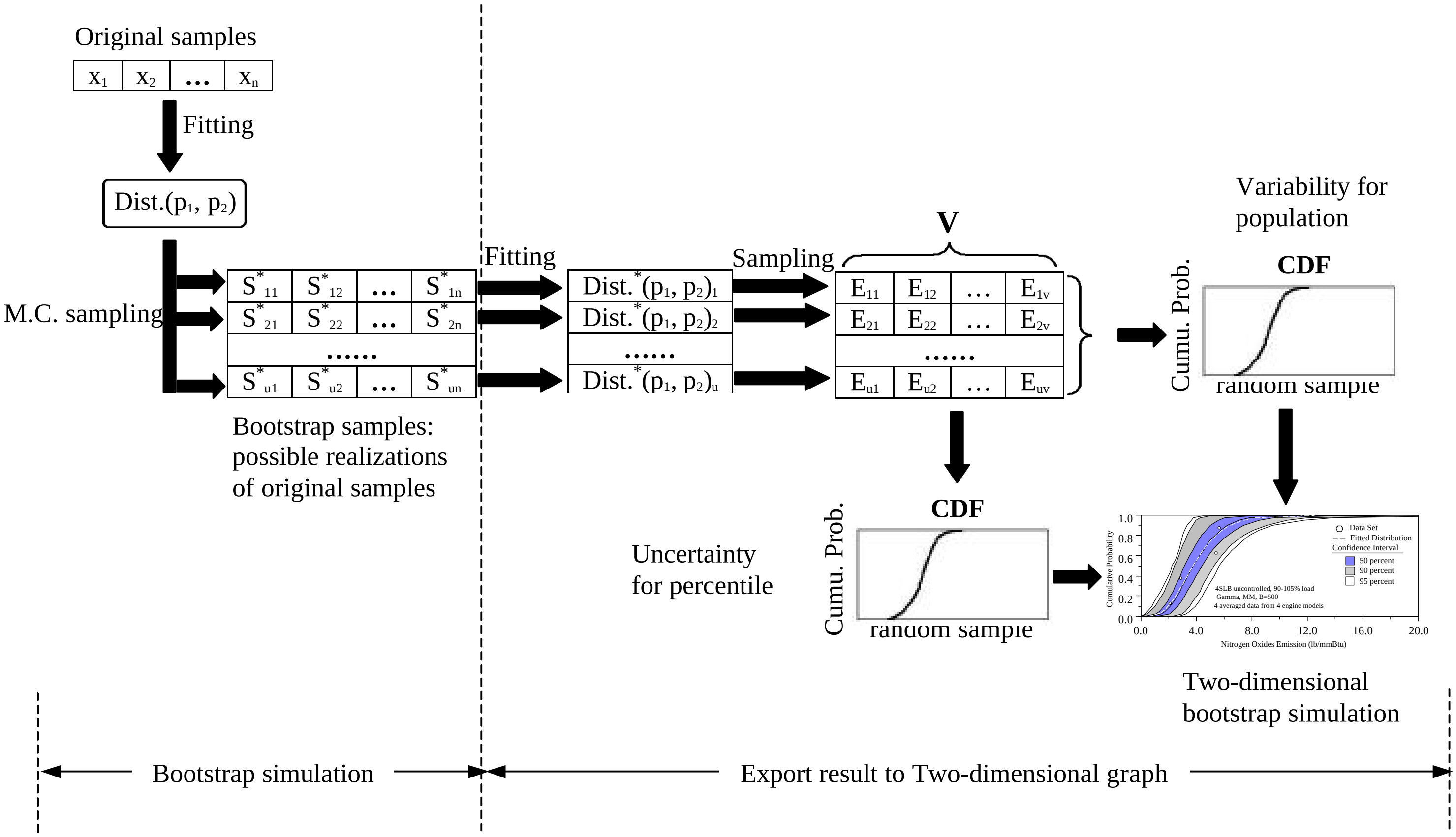


2.5 Bootstrap Simulation

Bootstrap simulation was introduced by Efron in 1979 for the purpose of simulating the sampling distribution for observed sample data by conducting statistical sampling experiments:

1. Construct the probability distribution $\hat{F}$ from a sample $x = (x_1, x_2, \ldots, x_n)$.
2. Draw random sample of size n, $S^* = (s_1^*, s_2^*, \ldots, s_n^*)$ from $\hat{F}$ using Monte Carlo sampling method. S^* is known as a bootstrap sample. A bootstrap sample has the same size of the original sample and is considered as one of many possible realizations of the original sample.
3. Repeat step 2 to generate a group of bootstrap samples $[(S^*)_1, (S^*)_2, \ldots, (S^*)_n]$.
4. Correspondingly, a group of uncertainty estimates $\{R[(S^*)_1, \hat{F}], R[(S^*)_2, \hat{F}], \ldots, R[(S^*)_n, \hat{F}]\}$ are taken as an approximation to the sampling distribution of the statistics R.

Figure 2.3. Bootstrap Simulation and Two-dimensional Visualization of Variability and Uncertainty



It is possible to separate variability and uncertainty under the scheme of the bootstrap simulation. The probability distribution estimated from observed sample reflects variability in the population. Then, uncertainty range of the fitted probability distribution of variability can be estimated from bootstrap samples. Typically, 500 to 2,000 bootstrap samples are simulated. The bootstrap simulation and the process of exporting simulation results into a two-dimensional graph are illustrated in Figure 2.3. An important advantage of the bootstrap simulation is that no restrictive assumption is required regarding normality. Thus, the bootstrap simulation can be used on a wide variety of problems.

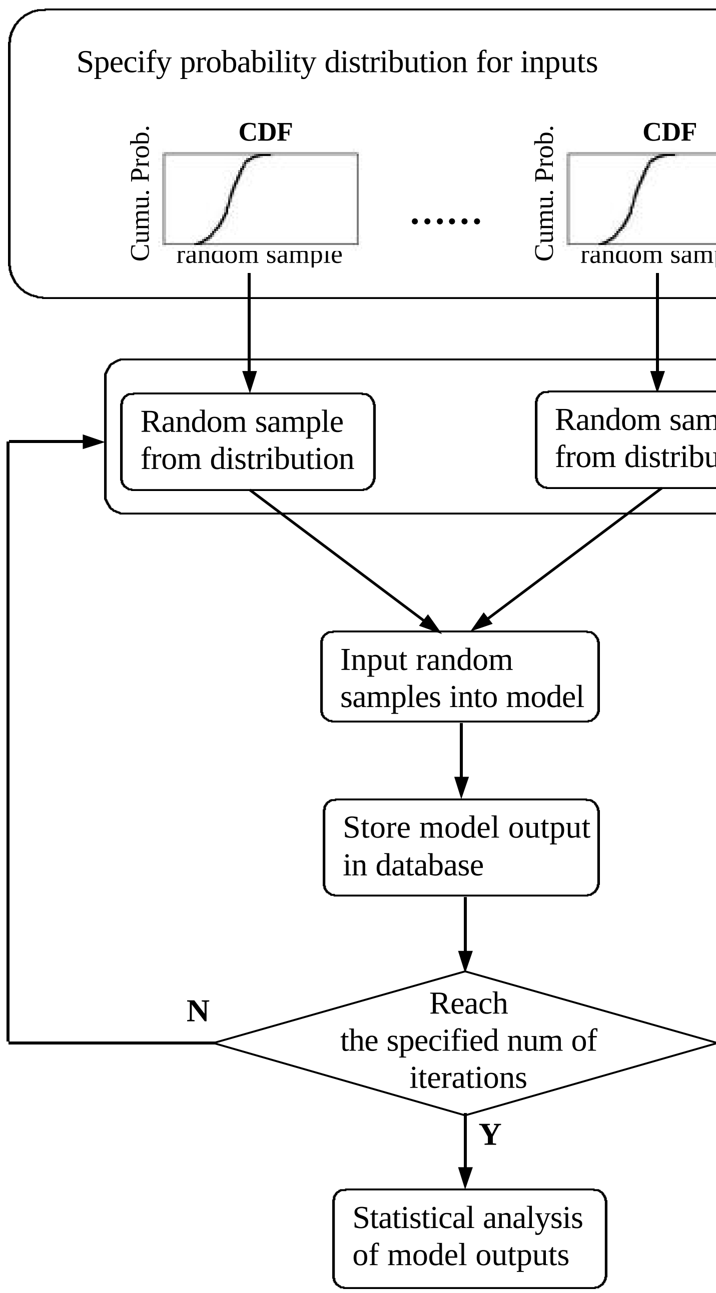
2.6 Propagation of Uncertainty through Models

Mathematical models are widely used in the abstractions and simulations of real-world systems. Uncertainty in the model output typically is attributed to two sources, the model uncertainty and input uncertainty (Cullen and Frey, 1999). The model uncertainty is associated with the model structure and arises due to the fact that the projection from a real system to a model is simplified. The limited knowledge regarding the underlying mechanism of a real system also adds uncertainty to model estimations. The input uncertainty refers to uncertainty existed in the model inputs. Increasing the model complexity may reduce the model uncertainty, but often inevitably increase the input uncertainty in that the number of inputs may increase. Hence, there always are tradeoffs.

Analytical and numerical methods can be used for propagation of input uncertainties in a mathematical model. Analytical methods are based upon error propagation equations, and often are not applicable if models are highly nonlinear (nonlinear equation may be expanded using Taylor expansion, but propagation may suffer from inaccuracies) or if probability distributions for model inputs are necessarily non-symmetric or there are significant covariance between inputs. Error propagation equations can be found in Mandel (1984).

Numerical methods, such as Monte Carlo simulation, have no restrictive assumption on the probability distributions assigned to model inputs and are typically applicable for complex models. The Monte Carlo simulation process is shown in Figure 2.4. The principle of Monte Carlo simulation is to draw random samples from specified probability distributions of model inputs and to calculate the corresponding model output. This procedure is repeated many times until the calculated the statistics, such as mean, for the model output are becoming stable and the probability distribution of the model output can be built up.

Figure 2.4. Numerical Propagation of Input Distributions through Models



A common recommendation associated with the application of Monte Carlo simulation is that the model inputs are independent. However, it is possible to simulate the dependence between model inputs using statistical techniques such as multivariate distributions or restricted pairing for sample generation. Weak dependence between input variables may have little effect on the overall modeling results. More discussions about input dependence can be found in Smith et al. (1992), and Cullen and Frey (1999).

One benefit of Monte Carlo simulation method is that it is possible to identify the key sources of uncertainties in model inputs contributing most to uncertainty in the model output by comparing the correlation coefficients of the model output and model inputs. A correlation coefficient, $r_{x,y}$, is a measure of the strength of the linear relationship between two variables x and y.

$$r_{x,y} = \frac{\sum_{k=1}^{m}(x_k - \bar{x})(y_k - \bar{y})}{[\sum_{k=1}^{m}(x_k - \bar{x})^2 \sum_{k=1}^{m}(y_k - \bar{y})^2]^{\frac{1}{2}}} \tag{2.42}$$

Where:

$r_{x,y}$ = correlation coefficient

x_k = model input

y_k = model output

m = number of iterations

$r_{x,y}$ = 1 implies positive linear dependence. $r_{x,y}$ = -1 implies negative linear dependence. And $r_{x,y}$ = 0 implies no linear dependence. For a typical probabilistic simulation, the large absolute value of the correlation coefficient between an input and an output indicates substantial dependence of the variation in the output on the variation of the input (Cullen and Frey, 1999).

However, if variables have different types of probability distributions, they are unlikely to be related linearly. In this circumstance, the correlation coefficient may have little meaning. One way to handle this problem is to use a rank value instead of the sample value to calculate the correlation coefficient. A rank value is determined by sorting sample data in an ascending order. Then the smallest sample data has a rank value of one, and the largest sample data has a rank value that equals to the total number of data points. The correlation coefficient calculated based upon rank values is referred as a rank correlation coefficient.

2.7 References

Ang, A. H-S., Tang, W. H., 1975. *Probability Concepts in Engineering Planning and Design*, John Wiley & Sons, Inc: New York

Casella, G., Berger, R. L., 1990. *Statistical Inference*, Duxbury Press: Belmont, CA

Chakravarti, I. M., Laha, R. G., Roy, J., 1967. *Handbook of Methods of Applied Statistics*, John Wiley & Sons, Inc: New York

Cullen, A. C., Frey, H. C., 1999. *Probabilistic Techniques in Exposure Assessment: A Handbook for Dealing with Variability and Uncertainty in Risk Analysis*; Plenum Press: New York

Efron, B., 1979. Bootstrap Methods: Another Look at the Jackknife, *Annals of Statistics*, 7(1), 1-26

Engineering Statistics Internet Handbook, (http://www.itl.nist.gov/div898/handbook/index.htm)

Frey, H. C., Rhodes, D. S., 1999. *Quantitative Analysis of Variability and Uncertainty in Environmental Data and Models, Volume 1. Theory and Methodology Based Upon Bootstrap Simulation*, Prepared by North Carolina State University for the U.S. Department of Energy, Germantown, MD

Holland, D. M., Fitz-Simons, T., 1982. Fitting Statistical Distributions to Air Quality Data by the Maximum Likelihood Method, *Atmospheric Environ.* 16, 1071-1076

IPCC National Greenhouse Gas Inventories Program, 2000. Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories. Intergovernmental Panel on Climate Change (IPCC)

ISO, 1993. Guide to the Expression of Uncertainty in Measurement. ISBN 92-67-10188-9. International Organization for Standardization (ISO), Geneva, Switzerland

Mage, D. T., 1988. Comment on “Parametric Distributions of Regional Lake Chemistry: Fitted and Derived”, Correspondence, Environ. Sci. Technol. 22(11), 1367-1368

Mandel, J., 1984. *The Statistical Analysis of Experimental Data*, Dover Publications: New York

Morgan, M. G., Henrion, M., 1990. *Uncertainty: A Guide to Dealing with Uncertainty in Quantitative Risk and Policy Analysis*. Cambridge University Press: Cambridge, Mass.

Smith, A. E., Ryan, P. B., Evans, J. S., 1992. The Effect of Neglecting Correlations when Propagating Uncertainty and Estimating the Population Distribution of Risk, *Risk Analysis*, 12, 467-474

Stephens, M. A. 1974. EDF Statistics for Goodness of Fit and Some Comparisons, *J. American Statistical Assoc.*, 69(347), 730-737

3.0 METHODS FOR QUANTIFYING VARIABILITY AND UNCERTAINTY IN AP-42 EMISSION FACTORS: CASE STUDIES FOR NATURAL GAS-FUELED ENGINES

H. Christopher Frey and Song Li

Department of Civil Engineering, North Carolina State University, Raleigh, NC 27695

Abstract

Quantitative methods for characterizing variability and uncertainty were applied to case studies of NO_x and Total Organic Carbon emission factors for lean burn natural gas-fueled internal combustion engines. Parametric probability distributions were fit to represent inter-engine variability in specific emission factors. Bootstrap simulation was used to quantify uncertainty in the fitted cumulative distribution function and in the mean emission factor. Some methodological challenges were encountered in analyzing the data. For example, in one instance, five data points were available, with each data point representing a different market share. Therefore, an approach was developed in which parametric distributions were fitted to population-weighted data. Uncertainty in mean emission factors ranges from as little as approximately plus or minus 10 percent to as much as minus 90 percent to plus 180 percent. The wide range of uncertainty in some emission factors emphasizes the importance of recognizing and accounting for uncertainty in emissions estimates. The skewness in some uncertainty estimates illustrates the importance of using numerical simulation approaches that do not impose

restrictive symmetry assumptions on the confidence interval for the mean. In this paper, the quantitative method, the analysis results, and key findings were presented.

3.1 Introduction

Uncertainty in emission factors, and in emission inventories, is typically not quantified. Therefore, it is not known, in many cases, how robust regulatory or management decisions are with respect to uncertainty. If management decisions are based upon point estimates of emissions that are biased, or if the range of uncertainty in emissions is much larger than any predicted change in emissions resulting from an air quality management strategy, then the decision-making process for developing management strategies could be ineffective. This paper focuses on one of the fundamental starting points for characterizing uncertainty in emission inventories, which is the emission factor. The case study application is stationary natural gas-fueled reciprocating engines. The key questions addressed in this paper are:

- What is the range of variability in emissions from one unit to another within a source category, such as natural gas-fueled engines?
- How well can a parametric probability distribution represent inter-engine variability?
- How can inter-engine variability be quantified when each available data point represents a different market share?
- What is the range of uncertainty in the average emission factor and is the range symmetric or skewed?
- What combination of existing or new methods is required to address the previous questions?

3.1.1 Variability and Uncertainty

Emissions vary from one specific source to another (e.g., one engine to another) within a source category because of variations in design, feedstock compositions, ambient conditions, and other operating conditions. For a given specific source (e.g., a particular engine), emissions vary over time because of differences in feedstock composition, ambient conditions, other operating characteristics, and maintenance and repair. Thus, there is typically some inherent variation in emissions that is revealed by measurements on multiple specific emission sources or by repeated measurements of the same emission source.

Uncertainty refers to lack of knowledge regarding the true but unknown value of a quantity, such as the true but unknown population average emission factor for a particular source category.[1] The average emission factor is subject to uncertainty for several possible reasons: (1) random sampling error; (2) measurement errors; (3) non-representativeness of available data; and/or (4) lack of information.[2] There is also the possibility of data entry mistakes. In this paper, the main focus is on quantification of random sampling error, which is the statistical random fluctuation in any statistic estimated from a finite random sample of data. Any statistic estimated from a random sample of data, such as the mean, is itself a random variable. The probability distribution for a statistic is referred to as the sampling distribution.[2] The sampling distribution can be used to develop confidence intervals for a statistic. Uncertainty due to random sampling error may often be a large or even dominant source of uncertainty for small data sets that are highly skewed.

3.1.2 Estimation of Uncertainty in Emission Factors

Some emission factors are accompanied by data quality ratings.[3] A method for qualitatively rating emission inventories, the Data Attribute Rating System (DARS) has been developed by the U.S. Environmental Protection Agency (EPA).[4] Some sources of uncertainty are difficult to quantify, such as non-representativeness of a data set. Therefore, there will always be a role for qualitative statements regarding non-quantifiable sources of uncertainty. However, qualitative rating systems should be used in combination with quantitative approaches, as suggested by the National Research Council (NRC).[5]

There is growing recognition of the importance of quantitative uncertainty analysis in environmental modeling and assessment. For example, the EPA has developed guidelines for Monte Carlo analysis of uncertainty.[6] The NRC has recommended to EPA that quantitative analysis of uncertainty be included in a variety of applications.[5,7]

In recent years, work has been underway to develop and demonstrate improved methods for quantifying uncertainty in emission inventories. In the area of mobile source emissions, for example, Kini and Frey developed quantitative estimates of uncertainty associated with the Mobile5b emission factor model estimates of light duty gasoline vehicle base and speed-corrected emissions.[8] Pollack *et al*. performed a similar study on California's EMFAC7G highway vehicle emission factor model.[9] Frey *et al*. revisited the earlier analysis of Mobile5b emission factor estimates to include uncertainties associated with temperature corrections.[10] Frey and Bammi estimated uncertainty in the emission factors for non-road mobile source categories.[11,12]

In the area of power plant emissions, various investigators have developed uncertainty estimates for emissions of hazardous air pollutants and NO_x.[10,13-17] Maurice et al. presented a methodological framework to quantitatively evaluate Uncertainty in life cycle inventories in coal power plants.[18] For other source categories, such as area sources, Li and Frey estimated uncertainty in VOC emission factors of consumer and commercial product use.[19] Methods for quantification of variability and uncertainty have been developed, evaluated, and demonstrated, including the use of Monte Carlo simulation and bootstrap simulation.[20-22]

In this paper, quantitative methods for characterizing variability and uncertainty are applied to the source category of stationary natural gas-fueled reciprocating engines. These engines are commonly used, for example, to power natural gas pipeline compressors. In some airsheds, such as for Charlotte, NC, this type of emission source is estimated to be a significant contributor to the total NO_x emission inventory.

3.2 Overview of Methods for Probabilistic Analysis of Emission Factors

The basic approach in probabilistic analysis is to quantify uncertainty in the inputs to a model, propagate the uncertainties through the model to make predictions of uncertainties in model outputs, and analyze the results. There are a variety of methods for quantification of uncertainty in environmental models, including analytical and numerical methods.[23] Numerical methods, such as Monte Carlo and bootstrap simulation, are typically more robust than analytical methods in that they can be applied to a wide range of problems without restrictive assumptions regarding probability distributions assigned to model inputs and for a wide variety of model formulations.

This paper focuses on the characterization of variability and uncertainty in emission factors, which are inputs to emission inventories. Methods for propagating both variability and uncertainty through models and for analyzing results are described elsewhere.[13,23] The key steps in characterizing variability and uncertainty for an emission factor data set are summarized here.

3.2.1 Characterizing Variability in a Data Set

A first step in characterizing variability in a data set is to obtain all relevant data and assess the quality of the data. A judgment must be made that the data are a reasonably representative sample of the population of interest, and that the data are free of significant errors. This step is the same regardless of whether one is developing a point estimate or a probabilistic estimate. This is perhaps the most critical step in the analysis.

A second step is to visualize the data to obtain insight regarding the range, central tendency, and skewness of the data, and any other noteworthy characteristics. A method often employed for this purpose is to plot the data as an empirical cumulative distribution function (CDF).[10,23]

It is convenient to represent a data set with a parametric probability distribution. Parametric distributions are described by a small number of parameters and therefore can concisely summarize variability in a data set. Parametric distributions enable interpolation within the range of observed data and extrapolation beyond the range of observed data. The latter is especially important for small data sets, in which the observed range of variability may not fully capture the actually range of the unknown population distribution. The plausibility of the extrapolation depends on selecting a theoretically-justified distribution model that is consistent with the observed data.[23,24]

In this study, lognormal, gamma, and Weibull distributions were considered as candidates for representing variability in emission factor data sets. There are several methods for estimating distribution parameters.[23] No method is necessarily the best one to use in all situations. Both Maximum Likelihood Estimation (MLE) and Method of Matching Moments (MoMM) are used and compared in this work.

3.2.2 Characterizing Uncertainty

Bootstrap simulation is used to quantify uncertainty based upon random sampling error.[25] The main assumption in bootstrap simulation is that the probability distribution estimated from the observed sample of data is the best estimate of the true but unknown population distribution. A synthetic data set, known as a *bootstrap sample*, is sampled at random from the assumed population distribution using Monte Carlo simulation. The bootstrap sample has the same number of data points as the original sample. The values of the samples in the bootstrap sample are one possible alternative random realization of the original data set. A large number of bootstrap samples are simulated, typically 500. For each bootstrap sample, one or more statistics of interest may be calculated, such as the mean. A statistic calculated from a bootstrap sample is referred to as a *bootstrap replication* of the statistic, and there will be random variation in the bootstrap replications. The 500 values of the bootstrap replicates of the statistic can be used to describe a sampling distribution of the statistic. From the sampling distribution, a confidence interval for the statistic can be inferred.

A key advantage of bootstrap simulation for estimation of confidence intervals is that no restrictive assumptions are required regarding normality, as is required to develop confidence intervals using common analytical methods. Thus, bootstrap simulation can be used on a wide variety of problems. The confidence intervals represent lack of knowledge regarding the true values of the statistics being estimated.

3.3 Natural Gas-Fueled Reciprocating Engines

Natural gas-fueled reciprocating engines are commonly used to provide mechanical shaft power to drive compressors, such as those used in natural gas pipelines.[26, 27] These engines are classified based upon three major designs: (1) 2-cycle lean burn, also referred to as 2-stroke lean burn (2SLB); (2) 4-stroke lean burn (4SLB); and (3) 4-stroke rich burn (4SRB). The capacity of these engines ranges from 50 brake horsepower (bhp) to 11,000 bhp. The air-to-fuel mass ratios of lean burn engines are typically higher than 24:1. Rich burn engines operate near a stoichiometric air-to-fuel mass ratio of 16:1.

Significant emissions from natural gas-fueled engines include NO_x and hydrocarbons (HC). Control technologies for natural gas-fueled engines are primarily aimed at reducing NO_x emissions. Emission factors for natural gas-fueled engines have been published by EPA.[3] Until recently, emission factors for this source category were based upon an October 1996 update.[26] However, an update was published in July 2000 based upon a different data set than the October 1996 version.[27] The October 1996 data set involves market-share weighted data for NO_x and Total Organic Carbon (TOC) uncontrolled emission factors, whereas the July 2000 data are assumed to be equally-weighted. To demonstrate a range of analysis methods, both sources of data are included in this study.

3.3.1 October 1996 Version of AP-42 Emission Factors

The analysis of the October 1996 version is focused upon lean burn engines, because these engines have high emission rates and are present in an airshed (Charlotte, NC) that is the subject of a case study in related work. The specific emission sources for which uncertainty in average emission factors were quantified include: (1) 2SLB uncontrolled engines; (2) 2-stroke "clean burn" controlled lean burn engines (2SCB); (3) 2-stroke pre-combustion chamber (PCC) controlled lean burn engines (2SPCC); and (4) 4SLB uncontrolled engines. For other control options, apparently only one data point was used by EPA to estimate emission factors.[28] Therefore, other control options were not analyzed statistically.

For the 2SLB and 4SLB uncontrolled engines, only average emissions data for selected manufacturers were available. In addition, the market share for each manufacturer, in terms of the percentage share of installed capacity, was reported. As an example, the data set for 2SLB engines is given in Table 3.1. No market share is available for the "Clean Burn" and PCC controlled engines.

The uncontrolled engine emission factors were assigned a data quality rating of "A" by EPA because they judged that the quantity and quality of the original test data were good and generally well documented, and that the engine types and population profile were known. The Clean Burn and Pre-Combustion Chamber controlled engine emission factors were rated as "C," based upon a judgment that the test data were of “A” quality, but that the amount of data was limited.[28]

3.3.2 July 2000 Version of AP-42 Emission Factors

After the October 1996 version was published, EPA initiated efforts to gather additional emissions data for combustion sources, including stationary reciprocating engines. EPA decided to base the emission factors for natural gas-fueled engines on original emission source test data.[29] The July 2000 emission factors are only for uncontrolled engines. However, the uncontrolled NO_x emission factors have been refined by estimating emissions separately for two different load ranges. EPA has made publicly available the data used to develop the new emission factors in a Microsoft Access database at the EPA TTN web site.[30] A summary of the average emission factor calculated from the database and of the emission factors reported in the July 2000 version of AP-42 is given in Table 3.2.[27] In some cases, it was possible to exactly reproduce the EPA emission factor.

Two alternative procedures were used to estimate emission factors from the database. In one procedure, referred to in Table 3.2 as "ungrouped", each data point in the database was given equal weight, even if some of the data represent repeated measurements of the same engine. In the other procedure, referred to as "grouped," all data for a single engine were averaged, and only the average value for each engine was used to calculate an average emission rate. Of the six emission factors shown in Table 3.2, it appears that for two of them (2SLB NO_x, both load ranges) it is possible to exactly recalculate the AP-42 emission factor from the available data using the “ungrouped” approach. For both of the TOC emission factors it is possible get a very close approximation to the AP-42 value using the "ungrouped" approach. For the emission fator of 4SLB NO_x, 90 to 105% load range, initially it was not possible to get a reasonable approximation to the AP-42 value using either approach. After consultation with EPA, test data from Colorado State University (CSU) were removed from the data set for the 4SLB case. The CSU test results were more than an order-of-magnitude less than that for the other tests and may have been from a controlled, rather than an uncontrolled, engine. After removing the CSU test data, the grouped average then is very close to the AP-42 value.

Although most ungrouped averages are within 15 percent or less of the reported AP-42 values, EPA and the supporting documentation for July 2000 version of AP-42 claimed that the "grouped" method was used in emission factor development.[29] The inconsistency could not be reconciled because of lack of complete documentation by EPA and its contractor regarding how the emission factors were actually calculated.

The emission factors of the uncontrolled 2SLB engines were assigned a quality rating "A" by EPA, and the emission factors of the uncontrolled 4SLB engines were assigned a quality rating of "B."[29] However, no explanations regarding the specific basis for these ratings were provided.

3.4 Quantification of Variability and Uncertainty in Emission Factors

Two sets of case studies are presented. In the first case study, each data point is assumed to be an equally likely random sample from the total population of emission sources. This type of case study applies to all of the emission factor data except for the October 1996 version uncontrolled 2SLB and 4SLB engine data, which are weighted by market share and described separately.

3.4.1 Equally-Weighted Randomly Sampled Data

In many cases, emission factor data are available for a sample of engines, representing different manufacturers, engine models, engine ages, and applications. In developing an emission factor, a judgment is made to group data from various specific engine measurements together because of similarities in engine design and operation. For example, expert judgment could be used as a basis for estimating the market share of each particular make and model of engine. In the absence of information, a common default assumption is to assume equal weight among the available data. Of course, this assumption could be wrong. At the same time, there may not be an empirical basis to justify other assumptions. Key assumptions in an analysis should be evaluated when interpreting the results of the analysis. Therefore, although equal weight for each data point is assumed, later this assumption will be critiqued.

Another factor that must be considered is how to handle replicate data. The available data sets include, in some cases, repeated measurements on the same engine. For example, in the case of the July 2000 data set for uncontrolled NO_x emissions from 4SLB engines operated at 90 percent to 105 percent load, there are 25 data points available from measurements on only 5 engine models. Repeated measurements on the same engine provide an indication of intra-engine variability in emissions. However, in calculating an emission factor, the objective is to quantify inter-engine variability in emissions for purposes of estimating the population distribution for variability within the source category. Therefore, it is necessary to prepare a data set representative of inter-engine variability. The approach taken here is to use an average value for repeated measurements of an individual engine as the representative emission rate for that engine, and to analyze the inter-engine variability in which each engine is represented by either one data point, if only one measurement is available, or the average of the available data, if repeated measurements are available.

As an example to illustrate the development of an emission factor database, Table 3.3 summarizes the NO_x emission data for five uncontrolled 4SLB engines operated at 90 to 105 percent load. The data for the Ingersoll Rand “KVS-412” and “KVS-12” engines were treated separately because they are reported separately in the data base and there is no evidence in the AP-42 supporting documentation that EPA treated them as the same engine in developing the AP-42 emission factors.[29] The CSU tests on Waukesha 3512GL engine may actually be based upon controlled emissions and, therefore, are removed from the data set as previously described.

The inter-engine variability in emissions for the uncontrolled 4SLB engines is shown in Figure 3.1. Of the several types of parametric distributions evaluated, the gamma distribution estimated using MoMM offered the best fit to the four data points. With only four data points, conventional statistical goodness-of-fit tests are not applicable. Instead, to evaluated the goodness-of-fit, bootstrap simulation was used to estimate confidence intervals for the CDF of the fitted parametric distribution. With only four data points, the confidence intervals are relatively wide. For example, the 95 percent confidence interval for the median, or 50^{th} percentile of the distribution, is from 2.3 lb/10^6 BTU to 5.7 lb/10^6 BTU, which is nearly as wide as the range of the observed data. The mean emission estimate obtained from the fitted distribution is 4.1 lb/10^6 BTU. The 95 percent confidence interval for the mean is from 2.5 lb/10^6 BTU to 6.1 lb/10^6 BTU, corresponding to a range of minus 39 percent to plus 49 percent.

An important characteristic of the confidence intervals of the mean, or of any other statistic, estimated based upon bootstrap simulation is that they need not be symmetric. With a very small data set of only four data points, and with positive skewness in the data set, the confidence interval on the mean is expected to be positively skewed. Therefore, the asymmetry of the confidence interval for the mean NO_x emission factor from 4SLB engines is expected. Because of the small number of data points and the wide range of variability of the data, the confidence interval is expected to be relatively wide, as it is in this case.

The adequacy of the fitted distribution can be evaluated, at least in part, by identifying what proportions of the data are contained with the confidence intervals of the CDF. On average, if the fit is a good one, half of the data should be enclosed within the 50 percent confidence interval, 90 percent of the data should be enclosed within the 90 percent confidence interval, and 95 percent of the data should be enclosed within the 95 percent confidence interval. In Figure 3.1, three of the four data points are contained within the 50 percent confidence interval, and all of the data are enclosed by the 90 percent confidence interval. This suggests that the gamma distribution is an adequate fit to the data.

3.4.2 Unequally-Weighted Data

In this section, an example case study is presented based upon emissions data that are not equally weighted. These data are from Table 3.1 for uncontrolled 2SLB engines, based upon the October

1996 version of AP-42. The five emissions values are shown in Figure 3.2 as an empirical CDF, along with three parametric distributions that have been fit to the data.

Because each of the five emissions values has a different market share-based weight, the method for fitting distributions to the data had to be modified compared to when data have equal weight. The approach taken here was to use 100 synthetic data points as a basis. The use of 100 basis data points allows for emission values to occur repeatedly in proportion to their market share. A portion of these 100 data points were assigned the emission factor associated with an engine, in proportion to the market share of that engine. For example, the Clark engines have 36 percent of the market share; therefore, 36 of the 100 basis data points were assigned the Clark engine emission value of 2.64 lb/10^6 BTU. Parametric distributions were fit to the 100 basis data points.

The Weibull distribution provides the best fit in the central portion of the distribution, and appears not to have as "heavy" of a tail at the upper end of the distribution. The lognormal and gamma distributions provide similar fits in this case. For comparison purposes, both the Weibull and lognormal distributions are included in the bootstrap simulation analyses, the results of which are given in Figures 3.3 and 3.4.

During bootstrap simulation, each simulated data point has equal weight. However, because the parametric distributions were fit to market share-weighted data, the shape of the parametric distributions reflects the frequency with which data should be sampled in different emission ranges. For example, the steepness of the fitted CDF in the range from approximately 2 lb/10^6 BTU to 3 lb/10^6 BTU means that there is a high probability that random samples of emissions will occur in this range, corresponding to the three engines that have the largest combined market share. In contrast, there is comparatively little probability that emissions values will be sampled for the two engines that, together, comprise only five percent of the total market share.

For comparison purposes, the results of the bootstrap simulation with the lognormal distribution are given in Figure 3.3. The 95 percent confidence interval encloses more than 95 percent of the empirical distribution of the data. However, the confidence intervals are very wide, and there appear to be biases in the fit. For example, the range of the empirical distribution from the 5^{th} to 50^{th} percentiles coincides with the high side of the confidence intervals, while the lower and upper tails of the empirical distribution coincide with the low side of the confidence interval. These assumptions suggest that the lognormal is not a particularly good distribution to use in this case.

The results of the bootstrap simulation with the Weibull distribution are given in Figure 3.4. These results imply more consistency between the assumed parametric distribution and the empirical distribution of the original data. In particular, only a small portion of the empirical distribution is not enclosed by the 95 percent confidence interval. The width of the confidence interval based upon the Weibull distribution, especially at the upper percentiles, is much narrower compared to the lognormal case, without compromising the apparent goodness-of-fit. Therefore, the Weibull distribution is selected over the lognormal distribution as a more appropriate basis for estimating uncertainty in the mean. The choice of parametric distribution influences the estimated confidence interval for the mean. The 95 percent confidence interval for the mean is 2.14 to 3.38 lb/10^6 BTU based upon the lognormal distribution, 2.25 to 3.26

$lb/10^6$ BTU based upon the gamma distribution, and 2.39 to 2.99 $lb/10^6$ BTU based upon the Weibull distribution. Of these three, the Weibull distribution leads to the narrowest estimate of the confidence interval.

In order to evaluate the influence of the market-share assumptions, this data set was also analyzed as equally weighted data. The result of bootstrap simulation based upon a Weibull distribution fitted to equally weighted data is given in Figure 3.5. When data are given equal weight, the mean is 1.95 $lb/10^6$ BTU, and the 95 percent confidence interval is from 1.22 to 2.75 $lb/10^6$ BTU. The equally weighted mean is 28 percent less than the market share weighted mean, and the confidence interval range is 160 percent larger. Moreever, the lower end of the confidence interval is 49 percent less than in the market share weighted case. In the equally weighted case, two engines with the lowest emission rate are treated equally with the other three data points even though their combined market share is only five percentage. The substantial difference between the two approaches suggests the importance, at least in this case, of appropriately weighting the data.

3.5 Summary of Quantified Variability and Uncertainty

The inter-engine variability in the emission factor data sets and the fitted parametric distributions are summarized in Table 3.4 for the October 1996 version AP-42 and in Table 3.5 for the July 2000 version AP-42. The range of variability in the October 1996 version emission factors is from as low as approximately a factor of 2.3 to as high as a factor of 11. Variability in the July 2000 version is from as low as approximately a factor of 2.7 to as high as a factor of 51.

Particularly, there is substantial variability in NO_x emission factors for engines with load smaller than 90% in the July 2000 version AP-42.

Parametric distributions were fitted to data sets to represent inter-engine variability in emission factors. The best fit was selected based upon the combined evaluations of the Kolmogorov-Smirnov GOF tests and graphical comparisons between the fitted distributions and bootstrap confidence intervals. The Kolmogorov-Smirnov GOF test was conducted using commercial software “Crystal Ball”. The Kolmogorov-Smirnov test statistics reported by “Crystal Ball” for all cases are smaller than the critical value at a significance level of 0.05.[31] Therefore, all fitted distributions are acceptable at the significance level of 0.05 based upon the Kolmogorov-Smirnov test results. For the cases that parametric distributions were fitted to the market-share weighted data, the Kolmogorov-Smirnov test is not applicable. The best fit was selected based upon graphically comparing the step-wise CDF of the synthetic data set and the bootstrap confidence intervals based upon the fitted distributions, as discussed for Figure 3.3 and 3.4.

A summary of estimates of uncertainties in emission factors for uncontrolled natural gas pipeline compressor engines are presented in Table 3.6. For the October 1996 version of AP-42, the analysis is based upon the complete dataset used by EPA to develop the AP-42 emission factors. For the July 2000 version, the methods and data actually used by EPA were not fully documented and therefore it was not possible to exactly reproduce the AP-42 emission factors except in a few cases as previously noted. However, the relative range of uncertainty estimated for these emission factors may still be useful in characterizing uncertainty. The AP-42 emission factors shown in Table 3.6 for the July 2000 version are believed to be close to the means calculated based upon "ungrouped" approach, whereas the mean values of the bootstrap means are based upon distributions fitted to data developed via the "grouped" approach. In general, these mean values are similar to the mean values calculated directly from the "grouped" data, as given in Table 3.3; however, means from the fitted distributions will differ from those estimated directly from data.

The summary tables indicate that the 95 percent range of uncertainty in the mean emission factor ranges from as low as approximately plus or minus 10 percent to as high as minus 90 to plus 180 percent. The range of uncertainty is influenced by a combination of the sample size and the range of variability in the data. Smaller sample sizes and/or larger inter-engine variability in the data will tend to contribute to wider ranges of uncertainty in the estimated mean emission factor.

3.6 Discussion and Conclusions

This paper demonstrates the successful application of quantitative probabilistic analysis to emission factor case studies, based upon the example of stationary natural gas-fueled reciprocating engines. The characterization of uncertainty is based upon random sampling error. The method includes: (1) development of a database; (2) visualization of the data using empirical CDFs; (3) evaluation of alternative parametric probability distributions fitted to the data; (4) bootstrap simulation to characterize confidence intervals in the fitted CDF; (5) selection of a judged best fit distribution based upon bootstrap simulation results; and (6) quantification of uncertainty in the mean based upon the bootstrap sampling distribution for the mean.

The probabilistic method was applied to several different types of analyses, including: (1) quantification of inter-engine variability in emissions and uncertainty in the mean for unequally weighted data points; and (2) quantification of inter-engine variability in emissions and uncertainty in the mean for equally weighted data points. The range of inter-engine variability, which often was a factor, in emissions suggests that the weights assigned to each engine emission estimate can significantly affect the estimate of the mean emission rate. Thus, the assumption of equal weighting of emissions data, as is often made, is likely to be a strong assumption in many cases and, therefore, can be a significant factor biasing emission factor estimates.

The range of inter-engine variability in emission factors was found as large as a factor of 51, and most were greater than 5. In this work, parametric distributions were fitted to data set for representing inter-engine variability in emission factors. The goodness of fits was evaluated based upon the combination of the Kolmogorov-Smirnov GOF tests and graphical comparisons between the fitted distributions and bootstrap confidence intervals. The Kolmogorov-Smirnov test statistics suggest that all fitted distributions are acceptable at a significance level of 0.05. The estimates of uncertainty in the mean are often asymmetric, indicating that skewness regarding observed variability in inter-engine emissions can lead to skewness in the estimate of uncertainty in the mean. Conventional analytical methods based upon normality assumptions can lead to errors in uncertainty estimates. The mean values estimated from the probabilistic analysis differ in some cases from the mean values estimated directly from the data because parametric probability distributions allow for interpolation within the range of observed data and for extrapolations beyond the range of observed data. For small data sets, it is unlikely that the observed sample of data truly includes the minimum and maximum possible values. On this basis, extrapolation is warranted.

Although three parametric distributions were typically evaluated, most often the Weibull distribution was found to provide a good fit to the data. The Weibull may take on many shapes, including negatively skewed, symmetric, or positively skewed. Furthermore, the Weibull distribution also tends to be less "tail-heavy" than the other two, and often provides a better empirical fit to the data for these reasons.

The quantitative analysis demonstrated here focuses on one important source of uncertainty. The range of uncertainty associated with random sampling error was found to be as large as minus 90 percent to plus 180 percent, and in most examples was greater than plus or minus 20 percent. Some other sources of uncertainty, such as potential lack of representativeness of the test cycles used in the measurements, or potential lack of representativeness of the sample of engines, are difficult to evaluate quantitatively. Therefore, it is recommended that qualitative methods for identifying sources of uncertainty *also* be used. However, there is not a direct relationship between the qualitative data rating and the range of uncertainty in the emission factor. Therefore, we do not recommend that data quality ratings be used to make inferences regarding quantitative ranges of uncertainty.

A significant difficulty encountered in this study was the lack of documentation of the data and calculation methods used for the July 2000 AP-42 emission factors. Complete documentation should include enough information so that others can reproduce the calculations and results.

Therefore, we recommend that EPA report the data actually used and the complete calculation method used for each emission factor. With the growing recognition of the importance of quantitative uncertainty analysis, it will be important for EPA and others to routinely report data regarding variability and uncertainty in emission factors.

3.7 Acknowledgements

This work was supported by U.S. Environmental Protection Agency STAR Grants Nos. R826766 and R826790. This paper has not been subjected to any EPA review. Therefore it does not necessarily reflect the views of the agency, and no official endorsement should be inferred. We thank Mr. Roy Huntley of U.S. EPA in Research Triangle Park, NC, for his assistance and recommendations regarding data sources.

3.8 References

1. Bogen, K. T.; Spear, R. C. Integrating Uncertainty and Interindividual Variability in Environmental Risk Assessment; *Risk Anal.* **1987**, 7, 427-436.

2. Frey, H. C.; Rhodes, D. S. *Quantitative Analysis of Variability and Uncertainty in Environmental Data and Models*; Prepared by North Carolina State University, Raleigh, NC, for US Department of Energy: Germantown, MD, 1999; Vol. 1.

3. US Environmental Protection Agency. *Compilation of Air Pollutant Emission Factors, AP-42, Fifth Edition*; US Environmental Protection Agency: 1995.

4. Beck, L.L.; Wilson, D. EPA's Data Attribute Rating System. In *Proceedings, Emission Inventory: Planning for the Future*, Air & Waste Management Assoc.: Pittsburgh, PA, 1997.

5. National Research Council. *Modeling Mobile-Source Emissions*; National Academy Press: Washington, DC, 2000.

6. US Environmental Protection Agency. *Guiding Principles for Monte Carlo Analysis*; EPA/630R-97/001; US Environmental Protection Agency: 1997.

7. National Research Council. *Science and Judgement in Risk Assessment*; National Academy Press: Washington, DC, 1994.

8. Kini, M.D.; Frey, H.C. *Probabilistic Evaluation of Mobile Source Air Pollution*; Prepared by North Carolina State University, Raleigh, NC, for Center for Transportation and the Environment: Raleigh, NC, 1997; Vol 1.

9. Pollack, A.K.; Bhave, P.; Heiken, J.; Lee, K.; Shepard, S.; Tran, C.; Yarwood, G.; Sawyer, R.F.; Joy, B.A. *Investigation of Emission Factors in the California EMFAC7G Model*; PB99-149718INZ, Prepared by ENVIRON International Corp, Novato, CA, for Coordinating Research Council: Atlanta, GA, 1999.

10. Frey, H.C.; Bharvirkar, R.; Zheng, J. *Quantitative Analysis of Variability and Uncertainty in Emissions Estimation*; Prepared by North Carolina State University, Raleigh, NC, for the U.S. Environmental Protection Agency: Research Triangle Park, NC, 1999.

11. Frey, H.C.; Bammi, S. Quantification of Variability and Uncertainty in Lawn and Garden Equipment NO_x and Total Hydrocarbon Emission Factors. *J. of Air & Waste Manage. Assoc*. **2002**, 52, 435-448.

12. Frey, H.C.; Bammi, S. Probabilistic Nonroad Mobile Source Emission Factors. *ASCE Journal of Environ. Eng*. Accepted May 2002, in press.

13. Frey, H. C.; Rhodes, D. S. Characterizing, Simulating, and Analyzing Variability and Uncertainty: An Illustration of Methods Using an Air Toxics Emissions Example; *Human Health and Ecological Risk Assessment*, **1996**, 2(4), 762-797.

14. Frey, H.C.; Bharvirkar, R. Quantification of Variability and Uncertainty: A Case Study of Power Plant Hazardous Air Pollutant Emissions; Chatper 10 in *The Risk Assessment of Environmental and Human Health Hazards: A Textbook of Case Studies*; Paustenbach, D., Ed.; John Wiley and Sons: New York, 2002, pp 587-617.

15. Rhodes, D.S.; Frey, H.C. Quantification of Variability and Uncertainty in AP-42 Emission Factors Using Bootstrap Simulation. In *Proceedings, Emission Inventory: Planning for the Future*, Air and Waste Management Assoc.: Research Triangle Park, NC, October 28-30, 1997.

16. Abdel-Aziz, A.; Frey, H. C. Quantification of Variability and Uncertainty in Hourly NO_x Emissions from Coal-Fired Power Plants. In *proceedings of the 95th Annual Meeting of the Air & Waste Management Association*, Baltimore, MD, June, 2002.

17. Frey, H.C.; Zheng, J. Quantification of Variability and Uncertainty in Utility NO_x Emission Inventories; *J. of Air & Waste Manage. Assoc.* in press.

18. Maurice, B.; Frischknecht, R.; Coelho-Schwirtz, V.; Hungerbuhler, K. Uncertainty Analysis in Life Cycle Inventory. Application to the Production of Electricity with French Coal Power Plants; *J. Cleaner. Prod.* **2000**, 8, 95-108.

19. Li, S.; Frey, H. C. Methods and Example for Development of a Probabilistic Per-Capita Emission Factor for VOC Emissions from Consumer/Commercial Product Use. In *proceedings of the 95th Annual Meeting of the Air & Waste Management Association*, Baltimore, MD, June, 2002.

20. Frey, H.C.; Rhodes, D.S. Characterization and Simulation of Uncertain Frequency Distributions: Effects of Distribution Choice, Variability, Uncertainty, and Parameter Dependence; *Human and Ecological Risk Assessment*, **1998**, 4(2), 423-468.

21. Frey, H. C.; Burmaster, D. E. Methods for Characterizing Variability and Uncertainty: Comparison of Bootstrap Simulation and Likelihood-Based Approaches; *Risk Analysis*, **1999**, 19, 109-129.

22. Zheng, J.; Frey, H.C. Quantitative Analysis of Variability and Uncertainty: An Illustration of Methods Using Mixture Distributions, In P*roceedings of the 94th Annual Meeting of the Air & Waste Management Association*, Orlando, FL, 2001.

23. Cullen, A. C.; Frey, H. C. *Probabilistic Techniques in Exposure Assessment: A Handbook for Dealing with Variability and Uncertainty in Risk Analysis*; Plenum Press: New York, 1999.

24. Report of the Workshop on Selecting Input Distributions for Probabilistic Assessments; Prepared by Eastern Research Group, Inc., Lexington, MA, for US. Environmental Protection Agency: Washington, DC, 1998.

25. Efron, B.; Tibshirani, R. J. *An Introduction to the Bootstrap*, Chapman & Hall: New York, 1993.

26. U.S. Environmental Protection Agency. *Compilation of Air Pollutant Emission Factors, AP-42, Fifth Edition, Volume I: Stationary Point and Area Sources, Chapter 3.2 Heavy-duty Natural Gas-fueled Pipeline Compressor Engines And Turbines*; U.S. Environmental Protection Agency; 1996.

27. U.S. Environmental Protection Agency. *Compilation of Air Pollutant Emission Factors, AP-42, Fifth Edition, Volume I: Stationary Point and Area Sources, Chapter 3.2 Natural Gas-fueled Reciprocating Engines*; U.S. Environmental Protection Agency; 2000.

28. Eastern Research Group. *Report on Revisions to 5th Edition AP-42, Section 3.2 Heavy-duty Natural Gas-fueled Pipeline Compressor Engines*; Prepared by Eastern Research Group, Morrisville, NC, for U.S. Environmental Protection Agency: RTP, NC, 1996.

29. Alpha-gamma Technologies, Inc. *Emission Factor Documentation for AP-42 Section 3.2, Natural Gas-fueled Reciprocating Engines*, Prepared by Alpha-gamma Technologies, Inc., Raleigh, NC, for U.S. Environmental Protection Agency, RTP: NC, 2000.

30. EPA emissions data web site, located December 2000. (http://www.epa.gov/ttn/chief/ap42/ch03/related/c03s02.html).

31. Ang, A. H-S.; Tang, W. H. *Probability Concepts in Engineering Planning and Design*; John Wiley & Sons, Inc: New York, 1975.

Table 3.1. Emissions data for Uncontrolled Natural-Gas Fueled 2-Stroke Lean Burn Engines (Source: Reference 28)

MAKE	**NO_x Emissions ($lb/10^6$ BTU)**	**TOC Emissions ($lb/10^6$ BTU)**	**Ratio of total installed capacity (%)**
Ajax	1.132	4.318	4
Clark	2.636	1.703	36
CB	3.009	1.164	47
Fairbanks-Morse	0.556	1.220	1
Worthington	2.466	1.618	12
Weighted average	2.710	1.539	

Table 3.2. Comparison Between EPA NO_x Emissions Database and Documentation of AP-42 Emission Factors for Uncontrolled 2SLB and 4SLB Natural Gas Engines Based Upon July 2000 Version of AP-42.

Engine Type	Pollutant	Engine Load	Average Calculated from Database[a] (lb/10^6 Btu)	AP-42 Emission Factor (lb/10^6 Btu)	Sample Size of Dataset Used to Develop AP-42 Emission Factor[b]
2SLB	NO_x	90 to 105%	3.17 (ungrouped), 3.05 (grouped)	3.17	34
		< 90%	1.94 (ungrouped), 2.15 (grouped)	1.94	57
	TOC[c]	Any load	1.61(ungrouped), 1.49 (grouped)	1.64	24
4SLB	NO_x	90 to 105%	4.40 (ungrouped)[d] 4.02 (grouped) [d]	4.08	25
		< 90%	0.739 (ungrouped) 1.44 (grouped)	0.847	13
	TOC[c]	Any load	1.42(ungrouped), 1.13 (grouped)	1.47	37

[a] Two average values were calculated from the available data in the database from the EPA TTN Web Site. The "Ungrouped" averages involve taking the average of all emissions tests for all engines. The "Grouped" averages involve first calculating the average emissions for engines that were tested more than once, and then calculating the average among all engines. For example, if we have 25 test data from 10 engines, the ungrouped average is based upon 25 equally weighted values. In contrast, the grouped average would be based upon the 10 average values for each different engine.
[b] The test identification numbers used in the on-line database are documented in Reference 29.
[c] Emission factors are reported on a TOC basis in AP-42. But they are reported as Total Hydrocarbons (THC) in database.[27,30]
[d] CSU test were removed.

Table 3.3. Summary of Emission Test Data Using in July 2000 Version of AP-42 for Uncontrolled 4SLB Natural Gas Engines Operated at 90 to 105 Percent of Load.

Engine Make and Model	**Engine Size (hp)**	**Engine Load Range (%)**	**Number of Tests**	**Range of Test Results (lb/10^6 BTU)**	**Average Emissions (lb/10^6 BTU)**
Caterpillar G339T	850	100	1	2.11	2.11
Cooper-Bessemer LSV-16	4,200	98-99	4	2.41 to 3.28	2.90
Ingersoll Rand KVS-412	2,000	91	2	5.24 to 5.63	5.44
Ingersoll Rand KVS-12	2,000	100	5	4.98 to 6.01	5.65
Waukesha 3521 GL (CSU tests)	736	100	13	0.11 to 0.38	0.21

Table 3.4. Fitted Parametric Distributions for Variability in NO_x and TOC Emission Factors for Natural Gas-fueled Lean Burn Engines, October 1996 AP-42 Data

Pollutant	**NO_x[a]**				**TOC[a]**			
Engine type	**2SLB**			**4SLB**	**2SLB**			**4SLB**
Control tech.	**none**	**CB**	**PCC**	**none**	**none**	**CB**	**PCC**	**none**
Min of data	0.56	0.67	0.26	0.35	1.16	0.17	0.50	0.63
Max of data	3.01	1.53	2.90	4.00	4.32	1.03	3.47	2.31
Ratio of Max to Min	5.41	2.29	11.2	11.43	3.71	5.91	6.99	3.66
Mean	/	0.83	0.85	/	/	0.77	1.75	/
Std. Dev.	/	0.25	0.57	/	/	0.38	0.75	/
Skewness	/	2.60	2.56	/	/	-1.12	0.34	/
Kurtosis	/	7.55	8.53	/	/	-0.84	-0.02	/
Fitted distribution	W	L	L	W	W	W	W	W
Parameter estimation method[b]	MLE	MLE	MLE	MLE	MLE	MLE	MLE	MLE
Shape parameter	9.9908	-0.2115	-0.3178	3.7167	2.4124	2.2006	2.5805	1.9748
Scale parameter	2.8505	0.2296	0.5361	3.5047	1.7279	0.8587	1.9783	1.3377
K-S test statistic[c]	n/a	0.2292	0.1308	n/a	n/a	0.3423	0.1121	n/a
Critical value at 0.05 significance level	n/a	0.40	0.29	n/a	n/a	0.40	0.29	n/a
Num. of Data	5	11	20	4	5	11	20	4
Percent of data in 50% bootstrap CI	/	36	70	/	/	18	75	/
Percent of data in 90% bootstrap CI	/	91	95	/	/	45	100	/
Percent of data in 95% bootstrap CI	/	91	100	/	/	55	100	/

[a] For uncontrolled emission factors, parametric distributions were fitted synthetic data sets.
[b] W = Weibull; L = Lognormal.
[c] Kolmogorov-Smirnov test is not applied for fits to synthetic data sets.

Table 3.5. Fitted Parametric Distributions for Variability in NO_x and TOC Emission Factors for Natural Gas-fueled Lean Burn Engines, July 2000 AP-42 Data

Pollutant	**NO_x**				**TOC**	
Engine type	**2SLB**		**4SLB**		**2SLB**	**4SLB**
Load range	**90-105%**	**<90%**	**90-105%**	**<90%**	**all**	**all**
Min of data set	1.31	0.16	2.11	0.11	0.19	0.22
Max of data set	5.60	5.08	5.65	5.65	2.14	1.65
Ratio of Max to Min	4.27	32.56	2.68	50.90	11.42	7.62
Mean	3.06	2.15	4.02	1.44	1.49	1.13
Std. Dev.	1.31	1.65	1.79	2.39	0.53	0.63
Skewness	0.36	0.79	-0.15	2.09	-1.05	-1.62
Kurtosis	-0.19	-0.91	-4.99	4.41	1.57	3.02
Fitted distribution[a]	W	W	G	G	W	G
Parameter estimation method	MLE	MLE	MoMM	MoMM	MLE	MoMM
Shape parameter	2.6640	1.3489	5.0730	0.3624	3.2514	3.2313
Scale parameter	3.4461	2.3423	0.7928	3.9670	1.6397	0.3484
K-S test statistic[b]	0.1553	0.2284	n/a	0.1668	0.1517	n/a
Critical value at 0.05 significance level	0.40	0.40	n/a	0.56	0.35	n/a
Total Num. of Data	11	11	4	5	14	4
Percent of data in 50% bootstrap CI	82	45	75	60	50	50
Percent of data in 90% bootstrap CI	100	100	100	100	93	100
Percent of data in 95% bootstrap CI	100	100	100	100	93	100

[a] W = Weibull, G = Gamma

[b] Kolmogorov-Smirnov test is not applicable for sample size smaller than 5.

Table 3.6. 95 Percent Confidence Interval for Mean NO_x and TOC Emission Factors for Natural Gas-fueled Lean Burn Engines

Engine and Emissions Control Technology	AP-42 Emission Factor[a]	Fitted Distrib.[b]	Bootstrap sample size	Mean of Bootstrap Sample Means[a]	Relative 95% CI on Mean[c]
October 1996 AP-42 Data, NO_x Emission Factor					
2SLB, Uncontrolled	2.710	Weibull	5	2.714	-11.8% to +9.36%
2SLB, Clean Burn	0.834	Lognormal	11	0.835	-14.1% to +15.4%
2SLB, PCC[d]	0.850	Lognormal	20	0.840	-23.7% to +28.5%
4SLB, Uncontrolled	3.225	Weibull	4	3.170	-27.2% to +30.8%
October 1996 AP-42 Data, TOC Emission Factor					
2SLB, Uncontrolled	1.539	Weibull	5	1.549	-36.0% to +42.7%
2SLB, Clean Burn	0.767	Weibull	11	0.770	-56.1% to +67.5%
2SLB, PCC[d]	1.756	Weibull	20	1.750	-17.1% to +18.3%
4SLB, Uncontrolled	1.261	Weibull	4	1.278	-47.6% to +55.7%
July 2000 AP-42 Data, NO_x Emission Factor					
2SLB, 90 to 105%	3.17	Weibull	11	3.05	-24% to +24%
2SLB, < 90%	1.94	Weibull	11	2.18	-41% to +46%
4SLB, 90 to 105%	4.08	Gamma	4	4.06	-39% to +49%
4SLB, < 90%	0.847	Gamma	5	1.45	-90% to +180%
July 2000 AP-42 Data, TOC Emission Factor					
2SLB, Uncontrolled	1.64	Weibull	14	1.45	-16% to +18%
4SLB, Uncontrolled	1.47	Gamma	4	1.12	-45% to +57%

[a] Units are $lb/10^6$ BTU.
[b] Parameter estimation: MLE for Weibull and lognormal distributions and MoMM for gamma distribution.
[c] Calculated based upon bootstrap simulation results.
[d] PCC=Pre-Combustion Chamber

Figure 3.1. Comparison of Empirical Cumulative Distribution of Average Uncontrolled 4-SLB Engine, 90-105% load, NO_x Emissions, Fitted Gamma Distribution, and Bootstrap Simulation Confidence Intervals, Based Upon July 2000 AP-42 Data.

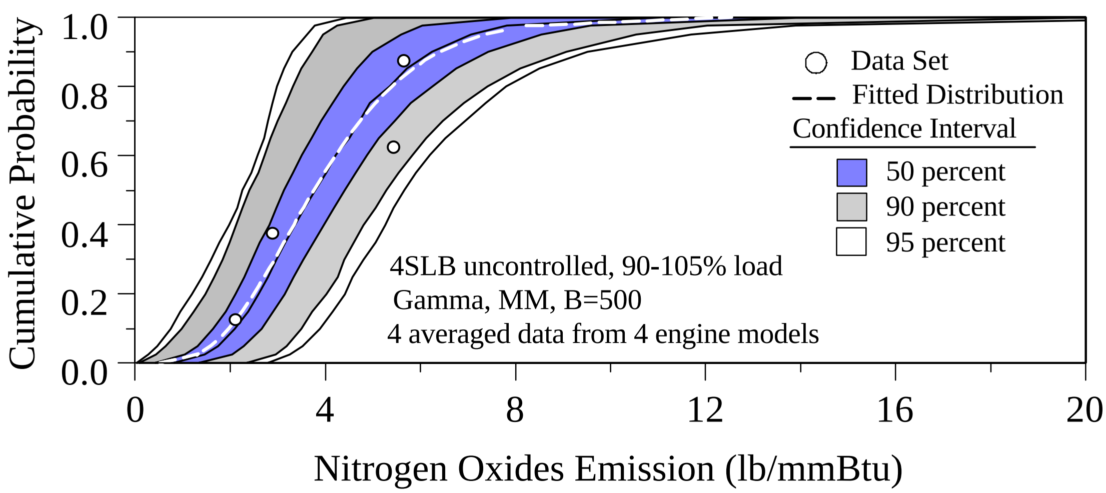


Figure 3.2. Empirical Distribution and Fitted Parametric Distributions for Market-Share Weighted NO_x Emissions Rates for Uncontrolled 2-Cycle Lean Burn Engines Based Upon October 1996 AP-42 Data

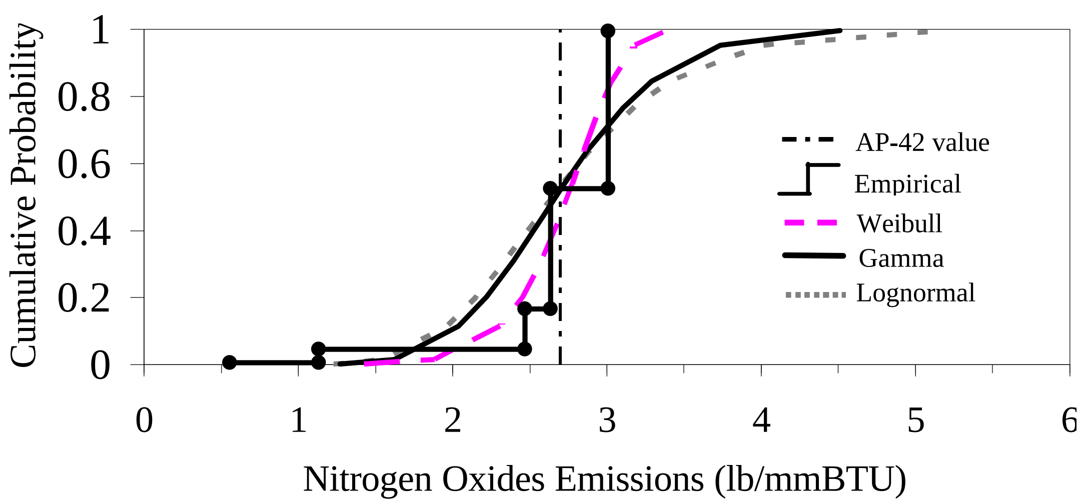


Figure 3.3. Comparison of the Empirical Distribution Bootstrap Simulation Results Based Upon a Lognormal Distribution for Market-Share Weighted NO_x Emissions Rates for Uncontrolled 2-Cycle Lean Burn Engines Based Upon October 1996 AP-42 Data

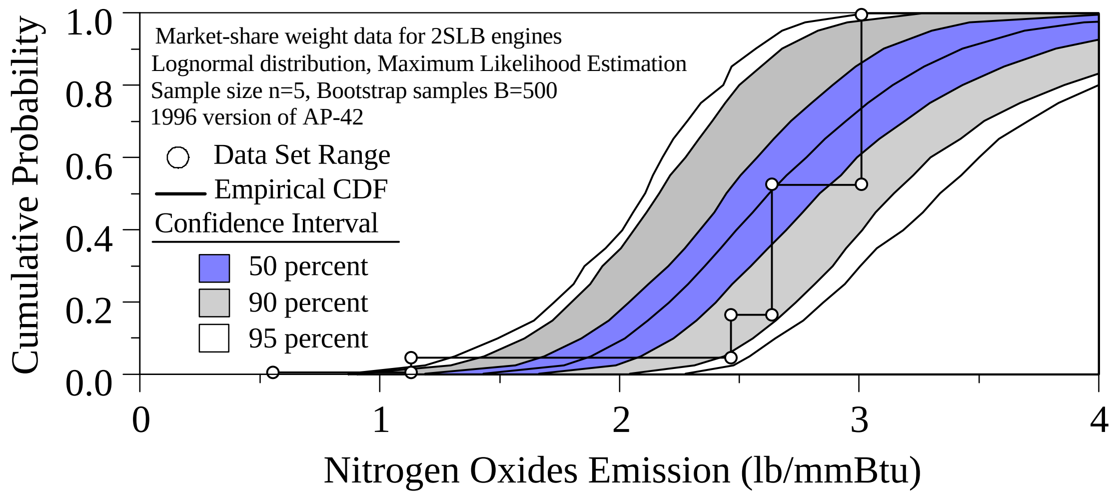


Figure 3.4. Comparison of the Empirical Distribution Bootstrap Simulation Results Based Upon a Weibull Distribution for Market-Share Weighted NO_x Emissions Rates for Uncontrolled 2-Cycle Lean Burn Engines Based Upon October 1996 AP-42 Data

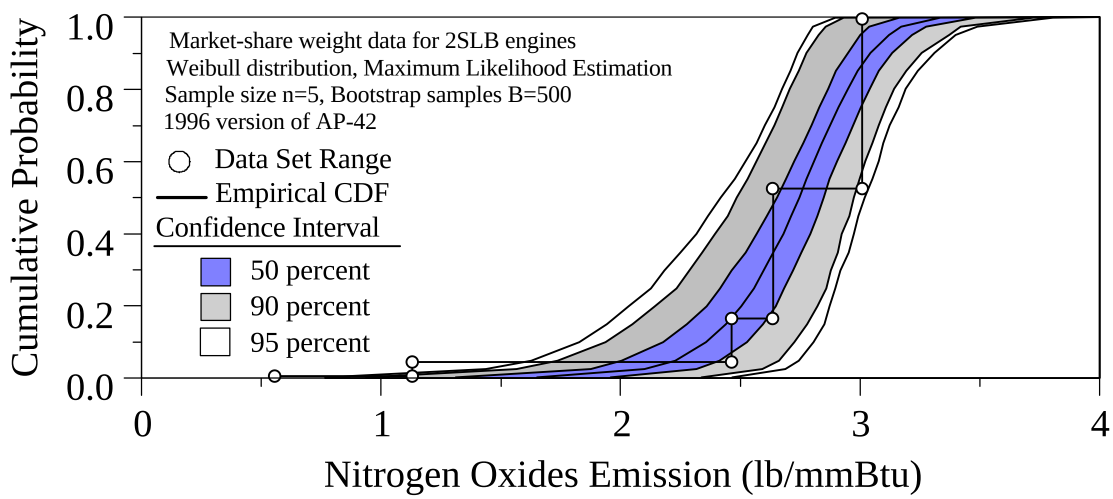
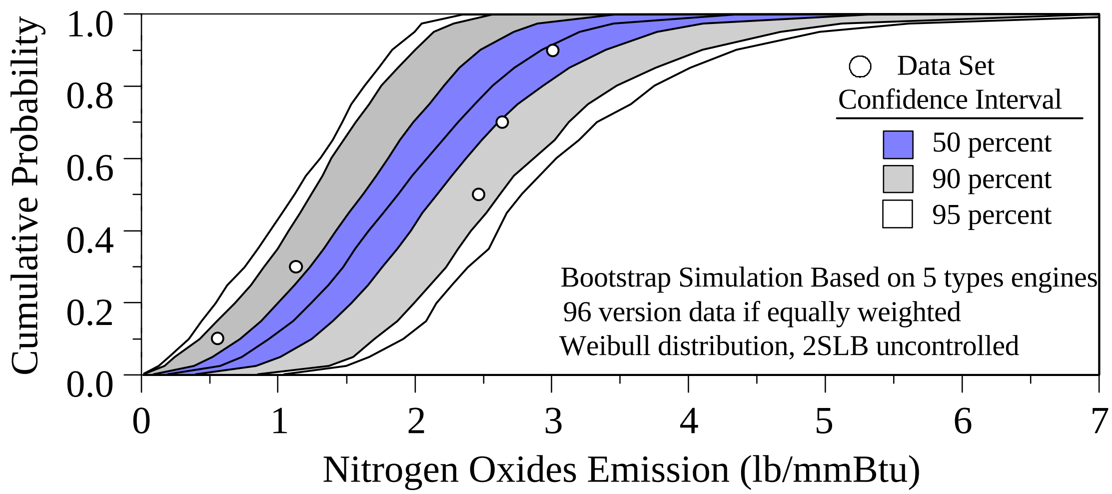


Figure 3.5. Comparison of the Empirical Distribution Bootstrap Simulation Results Based Upon a Weibull Distribution, Market-Share Weighted NO_x Emissions Rates, Treated as Unweighted data, Uncontrolled 2-Cycle Lean Burn Engines Based Upon October 1996 AP-42



4.0 METHODS AND EXAMPLE FOR DEVELOPMENT OF A PROBABILISTIC PER-CAPITA EMISSION FACTOR FOR VOLATILE ORGANIC COMPOUND EMISSIONS FROM CONSUMER/COMMERCIAL PRODUCT USE

Song Li and H. Christopher Frey

Department of Civil Engineering, North Carolina State University, Raleigh, NC 27695

Abstract

Quantitative methods for developing a probabilistic per-capita emission factor were applied for a case study of volatile organic compound (VOC) emissions from consumer/commercial product use. VOC profiles of 20 product categories were investigated. For each category, the beta distribution was fit to represent variability in the VOC contents of different formulations. Bootstrap simulation was used to quantify uncertainty in the mean VOC content for each category. Uncertainty in the mean VOC content for individual category is as large as minus 79 percent to plus 130 percent. Since no sample data was available, judgment was used to assign probability distributions for product use. Monte Carlo simulation was used to estimate uncertainty in the mean emission factor and to identify the key uncertainty contributors. Uncertainty in the mean emission factor was quantified as minus 7.7 percent to plus 8.4 percent. The key contributors of uncertainty was found including product use data of “Paints, primers, varnishes” and VOC content data of “Room deodorants and disinfectants”, “Caulking and

sealing compounds” and “Insect sprays”. To reduce uncertainty in mean emission factor, it is recommended to collect more data for the key contributors than the insignificant contributors.

4.1 Introduction

Emission factors are basic data to develop emission inventories, and emission inventories are widely used for air quality management purposes.[1] However, current practice typically ignores uncertainty in emission inventories as well as emission factors. Therefore, it is typically not known how robust air quality management decisions are with respect to uncertainty. It is also under considerable debate that the lack of quantification of uncertainty in current emission inventory development practice results in unnecessarily tight air quality standards and impedes opportunities to find cost-effective solutions.[2, 3]

The case study application is for a per-capita volatile organic compound (VOC) emission factor for consumer/commercial product use. VOCs are recognized precursors of tropospheric ozone, which is a criteria pollutant of NAAQS and of increasing concern, especially in urban areas. Consumer/commercial product use is among the largest emission sources of VOC emissions, such as in the Charlotte airshed, North Carolina.

4.1.1 Variability and Uncertainty in Emission Factors of Area Sources

Area sources include emission categories such as consumer/commercial product use, architecture coating, and asphalt paving. For a given area source category, emissions may vary from one specific area to another or/and from one particular time to another because of variations in user preference, economic situation and other geographic or temporal characteristics. For the purposes of developing emission factors, analysts are typically interested in the average emission rate for a particular area in a particular averaging time. This paper presents a case study of developing a national annual average emission factor for consumer/commercial product use. Further, in the case of consumer/commercial product use, the emission factor may also vary from one specific product category to another because of differences in formulations or manufacturers.

Typically, uncertainty arises due to lack of knowledge regarding the true value of an unknown quantity, such as the true but unknown emission factor for a particular source category.[4, 5] Other definitions of uncertainty can be found in ISO, Pukkala and Kangas, Lemons, Cullen and Frey and Mowrer.[6-10] The average emission factor is subject to uncertainty because of: (1) systematic errors, also referred as inaccuracy or bias, due to inaccurate measuring method or non-representativeness of data; and (2) random errors, also referred as imprecision, introduced by random measurement error and statistical random sampling error due to limited sample size.[11] The main focus of this case study is on the quantification of uncertainty that arises due to random sampling error, which is the statistical random fluctuation in any statistic estimated from a finite random sample of data. In this paper, sampling distributions were used as a method for quantifying uncertainty in the mean emission estimate associated with random sampling error.

4.1.2 Practice of Quantification of Uncertainty in Emission Estimates

There have been recent efforts to quantify uncertainty in emissions for some source categories, but to date there has not been an effort to quantify uncertainty in the mean emissions of consumer/commercial product use. For example, a number of efforts have been aimed at quantifying uncertainty in the emissions of coal-fired power plants, including hazardous air pollutants and nitrogen oxides (NO_x).[12-18] For nonroad mobile sources, uncertainty has been quantified associated with data used for both the Mobile5 and EMFAC7G models.[14, 19, 20] Probabilistic emission factors have recently been developed for selected nonroad mobile sources.[21, 22] Uncertainty in air pollutant emissions has been addressed for natural gas-fueled internal combustion engines.[23] Recently, the Intergovernmental Panel on Climate Change (IPCC) issued "Good Practice" guidance regarding methods for quantifying uncertainty in emission inventories.[1] The National Research Council, in a recent report on onroad mobile source emissions, has also recommended the application of quantitative uncertainty analysis for emissions factors and inventories.[24]

A methodology developed for the U.S. Environmental Protection Agency (EPA) is the underlying basis of the approach used in this paper.[14] The method is described in detail in the next section. Because most of the recent efforts to quantify uncertainty in specific source category emissions have been focused on point and mobile sources, it was deemed important to demonstrate the application of probabilistic methods to an important area source. Consumer/commercial product use was selected because it is a significant VOC emission source category and because uncertainty in the VOC emission factor for this category has not previously been quantified.

4.2 Overview of Probabilistic Analysis Methods

The primary approach of probabilistic analysis is to quantify uncertainties in the inputs to a model and to propagate the uncertainties through the model to obtain a probabilistic estimate of the model output. This paper focuses on the quantification of uncertainties in the inputs of a per-capita emission factor model and the propagation of the uncertainties through the model to develop a probabilistic emission factor.

4.2.1 Quantification of Uncertainty in Unknown Quantities

It is often useful to graphically visualize the sample data prior to performing uncertainty analysis. The typical approach to visualize data is the use of plotting position methods, which assign fractiles to samples and express them as an empirical cumulative distribution function (CDF). One limitation of an empirical CDF is that there is no probability assigned to any values other than the observed data. Fitting parametric probability distributions has benefits over the use of empirical distributions in that they can provide interpolations among the observed data and extrapolations beyond the range of observed data.[25] Parametric distributions also typically have an underlying theoretical basis and an appropriate distribution can be selected that is consistent with the procedure that generates the data.[9, 11]

Bootstrap simulation is a numerical method used to quantify uncertainties in statistics of a probability distribution that represents variability. The bootstrap method was introduced by Efron in 1979 for the purpose of numerically simulating the sampling distributions.[26] The main assumption in bootstrap simulation is that the probability distribution estimated from the observed sample of data is the best estimate of the true but unknown population distribution. Typically, 500 to 2,000 synthetic data sets, known as bootstrap samples, are randomly sampled from the assumed population distribution. Each bootstrap sample has the same number of data points as the original sample. Therefore, the bootstrap sample is one possible random realization of the original sample. Statistics, such as the sample mean, can be calculated from each bootstrap sample. Thus, there will be 500 to 2,000 estimates of the population mean, representing a sampling distribution of mean values. From the sampling distribution of mean, a confidence interval for the population mean can be inferred. Similarly, sampling distributions and confidence intervals can be inferred for other statistics, such as the standard deviation, distribution parameters, or percentiles of the cumulative distribution for variability.

4.2.2 Propagation of Distributions through Model

Analytical or numerical methods can be used for propagation of uncertainties in the model inputs through the model. Numerical methods, particularly the Monte Carlo simulation method, have no restrictive assumption on the probability distributions assigned to model inputs and are typically applicable for complex models.[9]

Another advantage of the Monte Carlo simulation method is that it is possible to identify the key sources of uncertainty in model inputs contributing most to uncertainty in model outputs by calculating the correlation coefficients between the each of the model output and model inputs. A correlation coefficient, $r_{x,y,}$ is a measure of the strength of the linear relationship between two variable x and y.[9] Larger magnitude of the correlation coefficient is often a useful indication of the important influence of a model input with respect to the range of uncertainty in a model output.

$$r_{x,y} = \frac{\sum_{k=1}^{m}(x_k - \bar{x})(y_k - \bar{y})}{[\sum_{k=1}^{m}(x_k - \bar{x})^2 \sum_{k=1}^{m}(y_k - \bar{y})^2]^{\frac{1}{2}}} \tag{4.1}$$

Where:

$r_{x,y}$ = correlation coefficient

x_k = model input

y_k = model output

m = number of iterations

In some cases, two distributions may have a non-linear but monotonic dependence. In such cases, one should use the rank value instead of the sample value to calculate the correlation coefficient. A rank value is determined by ordering the sample value in an ascending order. Then the smallest sample has a rank value of one, and the largest sample has a rank value that equals to the total number of samples. The correlation coefficient calculated based upon rank value is called the rank correlation coefficient (RCC).

4.3 VOC Emissions from Consumer/Commercial Product Use

VOC emission data and product use data used in this study were obtained from the EPA report.[27] In the EPA study, consumer/commercial products were organized in 47 categories, of which 20 categories account for 90 percent of total photochemically reactive organic compound (PROC) emissions.[28] Therefore, highest priority was given to these 20 categories. VOC profiles and product use for the 20 high priority categories were investigated.

4.3.1 Structure of the Database

Consumer/commercial product use is an emission process of evaporation loss associated with the use of organic solvents. Four types of information were needed for this study, including (1) Chemical composition of the products of interest (to determine the VOC content), (2) Market share of competing formulations, (3) National use of the products of interest, and (4) National population. The database structure is given in Figure 4.1. The database is organized in a hierarchical structure. Consumer/commercial products are separated into different product categories. For each product category, major formulations on the market were investigated.

According to EPA, chemical compositions of the competing formulations for a product were obtained from the chemical descriptions accompanied with the formularies or by contacting manufacturers.[28] To develop an emission factor, market share information for competing formulations would be needed. However, market share data were not readily available. Therefore, equal market share was assumed. This assumption will not substantially bias the results if chemical composition does not vary substantially from one formulation to another. Another assumption made by EPA is that all organic components in the consumer/commercial products are finally evaporated into the atmosphere. Product use data are typically obtained from market census, and only point estimates are available in this study.[27]

4.3.2 Method to Develop a Per-Capita Emission Factor

The emission inventory of consumer/commercial product use has been developed by EPA and many local authorities, such as NC Department of Environment and Natural Resources, based upon a per-capita emission factor. Equation 4.2 summaries the reported method to calculate the per-capita emission factor.[27]

$$EF = \frac{\sum_{i=1}^{m} WF_i \times U_i}{P} \tag{4.2}$$

Where:

EF = VOC per-capita emission factor, lb VOC/person-year

WF_i = VOC weight fraction for ith product, lb VOC/ lb product

U_i = product annual use for ith product, lb product/year

P = population, person

m = number of products

4.4 Development of Probabilistic Per-Capita Emission Factor

According to eq 4.2, in order to develop a probabilistic emission factor, uncertainties must be quantified in the: (1) VOC content data of each product; (2) annual use data of each product; and (3) population data. Then the Monte Carlo simulation can be used to propagate the uncertainties in the inputs through eq 4.2 to predict uncertainty in the emission factor.

4.4.1 Quantification of Uncertainty in VOC Content Data

VOC content data are available for different formulations in a product category. For example, there are eleven major formulations of engine degreaser on the market, and the average estimate of VOC weight percentage for each formulation is given in Table 4.1.

When quantifying uncertainty in VOC content data, an important consideration is to decide the market share for each formulation. In the absence of this information, a default assumption used by EPA is to assume equal market share for the available data. This assumption of course could be wrong. However, at the same time, there may not be an empirical basis to justify other assumptions. The equal market share assumption can be further reevaluated in the future when new information is released. In addition, possible biases if the assumption is wrong can be evaluated by comparing the formulations within the category. In the case of engine degreasers, there are three formulations with 25 weight percent or less of VOC, three formulations with 40 to 55 weight percent of VOC, and five formulations with approximately 80 to 95 weight percent VOC. If the market share is more heavily weighted toward the lower VOC formulations, then an emission factor based upon equally-weighted formulations will overestimate. If the market share is more heavily weighted toward high VOC formulations, then the true average VOC emissions will be underestimated.

Inter-formulation variability in the VOC content for a given product was represented with parametric probability distributions. Uncertainty in the average VOC content was then estimated using bootstrap simulation. As an example, the empirical cumulative distribution of the engine degreaser data, the fitted distribution for variability among degreasers and the bootstrap simulation confidence intervals for the fitted distribution are shown in Figure 4.2. The beta distribution was chosen because it is defined on a fixed range and can take on a wide variety of shapes. Therefore is suitable to describe distributions of with a lower bound of 0 and an upper bound of 1.

Goodness-of-fit (GOF) tests were conducted for evaluating the quality of fitting beta distributions. GOF tests typically have limitations on the minimum amount of data. For example, at least 25 data points should be available for the Chi-squared test and at least 5 data points should be available for the Kolmogorov-Smirnov test.[9] The Kolmogorov-Smirnov test was applied for engine degreaser data using a commercial software "Crystal Ball". The beta distribution was recommended by "Crystal Ball" as the best choice among all continuous parametric distributions. The Kolmogorov-Smirnov test statistic reported by "Crystal Ball" is 0.2113 for engine degreaser data. The critical value at a significance level of 0.05 is 0.40.[29] Therefore, the fit of beta distribution for engine degreaser data is acceptable at the significance level of 0.05. Bootstrap simulation also provides a plausible method to evaluate the adequacy of a fit by identifying the proportion of the data contained within the confidence intervals of the CDF. In this study, 500 bootstrap samples were simulated during the simulation process. In Figure 4.2, seven of the eleven data are enclosed by the 50 percent confidence interval, and all of the data are enclosed by the 90 percent confidence interval. This suggests that the beta distribution is a good fit to the data.

Confidence intervals for statistics of the fitted parametric distribution were estimated by the bootstrap simulation. For example, the 95 percent confidence interval for the median, or 50th percentile of the distribution, is from 0.22 VOC fraction to 0.87 VOC fraction. Similarly, for each bootstrap sample, the mean was calculated. Therefore, there are 500 estimates of the mean, representing a sampling distribution of mean values. From the sampling distribution, an average estimate and confidence intervals for the mean can be inferred. The average estimate of the mean fraction of VOC content for engine degreaser obtained from the sampling distribution is 0.53, which is the same as the mean VOC content calculated from the original data set. The 95 percent confidence interval for the mean is from 0.31 to 0.73, corresponding to a range of minus 42 percent to plus 38 percent compared to the mean. A characteristic of the confidence intervals of the mean, or of any other statistic, estimated based upon bootstrap simulation is that they need not be symmetric. The asymmetry in this case results from negative skewness of the data and the small sample size.

Summaries of parameters for fitted distributions and the proportions of data points enclosed by the bootstrap confidence intervals were given in Table 4.2. The bootstrap confidence intervals for "Hair sprays" and "Insect sprays" suggest that the fits might not be adequate. Thus, GOF tests were conducted for these two categories to further evaluate the quality of fit. The "Crystal Ball" reported that the Kolmogorov-Smirnov test statistic for "Hair sprays" is 0.2344, which is smaller than the critical value of 0.31 at a significance level of 0.05.[29] Therefore, this fit of beta distribution is acceptable at the significance level of 0.05 for the case of "Hair sprays." For the category of "Insect spray", the "Crystal Ball" reported a Kolmogorov-Smirnov test statistic of 0.5848, which is greater than the critical value of 0.41 at a significance level of 0.05.[29] The reason for the unsatisfied fit is that the sample data are highly negatively skewed, which has a skewness of -0.7377. Even then, the beta still provided a better fit than any other continuous distributions defined on a fix range.

A summary of probabilistic estimations of uncertainties in VOC content data of all 20 high priority categories is presented in Table 4.3. For the category of “Auto antifreeze” and “Engine starting fluids”, only one data point is available, therefore there is insufficient information to perform bootstrap simulation in these cases. For the categories of “Paints, primers, varnishes” and “Brake cleaners”, all reported formulations have the same VOC fraction of 1.0. Therefore, because of the lack of variability in the reported data, no distribution was fitted to these data and uncertainty could not be estimated based upon statistical analysis. These categories may be reinvestigated in the future if other data become available. Alternatively, expert judgment could be used to quantify uncertainty in those cases. However, in this work, uncertainty in the VOC content was solely quantified based upon empirical data.

For some product categories, such as “Caulking and sealing” and “Lubricants and silicones”, the data sets are very small, the confidence intervals therefore are very wide. Table 4.3 indicates that the relative 95 percent confidence interval of uncertainty in the average estimation of mean VOC content ranges from as low as approximately minus 1 percent to plus 1 percent to as high as minus 79 to plus 130 percent. The range of uncertainty is influenced by a combination of the sample size and the range of variability in the data. Smaller sample sizes and/or larger inter-formulation variability in the data will contribute to wider ranges of uncertainty. The skewness in some confidence intervals is because of skewness in the data, which is typical for nonnegative quantities with large relative variability.

4.4.2 Quantification of Uncertainty in Product Use and Population Data

The use of distributions based upon empirical evidence is certainly desirable; however, it is not always possible to obtain samples for all inputs under the conditions of interest. Where empirical information is scarce or unavailable, the use of judgment is necessary.[1]

In this study, only one point estimate of product annual use in the year of 1986 is available for each category. For example, the annual use of "Paints, primers, varnishes" was estimated to be 651,000,000 lb/year.[27] Subjective methods were used to quantify uncertainty in product use data. A normal distribution was assumed to represent uncertainty in the mean estimate of annual product use. The normal distribution is a typical parametric probability distribution recommended by the IPCC as the first choice to represent uncertainties unless the properties of the data suggest another distribution, such as highly non-symmetric population.[1]

After choosing the normal distribution, the next step is to estimate the parameters of the normal distribution. Based upon previous experience in the field of quantification of uncertainty in emission inventory data, a range of minus 10 percent to plus 10 percent of the point estimate was judged to represent the 95 percent confidence interval of uncertainty. Thus, the mean, m, of the normal distribution is taken to be the same as the point estimate value, and the standard deviation, s, of the normal distribution was derived to be a multiple of 0.051 of the mean value. Uncertainty in product use was assumed to be statistically independent among the product categories. The impact of these uncertainty assumptions with respect to the calculated probabilistic emission factor could be evaluated later when interpreting the results.

Expertise regarding uncertainty in the population data belongs in the field of demography. After consulting a demographist in the U.S. Census Bureau, it was decide not to assign a confidence interval to the population because the count of the population reported in the U.S. census tabulation is simply the result of doing a group of operations on the population and no sampling was applied to generate that number.[30]

4.4.3 Quantification of Uncertainty in Emission Factor and Emission Inventory

Monte Carlo simulation was used to propagate uncertainty in each model input given in the eq 4.2 to develop a probabilistic emission factor. A summary of the specified distributions for the inputs is given in Table 4.4. For the VOC content, an empirical CDF was defined based upon the bootstrap sampling distribution of the mean VOC content for each individual category. For the product use, a normal distribution described above was defined for each individual category. Thus, random samples for the VOC content and product use were generated from the specified empirical CDFs and the specified normal distributions, respectively. The random samples of inputs were propagated through the eq 4.2 using the Monte Carlo simulation. The random outputs of the eq 4.2 then were used to build up a probability distribution for emission factor.

A sample size of 10000 was used in the Monte Carlo simulation. The probability distribution for the estimated per-capita emission factor is presented in Figure 4.3. The mean per-capita emission factor was estimated to be 6.33 lb VOC/year-person. The 95 percent confidence interval of the per-capita emission factor is from 5.84 lb VOC/year-person to 6.86 lb VOC/year-person, corresponding to a relative range of minus 7.7 percent to plus 8.4 percent compared to the mean value. Although the relative uncertainty ranges in some product categories are large, the relative uncertainty range in the per-capita emission factor appears to be not substantial because the mean values of VOC content are small.

The EPA emission factor for commercial/consumer product use is 6.3 lb VOC/year-person.[27] The mean emission factor developed in this study is almost the same as the EPA value. However, insufficient documentation of how the EPA value was derived prevents a more detailed comparisons.

The U.S. population, for example, in the year of 1986 is 241 million. Based upon the probabilistic emission factor, a probabilistic estimation of the national inventory for the year of 1986 was calculated. The probability distribution of the national inventory is given in Figure 4.4. The mean estimate of national inventory is 1.526 billion lb VOC/year. The 95 percent confidence interval of the national inventory is from 1.408 billion lb VOC/year to 1.654 billion lb VOC/year. Therefore, although the relative confidence interval of the mean emission factor is not large, there is a substantial absolute range of uncertainty in the national inventory, which is approximately from minus 118 million lb VOC/year to plus 128 million lb VOC/year. Because this kind of effect of "zooming out", it is important to account for uncertainty emission factors.

4.5 Identification of Key Sources of Uncertainty in Mean Emission Factor

Knowledge of the key contributors to uncertainty in the mean per-capita emission factor will help guide future endeavors to reduce uncertainty by targeting the data collection where such data are most needed. Given that some assumptions were made in this analysis because of the absence of data, it is important to determine whether those assumptions significantly influence the results. The key sources of uncertainty were determined by calculating the RCC between the model output and each individual model input. The results are given in Table 4.5.

As shown in Table 4.5, four input variables have RCCs noticeable larger than other input variables. The RCCs of these four inputs are highlighted in bold and they are the product use of "Paints, primers, varnishes", and the VOC content of "Caulking and sealing compounds", "Room deodorants and disinfectants", and "Insect sprays". These quantities are considered the key contributors to total uncertainty in the per-capita VOC emission factor of consumer/commercial product use. Among them, the most correlated variable is the product use of "Paints, primers, varnishes" because this category has the largest annual sales in the market and has the highest mean value of VOC content. Another input variable with RCC greater than 0.4 is the VOC content of "Caulking and sealing compounds". The annual sales of this category ranked third and its uncertainty range, which is from minus 80 percent to plus 130 percent, is the most substantial one among all product categories. If there was a need to reduce uncertainty in the mean emission factor, it would be helpful to prioritize data and information collection on the above key contributors. In contrast, many of the other RCCs are either practically or statistically insignificant, indicating no important contribution to overall uncertainty in the emission factor from many of the model inputs.

4.6 Discussion and Conclusions

This paper demonstrated the application of quantitative methods to develop a probabilistic emission factor for VOC emissions from consumer/commercial product use. These methods include: (1) development of a database; (2) visualization of the data using plotting position method; (3) fitting and evaluation of beta distributions to the data; (4) bootstrap simulation to quantify uncertainty due to random sampling error; (5) quantification of uncertainty in point estimation data by judgment; (6) propagation of uncertainty through a model to develop a probabilistic emission factor; and (7) identification of key contributors of uncertainty in probabilistic emission factor.

The beta distribution was fit to represent VOC content data because it can be defined on the fixed range with a lower bound of 0 and an upper bound of 1. Uncertainty in the mean VOC content ranges from as much as minus 79 percent to plus 130 percent and in most examples was greater than minus 30 percent to plus 30 percent. The quantified uncertainty in the per-capita emission factor is minus 7.7 percent to plus 8.4 percent. For some product categories, relative uncertainty is large, but the mean values are small. Therefore, the relative range of uncertainty in the per-capita emission factor is not large. However, although the relative confidence interval of the mean emission factor is not large, there is a substantial absolute range of uncertainty in the national inventory, which is approximately from minus 118 million lb VOC/year to plus 128 million lb VOC/year. This “zooming out” effect emphasizes the importance of recognizing and accounting for uncertainty analysis.

The estimates of uncertainty in the VOC per-capita emission factor and in most of mean VOC content are asymmetric, which indicates that skewness and small sample size in the observed data set can lead to skewness in the estimates of uncertainty in the mean. Therefore, using numerical methods instead of analytical methods has the advantage that no normality is presumed, and avoids the introduction of bias in uncertainty estimation.

The key contributors of uncertainty in emission factor was found including product use data of “Paints, primers, varnishes” and VOC content data of “Room deodorants and disinfectants”, “Caulking and sealing compounds” and “Insect sprays”. This finding is important in that it allows for prioritization of future data collection or other efforts to improve the emission factor.

Besides random sampling error, some other sources of uncertainty, such as non-representativeness of the observed data, are difficult to evaluate quantitatively. Therefore, it is recommended that qualitative methods for identifying sources of uncertainty also be used. For example, for model inputs for which only point estimates are available, subjective methods can be used. *A prior*i knowledge of the theoretical basis for different distributions, and of the processes leading to uncertainty in a quantity, can aid in identifying candidate distributions and proposing a certainty confidence interval for that quantity.

4.7 Acknowledgements

This work was supported by U.S. Environmental Protection Agency STAR Grants Nos. R826766 and R826790. This paper has not been subjected to any EPA review. Therefore it does not necessarily reflect the views of the agency, and no official endorsement should be inferred. We thank Dr. Dean H. Judson at the U.S. Census Bureau for his advice.

4.8 References

1. IPCC National Greenhouse Gas Inventories Program, *Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories*. Intergovernmental Panel on Climate Change (IPCC), 2000.

2. Carraro, C., Hourcade, J. C., "Climate Modelling and Policy Strategies. The Role of Technical Change and Uncertainty", *Energy Econ*. 1998, 20, 463-471

3. Krupnick, A. J., *Cost-Benefit and Uncertainty Analysis for Ambient Ozone Reduction*; Resources for the Future (RFF) Project Summary. http://www.rff.org/proj_summaries/files/krupnick_costbenefit.htm (accessed January 2002)

4. Bogen, K. T., Spear, R. C., "Integrating Uncertainty and Interindividual Variability in Environmental Risk Assessment". *Risk Anal.* 1987, 7, 427-436

5. Hattis, D., Burmaster, D. E., "Assessment of Variability and Uncertainty Distributions for Practical Risk Analyses", *Risk Anal.*, 1994, 14, 713-730

6. ISO, *Guide to the Expression of Uncertainty in Measurement*, International Organization for Standardization (ISO), Geneva, Switzerland, 1993.

7. Pukkala, T., Kanagas, J., "A Method for Integrating Risk and Attitude toward Risk into Forest Planning", *Forest Science*. 1995, 42, 198-205

8. Lemons, J., *Scientific Uncertainty and Environmental Problem Solving*, Blackwell Science, Cambridge, Mass., 1996.

9. Cullen, A. C., Frey, H. C., *Probabilistic Techniques in Exposure Assessment: A Handbook for Dealing with Variability and Uncertainty in Risk Analysis*; Plenum Press: New York, 1999.

10. Mowrer, H. T., “Uncertainty in Natural Resource Decision Support System: Sources, Interpretation, and Importance”, *Computers & Electronics in Agriculture*, 2000, 27, 139-154

11. Morgan, M. G., Henrion, M., *Uncertainty: A Guide to Dealing with Uncertainty in Quantitative Risk and Policy Analysis*. Cambridge University Press: Cambridge, Mass., 1990.

12. Frey, H. C., Rhodes, D. S., “Characterizing, Simulating, and Analyzing Variability and Uncertainty: An Illustration of Methods Using an Air Toxics Emissions Example”, *Hum. Ecol. Risk Assess.* 1996, 2, 762-797

13. Rhodes, D. S., Frey, H. C., Quantification of Variability and Uncertainty in AP-42 Emission Factors Using Bootstrap Simulation. Emission Inventory: Planning for the Future (held October 28-30 in Research Triangle Park, NC), Air and Waste Management Association, Pittsburgh, PA, 1997.

14. Frey, H. C., Bharvirkar, R., Zheng, J., *Quantitative Analysis of Variability and Uncertainty in Emissions Estimation*, Prepared by North Carolina State University for the U.S. Environmental Protection Agency, Research Triangle Park, NC, 1999.

15. Frey, H.C., Bharvirkar, R., Quantification of Variability and Uncertainty: A Case Study of Power Plant Hazardous Air Pollutant Emissions. in *The Risk Assessment of Environmental and Human Health Hazards: A Textbook of Case Studies*. D. Paustenbach, Ed., John Wiley and Sons: New York, 2001.

16. Abdel-Aziz, A.; Frey, H. C. Quantification of Variability and Uncertainty in Hourly NOx Emissions from Coal-Fired Power Plants. In proceedings of the 95th Annual Meeting of the Air & Waste Management Association, Baltimore, MD, June, 2002.

17. Frey, H.C.; Zheng, J. Quantification of Variability and Uncertainty in Utility NOx Emission Inventories; *J. of Air & Waste Manage. Assoc*. in press

18. Maurice, B., Frischknecht, R., Coelho-Schwirtz, V., Hungerbuhler, K., “Uncertainty Analysis in Life Cycle Inventory. Application to the Production of Electricity with French Coal Power Plants”, *J. Cleaner. Prod.* 2000, 8, 95-108

19. Kini, M. D., Frey, H. C., *Probabilistic Evaluation of Mobile Source Air Pollution: Volume 1, Probabilistic Modeling of Exhaust Emissions from Light Duty Gasoline Vehicles*, Prepared by North Carolina State University for Center for Transportation and the Environment, Raleigh, 1997.

20. Pollack, A. K., Bhave, P., Heiken, J., Lee, K., Shepard, S., Tran, C., Yarwood, G., Sawyer, R. F., Joy, B. A., *Investigation of Emission Factors in the California EMFAC7G Model*. PB99-149718INZ, Prepared by ENVIRON International Corp, Novato, CA, for Coordinating Research Council, Atlanta, GA, 1999.

21. Frey, H.C.; Bammi, S. Quantification of Variability and Uncertainty in Lawn and Garden Equipment NOx and Total Hydrocarbon Emission Factors. *J. of Air & Waste Manage. Assoc.* 2002, 52, 435-448.

22. Frey, H.C.; Bammi, S. Quantification of Variability and Uncertainty for Selected Nonroad Mobile Source Emission Factors. In proceedings of the U.S. Environmental Protection Agency Emission Inventory Conference, Atlanta, GA, 2002.

23. Frey, H. C., Li, S., “Quantification of Variability and Uncertainty in Stationary Natural Gas-fueled Internal Combustion Engine NO_x and Total Organic Compounds Emission Factor”, Proceedings, Annual Meeting of the Air & Waste Management Association, Pittsburgh, PA, 2001.

24. National Research Council. Modeling Mobile-Source Emissions; National Academy Press: Washington, DC, 2000.

25. EPA, Report of the Workshop on Selecting Input Distributions for Probabilistic Assessments, EPA/630/R-98/004, Prepared by Eastern Research Group for Risk Assessment Forum, U.S. Environmental Protection Agency, Washington, DC, 1999

26. Efron, B., “Bootstrap Methods: Another Look at the Jackknife”, *Annals of Statistics*, 1979, 7(1), 1-26

27. Rognzen, M., Baca, R., *Compilation and Speciation of National Emissions Factors for Consumer/Commercial Solvent Use*, EPA-450/2-89-008, Prepared by Science Applications International Corporation for the U.S. Environmental Protection Agency, Research Triangle Park, NC, 1989.

28. Jones, A., Rich, H., Sewell, G., Rogozen, M., Katz, M., *Photochemically Reactive Organic Compound Emissions from Consumer and Commercial Products*, EPA-902/4-86-001, Prepared by Science Applications International Corporation for the U.S. Environmental Protection Agency, Region II, Air Programs Branch, New York, NY, 1986.

29. Ang, A. H-S.; Tang, W. H. *Probability Concepts in Engineering Planning and Design;* John Wiley & Sons, Inc: New York, 1975.

30. Personal communication with Dr. Dean H. Judson at the U.S. Census Bureau, January 14th, 2002.

Table 4.1. VOC Content Data for Different Formulas of Engine Degreasers

Formulas	**Average Percentage VOC by Weight**
1	25.0
2	0.0
3	79.8
4	80.0
5	81.0
6	40.0
7	40.0
8	54.2
9	94.8
10	80.0
11	5.0

Table 4.2. Fitted Parametric Distributions for Variability in VOC Content of Consumer/Commercial Product

Product Category	**Parameters of Beta Distribution**[a]		**Total Num. of Data**	**Percent of Data Within 50% CI**	**Percent of Data Within 90% CI**	**Percent of Data Within 95% CI**
		β				
Hair sprays	105.77	4.3052	18	44	78	89
All purpose cleaners	0.3640	5.7782	51	57	94	98
Insect sprays	0.2377	0.0461	10	40	60	70
Car polishes and waxes	0.3262	-0.9820	24	54	92	96
Room deodorants and disinfectants	1.1665	0.5681	4	100	100	100
Caulking and sealing compounds	0.8980	7.5180	3	33	100	100
Adhesives	0.1645	0.3165	7	71	100	100
Moth control products	67.790	0.5605	3	67	100	100
Window and glass cleaners	0.7358	5.9445	16	19	88	94
Herbicides, fungicides	0.2181	0.4632	14	64	93	100
Personal deodorants	3.1805	1.6118	3	100	100	100
Carburetor and choke cleaners	5.8320	1.0781	5	60	100	100
Engine degreasers	0.6737	0.6044	11	64	100	100
Rug and upholstery cleaners	0.3478	17.765	12	50	92	100
Lubricants and silicones	-0.2500	-0.2500	2	100	100	100
Metal cleaners and polishes	0.3059	2.5010	24	50	92	96

[a] is shape parameter, β is scale parameter.

Table 4.3. 95 Percent Confidence Interval Based upon Bootstrap Simulation for VOC Content of Consumer/Commercial Product

Product Category	**No. of data / Formulations**	**Mean VOC fraction from Original Data**	**Average Estimate of the Mean VOC fraction**[a]	**Absolute 95% CI for the Mean VOC fraction**[a]	**Relative 95% CI for the Mean VOC fraction**[a] **(%)**
Paints, primers, varnishes	18	1.0	No Uncertainty CI is Assigned		
Hair sprays	18	0.96	0.96	0.95 to 0.97	-1.0 to +1.0
All purpose cleaners	51	0.059	0.059	0.038 to 0.086	-36 to +46
Insect sprays	10	0.84	0.84	0.60 to 1.0	-29 to +19
Car polishes and waxes	24	0.25	0.25	0.14 to 0.36	-44 to +44
Room deodorants and disinfectants	4	0.67	0.68	0.38 to 0.91	-44 to +34
Caulking and sealing compounds	3	0.11	0.11	0.023 to 0.25	-79 to +130
Adhesives	7	0.34	0.34	0.08 to 0.64	-76 to +88
Moth control products	3	0.99	0.99	0.98 to 1.0	-1.0 to +1.0
Window and glass cleaners	16	0.11	0.11	0.062 to 0.16	-44 to +45
Herbicides, fungicides	14	0.32	0.33	0.16 to 0.54	-52 to +64
Personal deodorants	3	0.66	0.66	0.41 to 0.86	-38 to +30
Auto antifreeze	1	0.90	No Uncertainty CI is Assigned		
Carburetor and choke cleaners	5	0.84	0.84	0.71 to 0.94	-15 to +12
Brake cleaners	3	1.0	No Uncertainty CI is Assigned		
Engine degreasers	11	0.53	0.53	0.31 to 0.73	-42 to +38
Engine starting fluids	1	1.0	No Uncertainty CI is Assigned		
Rug and upholstery cleaners	12	0.019	0.020	0.0060 to 0.040	-70 to +100
Lubricants and silicones	2	0.50	0.51	0.0 to 1.0	-100 to +96
Metal cleaners and polishes	24	0.11	0.11	0.053 to 0.18	-52 to +64

[a] Based upon bootstrap sampling distribution for fitted beta distribution

Table 4.4. Probability Distributions Assigned to the Inputs of the Per-Capita VOC Emission Factor Model for Consumer/Commercial Product Use

Product Category	**Specified Probability Distribution**	
	Mean VOC Content	**Product Use**
Paints, primers, varnishes	Point estimation, no distribution assigned	Normal
Hair sprays	Bootstrap sampling distribution	Normal
All purpose cleaners	Bootstrap sampling distribution	Normal
Insect sprays	Bootstrap sampling distribution	Normal
Car polishes and waxes	Bootstrap sampling distribution	Normal
Room deodorants and disinfectants	Bootstrap sampling distribution	Normal
Caulking and sealing compounds	Bootstrap sampling distribution	Normal
Adhesives	Bootstrap sampling distribution	Normal
Moth control products	Bootstrap sampling distribution	Normal
Window and glass cleaners	Bootstrap sampling distribution	Normal
Herbicides, fungicides	Bootstrap sampling distribution	Normal
Personal deodorants	Bootstrap sampling distribution	Normal
Auto antifreeze	Point estimation, no distribution assigned	Normal
Carburetor and choke cleaners	Bootstrap sampling distribution	Normal
Brake cleaners	Point estimation, no distribution assigned	Normal
Engine degreasers	Bootstrap sampling distribution	Normal
Engine starting fluids	Point estimation, no distribution assigned	Normal
Rug and upholstery cleaners	Bootstrap sampling distribution	Normal
Lubricants and silicones	Bootstrap sampling distribution	Normal
Metal cleaners and polishes	Bootstrap sampling distribution	Normal

Table 4.5. Rank Correlation Coefficients of the Inputs of the Per-Capita VOC Emission Factor Model of Consumer/Commercial Product Use

Product Category	**Rank correlation coefficient**	
	Product VOC content	**Product use**
Paints, primers, varnishes	n/a[a]	**0.52**
Hair sprays	0	0.15
All purpose cleaners	0.13	0.03
Insect sprays	**0.36**	0.16
Car polishes and waxes	0.19	0.04
Room deodorants and disinfectants	**0.39**	0.10
Caulking and sealing compounds	**0.43**	0.03
Adhesives	0.10	-0.01
Moth control products	0.01	0.02
Window and glass cleaners	0.08	0.01
Herbicides, fungicides	0.12	0.02
Personal deodorants	0.08	0.03
Auto antifreeze	n/a[a]	0.02
Carburetor and choke cleaners	0.03	0.02
Brake cleaners	n/a[a]	0.02
Engine degreasers	0.03	0.01
Engine starting fluids	n/a[a]	0.04
Rug and upholstery cleaners	0.02	0.01
Lubricants and silicones	0.17	0.01
Metal cleaners and polishes	0	-0.01

[a] RCCs are not available because no uncertainty distribution is assigned.

Figure 4.1. Database Structure for Consumer/Commercial Product Use

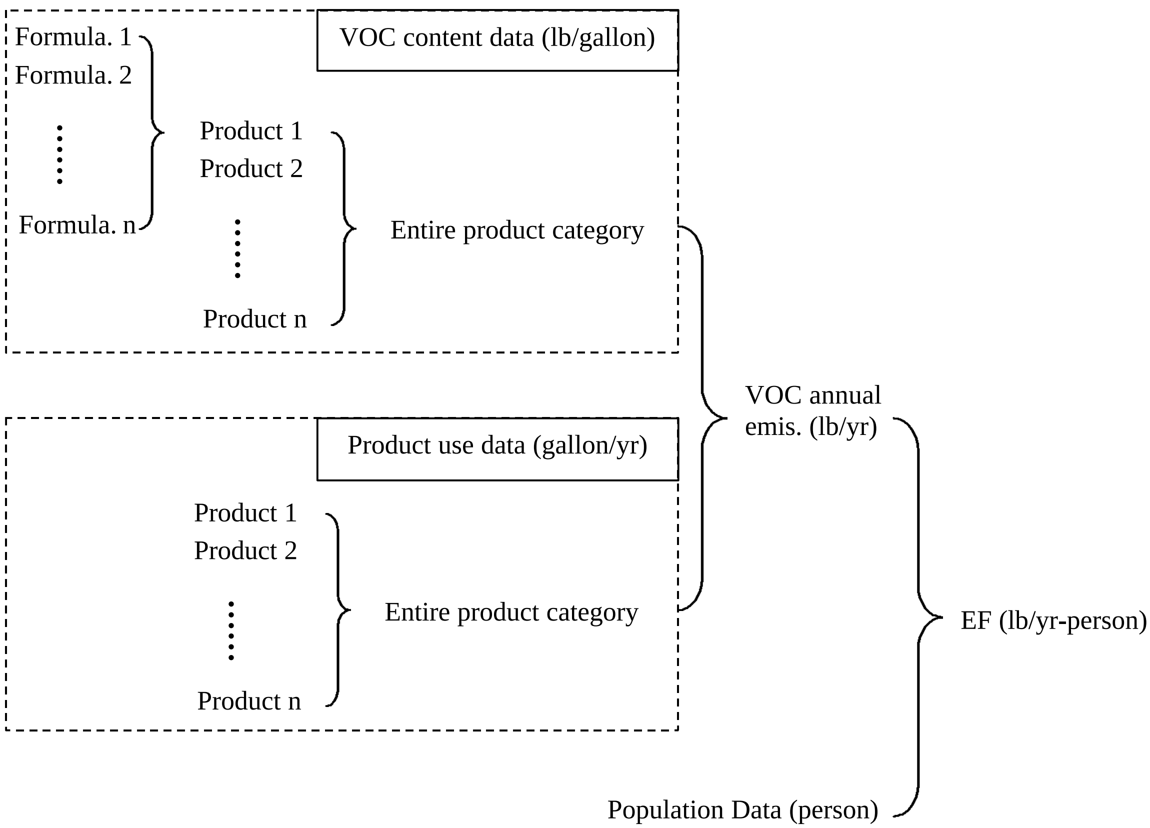


Figure 4.2. Comparison of Empirical Cumulative Distribution of VOC Content Data for Engine Degreasers, fitted Bata distribution, and Bootstrap Simulation Confidence Intervals

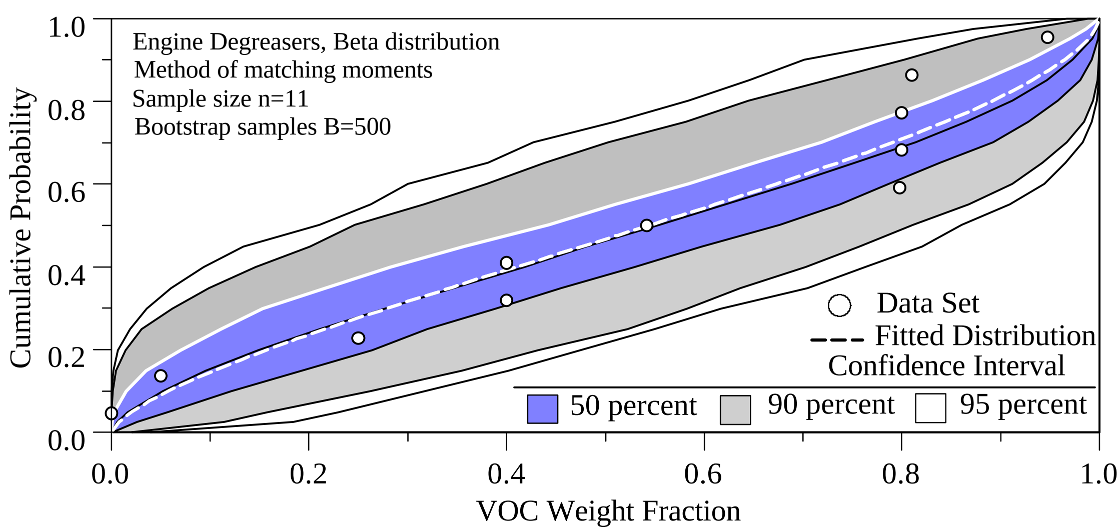


Figure 4.3. Mean and 95 Percent Confidence Interval of Per-Capita VOC Emission Factor for Consumer/Commercial Product Use

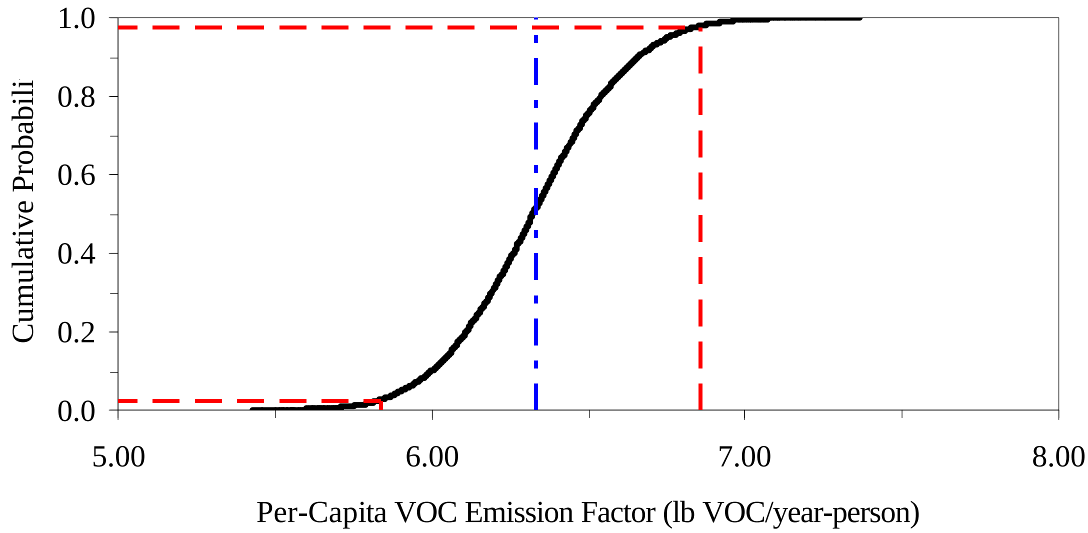
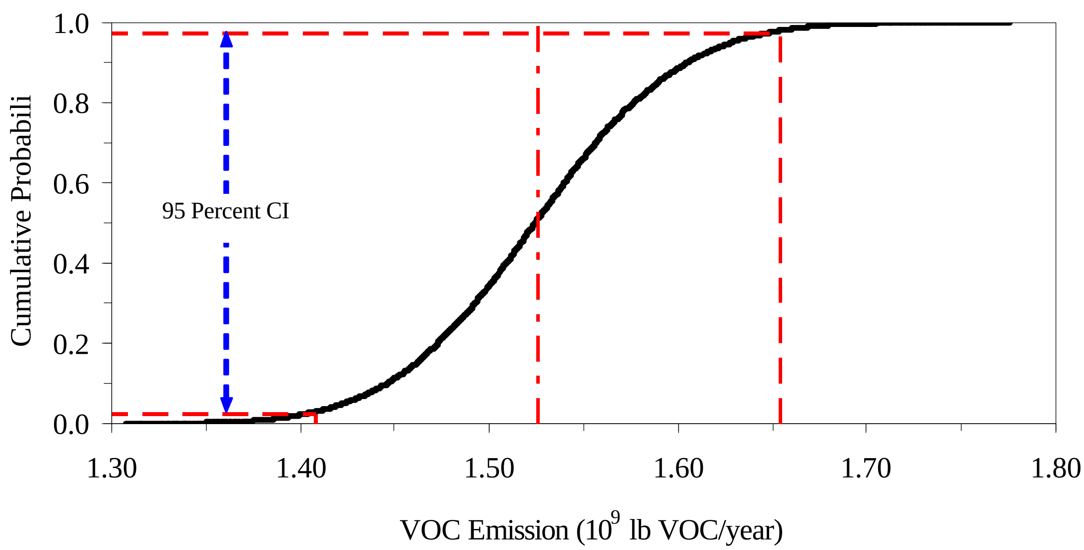


Figure 4.4. Mean and 95 Percent Confidence Interval of National Annual VOC Emissions from Consumer/Commercial Product Use



5.0 QUANTIFICATION OF VARIABILITY AND UNCERTAINTY IN EMISSION FACTORS OF GASOLINE TERMINAL LOADING LOSS

Song Li and H. Christopher Frey

Department of Civil Engineering, North Carolina State University, Raleigh, NC 27695

Abstract

In this paper, we demonstrated the application of quantitative approaches based upon real measurement data to characterize variability and uncertainty in air pollutant emissions. The approaches were illustrated for the case study of volatile organic compounds (VOCs) emissions from gasoline terminal loading process. We first characterized variability in measurement data using parametric probability distributions. Uncertainty due to statistical sampling error was quantified using a numerical method known as bootstrap simulation. In the emission factor development, it is important to distinguish intra-facility and inter-facility variability. Different analysis results based upon retaining and removing intra-facility variability were presented. The approach based upon removing intra-facility variability was recommended in that it is consistent with the real-world practice. Uncertainty in the mean VOC emission factors is approximately as high as minus 67 to plus 110 percent for a 95 percent probability range. The quantified confidence intervals for mean VOC emission factors are typically positive skewed, which reflects the skewness in emission measurement data and small sample size.

5.1 Introduction

Traditionally, investigators develop air pollutant emission inventory based upon point-estimates of emission rates, such as AP-42 emission factors developed by US Environmental Protection Agency (EPA).[1] However, a number of limitations of this approach have attracted increasing concern. In particular, emission factors and emission inventories are subjected to both variability and uncertainty. Failure to quantify them can lead to over-confident use of point estimates. This paper focuses on the demonstration of the quantitative methods based upon real measurements to characterize both variability and uncertainty in emission factors.

The case study application focuses on volatile organic compound (VOC) emissions from gasoline terminal loading processes. Gasoline terminal loading was selected for this case study because field test data are available and it is among the largest VOC emission sources in the Charlotte airshed, North Carolina, which is the subject of related case studies in other ongoing work.

5.2 Variability and Uncertainty in Emission factors

Statistically, variability refers to observed differences attributable to true heterogeneity or diversity in a population.[2] Many quantities are variable over time and space. For example, emission factors of gasoline loading processes may vary over time and space because of differences in gasoline composition, ambient temperature, and other system and operating characteristics. Uncertainty refers to a lack of knowledge regarding the true value of a quantity.[3] Uncertainties in emissions typically arise for several reasons, including bias or imprecision measurements, limited sample size and human errors, such as random mistakes in entering or processing data. The main focus in this paper is on quantifying uncertainty due to random sampling error.

Although the quantification of uncertainty in emission inventories is not yet a common practice, as recognized by the National Research Council (NRC) in 1991, the quality of emission inventories is hampered by significant, and yet poorly characterized uncertainties.[4] More recently, the NRC has made strong recommendations to EPA regarding quantification of uncertainty in mobile source emissions.[5] The Intergovernmental Panel on Climate Change (IPCC) has issued good practice guidance regarding uncertainty estimation for inventories of greenhouse gases.[6] The development and application of probabilistic methods has also been encouraged in the field of human health risk assessment, for which emissions estimation is an important component. For example, NRC recommended increased attention to the distinction between variability and uncertainty.[7] EPA issued a policy document regarding the use of Monte Carlo simulation that addressed at least some of the NRC recommendations.[8] Although EPA has long relied upon the use of qualitative ratings for emission factors, and in recent years has developed and applied the Data Attribute Rating System (DARS) to develop quality ratings of entire inventories, the NRC has pointed out that a qualitative approach is not sufficient.[1, 5, 9] Although not all sources of uncertainty are amenable to quantification, the NRC recommends that sources of uncertainty that can be quantified should be.[5]

There have been numerous specific efforts to quantify uncertainty in the inputs to emission inventories and in overall emission inventories. Examples of quantification of variability and uncertainty in emission factors include coal-fired power plants,[10-14] highway vehicles,[15-17] nonroad vehicles,[18, 19] selected area sources,[20] and a variety of specific AP-42 emission factors.[21, 22] Examples of quantification of uncertainty in emission inventories include inventories prepared for the National Acid Precipitation Assessment Program (NAPAP).[23, 24]

One of the challenges in quantifying uncertainty in the average emission factors for gasoline bulk loading terminals is that in some cases, replicate data are available for specific facilities. Thus, there is an explicit consideration of how to deal with the distinction between intra-facility variability and inter-facility variability when describing variability in emissions. The explicit quantification of two alternatives for quantifying variability is a key area of distinction of this paper compared to earlier work. In addition, this is the first known attempt to quantify uncertainty for this specific source category.

5.3 Overview of Probabilistic Analysis Applied to Emission Factors

Quantitative analysis of variability and uncertainty in emission factor data requires the development of a database, quantification of variability in the data, estimation of the mean emission factor, and estimation of uncertainty in the mean.

The starting point of quantitative analysis is to prepare an emission factor database and assess the quality of the data. This step is the same regardless of whether to develop a point estimate or a probabilistic estimate. For example, judgment must be made regarding which data are representative of the population, whether the data are well documented, and regarding methods to use to analyze the data. In this study, emission factor database was developed based upon real measurement data and any unclearly documented data were removed from our database.

Data sets from emissions measurements may typically be used to characterize variability based upon step-wise empirical distributions or fitted parametric distributions. The use of empirical distributions help to graphically visualize the sample data, thus a clear, graphical insight regarding the central tendency, degree of spread, shape and other characteristics of the data can be obtained. For small data sets, the real range of variability may be underestimated because variation in observed samples typically is much narrower than that in the population. Parametric probability distributions can provide a plausible means of interpolating and extrapolating to the unobserved part of the unknown population distribution.[25]

After choosing a candidate parametric distribution to characterize variability of a data set, the next step is to estimate its parameters based upon the observed data. Two methods for estimating distribution parameters, the method of matching moments (MoMM) and maximum likelihood estimation (MLE), were used and compared in this study. No parameter estimation method is always ideal for all circumstances. MLE is considered to be statistically efficient for large sample sizes. However, for small sample sizes, MLE does not always yield unbiased or robust estimates.[26]

Uncertainty in the average emission factor, based upon random sampling error, is influenced by the sample size and variability in the data. While it is commonplace to use an analytical approximation for estimating a 95 percent confidence interval for the mean, the typical analytical approximation is based upon an assumption of normality for the sampling distribution of the mean. However, with small data sets that are substantially skewed, which is often the case for emission factor data, the normality assumption is not valid. Therefore, a numerical method that does not impose a normality assumption is used.

The bootstrap simulation is a numerical method to estimate uncertainty due to random sampling error in a probability distribution. Basically, there are three steps in a bootstrap simulation process. The first step is to obtain statistical information from the sample data. An important assumption of this step is that the probability distribution estimated from the observed sample is the best estimate of the unknown population distribution.

The second step of the bootstrap simulation is to conduct random sampling experiments on a computer. Typically, 500 to 2,000 random samples, known as bootstrap samples, are simulated from the assumed population distribution. Each bootstrap sample has the same number of data points as the original sample, and therefore is a possible alternative realization of the original data set.

The third step of the bootstrap simulation is to develop sampling distributions for the statistics of interest. For example, one or more statistics, such as the sample mean, can be calculated from a bootstrap sample. Thus, there will be 500 to 2,000 replications of the mean. A sampling distribution of mean, which represents the random sampling error in the mean, then can be developed. Typically, uncertainty due to random sampling error is conveyed using a confidence interval based upon the simulated sampling distribution.

5.4 VOC Emission Data for Gasoline Terminal Loading Loss

Bulk gasoline terminals receive gasoline from refineries by pipeline, ship, or barge and dispense it into tank trucks for delivery to smaller bulk facilities or retail accounts. VOC emissions at a terminal occur during loading, unloading, and transfer processes. Loading losses are the primary source of emissions. The principal loading methods are the splash loading method and the submerged loading method. The submerged loading method has a lower emission rate than the splash loading method. There are two types of submerged loading methods, the submerged fill pipe method and the bottom loading method, which are reported to have the same emission factors.[1] In this paper, uncontrolled VOC emissions from the top splash loading and the bottom loading are investigated. There are some end-of-pipe control technologies available for the terminal loading process. However, no emission factor for controlled terminals was reported in the current version of AP-42.

The emission data are from a background information document published by EPA.[27] The document contains a summary of 22 VOC emission tests for bulk gasoline terminals, which were conducted by EPA throughout the United States between 1973 and 1978. EPA has not tested any uncontrolled emission on gasoline terminals since the late 1970's.[28] The 22 tests include measurement data for uncontrolled VOC emissions and controlled VOC emissions for six types of control technologies, including carbon adsorption, thermal oxidation, refrigeration, compression-refrigeration-absorption, compression-refrigeration-condensation, and lean oil absorption.

5.5 Quantification of Variability and Uncertainty in Emission Factors

In this section, quantitative methods were demonstrated to characterize variability in measurement data and uncertainty in mean VOC emission factors for the gasoline terminal loading loss. The quality of the sample data was first judged for the development of the emission database. Variability in measurement data was characterized by parametric probability distributions and uncertainty in the mean emission factor was estimated by bootstrap simulation.

The emission database includes not only measurements on different facilities but also repeated measurements on the same facility. The repeated measurements on the same facility represent the intra-facility variability. Measurements on different facilities represent the inter-facility variability from one facility to another. The main objective in the emission factor development is to quantify inter-facility variability. Therefore, it may necessary to separate the intra- and inter-facility variability. Two approaches were developed and compared to evaluate the importance of distinguishing intra- and inter-facility variability.

5.5.1 Preparation of Database for Analysis

Of 22 tests, in 6 cases, the type of loading method either was not specified or more than one type of loading method were simultaneously in operation during the test process.[27] Therefore, the data from these 6 tests were not included in the analysis database. In the database, two of the tests are for the top splash loading method. The remaining 14 tests are for the bottom loading method. Two of the bottom loading tests were conducted on the same facility; therefore, the measurements from these two tests were treated as repeated measurements on the same facility.

5.5.2 Quantification of Uncertainty Based upon Retaining Intra-Facility Variability

The first approach introduced in this study is based upon retaining intra-facility variability. In this approach, all measurement data were equally treated regardless of whether they are repeated measurements on the same facility or from different facilities. Lognormal, gamma and Weibull distributions were evaluated as possible candidates to characterize variability in the data. Bootstrap simulation with 500 replications was used to quantify uncertainty in the mean emission factor. An example of simulation results for the uncontrolled bottom loading is given in Figure 5.1. In this example, a fitted Weibull distribution is shown in comparison to an empirical cumulative distribution function (CDF) of 37 available measurements. Also displayed in the Figure 5.1 are the bootstrap confidence intervals for the fitted probability distribution.

Figure 5.1 illustrates that the Weibull distribution is a good fit to the data. The data are closed to the fitted distribution, especially at both the lower and upper tails of the distribution. A Kolmogorov-Smirnov goodness-of-fit (GOF) test was conducted for evaluating the quality of fitting the Weibull distribution. The Kolmogorov-Smirnov test statistic reported by “Crystal Ball”, a commercial software for risk analysis, is 0.0783, which is smaller than the critical value of 0.15 at a significance level of 0.05.[29] Therefore, the fit of Weibull distribution for the uncontrolled bottom loading data is acceptable at the significance level of 0.05.

The confidence intervals of different percentiles of the fitted probability distribution were estimated from bootstrap simulation results. For example, Figure 5.1 indicates the absolute 95 percent confidence interval of the median or 50th percentile of the fitted Weibull distribution is from 550 mg VOC/L gasoline loaded to 760 mg VOC/L gasoline loaded. The average estimate of mean emission factor is approximately 674 mg VOC/L gasoline loaded. The absolute 95 percent confidence interval of the mean emission factor ranges from 583 mg VOC/L gasoline loaded to 767 mg VOC/L gasoline loaded, corresponding to a relative interval of minus 14 percent to plus 14 percent compared to the mean.

Although the Weibull distribution offers a good fit to the data, it is also the case that both the lognormal and gamma distributions offer a good fit to the same data, as shown in Figures 5.2 and 5.3, respectively. The reported Kolmogorov-Smirnov test statistics for gamma and lognormal are 0.0866 and 0.0982, respectively. So in all three cases, a Kolmogorov-Smirnov GOF test indicates that none of these distributions can be rejected at the 0.05 significance level. However, the Weibull has the smallest Kolmogorov-Smirnov test statistic. Furthermore, the 95 percent confidence interval of the bootstrap results encloses all of the data in all three cases. However, a larger proportion of the data are enclosed by the 50 percent confidence interval for the Weibull distribution than for the other two distributions, and the Weibull distribution has less probability of large values (e.g., above 1,500 mg VOC/L gasoline) than the other two. Therefore, because the Weibull appears to be more consistent with the data and is less tail heavy, the Weibull distribution was selected as the basis for estimating uncertainty in the mean.

5.5.3 Quantification of Uncertainty Based upon Removing Intra-Facility Variability

An obvious drawback of the previous approach based upon non-distinguishing of intra- and inter-facility variability is that a facility with many repeated measurements was given more weight than a facility with few repeated measurements. The solution taken here is to remove the intra-facility variability before getting into uncertainty analysis for mean emission factor. The separation of intra- and inter-facility variability was actually based upon the fact that quantifying inter-facility variability is typically of more interested in the real-world practice of emission factor development.

To remove the intra-facility variability, repeated measurements from the same facility were first averaged and the average value was used as a representative emission level for that facility. Thus, in the emission level database, each facility was weighted equally regardless its measurement amount. Parametric distributions then were fitted to the emission level data set to characterize the inter-facility variability. Bootstrap simulation described above was used to quantify uncertainty in the fitted probability distribution and the mean emission factors. In this case, the bootstrap sample size was the same as the number of facilities. As an example, Figure 5.4 gives the bootstrap simulation result for uncontrolled bottom loading loss based upon removing intra-facility variability.

Summaries of fitted parametric distributions and proportions of data points enclosed by bootstrap confidence intervals for different loading methods are reported in Table 5.1. It is not always possible to employ a GOF test. The Kolmogorov-Smirnov GOF test has a relative looser requirement that minimally 5 data points should be available.[31] In Table 5.1, the Kolmogorov-Smirnov test results suggest that the fits of gamma distributions to uncontrolled and compression-refrigeration-absorption controlled bottom loading are acceptable at a significance level of 0.05. For those cases that are not satisfied to employ a GOF test, the large proportions of data points enclosed by the bootstrap confidence intervals also suggest that the fits are good. Typically, the method of matching moments (MoMM) provided better fit than the maximum likelihood estimation (MLE) for the small data set. As the sample size increasing, the MLE becomes more robust and tends to get a better fit than the MoMM. This finding is consistent with the literature reported.[26]

The quantified uncertainties in controlled and uncontrolled loading loss are given in Table 5.2. All control technologies are for the bottom loading method. For the thermal-oxidation controlled bottom loading, all measurements are from the same facility, thus only intra-facility variability could be characterized. Most confidence intervals of the mean emission factors based upon bootstrap simulation are positive skewed. For example, uncertainty in the mean VOC emission factor for carbon-adsorption controlled bottom loading is minus 67 percent to plus 110 percent. The skewness in the quantified uncertainties for mean emission factors reflects the skewness in the measurements and the small sample sizes. The relative 95 percent confidence intervals of uncertainty in mean emission factors range from as low as approximately minus 25 percent to plus 25 percent to as high as minus 67 to plus 110 percent. The range of uncertainty was dedicated to both sample size and the range of variability. Small sample size and large variability typically contribute to a wide range of uncertainty in the mean.

5.6 Discussion and Conclusions

In this paper, we presented the application of quantitative approaches based upon real measurement data to characterize variability and uncertainty in VOC emission factors for gasoline terminal loading loss. The quality of measurement data was first evaluated, and unclearly documented data were removed from database. The qualitative assessment is important in that nonrepresentativeness of data is difficult to be evaluated quantitatively.

Variability in the measurement data was characterized by fitting parametric probability distributions. Since emission values could not be negative, the commonly used nonnegative parametric distributions, including lognormal, gamma and Weibull distributions were fitted to emission data sets. The preferred fit was selected based upon the combinations of goodness-of-fit tests and graphical comparisons between the fitted distributions and the empirical CDFs of the data sets.

A special concern in the quantitative analysis of emission factors is how to handle the intra-facility and inter-facility variability. Different analyses based upon retaining and removing intra-facility variability were introduced and compared in detail. The approach based upon removing of intra-facility variability was recommended in that it avoids giving more weight to a facility with many repeated measurements than a facility with few repeated measurements.

Bootstrap simulation was applied to characterize uncertainty in the fitted probability distributions and mean emission factors. The relative 95 percent confidence interval of uncertainty in the mean emission factor is approximately as high as minus 67 percent to plus 110 percent. The absolute 95 percent confidence interval is approximately as large as minus 1000 to plus 1100 mg-VOC/l-gasoline. The wide range of uncertainty is attributed to small sample size and substantial inter-facility variability, and also supports the importance of quantifying uncertainty in this source category. The confidence intervals of uncertainty in the mean emission factors are positive skewed, indicating positive-skewness regarding variability in the emission measurement data. In this study, gamma distributions with MoMM parameter estimation were found likely to provide better fit than do lognormal and Weibull distributions.

5.7 Acknowledgements

This work was supported by U.S. Environmental Protection Agency STAR Grants Nos. R826766 and R826790. We thank Mr. Mr. Stephen Shedd in U.S. EPA Emission Standards Division for his advice and recommendations regarding data sources.

5.8 References

1. US Environmental Protection Agency. Compilation of Air Pollutant Emission Factors, AP-42, Fifth Edition; US Environmental Protection Agency: 1995.

2. ISO, Guide to the Expression of Uncertainty in Measurement. ISBN 92-67-10188-9. International Organization for Standardization (ISO), Geneva, Switzerland, 1993.

3. Frey, H. C., *Quantitative Analysis of Uncertainty and Variability in Environmental Policy Making*, 1992 Environmental Science and Engineering Fellows Program Reports, American Association for the Advancement of Science, Washington, DC, 1993, pp. 25-33.

4. National Research Council. Rethinking the Ozone Problem in Urban and Regional Air Pollution. National Academy Press: Washington, DC, 1991.

5. National Research Council. *Modeling Mobile-Source Emissions*; National Academy Press: Washington, DC, 2000.

6. IPCC National Greenhouse Gas Inventories Program, Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories. Intergovernmental Panel on Climate Change (IPCC), 2000.

7. National Research Council; Science and Judgment in Risk Assessment, National Academy Press: Washington, DC, 1994.

8. EPA. Policy for Use of Probabilistic Analysis in Risk Assessment at the U.S. Environmental Protection Agency, U.S. Environmental Protection Agency, Washington, DC, May 15, 1997.

9. Beck, L.L., Wilson, D; EPA's Data Attribute Rating System; *Proceedings, Emission Inventory: Planning for the Future*, Air & Waste Management Assoc., Pittsburgh, PA, 1997

10. Frey, H.C., and Rhodes, D.S., Characterizing, Simulating, and Analyzing Variability and Uncertainty: An Illustration of Methods Using an Air Toxics Emissions Example, *Human Health and Ecological Risk Assessment*, 1996, 2(4): 762-797.

11. Maurice, B., Frischknecht, R., Coelho-Schwirtz, V., Hungerbuhler, K., Uncertainty Analysis in Life Cycle Inventory. Application to the Production of Electricity with French Coal Power Plants, *J. Cleaner. Prod.* 2000, 8, 95-108

12. Frey, H.C.; Bharvirkar, R. Quantification of Variability and Uncertainty: A Case Study of Power Plant Hazardous Air Pollutant Emissions; In The Risk Assessment of Environmental and Human Health Hazards: A Textbook of Case Studies; Paustenbach, D. Ed.; John Wiley and Sons: New York, 2001.

13. Abdel-Aziz, A.; Frey, H. C. Quantification of Variability and Uncertainty in Hourly NOx Emissions from Coal-Fired Power Plants. In proceedings of the 95th Annual Meeting of the Air & Waste Management Association, Baltimore, MD, June, 2002.

14. Frey, H.C.; Zheng, J. Quantification of Variability and Uncertainty in Utility NOx Emission Inventories; *J. of Air & Waste Manage. Assoc*. in press

15. Kini, M. D., Frey, H. C., Probabilistic Evaluation of Mobile Source Air Pollution: Volume 1, Probabilistic Modeling of Exhaust Emissions from Light Duty Gasoline Vehicles, Prepared by North Carolina State University for Center for Transportation and the Environment, Raleigh, 1997.

16. Pollack, A. K., Bhave, P., Heiken, J., Lee, K., Shepard, S., Tran, C., Yarwood, G., Sawyer, R. F., Joy, B. A., Investigation of Emission Factors in the California EMFAC7G Model. PB99-149718INZ, Prepared by ENVIRON International Corp, Novato, CA, for Coordinating Research Council, Atlanta, GA, 1999.

17. Frey, H. C., Bharvirkar, R., Zheng, J., Quantitative Analysis of Variability and Uncertainty in Emissions Estimation, Prepared by North Carolina State University for the U.S. Environmental Protection Agency, Research Triangle Park, NC, 1999.

18. Frey, H.C.; Bammi, S. Quantification of Variability and Uncertainty in Lawn and Garden Equipment NOx and Total Hydrocarbon Emission Factors. *J. of Air & Waste Manage. Assoc.* 2002, 52, 435-448.

19. Frey, H.C.; Bammi, S. Quantification of Variability and Uncertainty for Selected Nonroad Mobile Source Emission Factors. In proceedings of the U.S. Environmental Protection Agency Emission Inventory Conference, Atlanta, GA, 2002.

20. Frey, H. C; Li, S. Methods and Example for Development of a Probabilistic Per-Capita Emission Factor for VOC Emissions from Consumer/Commercial Product Use. In proceedings of the 95th Annual Meeting of the Air & Waste Management Association, Baltimore, MD, June, 2002.

21. Rhodes, D. S., Frey, H. C., Quantification of Variability and Uncertainty in AP-42 Emission Factors Using Bootstrap Simulation; *Proceedings, Emission Inventory: Planning for the Future*, Air and Waste Management Association, Pittsburgh, PA, 1997.

22. Meyers, R., Compilation of Air Pollutant Emission Factors (AP-42), *Proceedings, Emission Inventory: Planning for the Future*, Air & Waste Management Association, Pittsburgh, PA. 1997.

23. Langstaff, J.E.; Wagner, J.K. *Estimation of Uncertainty for the 1980 NAPAP Emissions Inventory*; EPA/600/7-86/055, Prepared by Alliance Technologies Corporation for U.S. Environmental Protection Agency, Research Triangle Park, December 1986.

24. Langstaff, J.E.; Maiocco, L.J. *Development of Uncertainty Factors for the 1985 NAPAP Emissions Inventory, Draft Technical Memorandum*; Prepared by Alliance Technologies Corporation for U.S. Environmental Protection Agency, Research Triangle Park, April 1987.

25. EPA, *Report of the Workshop on Selecting Input Distributions for Probabilistic Assessments*; EPA/630/R-98/004; Prepared by Eastern Research Group for Risk Assessment Forum, U.S. Environmental Protection Agency, Washington, DC, 1999

26. Holland, D. M., Fitz-Simons, T., Fitting Statistical Distributions to Air Quality Data by the Maximum Likelihood Method, *Atmospheric Environ.* 1982, 16, 1071-1076

27. EPA, *Bulk Gasoline Terminals - Background Information For Proposed Standards*; EPA-450/3-80-038a, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1980

28. Personal communication with Mr. Stephen Shedd at the U.S. EPA, May 16th, 2000

29. Mage, D. T. Comment on "Parametric Distributions of Regional Lake Chemistry: Fitted and Derived", Correspondence, *Environ. Sci. Technol.* 1988, 22(11), 1367-1368

30. Ang, A. H-S., Tang, W. H., 1975. *Probability Concepts in Engineering Planning and Design*, John Wiley & Sons, Inc: New York

31. Cullen, A. C., Frey, H. C.; *Probabilistic Techniques in Exposure Assessment: A Handbook for Dealing with Variability and Uncertainty in Risk Analysis*; Plenum Press: New York, 1999

Figure 5.1. Comparison of Empirical Cumulative Distribution of Uncontrolled Bottom Loading, VOC Emissions, Fitted Weibull Distribution, and Bootstrap Simulation Confidence Intervals, Based Upon Retaining Intra-Facility Variability.

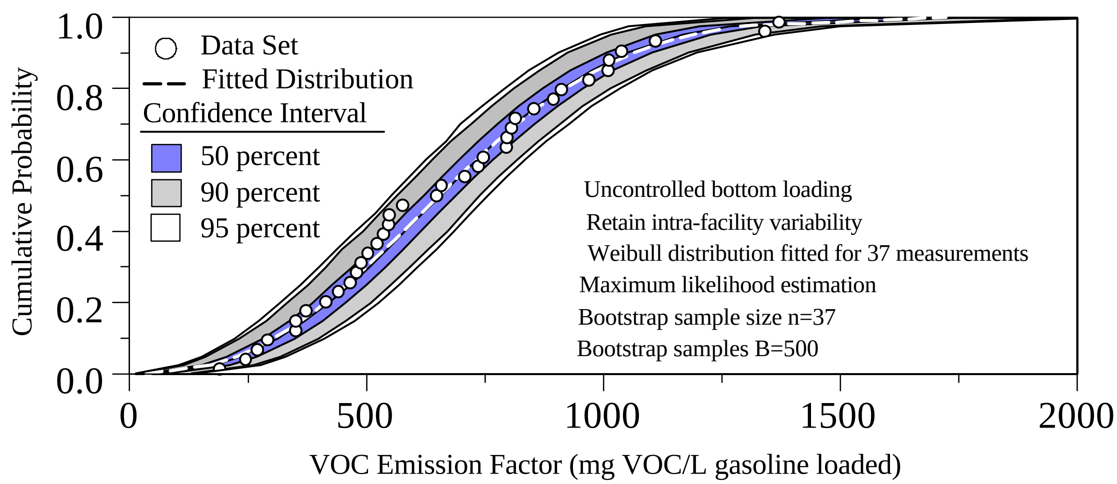


Figure 5.2. Comparison of Empirical Cumulative Distribution of Uncontrolled Bottom Loading, VOC Emissions, Fitted Lognormal Distribution, and Bootstrap Simulation Confidence Intervals, Based Upon Retaining Intra-Facility Variability.

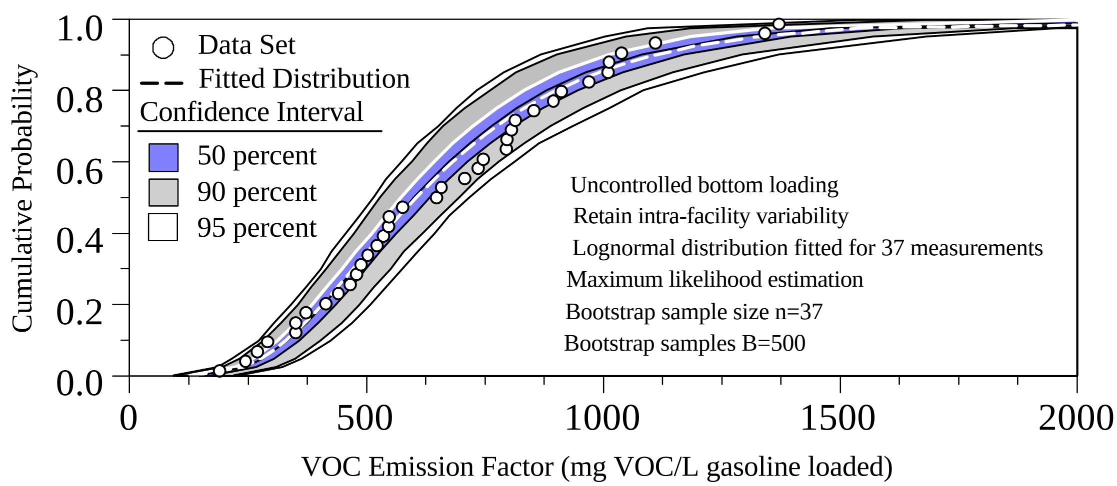


Figure 5.3. Comparison of Empirical Cumulative Distribution of Uncontrolled Bottom Loading, VOC Emissions, Fitted Gamma Distribution, and Bootstrap Simulation Confidence Intervals, Based Upon Retaining Intra-Facility Variability.

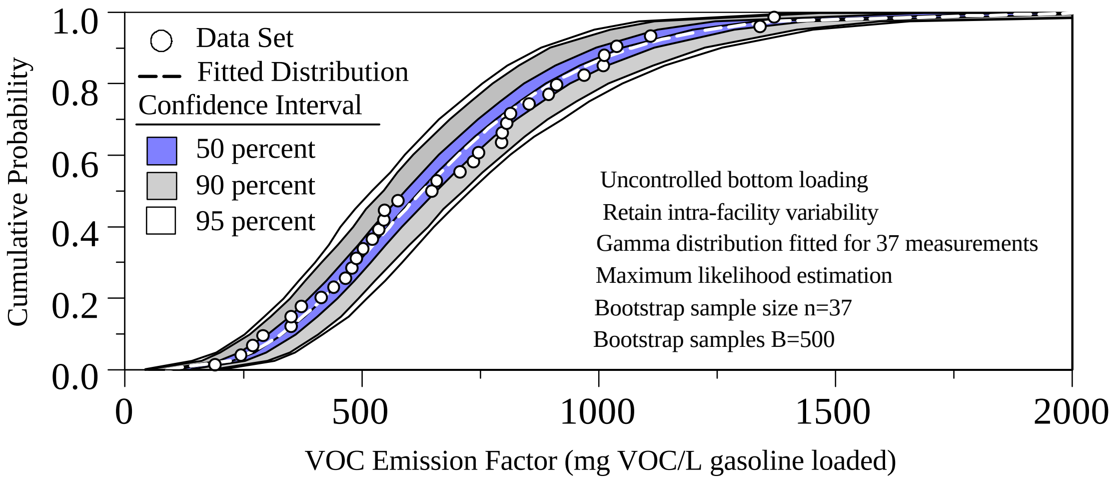


Figure 5.4. Comparison of Empirical Cumulative Distribution of Uncontrolled Bottom Loading, VOC Emissions, Fitted Gamma Distribution, and Bootstrap Simulation Confidence Intervals, Based Upon Removing Intra-Facility Variability.

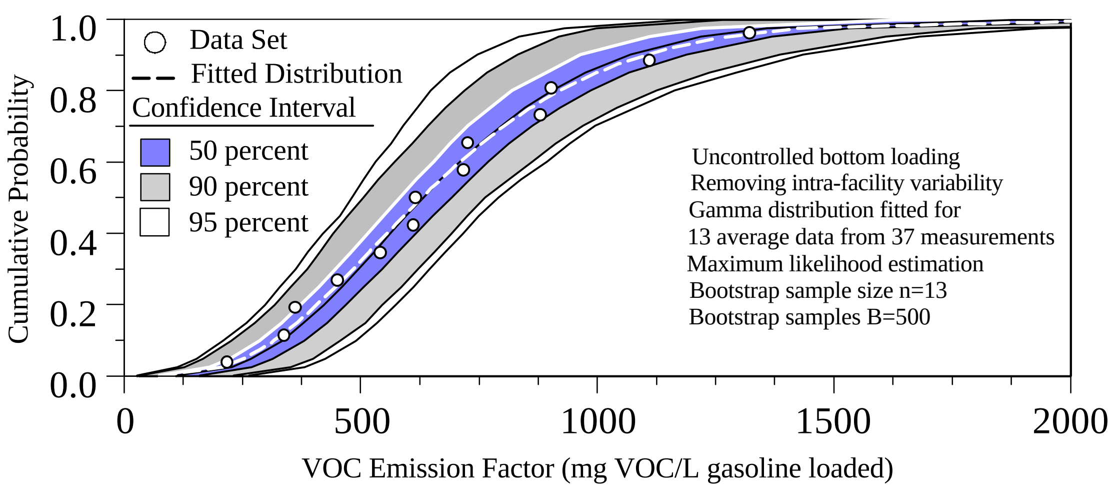


Table 5.1. Fitted Parametric Distributions for Variability in VOC Emission Factors of Gasoline Terminal Loading Loss

Loading method[a]	Fitted Dist.[b]	Para. Esti. Method.[c]	Parameters[d]		Total Num. of Data	Percent of Data Within 50% CI	Percent of Data Within 90% CI	Percent of Data Within 95% CI	K-S test statistics[e]	Critical Value at 0.05 significance level[f]
			r	λ						
Bottom, Uncontrolled	G	MLE	4.5840	147.87	13	92	100	100	0.1028	0.37
Top, Uncontrolled	G	MoMM	3.8536	429.76	2	100	100	100	n/a	n/a
Bottom, CA	G	MoMM	2.0832	2.6661	2	100	100	100	n/a	n/a
Bottom, CRA	G	MoMM	11.414	6.0167	5	80	100	100	0.2592	0.56
Bottom, Ref	G	MoMM	17.747	3.4658	4	100	100	100	n/a	n/a
Bottom, TO	G	MoMM	2.4803	22.376	4	100	100	100	n/a	n/a

[a] CA = Carbon Adsorption; CRA = Compression-Refrigeration-Absorption; Ref = Refrigeration; TO = Thermal Oxidation
[b] G=Gamma unit: mg VOC/L gasoline loaded
[c] MLE = Maximum Likelihood Estimation; MoMM = Method of Matching Moments
[d] r: shape parameter; λ: scale parameter
[e] Reported by "Crystal Ball"
[f] Sources: reference 29, 30

Table 5.2. Quantified Uncertainties for VOC Emission Factors of Gasoline Terminal Loading Process

Loading method[a]	Bootstrap sample size	Mean of bootstrap sample means[b]	Absolute 95% CI of bootstrap sample Means[b]	Relative 95% CI of bootstrap sample means, %
Bottom, Uncontrolled	13	681	-158 to +161	-23 to +24
Top, Uncontrolled	2	1599	-996 to +1123	-62 to +70
Bottom, CA	2	5.7	-3.8 to +6.3	-67 to +110
Bottom, CRA	5	69	-16 to +19	-23 to +28
Bottom, Ref	4	62	-14 to +15	-23 to +24
Bottom, TO	4	56	-28 to +39	-50 to +70

[a] CA = Carbon Adsorption; CRA = Compression-Refrigeration-Absorption; Ref = Refrigeration; TO = Thermal Oxidation
[b] unit: mg VOC/L gasoline loaded

6.0 QUANTIFICATION OF UNCERTAINTY IN EMISSION FACTORS OF EVAPORATIVE LOSS SOURCES: CASE STUDIES FOR ASPHALT PAVING AND ARCHITECTURAL COATINGS

Song Li and H. Christopher Frey

Department of Civil Engineering, North Carolina State University, Raleigh, NC 27695

Abstract

Volume-based emission factors are widely used for the development of emission inventories for evaporative loss sources. Two typical evaporative loss source categories, asphalt paving and architectural coating, were studied in this paper. However, different quantitative methods were used to characterize uncertainty in volatile organic compound (VOC) emission factors of these two categories. The quantitative analysis for asphalt paving was based upon the combination of limited known characteristics and judgment. The quantitative analysis for architectural coatings was based upon real sample data. For the case study of architectural coatings, market share information is also available. Thus, emission data should not be weighted equally. A method referred as synthetic data set was introduced for enabling fitting parametric probability distribution to unequally weighted emission data. In the quantitative analysis based upon sample data, bootstrap simulation was used to quantify uncertainty in mean emission factors. The procedures and results of the above two different quantitative analyses were discussed in detail in this paper.

6.1 Introduction

Emission inventories are used for a variety of purposes, from as wide as national emission trends estimation to as detailed as source compliance analysis. Non-quantified uncertainties in emission inventories possibly lead to biased conclusions regarding emission estimations and in turn result in erroneous management decisions. Therefore, it is important to account for uncertainties in the emission inventory development.

Emission factors are a starting point of emission inventory development, especially for area sources. An ideal emission factor would be derived from source-specific sample data. However, it is not practical to sample every source category. Hence, emission factors are often based upon the known characteristics of a typical source.[1]

This paper focuses on the demonstration of quantitative methods to characterize variability and uncertainty in emission factors for area sources. Two case studies for cutback asphalt paving and architectural coating were presented. These two categories are typical area sources of evaporative loss, for which volume-based emission factors are commonly used to develop emission inventories.

However, the first case study of cutback asphalt paving targeted on demonstrating an uncertainty analysis for an emission factor based upon the combination of limited known characteristics and judgment. The second case study of architectural coating demonstrated an uncertainty analysis for an emission factor based upon sample data.

Some key issues were addressed in this paper, including: (1) How to characterize uncertainty based upon judgment in the situation that information is limited? (2) How to characterize uncertainty based upon sample data? (3) How market share information could be incorporated into uncertainty analysis? (4) What is the typical range of uncertainty in emission factors of asphalt paving and architectural coatings since uncertainties in these two source categories have never been analyzed quantitatively?

6.2 Overview of Uncertainty Analysis

Uncertainty refers to lack of knowledge regarding the true value of a quantity.[2] Typically, uncertainty arise due to lack of data, nonrepresentativeness of data, limited sample size, use of surrogate data, or human errors. There are a number of recommendations to U.S. Environmental Protection Agency (EPA) that addressed on the importance of uncertainty analysis. The National Research Council (NRC) has recommended uncertainty analysis in the fields of modeling mobile emissions and risk assessment.[3, 4] The Intergovernmental Panel on Climate Change (IPCC) has developed "good practices guidance and uncertainty management" on the request from the United Nations Framework Conversion on Climate Change (UNFCCC).[1] The U.S. Department of Energy (DOE) also recommended using Monte Carlo simulations of uncertainty in U.S. greenhouse gas emission estimates.[5] The National Council on Radiation Protection and Measurements (NCRP) has published guides for uncertainty analysis in dose and risk assessments related to environmental contaminations.[6]

Basically, there are two types of uncertainty analysis, sample-based method and judgment-based method. The sample-based method, such as bootstrap simulation, is certainly desirable. However, when sample information is scarce or unavailable, the use of judgment to define uncertainty range is necessary.[1] In practice, these two methods are used in compensation to each other.

6.3 Case Study 1: VOC Emissions from Cutback Asphalt Paving

The major source of VOC emission from asphalt paving is cutback asphalt. VOC emissions from cutback asphalts result from the evaporation of the petroleum distillate solvent that is used to liquefy the asphalt cement.[7] This case study focuses on the medium cure cutback asphalt, which is the prevailing approach in the Charlotte airshed, North Carolina, which is the studing domain of a ongoing related work. However, quantitative methods demonstrated here can also be applied to the emission factors of other types of cutback asphalts.

No sample data is available for VOC emissions from cutback asphalt paving, thus a mass-balance model based upon known characteristics of the cutback asphalt was proposed by EPA for this source category. The mass-balance model for VOC emissions from cutback asphalt paving is given by Eq. 6.1.

$$EF = DC \times r \times EV \tag{6.1}$$

Where:

EF, volume-based VOC emission factor, kg VOC/liter asphalt

DC, diluent content, liter diluent/liter asphalt

r, diluent density, kg/liter diluent

EV, percent of diluent evaporated, %.

Theoretically, both model uncertainties and input uncertainties contribute to uncertainty in the model prediction. Model uncertainties arise due to the fact that the model is a simplified representation of the real system. For example, VOC emissions from the asphalt paving are also influenced by temperature, thus a temperature adjustment factor may be added to Eq. 6.1. Input uncertainties refer to uncertainties that exist in the model inputs. As far as this case study, only input uncertainties were addressed.

Some known characteristics for the model inputs were available in EPA publications. The diluent used for medium cure is kerosene.[7] The reported diluent content typically varies between 0.25-0.45 liter-diluent/liter-asphalt according to the AP-42, or 0.20-0.50 liter-diluent/liter-asphalt according to the EPA guideline series.[7, 8] A typical value of 0.35 liter-diluent/liter-asphalt for the diluent content may be assumed for the inventory purpose.[7] The percentage of diluent evaporated is estimated to be 60-80%.[8] And a typical value of 70% is assumed for the inventory purpose.[7] The above reported characteristics help to identify the ranges of variability in diluent content and percentage of diluent evaporated.

Because no sample data is available for the model inputs, the judgment-based method was used to quantify uncertainty ranges in the mean diluent content and mean percentage of diluent evaporated. First, normal distributions were assumed to represent uncertainties in the means. The normal distribution was chosen because it is a typical parametric probability distribution recommended by IPCC as the first choice to represent uncertainties unless the characteristics of the data suggest a highly non-symmetric population.[1]

After choosing the normal distribution, the next step is to define the range of uncertainty. For the diluent content, a range of minus 10 percent to plus 10 percent of the typical value was judged to represent the 95 percent confidence interval of uncertainty in the mean diluent content. For the percentage of diluent evaporated, since variability is not large, a range of minus 5 percent to plus 5 percent of the typical value was judged to represent the 95 percent confidence interval of uncertainty in the mean estimate. The density for kerosene is 0.8 kg/liter. Kerosene has a standard Chemical Abstracts Service (CAS) code of 8008-20-6, and its compositions are well known in the chemical industry.[9] Therefore, we wouldn't expect much uncertainty in the estimation of kerosene density. In this study, a range of minus 1 percent to plus 1 percent of the 0.8 kg/liter was judged to represent the 95 percent confidence interval of uncertainty in the kerosene density. Based upon the assumed range of uncertainty, the mean of normal distribution is the same as the typical value of the model input, and the standard deviation of the normal distribution was derived as a multiple of 0.51 of the absolute uncertainty range. Input uncertainty assumptions are summarized in Table 6.1.

Uncertainty in each model input was assumed to be statistically independent. The Monte Carlo simulation was used to propagate the input uncertainty distributions through Eq. 6.1. A sample size of 10000 was used in the simulation process. The probability distribution for the simulated volume-based emission factor is presented in Figure 6.1. The average estimate of mean emission factor is 1.64 lb-VOC/gallon-asphalt. The absolute 95 percent confidence interval of the mean emission factor is from 1.46 to 1.83 lb-VOC/gallon-asphalt, corresponding to a range of minus 11 percent to plus 12 percent compared to the mean value. The relative confidence interval of the mean emission factor appears not large, however, it may convert to a substantial absolute range of uncertainty in the inventory estimation. For example, the point estimate of VOC emissions from cubtack asphalt paving in Charlotte airshed, North Carolina, was 14132 tons/year in 1995. If uncertiany in the emission factor had been taken into consideration, it would lead to thousdands of tons uncertainty estimation in the emission inventory of Charlotte airshed.

6.4 Case Study 2: VOC Emissions from Architectural Coatings

VOC Emission factors for architectural coatings are based upon sample data. Data used in this case study are from a 1992 industry survey and were reported by EPA in 1996.[10] Emission data and annual sales information for 73 types of coatings were collected in this survey. Coatings fall into two technology groups, solvent-borne and water-borne, based upon their carrier mediums. 34 types of coatings are solvent-borne coatings and 30 types of coatings are water-borne coatings. The carrier mediums of remainning 9 types of coatings are unknown.

It was expected that solvent-borne coatings and water-borne coatings would yield different average emission rates. Therefore, they were analyzed seperatly and the coatings with unknown carrier mediums were not used. The categorization of database into small groups has statistical benefits in that it increases the precision of estimates by avoiding to lump heterogeneous items together.

In this case study, sample-based method was demonstrated for quantifying uncertainty in mean emission factors of arcihtectural coatings. Because different coatings have different market shares, a method refered to the synthetic data set (SDS) was introduced for the analysis of market-share weighted emission data.

6.4.1 Overview of General Methodology

In the sample-based quantitative analysis, sample data are typically visualized as an empirical cumulative distribution function (CDF) and variability in population can be characterized by fitting a parametric probability distribution to the sample data. The bootstrap simulation was used to characterize uncertainties in the probability distribution of variability and mean emission factors. In the bootstrap simulation, random sampling process was repeated simulated for, typically, 500 to 2000 times. Each time, a simulated data set, known as a *bootstrap sample*, is sampled at random from the fitted probability distribution.[11] The bootstrap sample has the same number of data points as the original sample and therefore is a possible random realization of the original sample. Statistics, such as the mean, can be calculated for each bootstrap sample. The 500 to 2000 bootstrap replications of the statistics can be used to build up a sampling distribution, and confidence intervals of those statistics can be inferred.

6.4.2 Development of Synthetic Data Sets

Synthetic data sets were developed in order to fit parametric probability distributions to market-share weighted sample data. In the synthetic data set, a portion of the data points were assigned with the emission value associated with a type of coating, in proportion to the market share of that coating. For example, shellacs has a VOC emission rate of 4.51 lb-VOC/gallon-coating and 0.2071 percentage of total market share. In a synthetic data set with 1000 data points, 2 of the 1000 data points were assigned with the shellacs's emission value of of 4.51 lb-VOC/gallon-coating. Thus, the use of synthetic data set allows emission values to occur repeatedly in proportion to their market shares. Then parametric distributions were fit to the synthetic data sets.

6.4.3 Quantifications of Variability in Data Sets

A concern in the SDS method is that the emission values with market share less than $\frac{0.5}{n}$, where n is the size of synthetic data set, will not occur in the synthetic data set. Judgements were first made that fitted parametric probability distributions based upon synthetic data sets represent the original database well.

In this case study, synthetic data sets of 1000 data points were used. Summaries of the synthetic data sets and selected parametric probability distributions for variability are presented in Table 6.2. Because parametric distributions were fitted to the synthetic data sets, conventional Goodness-of-Fit tests, such as Kolmogorov-Smirnov test, are not applicable. Therefore, the goodness of fitted parametric distribution was evaluated based upon visualizing of the data set and comparing empirical CDF with the fitted parametric distribution.

A comparison of a fitted gamma distribution, a stepwise empirical CDF of the synthetic data set, and the original coating data set for solvent-borne coatings is presented in Figure 6.2. The original coating data set was plotted as a discrete empirical CDF based upon cumulative market shares. Variability in the emission factor of solvent-borne coatings is more than a factor of 3, from 2 to 6 lb/gal. The gamma distribution was fitted to the synthetic data set. The comparison suggests that the gamma distribution agrees with the discrete CDF of the original coating data set.

The same comparison for the water-borne coatings is presented in Figure 6.3. Figure 6.3 shows that a fitted Weibull distribution can capture the overall trends of the discrete CDF of the original coating data set. Variability in the emission factor of water-borne coatings is from 0.03 to 3 lb/gal, with a factor of 100, and major coatings on the market have emission rates less than 0.7 lb/gal. The fitted Weibull distribution also supports that there is little probability that emission values larger than 1 lb/gal will be sampled for water-borne coatings since they only comprise less than 1 percent of the total market share.

6.4.4 Quantification of Uncertainty in the Mean Emission Factors

Bootstrap simulation was used to quantify uncertainties in the fitted distribution. In Figure 6.4, quantitative analysis results based upon fiting gamma distribution are shown for solvent-borne coatings. The confidence intervals for different percentiles are plotted over the fitted gamma distribution. For example, the 95 percent confidence interval for median is from 3.25 to 3.9 lb/gal. Similarly, the confidence interval of mean emission rate can be obtained.

The quantified uncertainties in the mean emission factors for architectural coatings are summarized in Table 6.3. For solvent-borne coatings, the mean emission rate is 3.65 lb/gal, corresponding to approximately the 55^{th} percentile of the fitted gamma distribution. The cumulative probability of the mean is above the median, which suggests slightly positive skewness in the data set. The absolute 95 percent confidence interval of the mean emission factor for solvent-borne coatings is from 3.35 to 3.99 lb/gal, corresponding to a relative range of minus 8.2 percent to plus 9.3 percent of the mean value. The absolute 95 percent confidence interval of mean emission factor for water-borne coatings is from 0.39 to 0.59 lb/gal, representing minus 20 percent to plus 20 percent of the mean value. The wide range of relative confidence interval for water-borne coatings is due to the small sample size and the small mean value.

6.5 Discussion and Conclusions

Evaporative loss sources are important contributors to the VOC emission inventories. In this paper, we briefly presented two case studies on the quantification of uncertainties in the VOC emission factors of asphalt paving and architectural coatings. Typically, a quantitative analysis based upon real sample data is desirable. However, instead of sample data, often only limited known characteristics, such as upper and lower bound information, are available for an emission source category. Therefore, judgment based upon those limited known characteristics was made for the quantitative analysis.

In the case study of VOC emissions from asphalt paving, uncertainties in the mean estimates of diluent content, diluent density and evaporation percentage were characterized based upon judgment. The Monte Carlo simulation method was used to propagate input uncertainties in diluent content, diluent density and evaporation percentage through the emission factor model for the development of a probabilistic volume-based emission factor. The 95 percent confidence interval of the mean emission factor for asphalt paving was quantified with a absolute range of 1.46 to 1.83 lb-VOC/gallon-asphalt, corresponding to a relative range of minus 11 percent to plus 12 percent compared to the mean value.

The case study of architectural coating represents an ideal scenerio of uncertainty analysis in that sample data are available. However, because different sample data have different market shares, conventional statistical methods were modified in order to fit parametric distributions to unequally weighted data. In this case study, a synthetic data set, which allows emission values to occur repeatedly in proportion to their market shares, was first developped. Parametric distributions thus were fitted to the synthetic data set. Bootstrap simulation was used to quantify uncertainty in mean emission factors based upon the fitted parametric distribution. The 95 percent confidence interval for the solvent-borne coatings was quantified to be approximately minus 8 percent to plus 9 percent of the mean of 3.65 lb-VOC/gallon-coating. The 95 percent confidence interval for the water-borne coatings was quantified to be minus 20 percent to plus 20 percent of the mean of 0.49 lb-VOC/gallon-coating.

The classification of coatings as either waterborne or solvent-borne was based upon an a *priori* expectation that these two categories would produce different average emission rates. The quantitative analysis results demonstrate that the average emission rates for these two categories are statistically significantly different from each other. For example, the upper 95 percent confidence interval for waterborne coatings is 0.59 lb/gallon, versus a lower 95 percent confidence interval for solvent-borne coatings of 1.19 lb/gallon. Therefore, the *priori* expectation is confirmed and the stratification of data with respect to the type of carrier medium is justified.

6.6 Acknowledgements

We thank the U.S. Environmental Protection Agency for supporting this work with STAR Grants Nos. R826766 and R826790.

6.7 References

1. IPCC National Greenhouse Gas Inventories Program, Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories, Intergovernmental Panel on Climate Change (IPCC), 2000.

2. Frey, H. C., *Quantitative Analysis of Uncertainty and Variability in Environmental Policy Making*, 1992 Environmental Science and Engineering Fellows Program Reports, American Association for the Advancement of Science, Washington, DC, 1993, pp. 25-33.

3. National Research Council. *Science and Judgment in Risk Assessment*; National Academy Press: Washington, DC, 1994.

4. National Research Council. *Modeling Mobile-Source Emissions*; National Academy Press: Washington, DC, 2000.

5. U.S. DOE, Monte Carlo Simulations of Uncertainty in U.S. Greenhouse Gas Emissions Estimates and Related Support Work, prepared by Science Applications International Corporation for U.S. Department of Energy (DOE) 2001.

6. NCRP, A Guide for Uncertainty Analysis in Dose and Risk Assessments Related to Environment Contamination. National Council on Radiation Protection and Measurements (NCRP) 1996.

7. EPA. *Compilation of Air Pollutant Emission Factors, AP-42, Fifth Edition, Chapter 4.5: Asphalt Paving Operation*; U.S. Environmental Protection Agency, Research Triangle Park, NC, 1995.

8. Makwordt, D. W. Guideline Series: Control of Volatile Organic Compounds from Use of Cutback Asphalt, EPA 450/2-77-037, Environmental Protection Agency, RTP, NC, 1977

9. Chemical Abstracts Service code is available at http://www.cas.org/

10. EPA Emission Standards Division, *Architectural Coatings: Background for Proposed Standards : Draft*; EPA-453/R-95-009a, U.S. Environmental Protection Agency Research Triangle Park, NC, 1996

11. Efron, B., “Bootstrap Methods: Another Look at the Jackknife”, *Annals of Statistics*, 1979, 7(1), 1-26

Figure 6.1. Mean and 95 Percent Confidence Interval of Volume-based VOC Emission Factor for Cutback Asphalt Paving

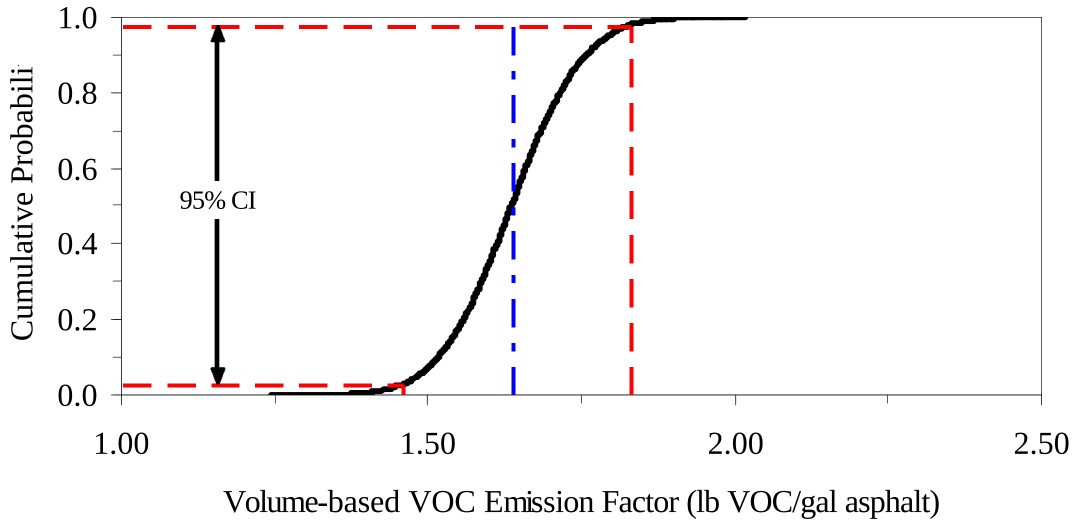


Figure 6.2. Comparison of Fitted Gamma Distribution, Stepwise Empirical CDF of the Synthetic Data Set and Cumulative Market Share of the Original Coating Database, VOC Emission Factor of Solvent-Borne Architectural Coatings

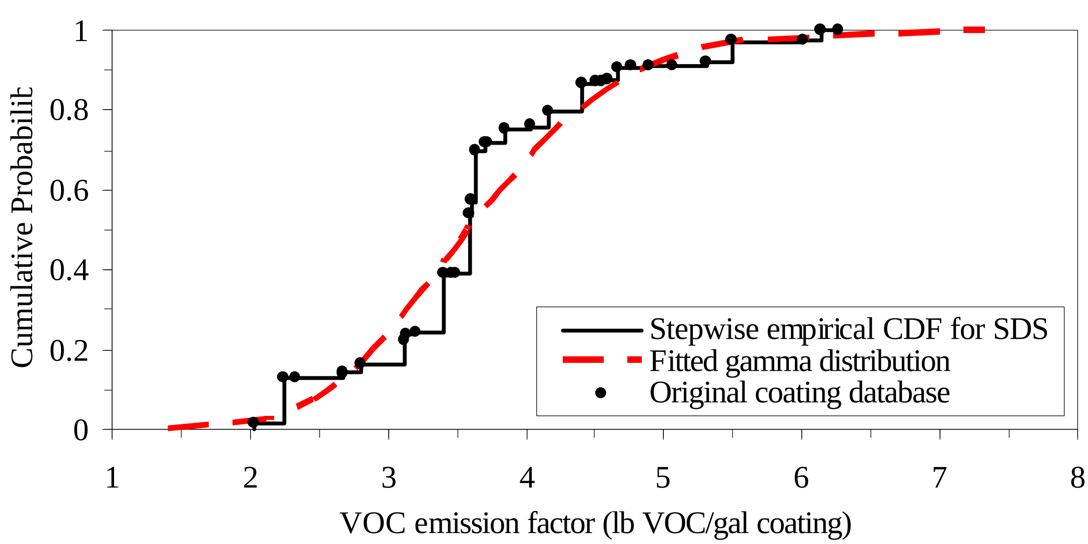


Figure 6.3. Comparison of Fitted Weibull Distribution, Stepwise Empirical CDF of the Synthetic Data Set and Cumulative Market Share of the Original Coating Database, VOC Emission Factor of Water-Borne Architectural Coatings

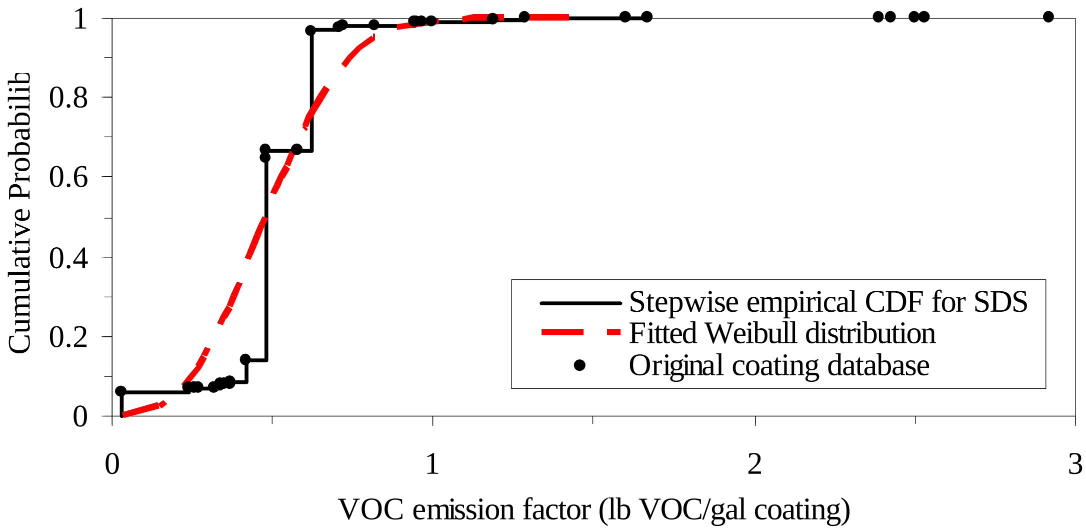


Figure 6.4. Bootstrap Simulation Results Based Upon a Fitted Gamma Distribution for Market-Share Weighted VOC Emission Factor of Solvent-Borne Architectural Coatings

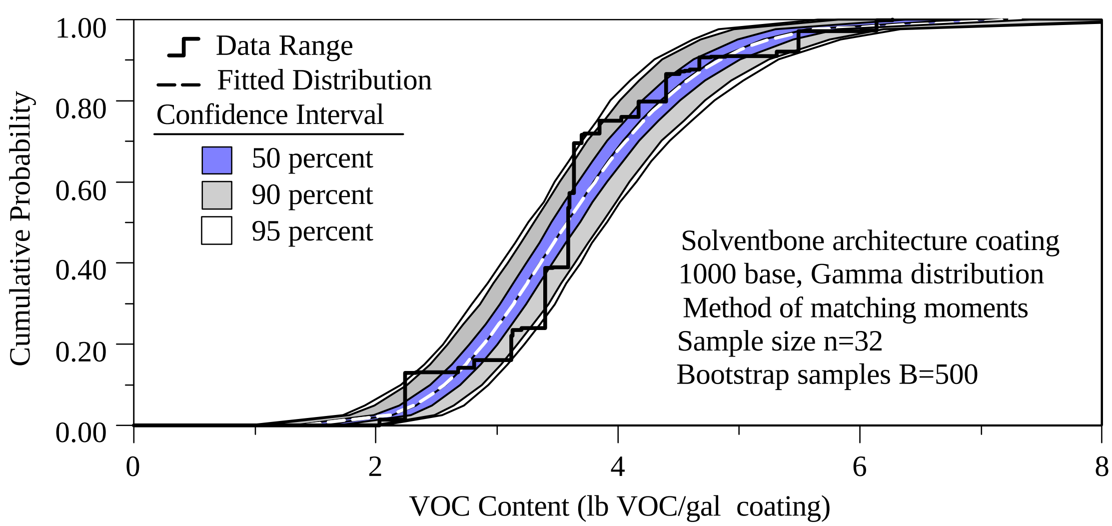


Table 6.1. Input Assumptions for Cutback Asphalt Paving Emission Factor Model

Model Inputs	Uncertainty Dist.	Parameters	
		Mean	Std. Deviation
Diluent content	Normal	0.35	0.018
Percent of diluent evaporated	Normal	70%	1.8%
Diluent density	Normal	0.8	0.0041

Table 6.2. The Synthetic Data Sets and Variability Charaterized by Fitted Parametric Probability Distribuions for Architectural Coatings

Coating category	Total No. of coating in database	No. of coating enclosed in SDS	Total market share of the coatings enclosed in SDS (%)	VOC emission percent of coatings enclosed in SDS (%)	Fitted Dist.[a]	Parameter	
						shape	scale
Solvent-borne	34	32	99.97	99.97	G	16.697	0.2188
Water-borne	30	16	99.84	99.56	W	2.8234	0.5493

[a] G = gamma, MoMM parameter estimation; W = Weibull, MLE parameter estimation.

Table 6.3. Quantified Uncertainty in Mean VOC Emissions Factors of Architectural Coatings

Coating category	Fitted Dist.	Bootstrap sample size	Mean of Bootstrap sample means (lb/gal)	Absolute 95% CI of Bootstrap sample means (lb/gal)	Relative 95% CI of Bootstrap sample means (%)
Solvent-borne	Gamma	32	3.65	3.35 to 3.99	-8.2 to 9.3
Water-borne	Weibull	16	0.49	0.39 to 0.59	-20% to 20

7.0 QUANTIFICATION OF VARIABILITY AND UNCERTAINTY IN EMISSION FACTORS AND COATING USAGE FACTOR FOR WOOD FURNITURE COATING PROCESS

Song Li and H. Christopher Frey

Department of Civil Engineering, North Carolina State University, Raleigh, NC 27695

Abstract

Emission factors are important starting point of emission inventories. Emission inventories in turn are widely used in air quality prediction and management purposes. Typically, uncertainties in emission factors and emission inventories are not quantified. Therefore, it is unknown how robust regulatory and management decisions are with respect to uncertainty. Quantitative methods to characterize variability and uncertainty based upon parametric probability distributions and bootstrap simulation were demonstrated in this paper with respect to a case study for VOC emissions from wood furniture coatings. The 95 percent confidence intervals of uncertainty for the mean volume-based emission factors and coating usage factor were calculated. Uncertainty distributions in volume-based emission factors and usage factor were propagated trough equation to develop a probabilistic employee-based emission factor. These quantitative measures of uncertainties convey information regarding the quality of the emission factors and serve as a guideline for future work to improve the quality of emission factors as well as emission inventories for wood furniture coatings.

7.1 Introduction

This paper demonstrates quantitative approaches to characterize variability and uncertainty in Volatile Organic Compound (VOC) emissions from the coating process of wood furniture industry. This work is a part of a large project sponsored by US EPA to develop and demonstrate methods for the quantification of variability and uncertainty in emission factors and to apply these methods for a variety of emission source categories. The quantified uncertainties in emission factors thereby serve as a basis to quantify uncertainties in emission inventories, which will finally be inputted into air quality models for the probabilistic prediction of ambient ozone level.

The target pollutant in this study is VOC. VOCs and nitrogen oxides (NO_x) react in the presence of sunlight to form tropospheric ozone, a regulated pollutant in the federal and state ambient air quality standards. Therefore, the estimations of VOC emissions are important to photochemical air quality models for the ozone prediction. The target category is wood furniture coating, which is the largest VOC emission source in the research domain, Charlotte airshed, North Carolina.[1] Some key questions addressed in this papers include: (1) How to characterize variability in the volume-based VOC emission factors? (2) How to characterize the inter-factory variability in coating usage factor? (3) Whether there are significant differences in emission factors between water based and solvent-based coatings? (4) What are the ranges of uncertainty in the mean estimates of the volume-based VOC emission factors? (5) What is the range of uncertainty in mean coating usage factor? and (6) How to develop a probabilistic employee-based VOC emission factor for wood furniture coatings?

7.2 Variability and Uncertainty

Variability refers to observed differences attributable to true heterogeneity or diversity in a population.[2] For example, emission factors and usage factor for wood furniture coatings may vary from one factory to another because of variations in coating type, specific formulation, ambient temperature, and other operating conditions. Uncertainty refers to lack of knowledge regarding the true value of an unknown quantity.[3] Uncertainty can be further separated into systematic errors and random errors. This study focuses on the quantification of uncertainty due to random sampling errors.

Systematic errors, which are also referred as inaccuracy or bias, come from inaccurate measuring methods or non-representativeness of data.[3] Statistic techniques generally do not have enough power to characterize the systematic errors. Therefore, it’s important to carefully judge the quality of data before uncertainty analysis.

Random errors are also referred as imprecision. Sources of random errors typically include random measurement errors and random sampling errors due to the limited sample size. In the case that methods used to measure emissions are of good quality and well calibrated, it is expected that random measurement errors are not large compared with the random sampling errors. In particular, when the sample size is small, random sampling error is typically a dominant source of uncertainty. Therefore, this study focuses on the quantification of uncertainty associated with random sampling errors.

7.3 Needs of Probabilistic Analysis

Uncertainties in emission factors and emission inventories are typically not reported in current practice. As a surrogate for uncertainty estimates, AP-42 emission factors are accompanied with data quality ratings.[4] For example, “A” to E” qualitative ratings are assigned to emission factors as a indicator of their quality. A method for qualitatively rating emission inventories, known as the Data Attribute Rating System (DARS) has also been developed by EPA.[5] Qualitative ratings of emission factors and emission inventories are important. Some sources of uncertainty are difficult to quantify, such as non-representativeness of a data set. Therefore, there will always be a role for qualitative statements regarding non-quantifiable sources of uncertainty. However, qualitative rating systems should be used in combination with quantitative approaches.

The National Research Council (NRC) and the EPA have increasingly recognized the need for a quantitative uncertainty analysis in environmental modelings and decision-makings. For example, the NRC has recommended to EPA the quantitative analysis of uncertainty as early as the year of 1994.[6] A recent NRC report again recommended the EPA to "undertake the necessary measures to conduct quantitative uncertainty analyses of the mobile source emissions."[7] The EPA also has developed guidelines for Monte Carlo analysis of uncertainty in the context of human exposure and risk analysis.[8]

7.4 VOC Emission from Wood Furniture Coatings

The major pollutant emitted from wood furniture coating process is VOC. In the wood furniture industry, coatings are usually applied in either manual or automatic spray booths. The booths generally do not have any temperature or humidity control, and are maintained at ambient conditions.[9] This research focuses on uncontrolled VOC emissions. An assumption made by EPA for the surface coating area sources is that all VOCs in coatings are eventually emitted into the atmosphere.[10]

The Standard Industrial Classification (SIC) code of 25 is created by the Bureau of the Census to track the practices in the furniture and fixtures industry. SIC 25 actually covers a diverse groups of products. This research focuses on wood furniture manufacturing industry that belongs to the following SIC codes:

- SIC 2511: Wood Household Furniture, Except Upholstered
- SIC 2512: Wood Household Furniture, Upholstered
- SIC 2521: Wood Office Furniture

We originally intend to collect the emission data that was exactly used by the EPA in developing its emission factor for wood furniture coatings. However, these data was not easily available. Given the difficulty to obtain a complete EPA data set, we decided instead to search for emission data for wood furniture coatings from other sources. The data used in this study are from a survey conducted by the University of California at Davis (UC Davis) in the middle of 1990's for California Air Resources Board (CARB).[11]

Volume-based VOC emission factor and annual sales data of more than two hundred coating products were collected in the CARB survey.[11] In the survey database, coatings were organized in 8 categories according to functional taxonomy. These categories include colored coatings, enamels, fillers, sealers, stains thinners, topcoats and washcoats. Similar functional taxonomy can be found in several EPA publications regarding wood furniture industry.[9, 12] Three are 18 unclassified coatings in the survey database, and thereby were not used in this study.

For each of coating category except for thinners, coatings can be further divided into two subgroups according to their carrier mediums: water-based coatings and solvent-based coatings that are commonly referred as conventional coatings. It was expected that the solvent-based coatings and water-based coatings would produce different average emission rates. Therefore, they were analyzed separately in this study. Typically, uncertainty in the mean is influenced by variability in the data set. Dividing sample data set into homogeneous subgroups will reduce variability due to lumping heterogeneous items together.

This database has been used by UC Davis to quantify uncertainty in emission factors. In their research, truncated normal distributions were used to represent variability in emissions, and based upon normality assumption, student-t distributions were used to analytically quantify uncertainty in mean emission factors. The normality assumption and the use of analytical method resulted in absolute symmetric estimates of uncertainty in their emission factors.[11]

In our study, non-negative parametric distributions, including lognormal, gamma and Weibull distributions, were used to represented variability in emission data set, and numerical methods based upon bootstrap simulation was used to quantify uncertainty in the mean emission factors.

7.5 Methods to Quantify Variability and Uncertainty

The very first step in any uncertainty analysis is to prepare sample database and assess the quality of the sample. A judgment must be made that the data are a reasonably representative sample of the population of interest. It is often useful to graphically visualize the sample data to obtain a clear insight of the range, central tendency, skewness and other characteristics of the sample. The typical approach to visualize data is assigning certain fractiles to sample data and expressing them as an empirical cumulative distribution functions (CDF). There are several candidate plotting position functions can be used to estimate the fractiles for a sample. The Hazen plotting position was used in this study.[13] An empirical CDF is also a valid description of variability in a sample. However, one limitation of the empirical CDF is that there is no extrapolation beyond the range of observed data. Thus, for small data set, the range of variability of the population may be underestimated because the variation in sample data observed may be much narrower than the variation in the actual population.[13]

In this study, parametric probability distributions were fitted to the sample data for a plausible means to interpolate within the range of observed sample data and to extrapolate to the unobserved portion of the unknown population distribution. The parametric probability distributions evaluated were lognormal, gamma and Weibull distributions. The selections of parametric distributions were based upon both theoretical and empirical considerations. For example, emissions data are nonnegative and typically skewed. The symmetric distributions, such as normal, are often inappropriate when sample size is small and variability is large. While, the lognormal distribution is non-negative and positively skewed and is often useful for fitting to physical quantities, such as pollutant concentrations. The gamma and Weibull distributions are similar to the lognormal, but are more flexible than the lognormal to assume different shapes for variability. [14]

Bootstrap simulation was used to estimate uncertainty in the population distribution and mean emission factors. The objective of bootstrap simulation is to numerically simulate sampling distributions for statistics. In the bootstrap simulation process, multiple random samples, known as *bootstrap samples*, were drawn from the assumed probability distribution using Monte Carlo sampling method. In general, the bootstrap sample has the same number of data points as the observed sample. Thus, the bootstrap sample is a computer-simulated alternative realization of the original sample. Typically, 500 to 2,000 bootstrap samples are simulated and statistics, such as the mean, are calculated from each bootstrap sample. Therefore, 500 to 2,000 estimates of the statistics are obtained to build the sampling distributions for statistics. From the sampling distribution, a confidence interval for uncertainty can be inferred.[15] Results of bootstrap simulation are typically exported to a two-dimensional graph.

7.6 Quantification of Variability and Uncertainty in Volume-Based Emission Factors

Because different coatings have different annual sales, emission rates of different coatings should be weighted unequally when estimating uncertainty in average emission factors. In this case study, a method refered as synthetic data set (SDS) was introduced to enable fitting parametric distributions for unequally-weight sample data. This method has been successfully applied on other source categories, such as natural gas engine emissions.[16]

In the SDS method, the market shares of coatings were first calculated based upon their annual sales. Then a synthetic data set, in which a portion of data points were assigned the emission value of a coating in proportion to its market share, was developed. For example, suppose a coating has a VOC emission rate of 2 lb-VOC/gal-coating and a market share of 5 percent. In a synthetic data set with 100 data points, 5 of the 100 data points will be assigned with the emission value of of 2 lb-VOC/gal-coating. Thus, the use of synthetic data set allows emission values to occur repeatedly in proportion to their market shares.

Finally, parametric probability distributions were fitted to the synthetic data set of each coating category. Commonly used non-negative parametric distributions, including lognormal, gamma and Weibull, were chosen as candidates of fitting in this study. As an example, fitted parametric distributions are plotted with the empirical stepwise CDF of the synthetic data set in Figure 7.1 for solvent-based stains. According to Figure 7.1, variability in emission rates ranges from 3 to 7 lb/gal, with a factor of more than 2. Most of the sample data have emission values between 5 and 6 lb/gallon, which represent approximately 80 percent of total sales. Because distributions were fitted to synthetic data sets, conventional goodness-of-fit tests are not applicable. The preferred fitting was selected based upon graphically comparison between the fitted distributions and the empirical CDF of the sample data. For example, Figure 7.1 shows that the Weibull distribution agrees more with the data set than do the lognormal and gamma, especially in the central portion of the distribution. Further, the lognormal and gamma distributions are noticeably more tail-heavy than the Weibull. Thus, the Weibull was selected as the best fit in this case to represent variability in emission rates.

Table 7.1 summarizes the fitted parametric distributions for variability in different coating categories. Some water-based coating categories have large factors of variability, such as a factor of 1250 for water-based stains, because their minimum emission rates are small. Solvent-based coating categories typically have factors of variability from 1.5 to 3. In most cases, the Weibull distribution is more likely to provide a better fit than do the other two distributions because it is typically less tail-heavy and much flexible to assume different shapes.

Bootstrap simulation was used to quantify uncertainties in the CDF and mean of the fitted distribution for each coating category. Quantified uncertainty for solvent-based stains is shown in Figure 7.2. Confidence intervals of uncertainty from bootstrap simulation are overlapped over the fitted Weibull distribution. For example, the absolute 95 percent confidence interval of the median is from 5.4 lb/gallon to 5.9 lb/gallon. In this case, the sample size is large, thus the confidence interval is relative small. The average estimate of the mean is 5.53 lb/gallon, and the absolute 95 percent confidence interval of the mean is from 5.33 to 5.73 lb/gallon. The average estimate of the mean approximates the 44 percentile of the fitted distribution. The percentile of mean is smaller than 50 percentile, which suggests negative skewness in the data set. Figure 7.3 shows bootstrap simulation results based upon a fitted gamma distribution for solvent-based fillers. In this case, variability in emission rates ranges from 3 to 6 lb/gal and the emission value of 3 lb/gal represents approximately 97 percent of total sales. Because only 3 data points are available, the 95 percent confidence interval of the mean is relative wide, with an absolute range of 2.61 to 3.52 lb/gallon and a relative range of minus 15 percent to plus 15 percent.

The quantified uncertainty in the mean emission factors for different coating categories are summarized in Table 7.2. As shown in Table 7.2, the minimum uncertainty range for water-based coatings is approximately from minus 18 percent to plus 21 percent and the maximum uncertainty range is approximately from minus 56 percent to plus 65 percent. Therefore, there are substantial quantified uncertainties in the mean emission factors of water-based coatings. Quantified uncertainties in water-based coatings are all asymmetric. 5 of 7 coatings have positive-skewed confidence intervals for mean emission factors. The confidence intervals for the water-based enamels and fillers are slightly negative-skewed. The asymmetric confidence intervals reflect skewness and small sample size in emission data set.

Except for the colored coatings and fillers, the absolute ranges of uncertainty in the mean emission factors of solvent-based coatings are larger than those of water-based coatings. The relative ranges of uncertainty of solvent-based coatings are all much narrower than those of water-based coatings because the sample sizes and the mean values of solvent-based coatings are typically larger than those of water-based coatings. As shown in Tables 3, 6 of 8 solvent-based coatings have relative uncertainty ranges of smaller than minus 10 percent to plus 10 percent. Further, as the sample size getting large, the uncertainties in mean emission factors of solvent-based coatings are approaching to normality based upon the Central Limit Theorem.

Knowledge of the range of uncertainty also enables rigorous comparison among different coating technology groups. For example, it is clear that water-based coatings have much different average VOC emission rates from the solvent-based coatings because their confidence intervals for the mean emissions never overlap.

7.7 Quantification of Variability and Uncertainty in Coating Usage Factor

The coating usage factor is for all wood furniture coatings combined and has a unit of gallon-coating/employee-year. The coating usage factor is used to estimate the employee level coating consumptions. 44 sample data of usage factor from 44 factories are available in the CARB survey database.[11] These 44 factories all belong to SIC 2511, 2512 and 2521.

Parametric probability distributions were fitted to represent inter-factory variability in the coating usage factor. Bootstrap simulation was used to quantify uncertainty in the mean coating usage factor. However, in this case, sample data were weighted equally because it is not necessary to discriminate different wood furniture factories. The quantitative result for usage factor is given in Figure 7.4.

As shown in Figure 7.4, there is substantial inter-factory variability in the coating usage factor. The sample data vary from approximately 0.25 to approximately 220 gallons per employee-year. The substantial inter-factory variability possibly is attributed to the substantial variations in the size of these 44 factories. Among them, the smallest factory has only 1 worker with a usage factor of 0.25 gal/employee-year, and the largest factory has 250 workers with a usage factor of 106 gal/employee-year. The largest coating usage factor of 218 gal/employee-year occurred at a factory with 45 workers. Therefore the substantial inter-factory variability represents the substantial variations in the employee numbers, work efficiency and other operation conditions among different wood furniture factories.

A fitted Weibull distribution is shown in Figure 7.4 in comparison with the empirical CDF of the data. The shape and scale parameters of the Weibull distribution are 0.7735 and 57.6446, respectively. There is scatter of the data either above or below the fitted distribution, especially in the central part and the tail of the Weibull distribution. However, the deviations of the data are all within the 95 percent confidence interval of the CDF of the Weibull distribution. The mean usage factor was estimated to be 67 gallon/employee-year. The 95 percent confidence interval of the mean usage factor is from 44 to 100 gallon/employee-year, corresponding to a range of minus 35 percent to plus 49 percent compared to the mean value. The skewness in the quantified uncertainty suggestes the skewness in the data set. Although the sample size is relative large, the range of uncertainty is still quite wide, which is attributed to the wide range of inter-factory variability in the data set.

7.8 Development of Probabilistic Employee-Based Emission Factor

For the evaporative loss sources like wood furniture coatings, it is not always possible that sales data for different coatings are readily available for the emission inventory development. Therefore, an employee-based emission factor is used when sales data are absent. Typically, employee- or population-based emission factors for general surface coatings are developed based upon material balance.[3] However, no detailed equation to develop an employee-based emission factor is proposed by EPA in the AP-42. In this study, a material-balance model to develop an employee-based emission factor for wood furniture coatings was proposed. As shown in Eq. 7.1, this model is based upon volume-based emission factors and coating usage factor.

$$EEF = \frac{\sum_{i=1}^{n} VEF_i \times S_i}{\sum_{i=1}^{n} S_i} \times CUF \qquad (7.1)$$

Where:

EEF = employee-based emission factor, lb-VOC/employee-year

VEF_i = volume-based emission factor for i^{th} coating category, lb-VOC/gal-coating

S_i = coating annual sales for i^{th} coating category, gal-coating/year

CUF = coating usage factor, gal-coating/employee-year

n = total number of coating cateogries

In this case study, the Monte Carlo simulation method was used to propagate the probability distributions of uncertainty in model inputs through Eq. 7.1. The simulation was conducted using a commercial software "Crystal Ball." For the volume-based emission factor of each coating category, the input probability distribution is exactly the bootstrap sampling distribution for the mean emission factor. The input probability distribution for the coating usage factor also is the bootstrap sampling distribution. Because there is no sample data available for coating annual sales, judgment was made regarding uncertainty level in coating sales. In this study, normal distribution was assumed to represent uncertainty in average coating sales and a range of minus 10 percent to plus 10 percent of the point estimate of coating sales was assumed to be the 95 percent confidence interval of uncertainty. This assumption was based upon the recommendation of Intergovernmental Panel on Climate Change (IPCC) that the normal distribution is the first choice to represent uncertainties unless the properties of the data suggest another distribution, such as highly non-symmetric data.[17]

A sample size of 1000 was used in the Monte Carlo simulation process. The probability distribution for the employee-based VOC emission factor is presented in Figure 7.5. The mean emission factor was estimated to be 281 lb-VOC/employee-year. The 95 percent confidence interval of the mean emission factor is from 178 to 413 lb-VOC/employee-year, corresponding to a range of minus 37 percent to plus 47 percent compared to the mean value.

The Monte Carlo simulation method also enables the identification of the key sources of uncertainty in model inputs contributing mostly to uncertainty in model output by comparing the rank correlation coefficients (RCCs) between the model inputs and the model output. Typically, a larger RCC of indicates strong dependence of the variation in the model output on the variation of the model input.[13] The reported RCCs by “Crystal Ball” are shown in Figure 7.6. In this case study, the coating usage factor has a RCC close to 1, and all other inputs of the Eq. 7.1 have RCCs smaller than 0.1. Therefore, uncertainty in the usage factor actually dominates the overall uncertainty in the employee-based emission factor. In order to reduce uncertainty in the employee-based emission factor, we strongly recommended more data to be collected for coating usage factor in the future work.

7.9 Conclusions

The procedures of quantification of variability in emission factors and uncertainty in mean emission factors were demonstrated with respect to a case study of wood furniture coatings. First, the large coating database was divided into different categories based upon functional taxonomy. For each coating category, it was initially expected that solvent-based coatings and water-based coatings would product different emission rates. Although it is not possible to conduct hypothesis tests on the population mean because the sample size is not large enough and we would not like to assume normality for the emission data, this *priori* expectation was demonstrated since the quantified confidence intervals for the mean emission factors of solvent-based and water-based coatings never overlap.

Uncertainty associated with statistical random sampling error was quantified based upon bootstrap simulation. Random measurement errors can potentially be another source of uncertainty. However, in the judgment of the investigators, the methods used to measure VOC content in coatings were assumed relatively well-known and of high quality. Therefore, it is expected that the measurement errors are not large with respect to the random sampling errors. Another argument can be made is that if the data contain measurement errors, so do the quantified uncertainties in mean emission factors. As the National Research Council noted in its recent report on mobile source emissions, it is not possible to quantify all sources of uncertainty. Nonetheless, the quantifiable portion of uncertainty should be taken into account when reporting and using emission factors.[7]

In this study, uncertainty ranges in mean volume-based emission factors for water-based coatings were found above minus 30 percent to plus 30 percent in most cases and are not necessary to be symmetric due to skewness in data sets and small sample sizes. Thus, the normality assumption made in early study by UC Davis would be biased, especially for the water-based color coatings, sealers, stains and washcoats.

The quantified uncertainties in mean volume-based emission factors for solvent-based coatings are typically less than minus 10 percent to plus 10 percent because of the large sample sizes. The substantial inter-factory variability in coating usage factor leads to a wide uncertainty range of minus 35 to plus 49 percent in the mean coating usage factor. These observations suggest that uncertainty in the mean is affected by both sample size and variability in population.

Furthermore, a probabilistic employee-based VOC emission factor was developed using Monte Carlo simulation method based upon volume-based emission factors and coating usage factor. The analysis of rank correlation coefficient indicates that uncertainty in coating usage factor actually dominates the overall uncertainty in employee-based emission factor. Keeping the understanding of the key contributor of uncertainty in mind, resources can be prioritized to reduce uncertainty in employee-based emission factor by collecting better and more data for the coating usage factor. Thus, the quantitative methodology demonstrated in this paper is not only for the quality evaluation of the current emission inventories but also for the future emission inventory improvement planning.

7.10 Acknowledgements

We thank U.S. Environmental Protection Agency for the support of this research with STAR Grants Nos. R826766 and R826790. We also especially thank Dr. Robert P. Anex and Dr. Jay R. Lund for providing us the coating survey data.

7.11 References

1. Supplement to the Redesignation Demonstration and Maintenance Plan for the Charlotte/Gastonia Ozone Nonattainment Area, Air Quality Section, NC Department of Environment, Heath and Natural Resources, 1994

2. ISO, Guide to the Expression of Uncertainty in Measurement. ISBN 92-67-10188-9. International Organization for Standardization (ISO), Geneva, Switzerland, 1993.

3. Frey, H. C. Quantitative Analysis of Uncertainty and Variability in Environmental Policy Making, 1992 Environmental Science and Engineering Fellows Program Reports, 1992.

4. EPA, Compilation of Air Pollutant Emission Factors, AP-42, Fifth Edition. US Environmental Protection Agency, 1995.

5. Beck, L. L., Wilson, D. EPA's Data Attribute Rating System, Proceedings, Emission Inventory: Planning for the Future, Air & Waste Management Assoc., Pittsburgh, PA, 1997.

6. National Research Council, *Science and Judgement in Risk Assessment*. National Academy Press: Washington, DC, 1994.

7. National Research Council, Modeling Mobile-Source Emissions. National Academy Press: Washington, DC, 2000.

8. EPA, Guiding Principles for Monte Carlo Analysis, EPA/630R-97/001, US Environmental Protection Agency, DC, 1997.

9. EPA Office of Compliance Sector Notebook Project, Profile of the Wood Furniture and Fixtures Industry, EPA 310-R-95-003, US Environmental Protection Agency, DC, 1995.

10. Procedures for the Preparation of Emission Inventories for Carbon Monoxide and Precursors of Ozone, Vol. I: General Guidance for Stationary Sources, EPA-450/4-91-016, prepared by Alliance Technologies Corporation for EPA, Research Triangle Park, NC, 1991.

11. Anex, R. P., Lund, J. R., Chang, D. P. Y., *Industrial Surface Coatings – Wood Furniture and Fixtures Emission Inventory Development: Final Report*; Prepared by University of California, Davis for California Air Resources Board Research Division, Sacramento, CA, 1998

12. Noordwyk, H. V., Reducing Emissions from the Wood Furniture Industry with Waterborne Coatings, EPA-600/2-80-160, Prepared by Acurex Corporation for U.S. EPA, Cincinnati, OH, 1980

13. Cullen, A. C., Frey, H. C. Probabilistic Techniques in Exposure Assessment: A Handbook for Dealing with Variability and Uncertainty in Risk Analysis; Plenum Press: New York, 1999.

14. Report of the Workshop on Selecting Input Distributions for Probabilistic Assessments; Prepared by Eastern Research Group, Inc., Lexington, MA, for US. Environmental Protection Agency: Washington, DC, 1998.

15. Efron, B., “Bootstrap Methods: Another Look at the Jackknife”, *Annals of Statistics*, 1979, 7(1), 1-26

16. Frey, H. C., Li, S., “Quantification of Variability and Uncertainty in Stationary Natural Gas-fueled Internal Combustion Engine NOx and Total Organic Compounds Emission Factor”, Proceedings, Annual Meeting of the Air & Waste Management Association, Pittsburgh, PA, 2001.

17. IPCC National Greenhouse Gas Inventories Program, Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories. Intergovernmental Panel on Climate Change (IPCC), 2000.

Table 7.1. Fitted Parametric Distributions for Variability in Volume-Based VOC Emission Factors for Wood Furniture Coatings

Coating Category	Carrier Medium	Min [a]	Max [a]	Ratio, Max to Min	Fitted Dist.[b]	Shape Parameter	Scale Parameter
Colored coatings	Water	0.040	2.09	52	W	1.5799	0.2593
	Solvent	2.50	7.10	2.8	W	8.7575	5.7055
Enamels	Water	1.05	2.09	2.0	W	4.4100	1.8991
	Solvent	2.92	5.38	1.8	W	7.9955	4.8126
Fillers	Water	0.310	2.20	7.1	W	4.1609	1.6832
	Solvent	3.00	6.00	2.0	G	50.882	0.0603
Sealers	Water	0.088	2.50	28	W	1.3875	1.7984
	Solvent	3.34	6.00	1.8	W	38.318	5.6474
Stains	Water	0.002	2.50	1250	W	1.0619	0.7240
	Solvent	2.92	6.70	2.3	W	10.144	5.8080
Thinners	Solvent	5.34	8.00	1.5	W	16.343	6.7196
Topcoats	Water	0.83	2.50	3.0	W	2.5589	1.5684
	Solvent	3.75	5.80	1.6	W	16.117	5.6182
Washcoats	Water	0.26	2.29	8.8	W	1.9137	1.8269
	Solvent	3.50	5.50	1.6	W	12.150	5.3412

[a] Unit: lb-VOC/gallon-coating.

[b] W = Weibull, MLE parameter estimation; G = gamma, MoMM parameter estimation.

Table 7.2. Quantified Uncertainty in Mean Volume-Based VOC Emission Factors for Wood Furniture Coatings

Coating Category	Carrier Medium	Bootstrap Sample Size	Mean of Bootstrap Means[a,b]	Absolute 95% CI of Mean[a,b]	Relative 95% CI of Mean (%)[b]
Colored coatings	Water	6	0.23	0.12 to 0.36	-46 to 55
	Solvent	17	5.39	5.01 to 5.77	-7.1 to 7.0
Enamels	Water	3	1.72	1.19 to 2.23	-31 to 29
	Solvent	6	4.52	3.99 to 5.02	-12 to 11
Fillers	Water	4	1.54	1.10 to 1.90	-28 to 24
	Solvent	3	3.05	2.61 to3.52	-15 to 15
Sealers	Water	11	1.66	1.03 to 2.45	-38 to 48
	Solvent	28	5.57	5.49 to 5.63	-1.3 to 1.2
Stains	Water	17	0.70	0.43 to 1.03	-39 to 48
	Solvent	46	5.53	5.33 to 5.73	-3.6 to 3.5
Thinners	Solvent	37	6.51	6.35 to 6.68	-2.5 to 2.6
Topcoats	Water	20	1.39	1.14 to 1.67	-18 to 21
	Solvent	33	5.44	5.30 to 5.58	-2.5 to 2.6
Washcoats	Water	3	1.64	0.73 to 2.71	-56 to 65
	Solvent	6	5.13	4.69 to 5.50	-8.6 to 7.3

[a] Unit: lb-VOC/gallon-coating.
[b] Estimated from bootstrap simulation based upon fitted parametric distributions for variability..

Table 7.3. Input Uncertainty Assumptions for Employee-Based Emission Factor Model for Wood Furniture Coatings

Model inputs		Input assumption of uncertainty
Water-based colored coatings	Volume-based emission factor	bootstrap sampling distribution for the mean
	Annual sales	Normal distribution
Solvent-based colored coatings	Volume-based emission factor	bootstrap sampling distribution for the mean
	Annual sales	Normal distribution
Water-based enamels	Volume-based emission factor	bootstrap sampling distribution for the mean
	Annual sales	Normal distribution
Solvent-based enamels	Volume-based emission factor	bootstrap sampling distribution for the mean
	Annual sales	Normal distribution
Water-based fillers	Volume-based emission factor	bootstrap sampling distribution for the mean
	Annual sales	Normal distribution
Solvent-based fillers	Volume-based emission factor	bootstrap sampling distribution for the mean
	Annual sales	Normal distribution
Water-based sealers	Volume-based emission factor	bootstrap sampling distribution for the mean
	Annual sales	Normal distribution
Solvent-based sealers	Volume-based emission factor	bootstrap sampling distribution for the mean
	Annual sales	Normal distribution
Water-based stains	Volume-based emission factor	bootstrap sampling distribution for the mean
	Annual sales	Normal distribution
Solvent-based stains	Volume-based emission factor	bootstrap sampling distribution for the mean
	Annual sales	Normal distribution
Solvent-based thinners	Volume-based emission factor	bootstrap sampling distribution for the mean
	Annual sales	Normal distribution
Water-based topcoats	Volume-based emission factor	bootstrap sampling distribution for the mean
	Annual sales	Normal distribution
Solvent-based topcoats	Volume-based emission factor	bootstrap sampling distribution for the mean
	Annual sales	Normal distribution
Water-based washcoats	Volume-based emission factor	bootstrap sampling distribution for the mean
	Annual sales	Normal distribution
Solvent-based washcoats	Volume-based emission factor	bootstrap sampling distribution for the mean
	Annual sales	Normal distribution
Coating Usage Factor		bootstrap sampling distribution for the mean

Figure 7.1. Fitted Parametric Probability Distributions and Market-share Weighted Empirical Cumulative Distribution Function for VOC Emission factor of Solvent-Based Stains

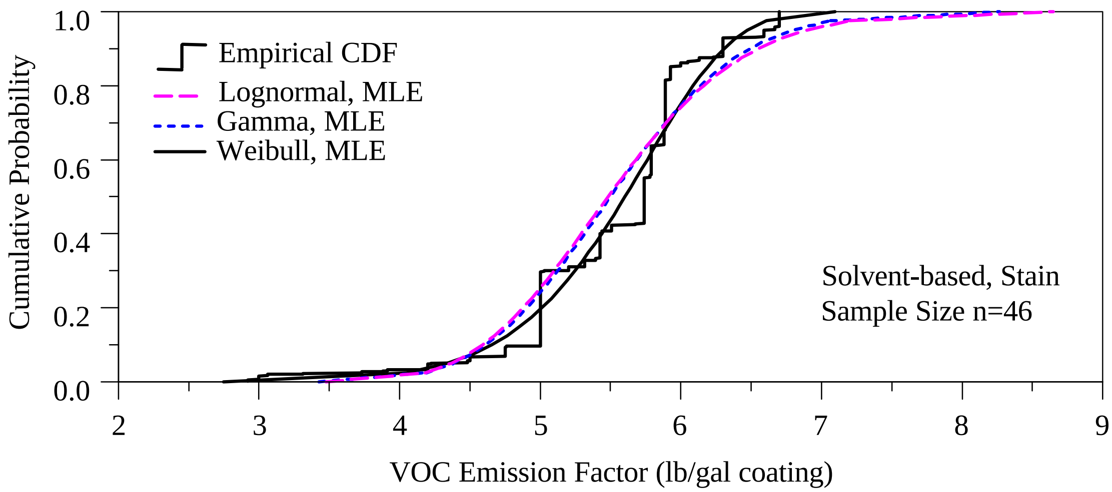


Figure 7.2. Bootstrap Simulation Results Based Upon Fitted Weibull Distribution for Market-Share Weighted VOC Emission factor of Solvent-Based Stains

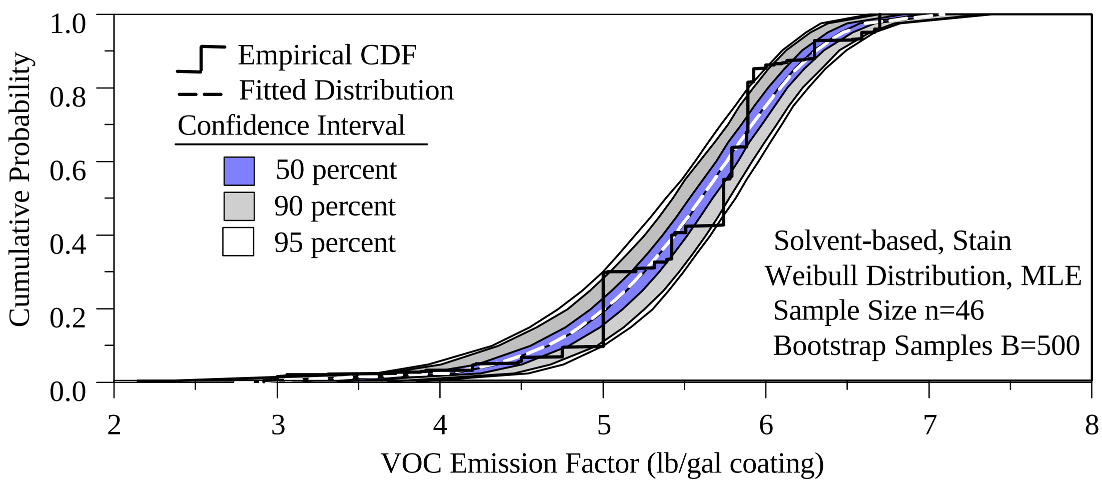


Figure 7.3. Bootstrap Simulation Results Based Upon Fitted Gamma Distribution for Market-Share Weighted VOC Emission factor of Solvent-Based Fillers

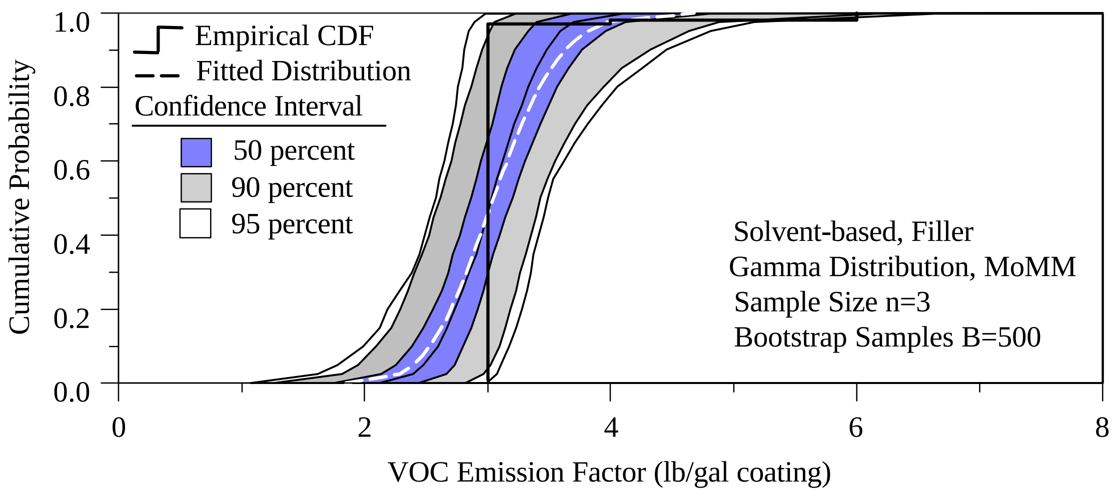


Figure 7.4. Bootstrap Simulation Results Based Upon Fitted Weibull Distribution for Architecture Coating Usage Factor

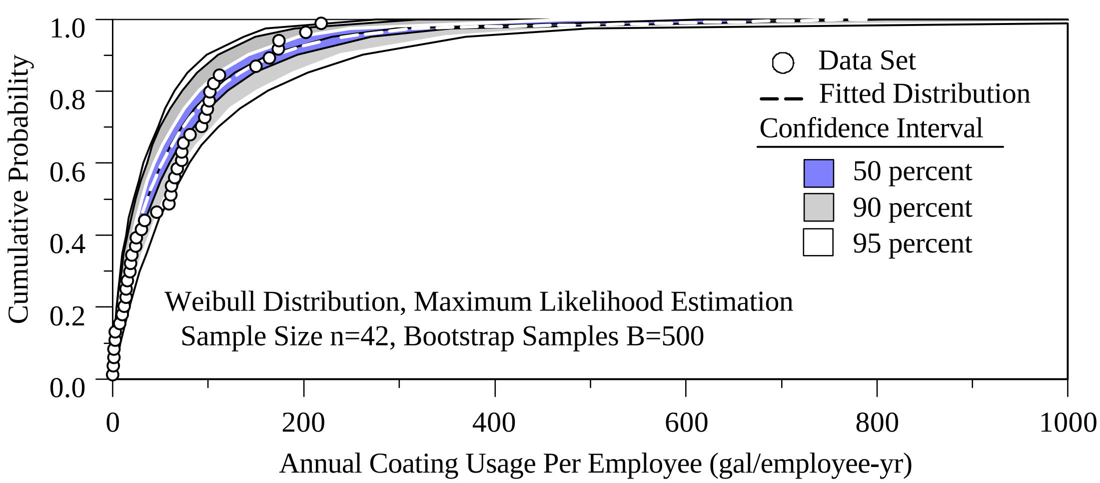


Figure 7.5. Quantified Uncertainty in the Per-Employee VOC Emission Factor for Wood Furniture Coatings

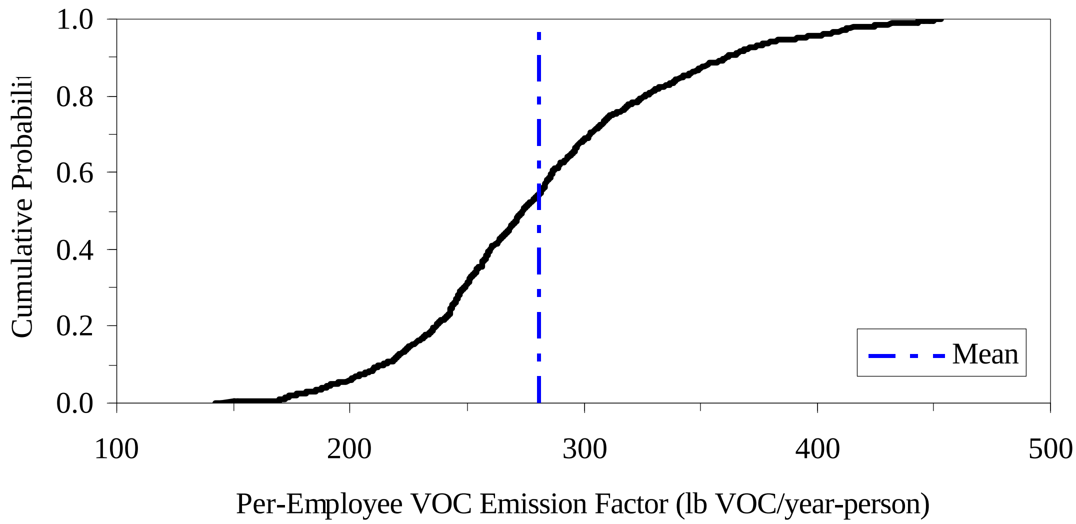
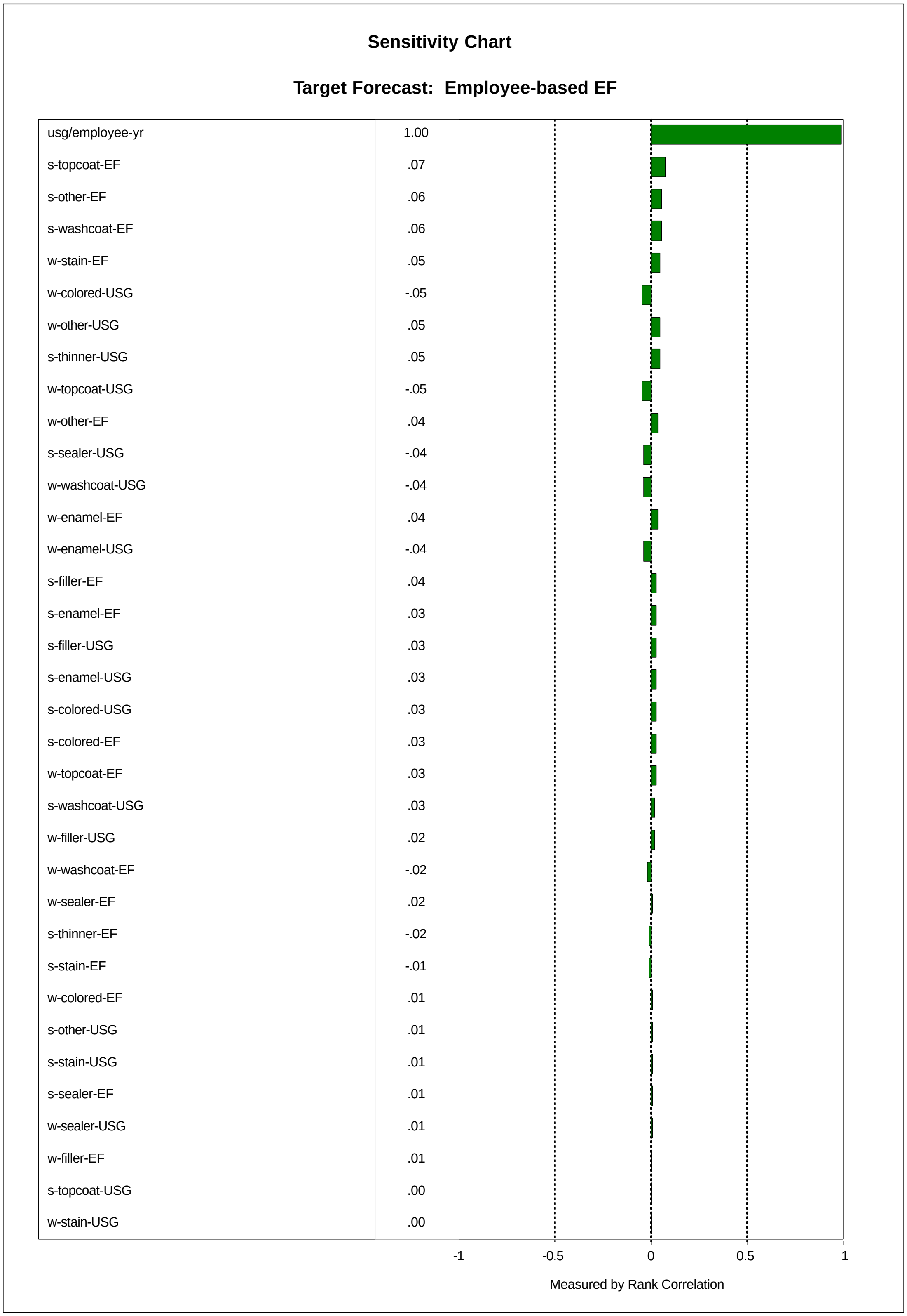


Figure 7.6. Rank Correlation Coefficients Reported by "Crystal Ball" for Input Assumptions of Employee-Based Emission Factor Model for Wood Furniture Coatings



8.0 DISCUSSION AND RECOMMENDATIONS

This work demonstrated new applications of quantitative methods for characterizing variability and uncertainty in emission estimates. The methods were demonstrated with respect to cases studies on NO_x and VOC emissions from natural gas-fueled internal combustion engines, VOC emissions from consumer/commercial product use, VOC emissions from gasoline terminal loading, VOC emissions from cutback asphalt paving, VOC emissions from architectural coatings and VOC emissions from wood furniture coatings. Except for wood furniture coatings, this work is the first known effort to characterize variability and uncertainty in these source categories.

The key questions addressed in this study include:

- Why should variability and uncertainty be distinguished?
- What methods should be used to quantify uncertainty in emission factors?
- How should intra-engine/facility variability be handled in quantitative analysis for mean emission factors?
- What method can be used for unequally weighted data?
- What is the range of variability in product compositions and emission estimates?
- What is the range of uncertainty in mean emission factors?

8.1 Distinction of Variability and Uncertainty

Emission factors are subject to both variability and uncertainty. Variability refers to observed differences attributable to true heterogeneity or diversity in emissions.

Uncertainty refers to lack of knowledge regarding the true value of emissions. Separation of variability and uncertainty provides different insights into emission estimations. Characterization of variability aids in understanding how emissions vary with respect to time, space and other factors. Quantification of uncertainty aids in establishing the level of confidence with respect to emission estimates and benefits future efforts of data collection to reduce uncertainty.

8.2 Methodology for Quantification of Uncertainty in Emission Factors

Emission sample data must be nonnegative, typically are positively skewed and have limited sample size. The restrictive assumption of normality used in analytical methods can lead to biased results in uncertainty estimates. Therefore, in this work, numerical methods based upon fitting parametric distributions and bootstrap simulation were applied to quantify uncertainties in emission sample data.

Typically, a quantitative analysis based upon sample data is desirable. However, as the IPCC pointed out in its good practice guidance, when sample information is scarce or unavailable, the use of judgment to define uncertainty range is necessary. Therefore, in practice, there will always be a role for judgment-based approaches to be used in compensation to sample-based approaches.

Some sources of uncertainty are difficult to quantify, such as non-representativeness of a data set. Therefore, qualitative assessment regarding non-quantifiable uncertainty is important. It is critical to judge the quality of data and prepare the data with good representativeness for quantitative analysis. Thus, an argument can be made that qualitative assessment should be used in combination with quantitative approaches. As the National Research Council noted in its recent report, it is not possible to quantify all sources of uncertainty. Nonetheless, the quantifiable portion of uncertainty should be taken into account when reporting and using emission factors.

8.3 Separation of Intra- and Inter-Facility/Engine Variability

A special concern in the quantitative analysis of emission factors is to properly distinguish intra- and inter-facility/engine variability. The main objective in the emission factor development is to quantify the inter-facility/engine variability because an emission factor represents the emission rate for entire population, and not for a specific engine/facility. If the intra-facility/engine variability was not separated from the inter-facility/engine variability, a facility/engine with many repeated measurements would be given more weight than a facility with few repeated measurements. Therefore, it is important to remove the intra-facility/engine variability by averaging the repeated measurements before the quantification of uncertainty in emission factors.

8.4 Methodology for Unequally Weighted Data

Emission values sometime come with market share information. Because different emission values have different market shares, they should not be weighted equally in the characterization of uncertainty in average emission factors. In this case, the conventional method for fitting distributions to the data was modified compared to when data were equally weighted. The approach taken in this work was to use a synthetic data set as a basis, in which a portion of the data points were assigned the emission value in proportion to its market share. Thus, the use of the synthetic data set allows for emission values to occur repeatedly in proportion to their market share and distributions could be fitted to a synthetic data set that contains unequally weighting information.

Table 8.1. Typical Parametric Distributions for Representing Variability and Highest Quantified Uncertainty in Selected Emission Source Categories

Quantity[a]	Typical Parametric Distribution for Variability	Highest Relative 95 Percent CI of Uncertainty (%)
EF, Natural Gas Engine, 1996 version	Weibull	-56 to +67
EF, Natural Gas Engine, 2000 version	Gamma and Weibull	-90 to +180
VOC Content, Consumer Product	Beta	-79 to +130
Per-Capita EF, Consumer Product[b]	N/A	-7.7 to +8.4
EF, Gasoline Terminal	Gamma	-67 to +110
Volume-Based EF, Cutback Asphalt Paving[b]	N/A	-11 to +12
Volume-Based EF, Solvent-Borne Architectural Coating	Gamma	-8.2 to +9.3
Volume-Based EF, Water-Borne Architectural Coating	Weibull	-20 to +20
Volume-Based EF, Solvent-Borne Wood Furniture Coating	Weibull	-15 to +15
Volume-Based EF, Water-Borne Wood Furniture Coating	Weibull	-56 to +65
Employee-Based EF, all Wood Furniture Coating[b]	N/A	-37 to +47
Usage Factor, all Wood Furniture Coating	Weibull	-35 to +49

[a] EF = emission factor
[b] Based upon Monte Carlo Simulation results for uncertainty, no sample data was available to quantify variability

8.5 Quantified Variability and Uncertainty in Selected Emission Source Categories

A summary of results is given in Table 8.1, showing the typical parametric distributions selected to represent variability and the highest quantified uncertainty for the selected emission source categories. The quantified uncertainty is approximately as much as minus 90 percent to plus 180 percent in a relative basis. The wide range of uncertainty in some emission factors emphasizes the importance of quantitative uncertainty analysis.

8.6 Recommendations

It is worthy to mention that the quantified source categories merely account for 27 percent of total VOC emissions in Charlotte airshed, and other important VOC source categories, such as printing industry, are recommended to be quantitatively analyzed in the future.

A significant difficulty encountered in this study was to obtain complete and well-documented emission database. For example, it was difficult to get some supporting test reports and database from EPA and local environmental protection agencies. In the case of natural gas-fueled engines, although the database is available, the lack of detailed documentation of the data and calculation methods prevents others from reproducing the calculations and results. Therefore, we recommend that EPA report the data actually used and the complete calculation methods used for each emission factor. Such information is ideally compiled in a straightforward format, subject to quality assurance and widely available to publics, such as online database. Furthermore, with the growing recognition of the importance of quantitative uncertainty analysis, it will be important for EPA and others to routinely report data regarding variability and uncertainty in emission factors.

APPENDIX A. DEVELOPMENT OF UNCERTAINTY FACTOR OF EMISSION INVENTORY FOR SELECTED SOURCE CATEGORIES

Equation for point estimate of emission inventory:

$$EI_{point} = EF \times AF \tag{A.1}$$

Where:

EI_{point}, point estimate of emission inventory

EF, emission factor

AF, activity factor

Equation for Probabilistic estimate of Emission Inventory:

$$\begin{aligned} & EI_{prob} \\ & = (EF \times UF_{EF}) \times (AF \times UF_{AF}) \\ & = (EF \times AF) \times (UF_{EF} \times UF_{AF}) \\ & = EI_{point} \times UF_{EI} \end{aligned} \tag{A.2}$$

Where:

EI_{prob}, probabilistic estimate of emission inventory

EF, emission factor

AF, activity factor

UF_{EF}, uncertainty factor for emission factor

UF_{AF}, uncertainty factor for activity factor

EI_{point}, point estimate of emission inventory

UF_{EI}, uncertainty factor for emission inventory

$$UF_{EI} = UF_{EF} \times UF_{AF} \tag{A.3}$$

Monte Carlo Simulation is used to propagate UF_{EF} and UF_{AF}, through Eq. A.3 to develop a UF_{AF}. Input assumptions are given in Table A.1. Input empirical sampling distributions were normalized, which were obtained by dividing empirical sample data points by the mean of the sample. Thus, a normalized sampling distribution has the mean of 1.

Table A.1 Input Assumptions for Uncertainty Factor of Emission Inventory for Selected Source Categories

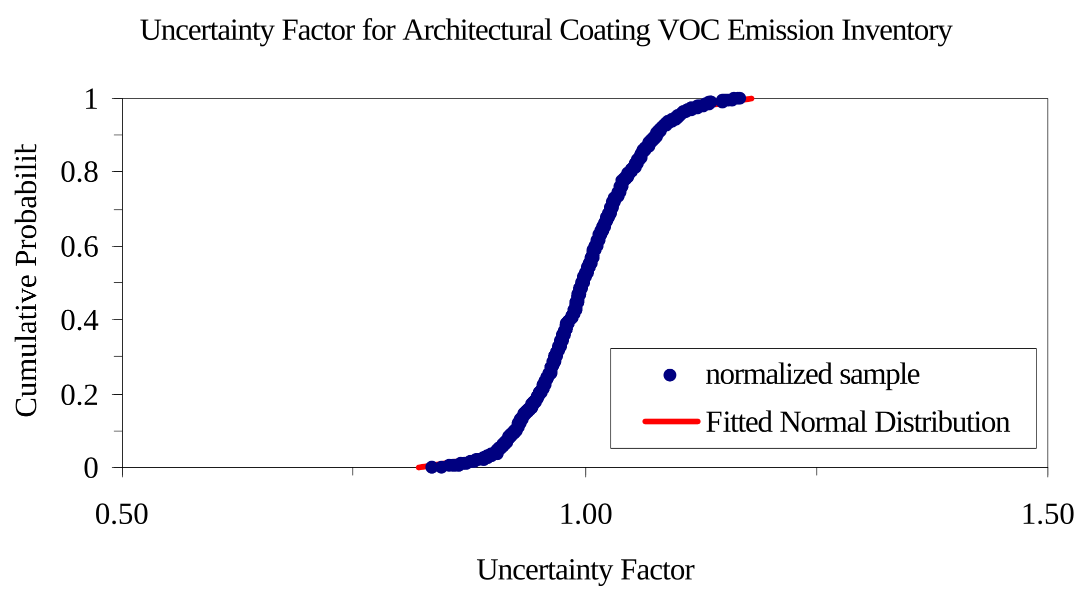
Source Category	Emission factor type	UF_{EF}, uncertainty factor for emission factor[a]	Activity factor type	UF_{AF}, uncertainty factor for activity factor[a,b]
2-stroke lean burn uncontrolled Natural Gas-fueled Compressor Engine[c]	lb NO_x per BTU	normalized bootstrap sampling distribution	Annual BTU	N(1, 0.0026)
Wood Furniture Coating	Per-employee	normalized Monte Carlo sampling distribution	Num of employee	point estimate, no distribution assigned
Cutback Asphalt paving	Volume-based	normalized Monte Carlo sampling distribution	Annual usage volume	N(1, 0.0026)
Consumer solvents	Per-capita	normalized Monte Carlo sampling distribution	Population	point estimate, no distribution assigned
Architectural coating	Volume-based	normalized bootstrap sampling distribution	Annual sales volume	N(1, 0.0026)
Gasoline terminal	mg VOC per liter gas loaded	normalized bootstrap sampling distribution	Annual gas loaded	N(1, 0.0026)

[a] no unit, normalized sampling distribution has mean equals to 1.
[b] N(1, 0.0026) refers to normal distribution with mean = 1 and variance = 0.0026
[c] only 2-stroke lean burn uncontrolled engines are installed in Charlotte airshed.

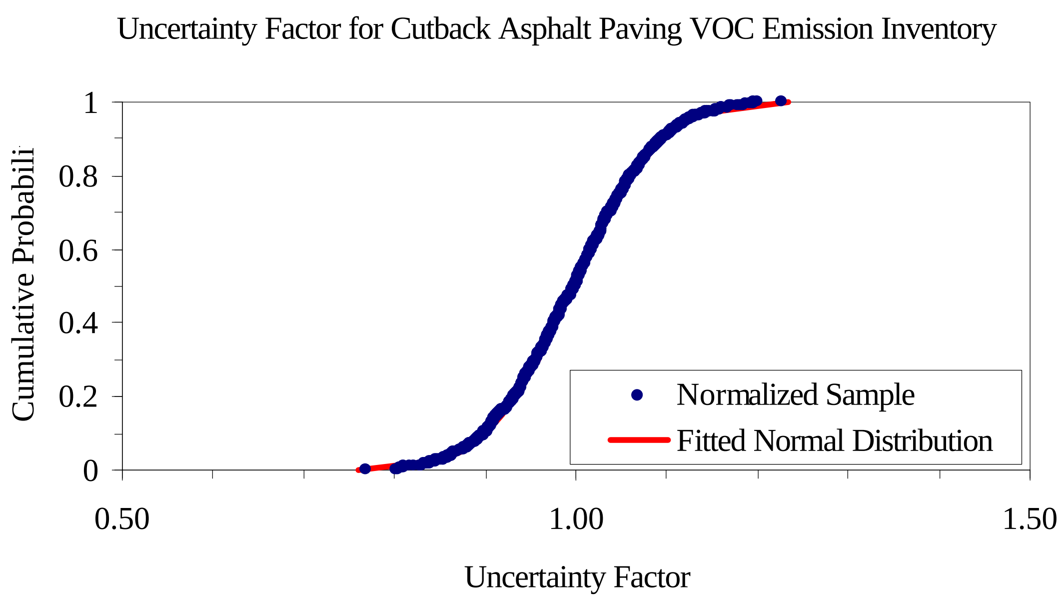
Table A.2 Fitted Parametric Distributions for Uncertainty Factors of Emission Inventories for Selected Source Categories

SCC	SCC description	Dist.[a]	Parameters[b]	
			1st para.	2nd para.
VOC				
2401001000	Surface Coating - Architectural Coatings	N	1	0.058
2461021000	Cutback Asphalt Paving	N	1	0.077
2465900000	Consumer/Commercial Products	N	1	0.040
40600301	Transportation and Marketing of Petroleum Products – Major Groups 44, 45, & 51, Gasoline Retail Operations – Stage I, Splash Filling	G	12.7	0.0785
40600302	Transportation and Marketing of Petroleum Products – Major Groups 44, 45, & 51, Gasoline Retail Operations – Stage I, Submerged Filling w/o Controls	N	1	0.14
40201901	Surface Coating Operations - Major Groups 22-37, Wood Furniture Surface Coating, Coating	G	24.56	0.41
20200202	2SLB Internal Combustion Engines - Industrial, Natural Gas, Reciprocating	G	98.48	0.0101
NO_x				
20200202	2SLB, 90% to 105% load, Internal Combustion Engines - Industrial, Natural Gas, Reciprocating	N	1	0.13

a N=normal distribution; W=Weibull distribution; G=gamma distribution
b Normal distribution: 1st parameter is mean; 2nd parameter is standard deviation; gamma distribution: 1st parameter is shape parameter *r*, 2nd parameter is scale parameter l.

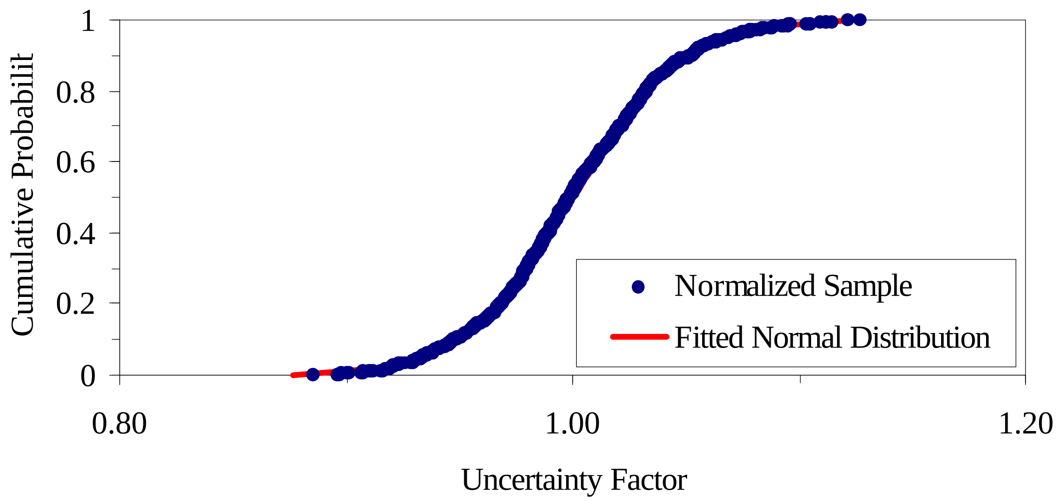


Uncertainty Factor for Architectural Coating VOC Emission Inventory
Cumulative Probabilit
1
0.8
0.6
0.4
0.2
0
0.50
1.00
1.50
Uncertainty Factor
normalized sample
Fitted Normal Distribution

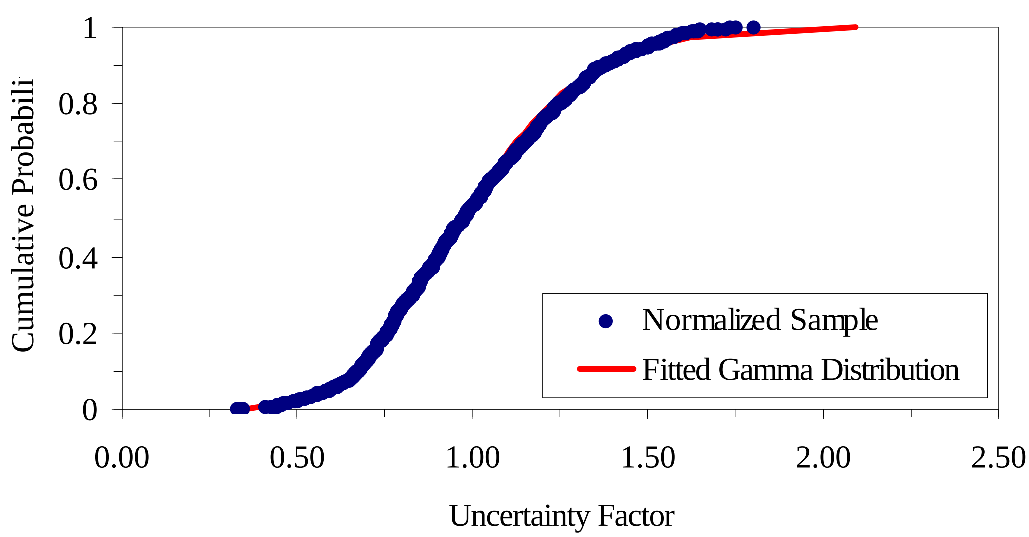


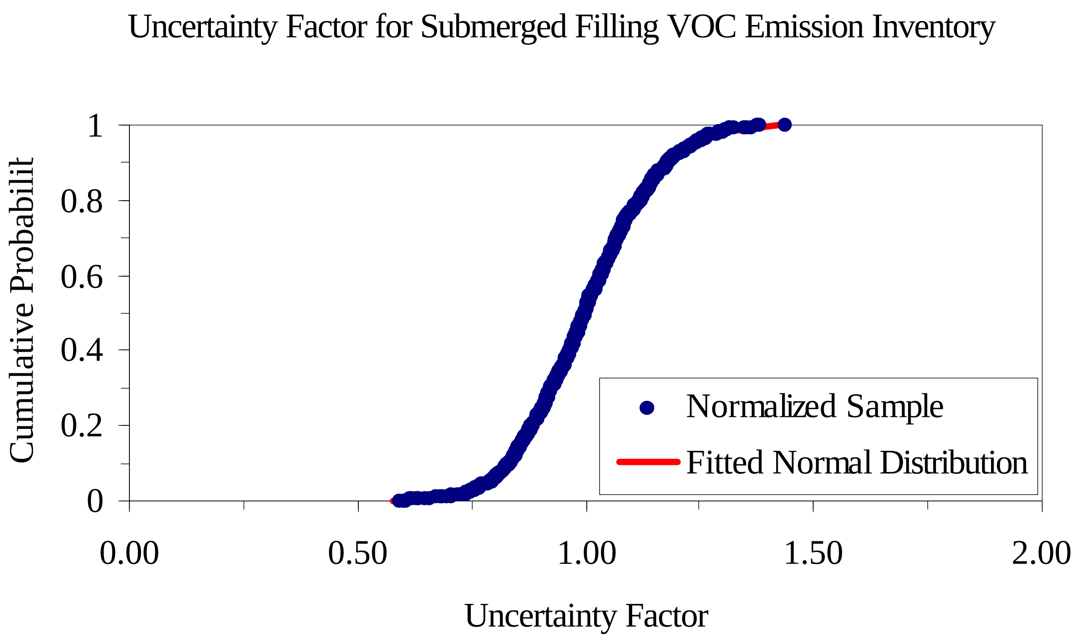
Uncertainty Factor for Cutback Asphalt Paving VOC Emission Inventory
Cumulative Probabili
1
0.8
0.6
0.4
0.2
0
0.50
1.00
1.50
Uncertainty Factor
Normalized Sample
Fitted Normal Distribution

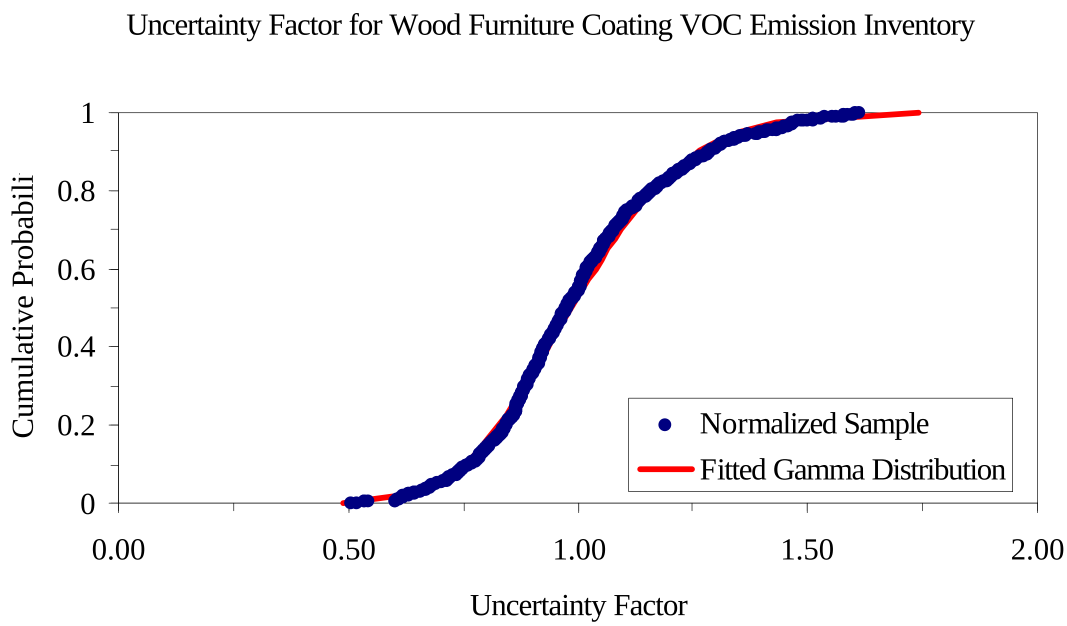
Uncertainty Factor for Consumer Solvent VOC Emission Inventory



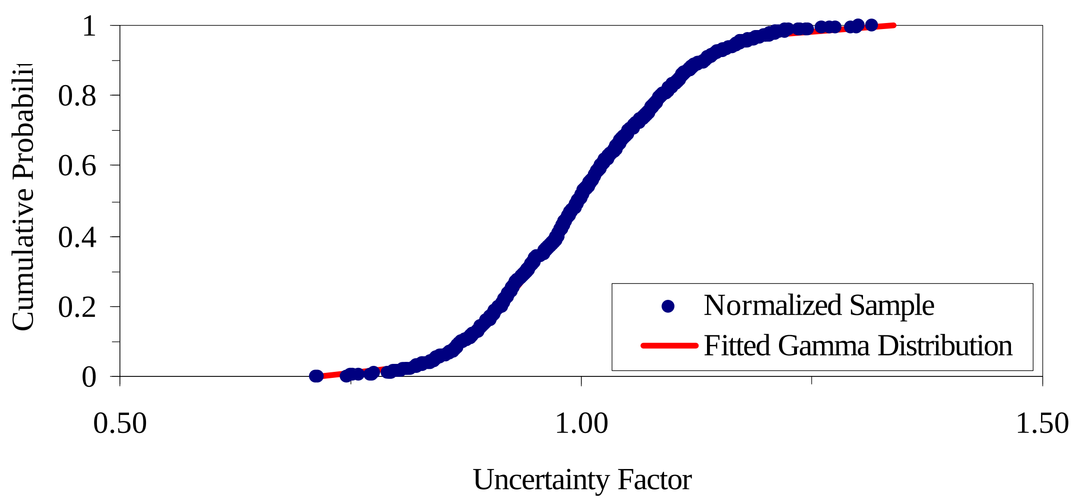
Uncertainty Facotr for Splash Filling VOC Emission Inventory



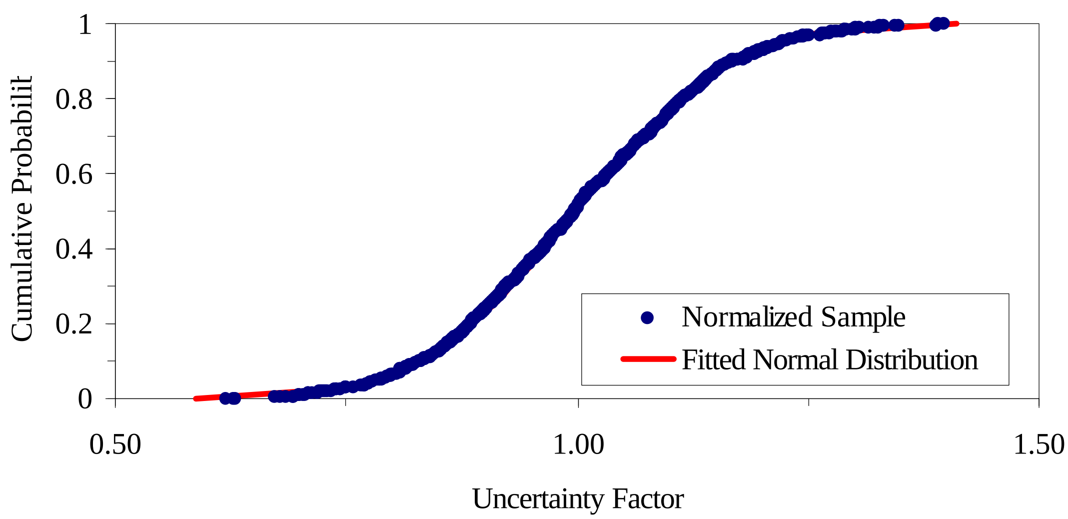

Uncertainty Factor for Submerged Filling VOC Emission Inventory
Cumulative Probabilit
1
0.8
0.6
0.4
0.2
0
0.00
0.50
1.00
1.50
2.00
Uncertainty Factor
Normalized Sample
Fitted Normal Distribution


Uncertainty Factor for Wood Furniture Coating VOC Emission Inventory
Cumulative Probabili
1
0.8
0.6
0.4
0.2
0
0.00
0.50
1.00
1.50
2.00
Uncertainty Factor
Normalized Sample
Fitted Gamma Distribution

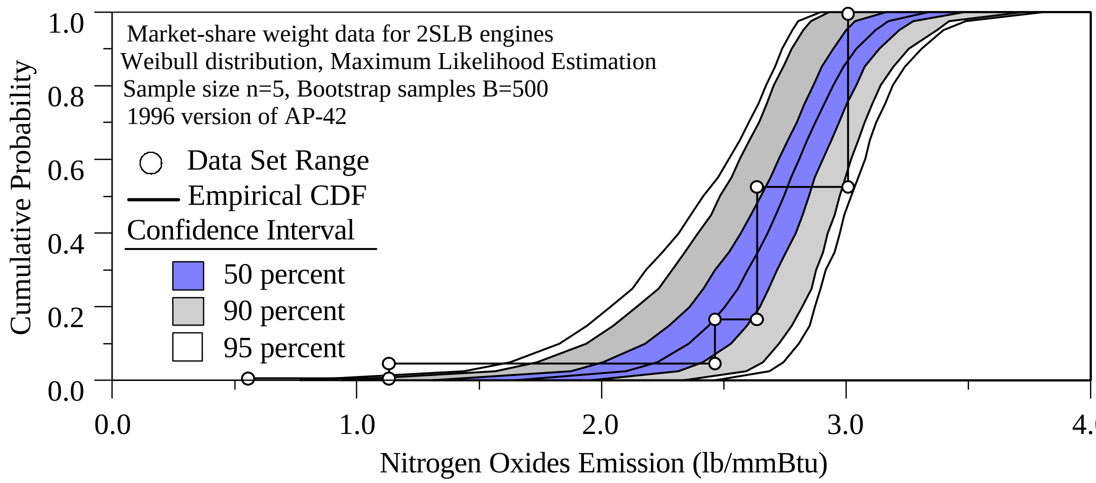
Uncertainty Factor for 2-Stroke Lean Burn Natural Gas Engine VOC Emission Inventory

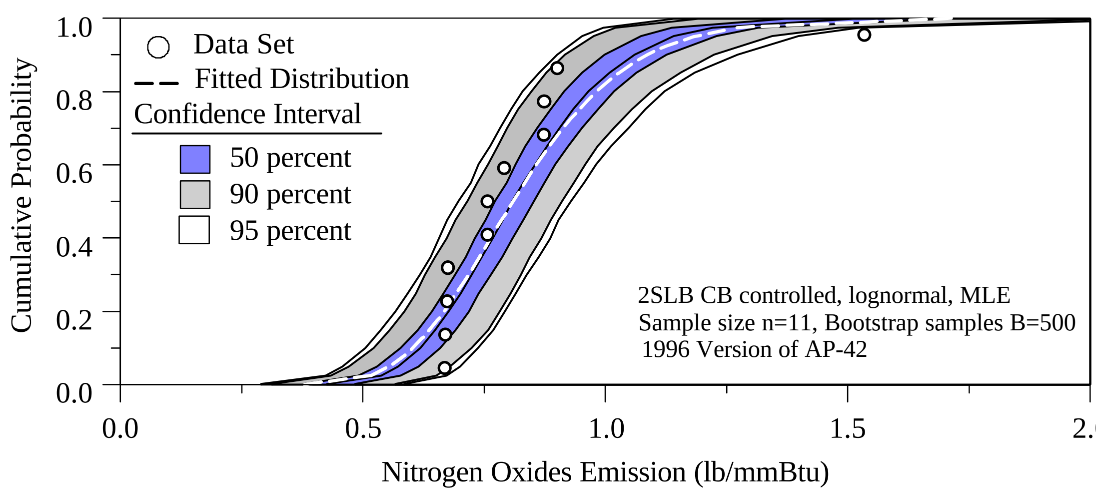


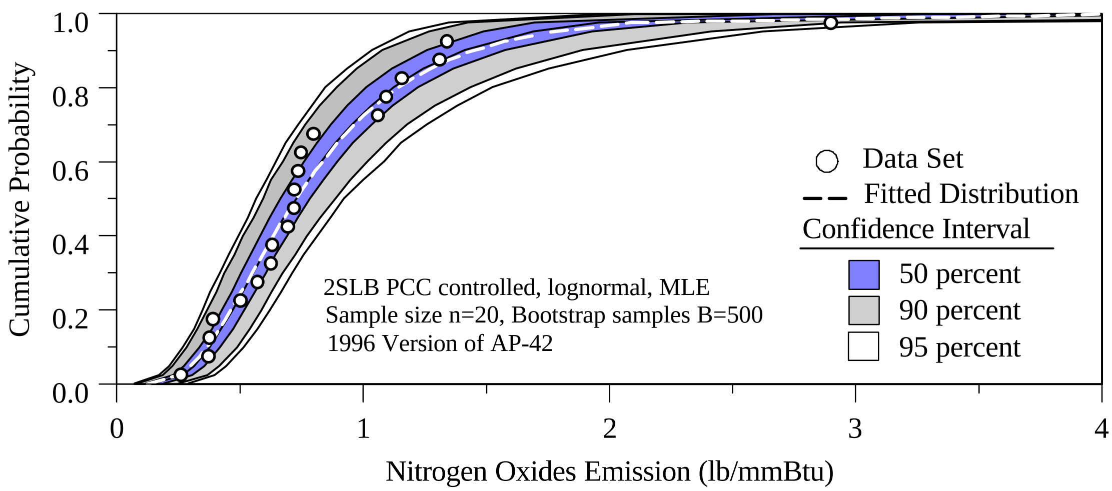
Uncertainty Factor for 2-Stroke Lean Burn (90-105% load) Natural Gas Engine NO_x Emission Inventory

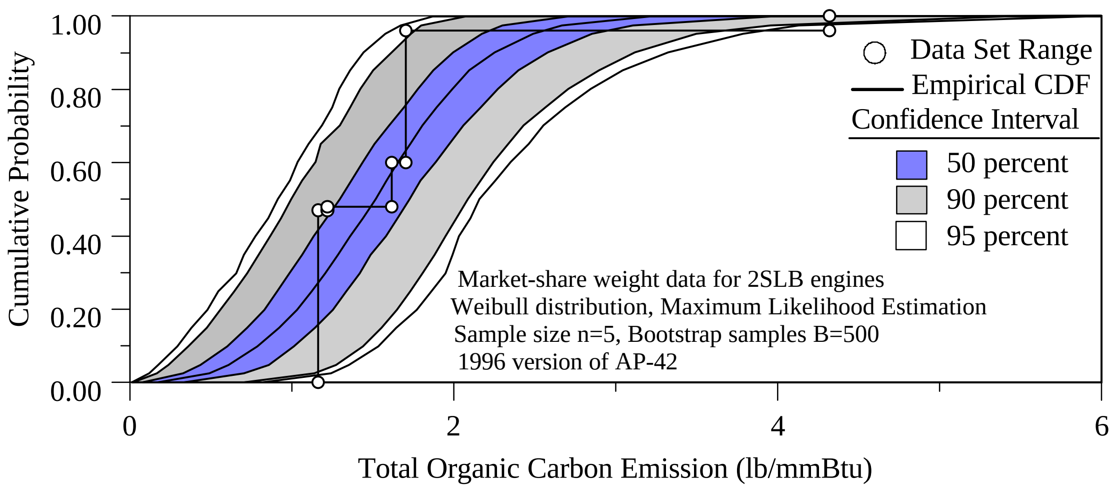


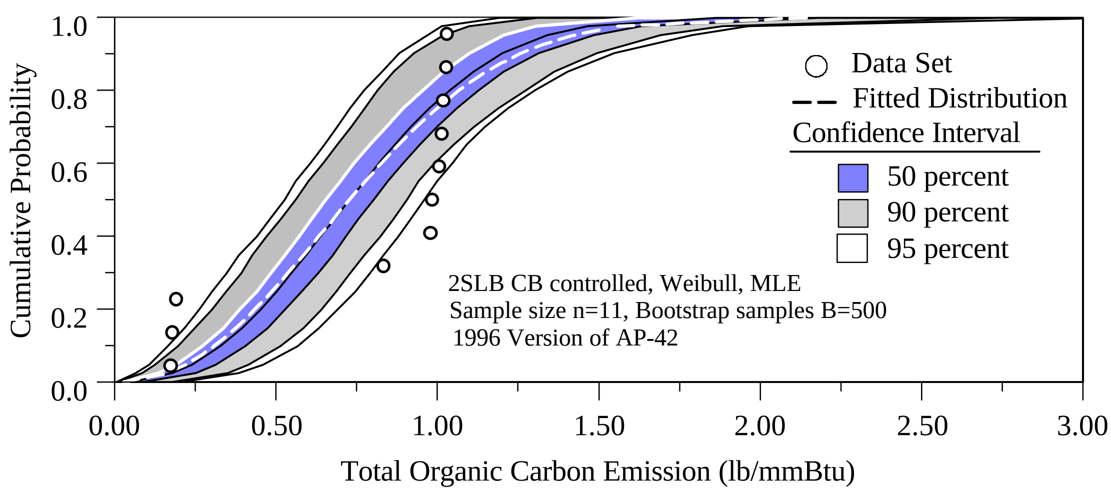
APPENDIX B. BOOTSTRAP SIMULATION GRAPHS FOR NATURAL GAS-FUELED INTERNAL COMBUSTION ENIGNES

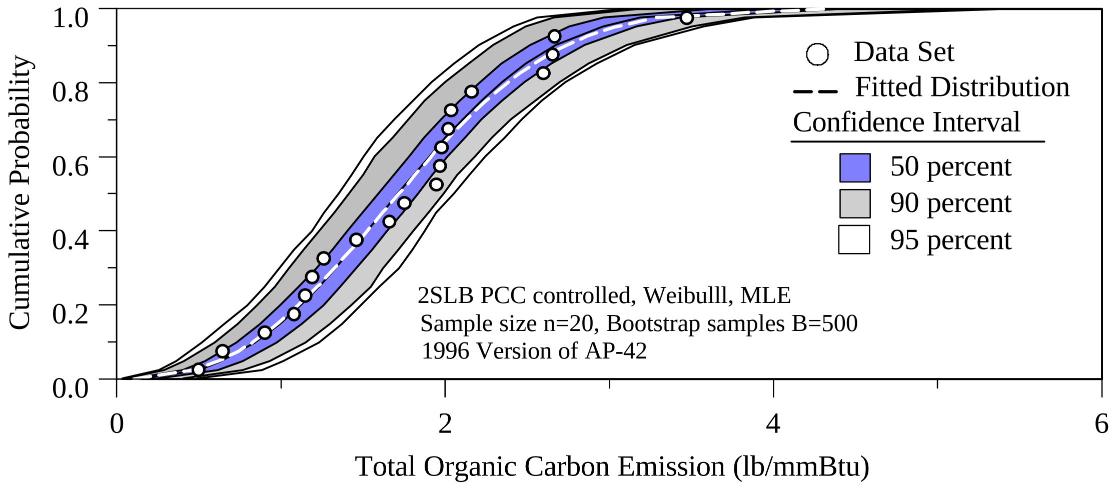


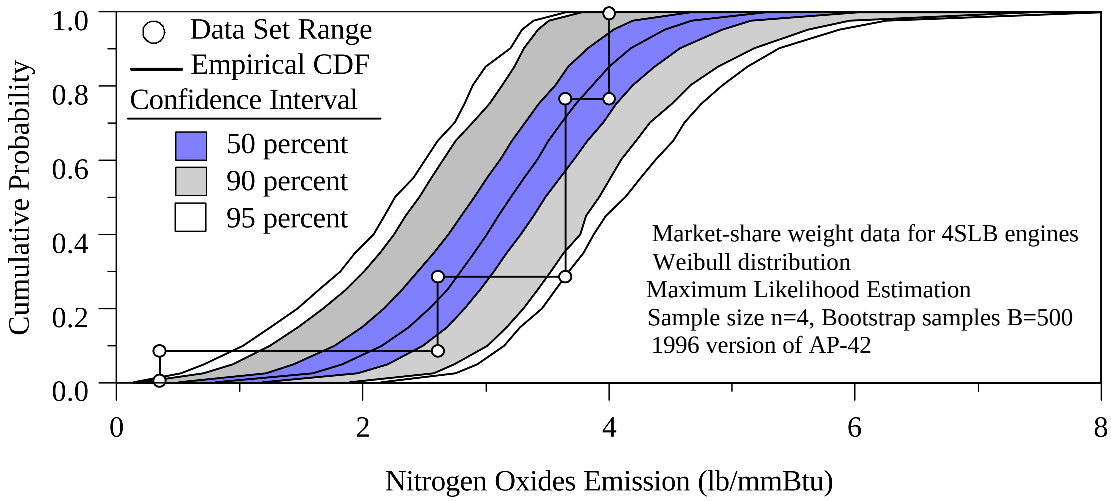


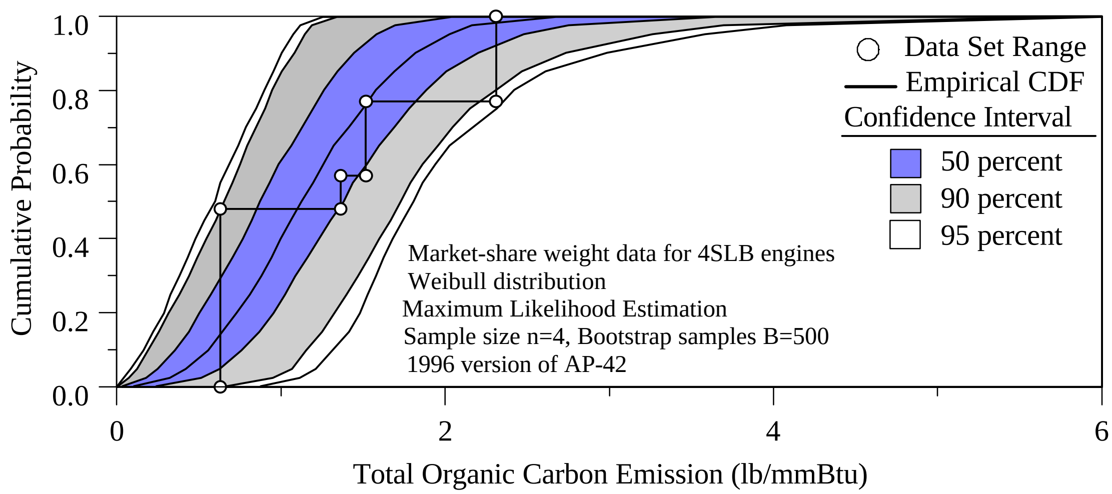

Cumulative Probability
1.0
0.8
0.6
0.4
0.2
0.0
0
1
2
3
4
Nitrogen Oxides Emission (lb/mmBtu)
Data Set
Fitted Distribution
Confidence Interval
50 percent
90 percent
95 percent
2SLB PCC controlled, lognormal, MLE
Sample size n=20, Bootstrap samples B=500
1996 Version of AP-42

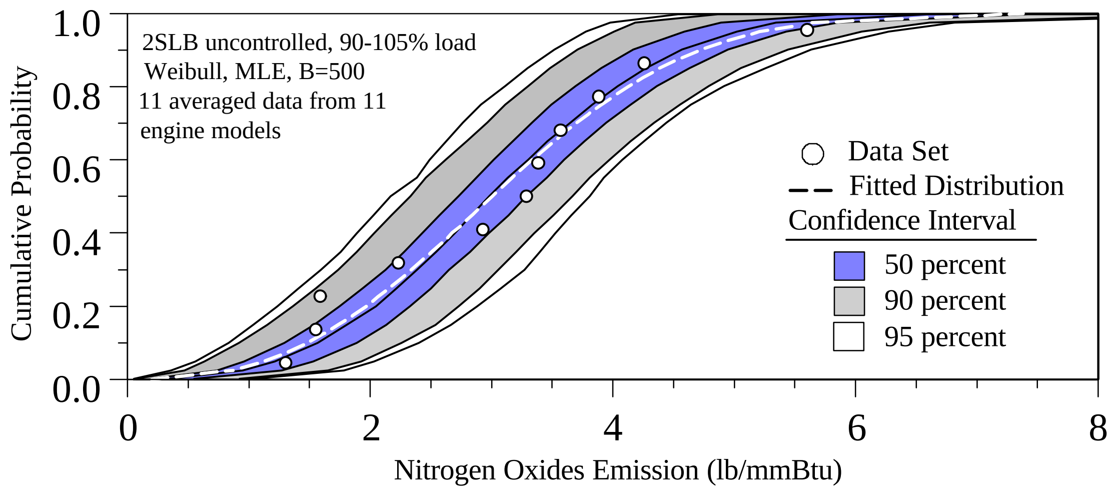

Cumulative Probability
1.00
0.80
0.60
0.40
0.20
0.00
0
2
4
6
Total Organic Carbon Emission (lb/mmBtu)
Data Set Range
Empirical CDF
Confidence Interval
50 percent
90 percent
95 percent
Market-share weight data for 2SLB engines
Weibull distribution, Maximum Likelihood Estimation
Sample size n=5, Bootstrap samples B=500
1996 version of AP-42

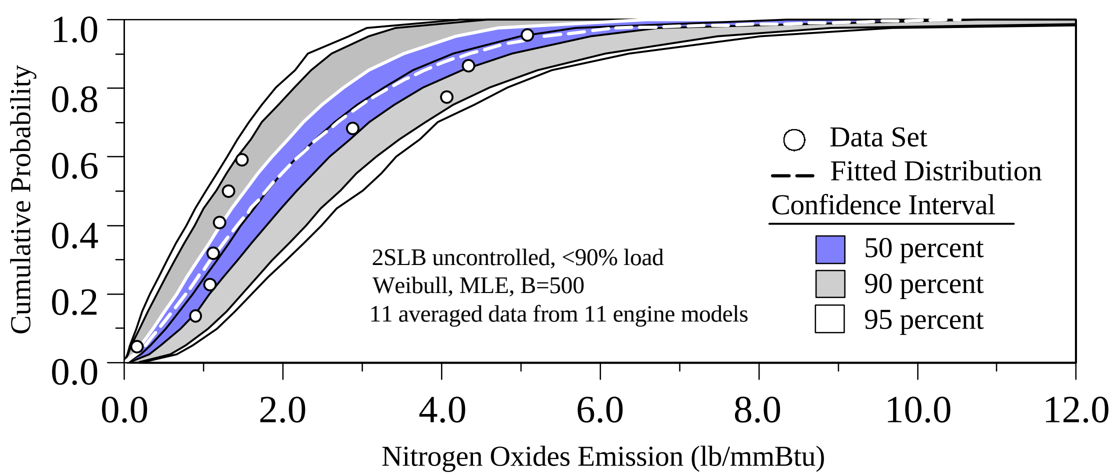

Cumulative Probability
1.0
0.8
0.6
0.4
0.2
0.0
0.00
0.50
1.00
1.50
2.00
2.50
3.00
Total Organic Carbon Emission (lb/mmBtu)
Data Set
Fitted Distribution
Confidence Interval
50 percent
90 percent
95 percent
2SLB CB controlled, Weibull, MLE
Sample size n=11, Bootstrap samples B=500
1996 Version of AP-42

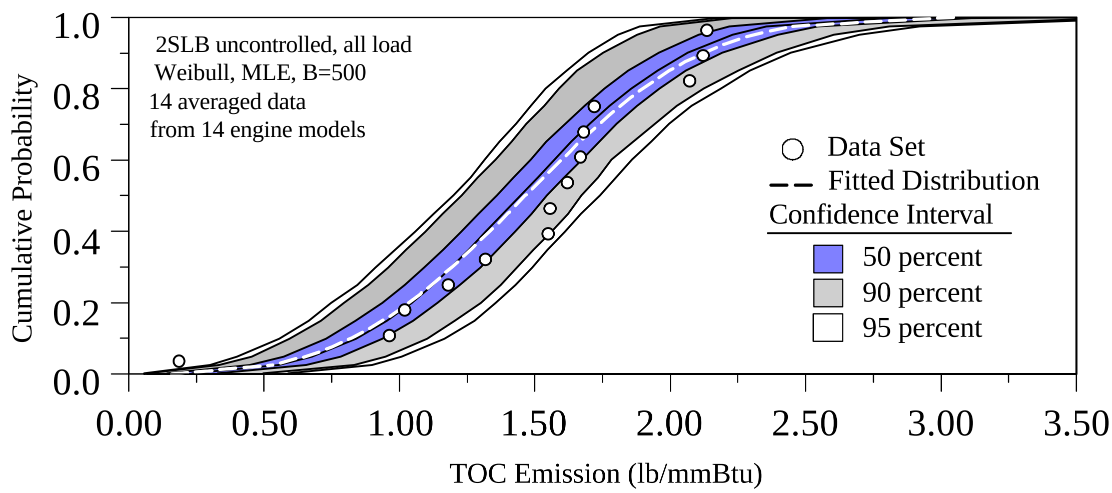

Cumulative Probability
1.0
0.8
0.6
0.4
0.2
0.0
0
2
4
6
Total Organic Carbon Emission (lb/mmBtu)
Data Set
Fitted Distribution
Confidence Interval
50 percent
90 percent
95 percent
2SLB PCC controlled, Weibulll, MLE
Sample size n=20, Bootstrap samples B=500
1996 Version of AP-42

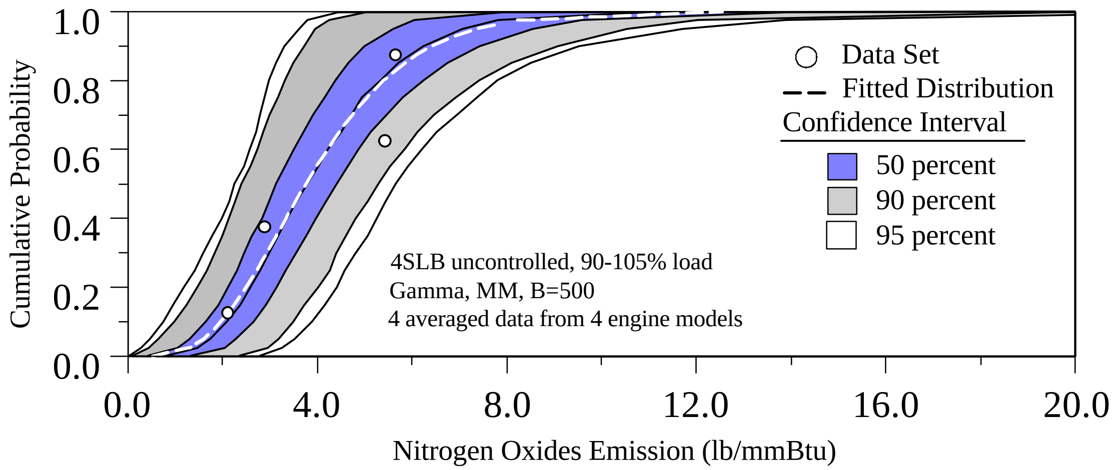

Cumulative Probability
1.0
0.8
0.6
0.4
0.2
0.0
0
2
4
6
8
Nitrogen Oxides Emission (lb/mmBtu)
Data Set Range
Empirical CDF
Confidence Interval
50 percent
90 percent
95 percent
Market-share weight data for 4SLB engines
Weibull distribution
Maximum Likelihood Estimation
Sample size n=4, Bootstrap samples B=500
1996 version of AP-42

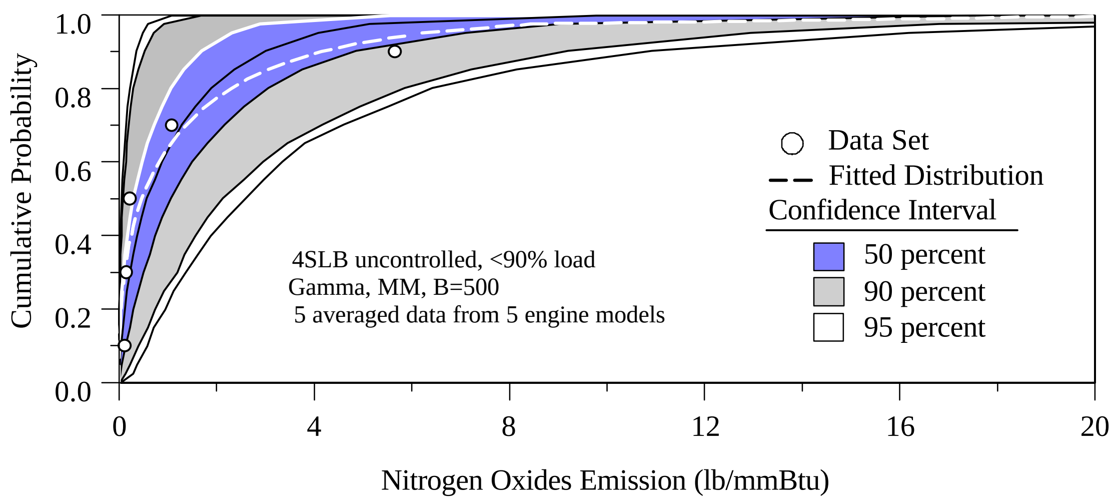

Cumulative Probability
1.0
0.8
0.6
0.4
0.2
0.0
0
2
4
6
Total Organic Carbon Emission (lb/mmBtu)
Data Set Range
Empirical CDF
Confidence Interval
50 percent
90 percent
95 percent
Market-share weight data for 4SLB engines
Weibull distribution
Maximum Likelihood Estimation
Sample size n=4, Bootstrap samples B=500
1996 version of AP-42

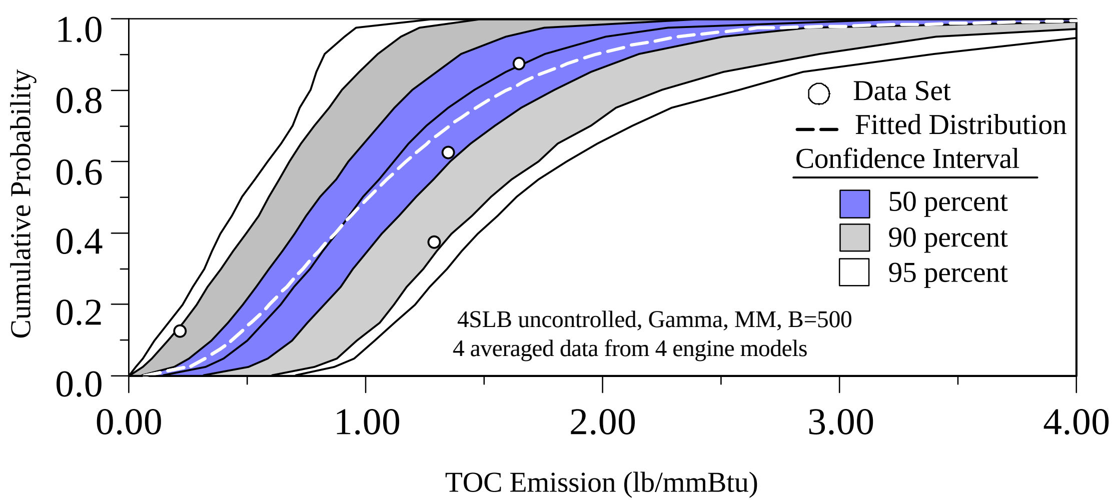

2SLB uncontrolled, 90-105% load
Weibull, MLE, B=500
11 averaged data from 11
engine models
Data Set
Fitted Distribution
Confidence Interval
50 percent
90 percent
95 percent
Cumulative Probability
0.0
0.2
0.4
0.6
0.8
1.0
0
2
4
6
8
Nitrogen Oxides Emission (lb/mmBtu)


Data Set
Fitted Distribution
Confidence Interval
50 percent
90 percent
95 percent
2SLB uncontrolled, <90% load
Weibull, MLE, B=500
11 averaged data from 11 engine models
Cumulative Probability
0.0
0.2
0.4
0.6
0.8
1.0
0.0
2.0
4.0
6.0
8.0
10.0
12.0
Nitrogen Oxides Emission (lb/mmBtu)

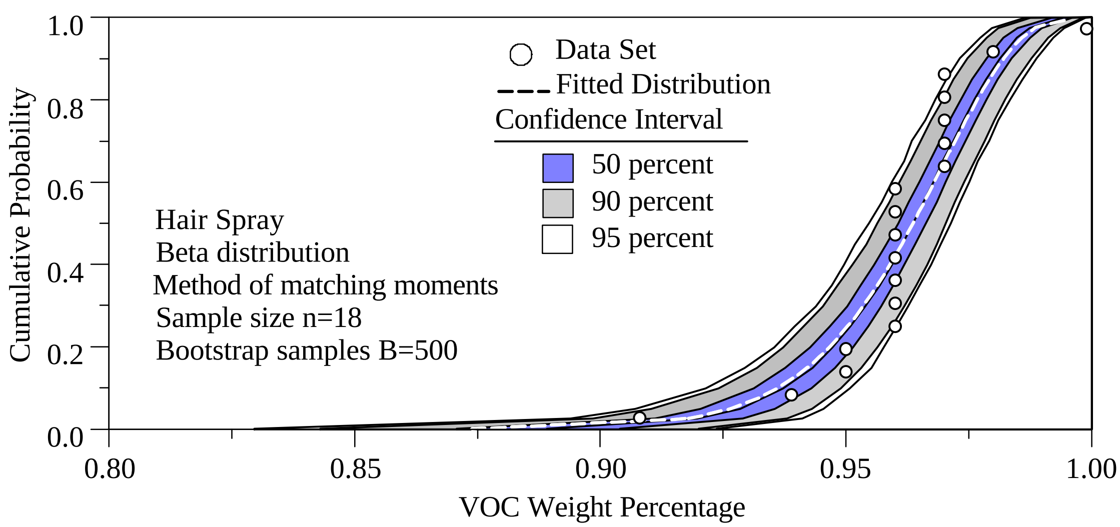

2SLB uncontrolled, all load
Weibull, MLE, B=500
14 averaged data
from 14 engine models
Data Set
Fitted Distribution
Confidence Interval
50 percent
90 percent
95 percent
Cumulative Probability
0.0
0.2
0.4
0.6
0.8
1.0
0.00
0.50
1.00
1.50
2.00
2.50
3.00
3.50
TOC Emission (lb/mmBtu)

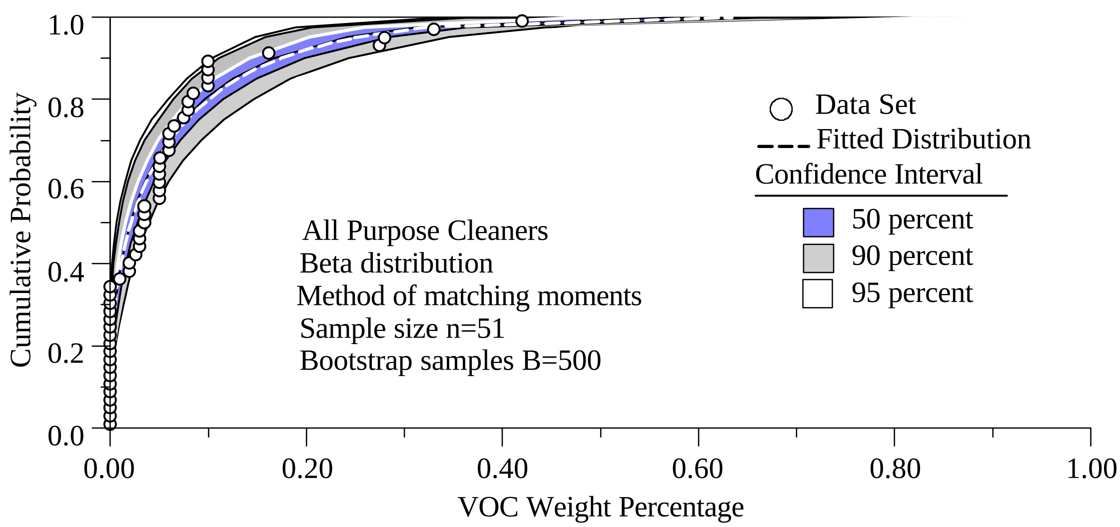

1.0
0.8
0.6
0.4
0.2
0.0
Cumulative Probability
0.0
4.0
8.0
12.0
16.0
20.0
Nitrogen Oxides Emission (lb/mmBtu)
Data Set
Fitted Distribution
Confidence Interval
50 percent
90 percent
95 percent
4SLB uncontrolled, 90-105% load
Gamma, MM, B=500
4 averaged data from 4 engine models

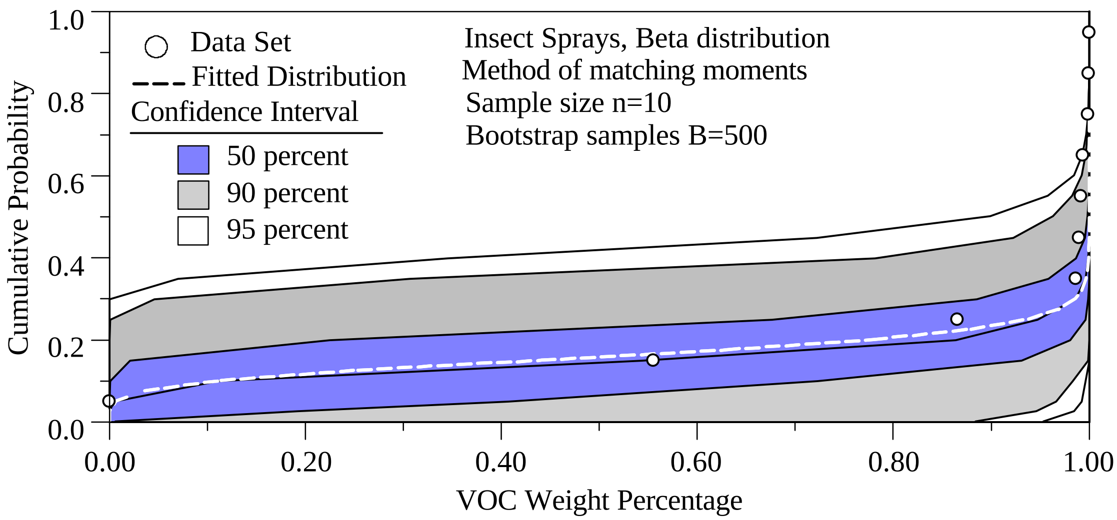

1.0
0.8
0.6
0.4
0.2
0.0
Cumulative Probability
0
4
8
12
16
20
Nitrogen Oxides Emission (lb/mmBtu)
Data Set
Fitted Distribution
Confidence Interval
50 percent
90 percent
95 percent
4SLB uncontrolled, <90% load
Gamma, MM, B=500
5 averaged data from 5 engine models

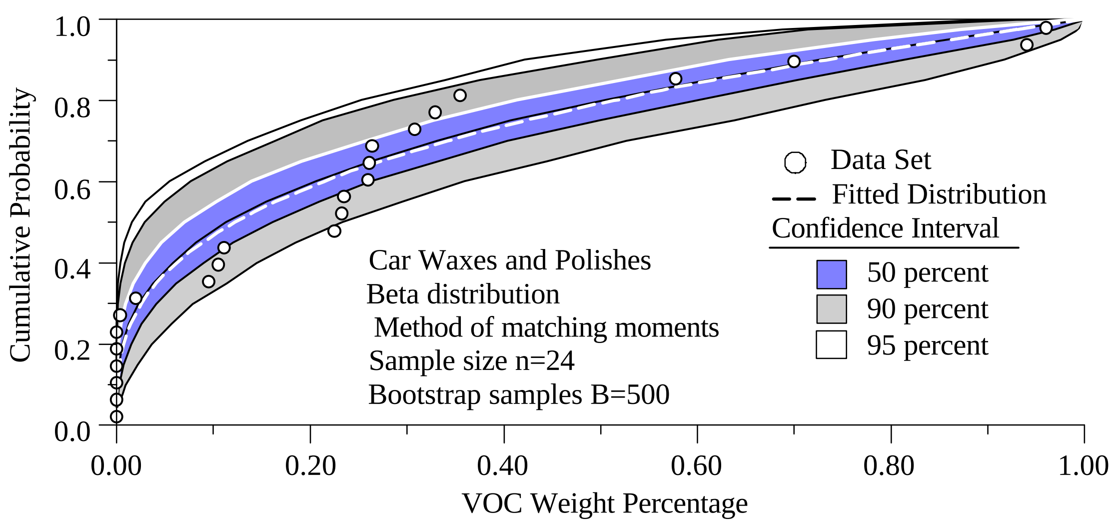

1.0
0.8
0.6
0.4
0.2
0.0
Cumulative Probability
0.00
1.00
2.00
3.00
4.00
TOC Emission (lb/mmBtu)
Data Set
Fitted Distribution
Confidence Interval
50 percent
90 percent
95 percent
4SLB uncontrolled, Gamma, MM, B=500
4 averaged data from 4 engine models

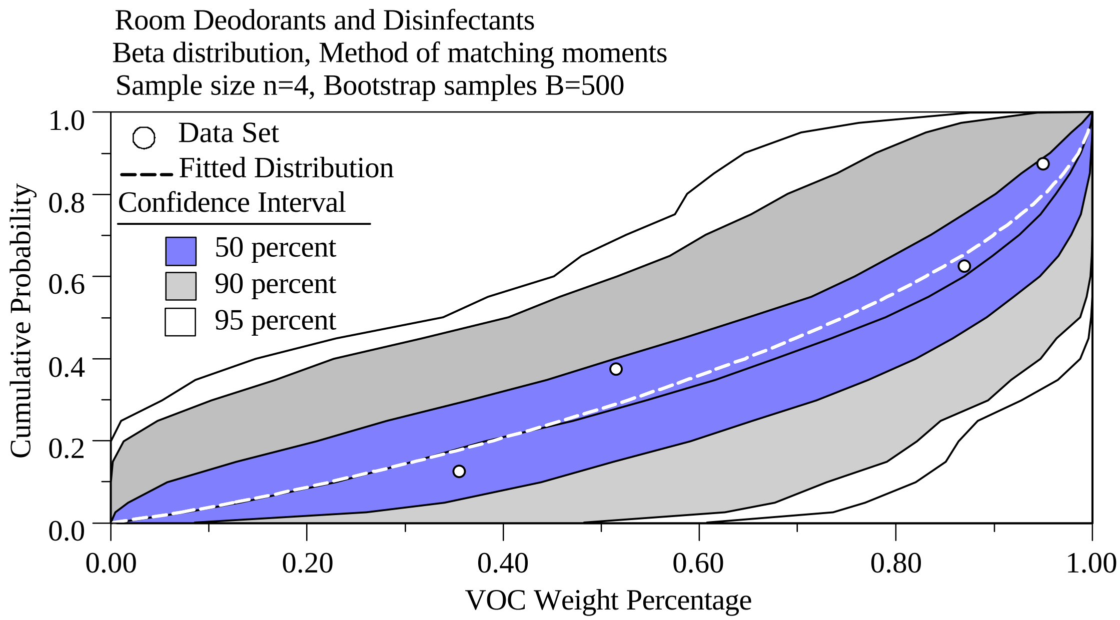
APPENDIX C. BOOTSTRAP SIMULATION GRAPHS FOR CONSUMER/COMMERCIAL PRODUCT USE

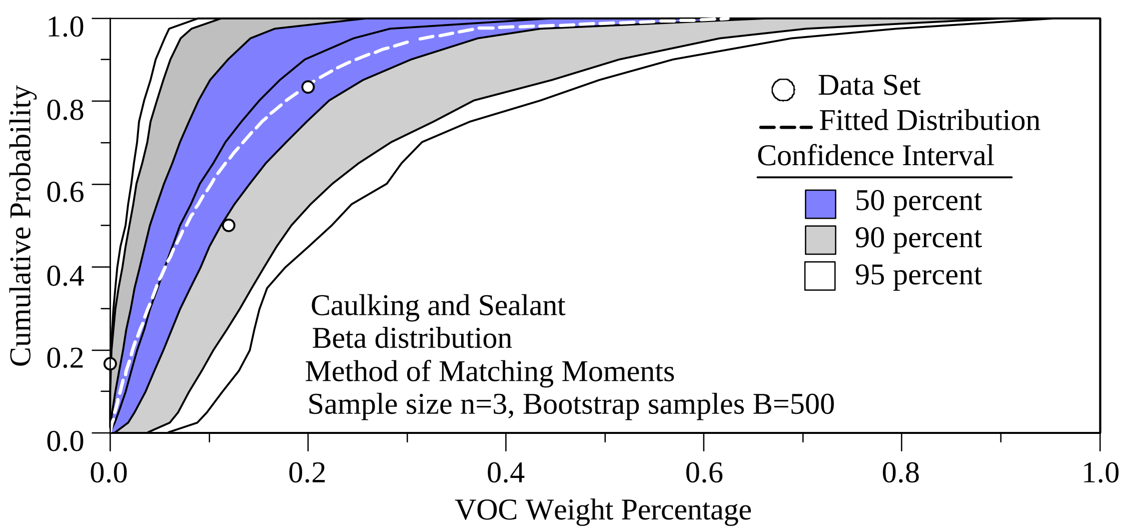


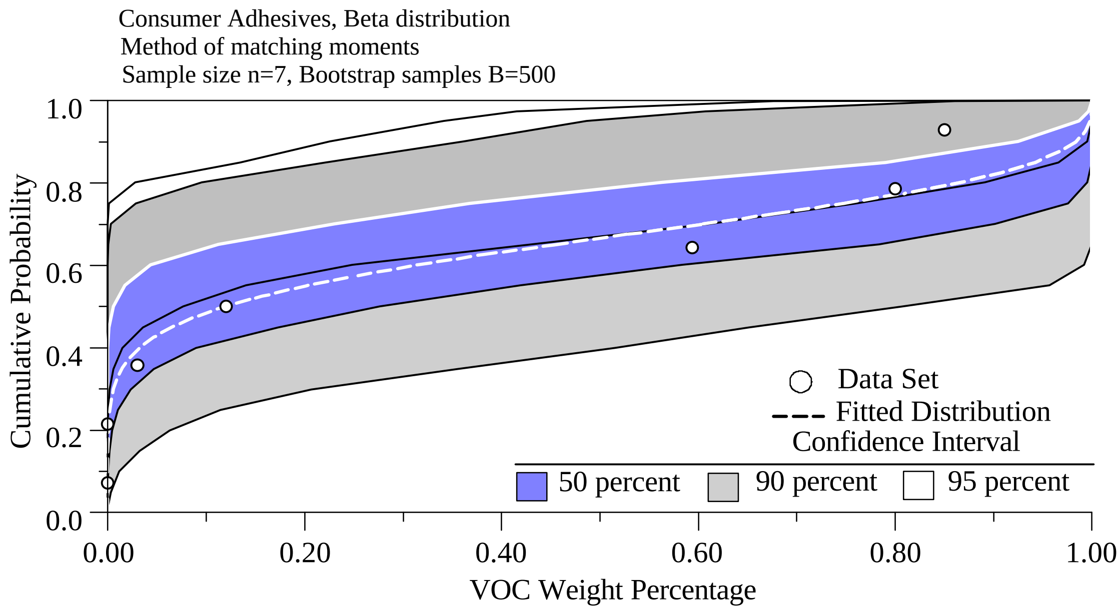


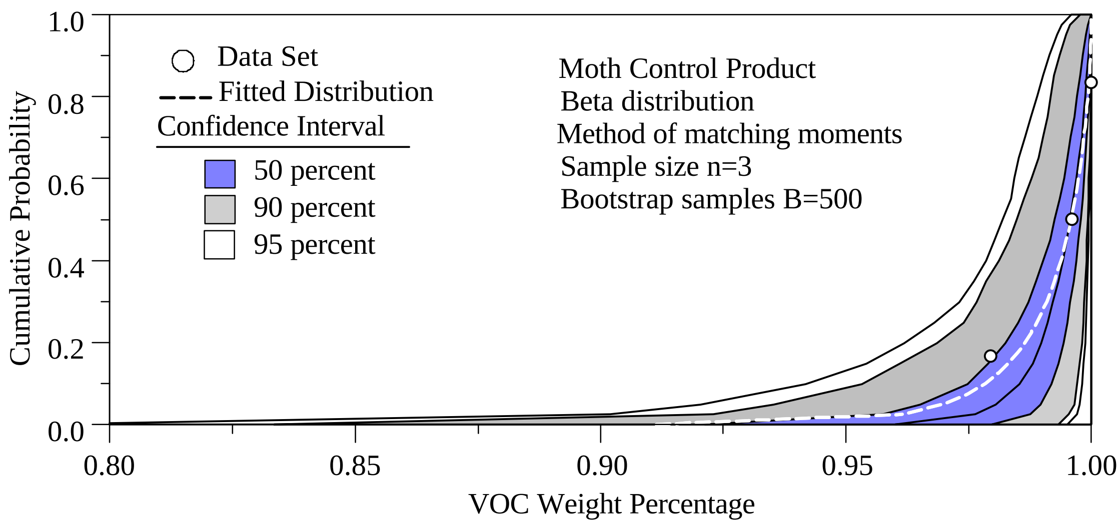

1.0
0.8
0.6
0.4
0.2
0.0
Cumulative Probability
Data Set
Fitted Distribution
Confidence Interval
50 percent
90 percent
95 percent
Insect Sprays, Beta distribution
Method of matching moments
Sample size n=10
Bootstrap samples B=500
0.00
0.20
0.40
0.60
0.80
1.00
VOC Weight Percentage

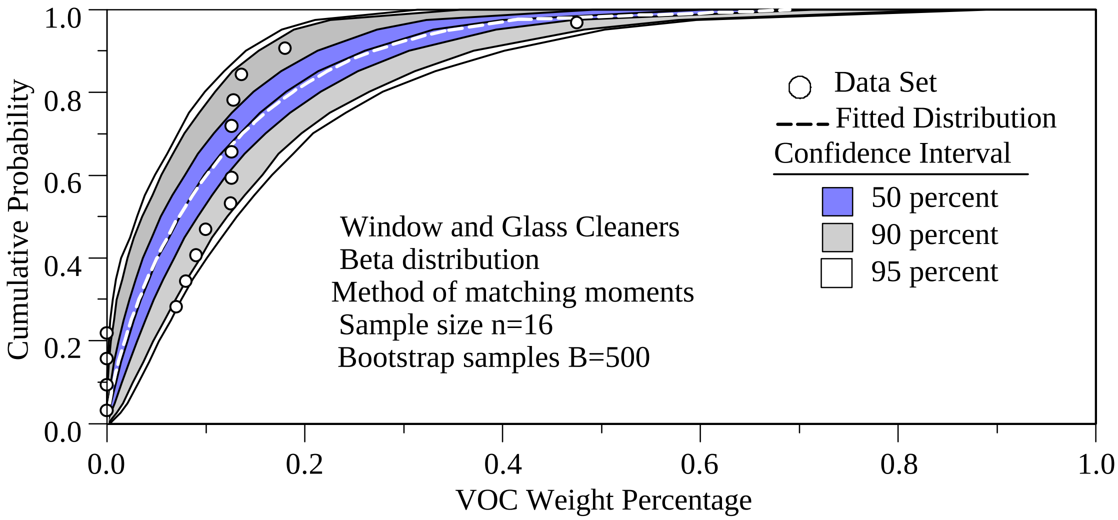

1.0
0.8
0.6
0.4
0.2
0.0
Cumulative Probability
Data Set
Fitted Distribution
Confidence Interval
50 percent
90 percent
95 percent
Car Waxes and Polishes
Beta distribution
Method of matching moments
Sample size n=24
Bootstrap samples B=500
0.00
0.20
0.40
0.60
0.80
1.00
VOC Weight Percentage

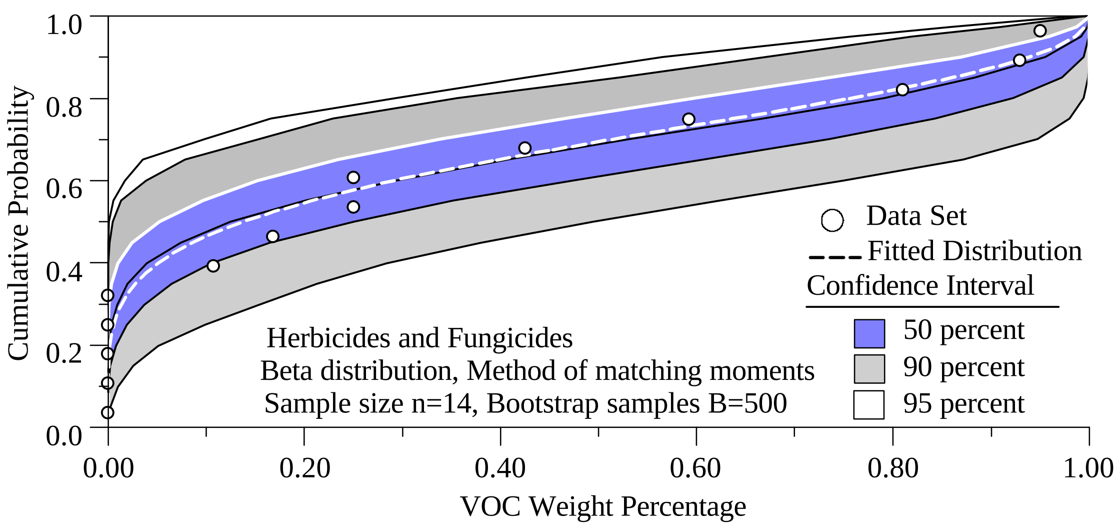

Room Deodorants and Disinfectants
Beta distribution, Method of matching moments
Sample size n=4, Bootstrap samples B=500
Data Set
Fitted Distribution
Confidence Interval
50 percent
90 percent
95 percent
Cumulative Probability
0.0
0.2
0.4
0.6
0.8
1.0
0.00
0.20
0.40
0.60
0.80
1.00
VOC Weight Percentage

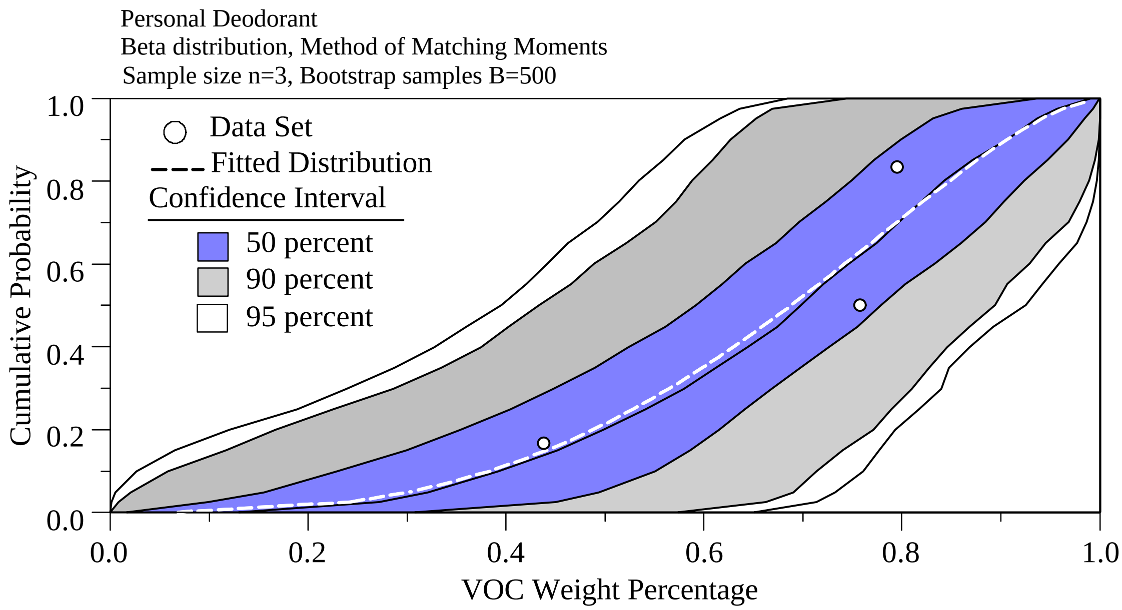

Data Set
Fitted Distribution
Confidence Interval
50 percent
90 percent
95 percent
Caulking and Sealant
Beta distribution
Method of Matching Moments
Sample size n=3, Bootstrap samples B=500
Cumulative Probability
0.0
0.2
0.4
0.6
0.8
1.0
0.0
0.2
0.4
0.6
0.8
1.0
VOC Weight Percentage

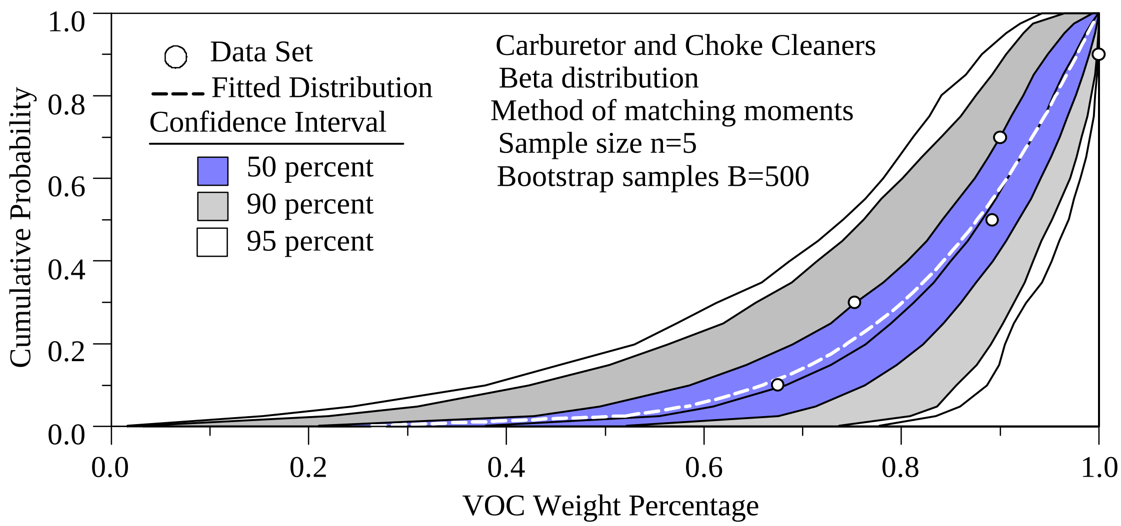

Consumer Adhesives, Beta distribution
Method of matching moments
Sample size n=7, Bootstrap samples B=500
Cumulative Probability
1.0
0.8
0.6
0.4
0.2
0.0
0.00
0.20
0.40
0.60
0.80
1.00
VOC Weight Percentage
Data Set
Fitted Distribution
Confidence Interval
50 percent
90 percent
95 percent

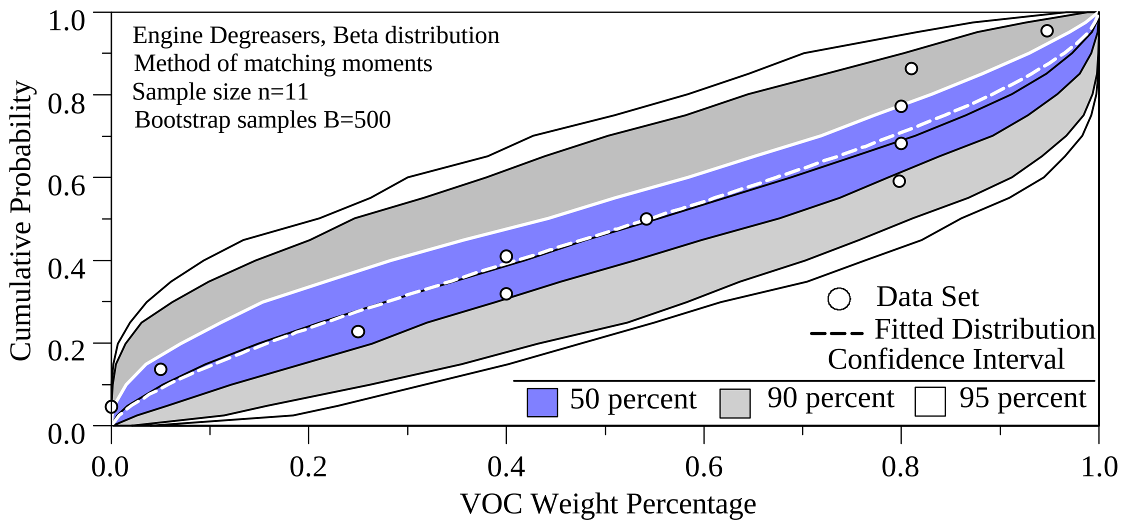

Data Set
Fitted Distribution
Confidence Interval
50 percent
90 percent
95 percent
Moth Control Product
Beta distribution
Method of matching moments
Sample size n=3
Bootstrap samples B=500
Cumulative Probability
1.0
0.8
0.6
0.4
0.2
0.0
0.80
0.85
0.90
0.95
1.00
VOC Weight Percentage

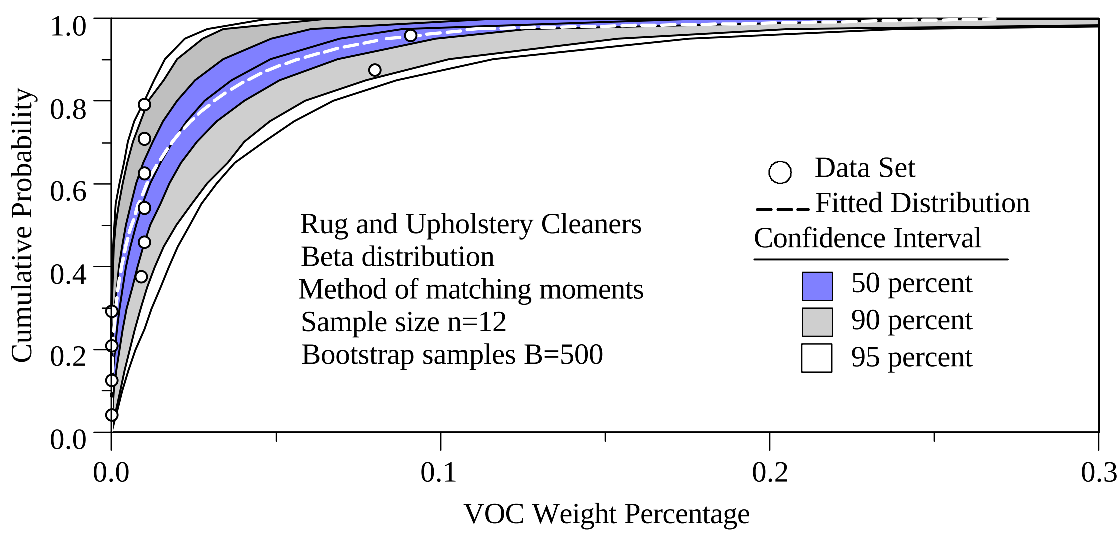

1.0
0.8
0.6
0.4
0.2
0.0
Cumulative Probability
0.0
0.2
0.4
0.6
0.8
1.0
VOC Weight Percentage
Data Set
Fitted Distribution
Confidence Interval
50 percent
90 percent
95 percent
Window and Glass Cleaners
Beta distribution
Method of matching moments
Sample size n=16
Bootstrap samples B=500

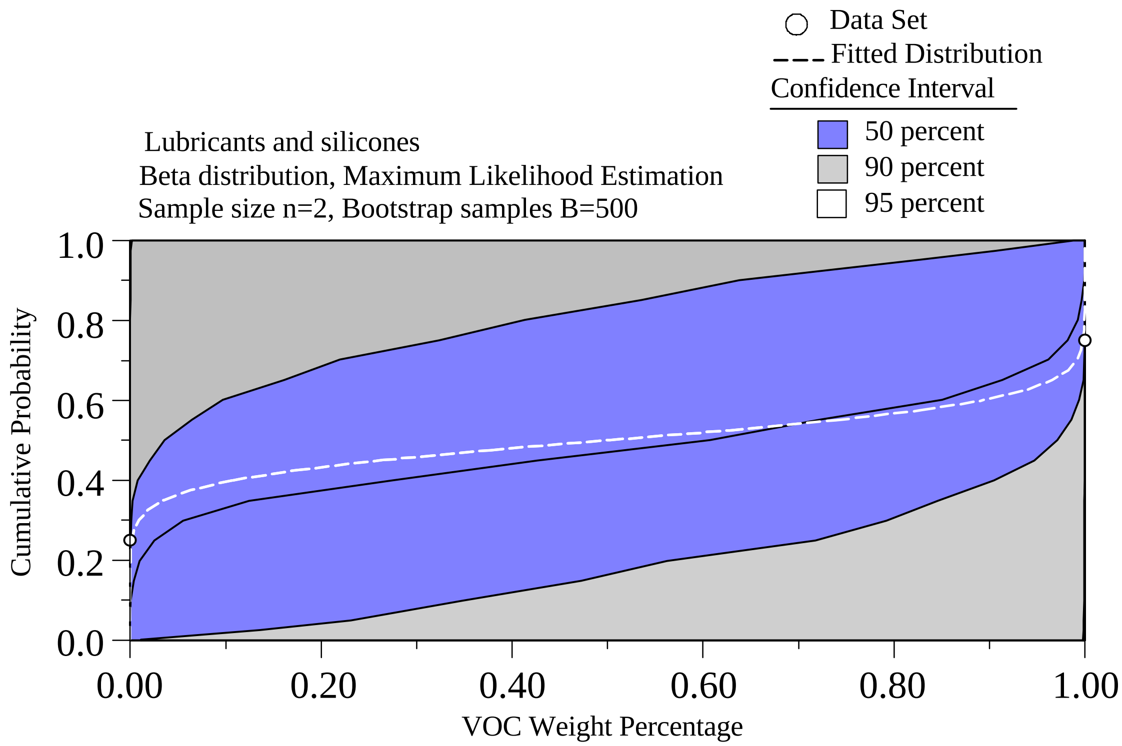

1.0
0.8
0.6
0.4
0.2
0.0
Cumulative Probability
0.00
0.20
0.40
0.60
0.80
1.00
VOC Weight Percentage
Data Set
Fitted Distribution
Confidence Interval
50 percent
90 percent
95 percent
Herbicides and Fungicides
Beta distribution, Method of matching moments
Sample size n=14, Bootstrap samples B=500

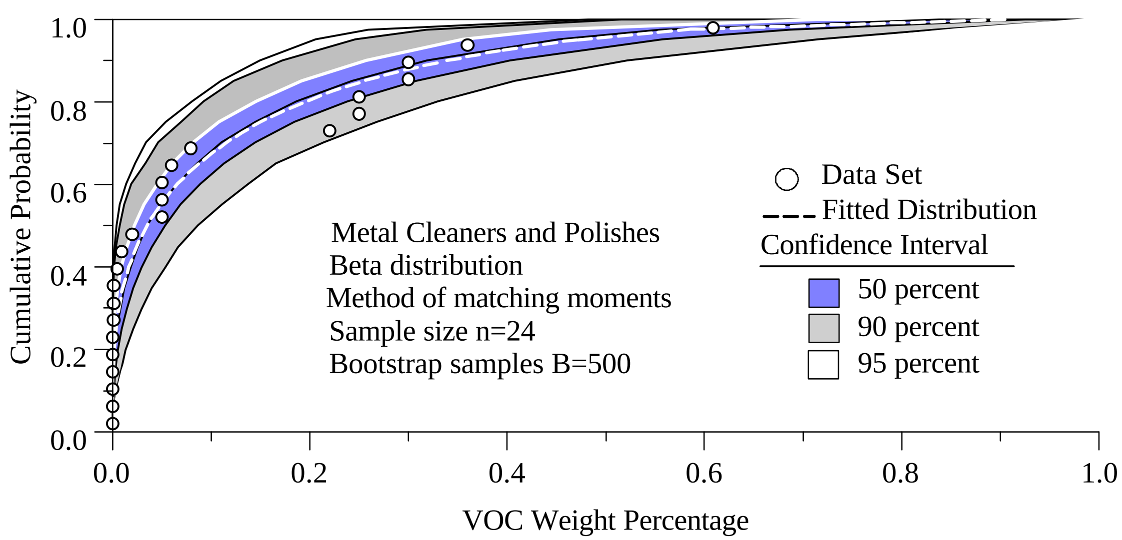

Personal Deodorant
Beta distribution, Method of Matching Moments
Sample size n=3, Bootstrap samples B=500
Data Set
Fitted Distribution
Confidence Interval
50 percent
90 percent
95 percent
Cumulative Probability
VOC Weight Percentage
0.0
0.2
0.4
0.6
0.8
1.0


Data Set
Fitted Distribution
Confidence Interval
50 percent
90 percent
95 percent
Carburetor and Choke Cleaners
Beta distribution
Method of matching moments
Sample size n=5
Bootstrap samples B=500
Cumulative Probability
VOC Weight Percentage
0.0
0.2
0.4
0.6
0.8
1.0

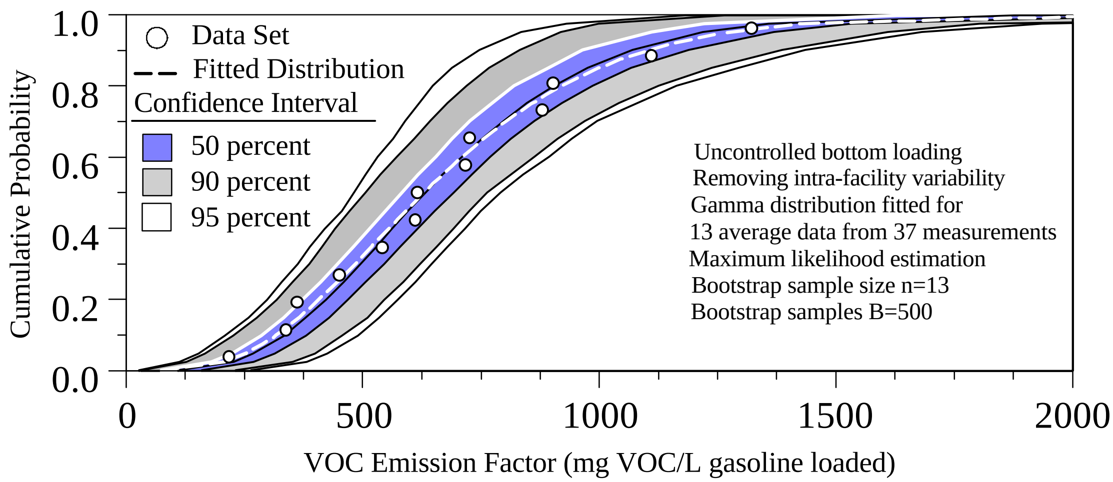

Engine Degreasers, Beta distribution
Method of matching moments
Sample size n=11
Bootstrap samples B=500
Data Set
Fitted Distribution
Confidence Interval
50 percent
90 percent
95 percent
Cumulative Probability
VOC Weight Percentage
0.0
0.2
0.4
0.6
0.8
1.0

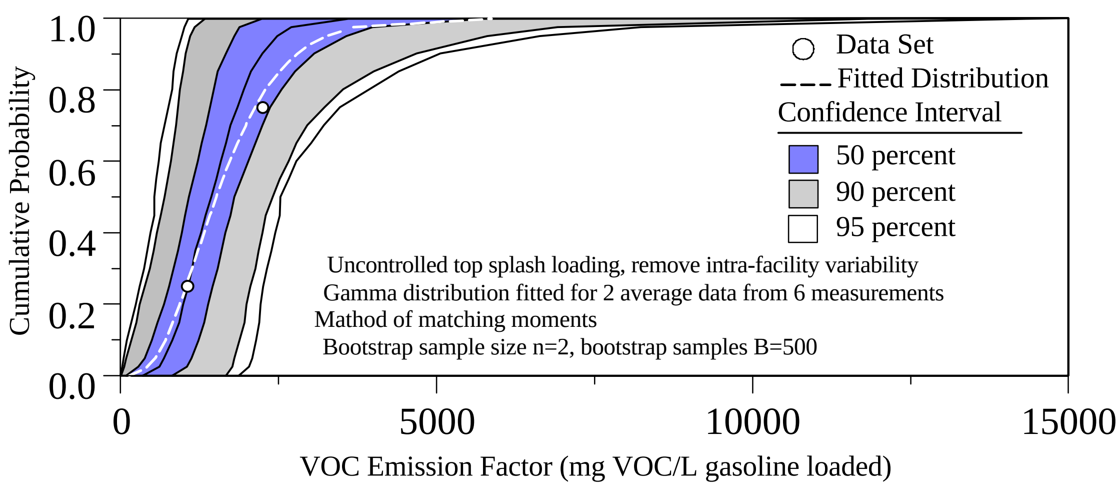

Rug and Upholstery Cleaners
Beta distribution
Method of matching moments
Sample size n=12
Bootstrap samples B=500
Data Set
Fitted Distribution
Confidence Interval
50 percent
90 percent
95 percent
Cumulative Probability
VOC Weight Percentage
0.0
0.1
0.2
0.3
0.4
0.6
0.8
1.0

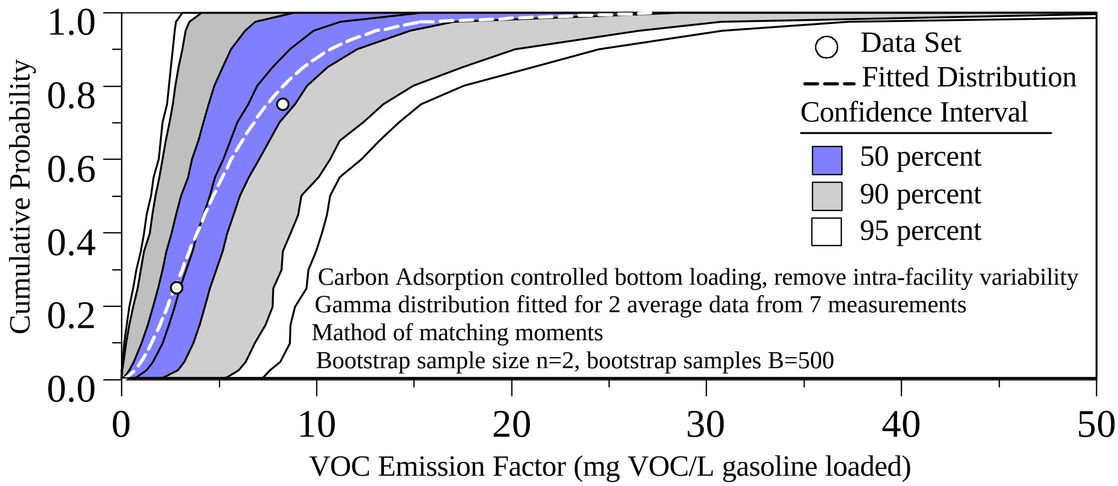

Data Set
Fitted Distribution
Confidence Interval
50 percent
90 percent
95 percent
Lubricants and silicones
Beta distribution, Maximum Likelihood Estimation
Sample size n=2, Bootstrap samples B=500
1.0
0.8
0.6
0.4
0.2
0.0
Cumulative Probability
0.00
0.20
0.40
0.60
0.80
1.00
VOC Weight Percentage

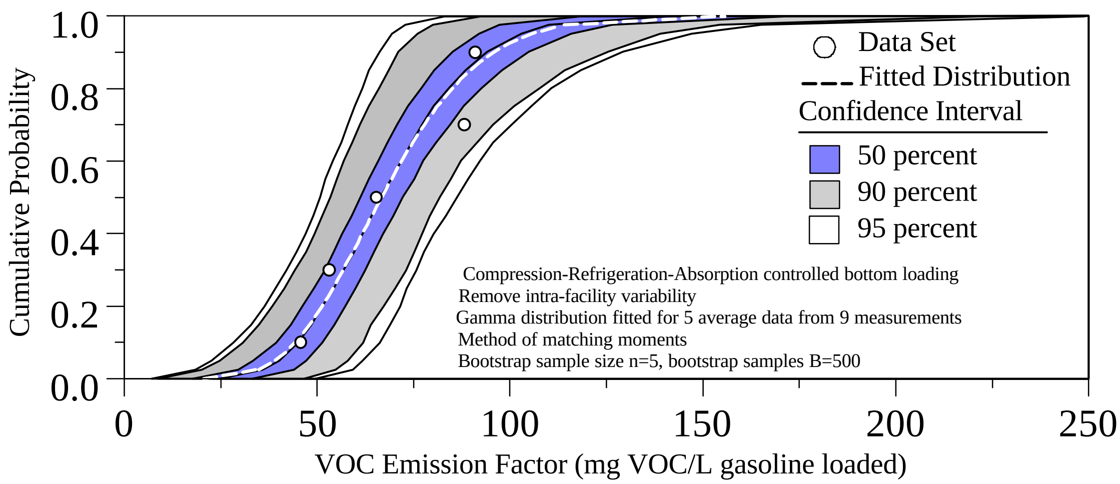

1.0
0.8
0.6
0.4
0.2
0.0
Cumulative Probability
Data Set
Fitted Distribution
Confidence Interval
50 percent
90 percent
95 percent
Metal Cleaners and Polishes
Beta distribution
Method of matching moments
Sample size n=24
Bootstrap samples B=500
0.0
0.2
0.4
0.6
0.8
1.0
VOC Weight Percentage

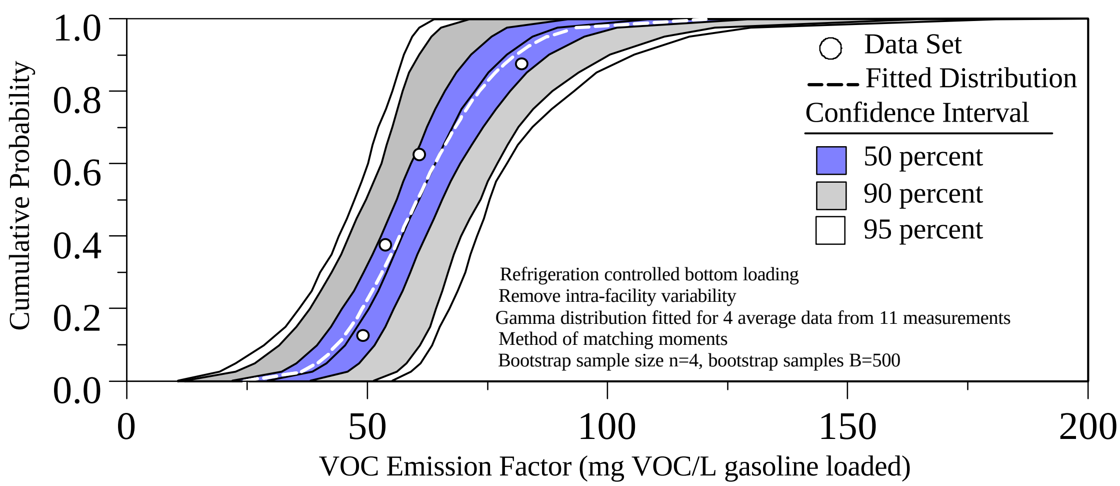
APPENDIX D. BOOTSTRAP SIMULATION GRAPHS FOR GASOLINE TERMINAL LOADING LOSS

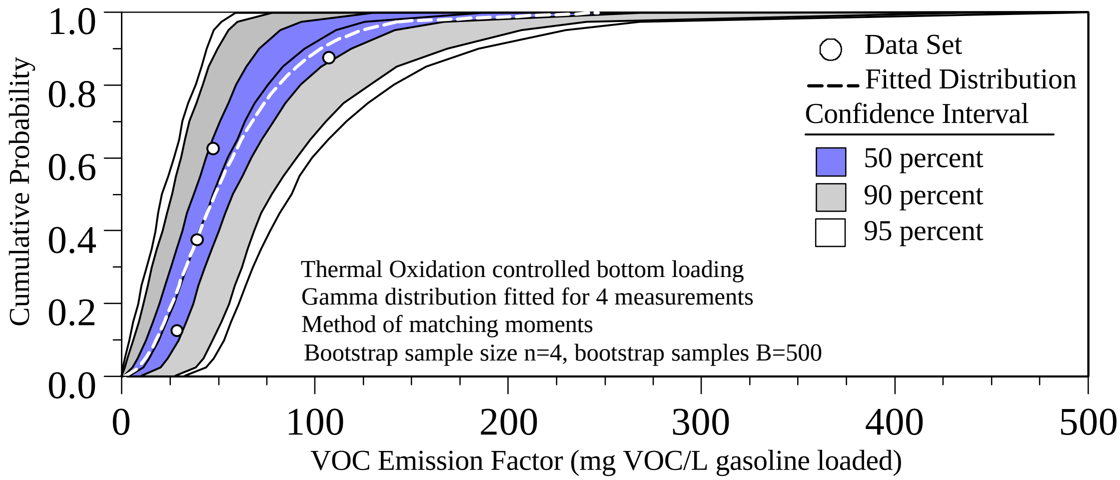




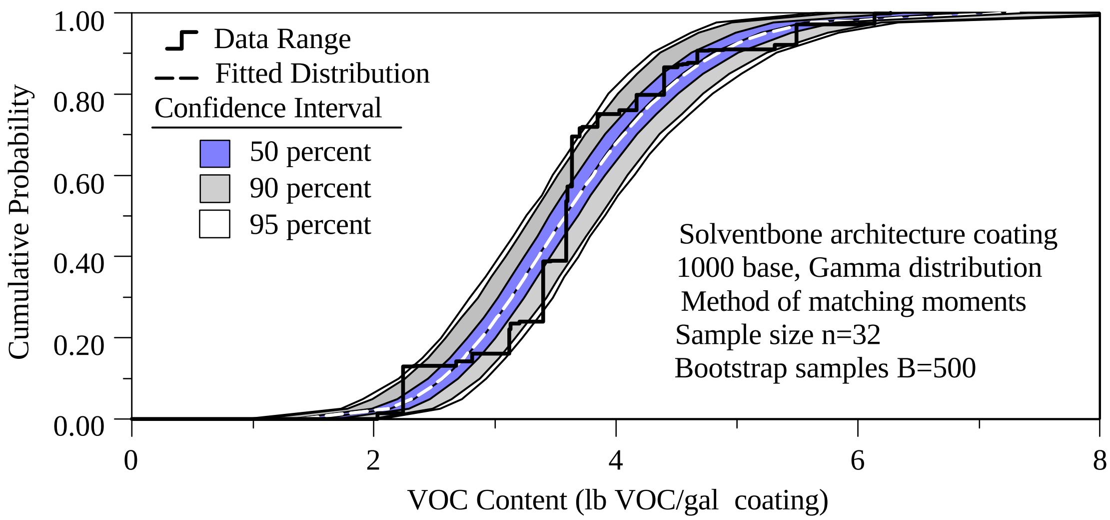

Cumulative Probability
1.0
0.8
0.6
0.4
0.2
0.0
0
10
20
30
40
50
VOC Emission Factor (mg VOC/L gasoline loaded)
Data Set
Fitted Distribution
Confidence Interval
50 percent
90 percent
95 percent
Carbon Adsorption controlled bottom loading, remove intra-facility variability
Gamma distribution fitted for 2 average data from 7 measurements
Mathod of matching moments
Bootstrap sample size n=2, bootstrap samples B=500

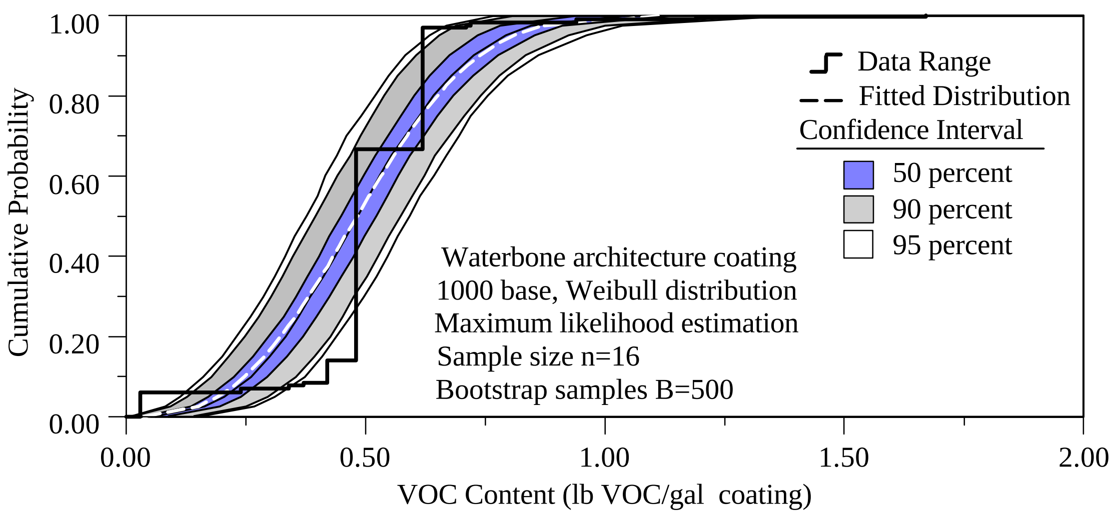

Cumulative Probability
1.0
0.8
0.6
0.4
0.2
0.0
0
50
100
150
200
250
VOC Emission Factor (mg VOC/L gasoline loaded)
Data Set
Fitted Distribution
Confidence Interval
50 percent
90 percent
95 percent
Compression-Refrigeration-Absorption controlled bottom loading
Remove intra-facility variability
Gamma distribution fitted for 5 average data from 9 measurements
Method of matching moments
Bootstrap sample size n=5, bootstrap samples B=500


Cumulative Probability
1.0
0.8
0.6
0.4
0.2
0.0
0
50
100
150
200
VOC Emission Factor (mg VOC/L gasoline loaded)
Data Set
Fitted Distribution
Confidence Interval
50 percent
90 percent
95 percent
Refrigeration controlled bottom loading
Remove intra-facility variability
Gamma distribution fitted for 4 average data from 11 measurements
Method of matching moments
Bootstrap sample size n=4, bootstrap samples B=500

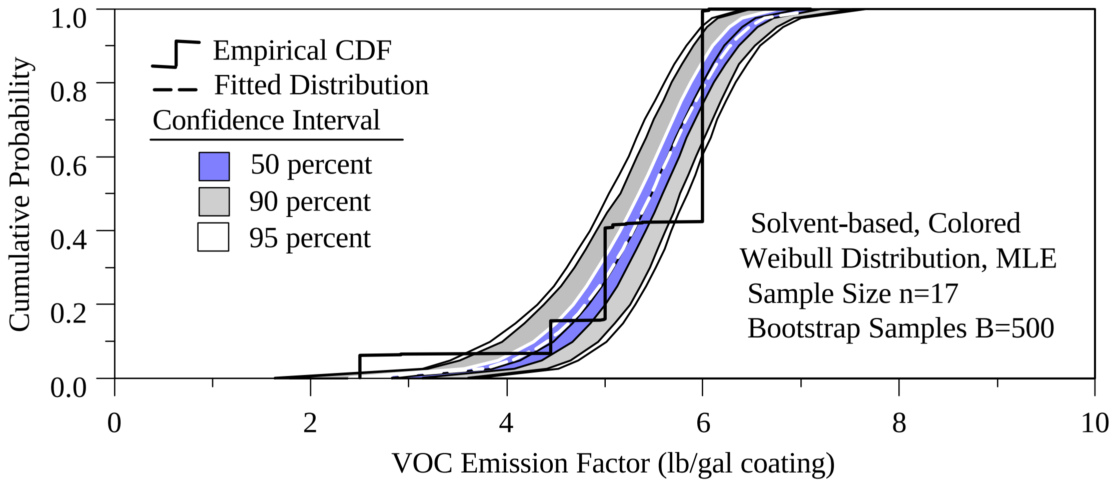

1.0
0.8
0.6
0.4
0.2
0.0
Cumulative Probability
0
100
200
300
400
500
VOC Emission Factor (mg VOC/L gasoline loaded)
Data Set
Fitted Distribution
Confidence Interval
50 percent
90 percent
95 percent
Thermal Oxidation controlled bottom loading
Gamma distribution fitted for 4 measurements
Method of matching moments
Bootstrap sample size n=4, bootstrap samples B=500

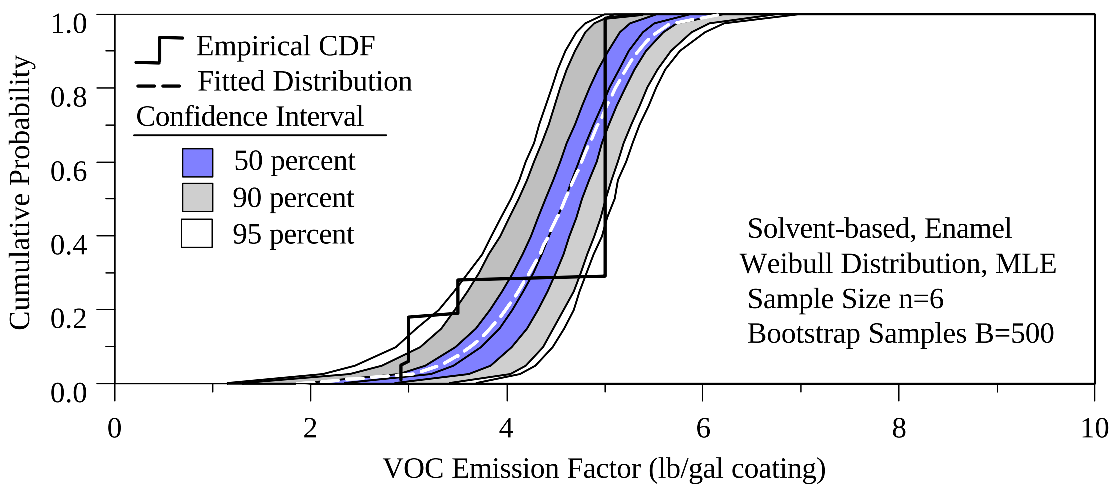
APPENDIX E. BOOTSTRAP SIMULATION GRAPHS FOR ARCHITECTURAL COATINGS

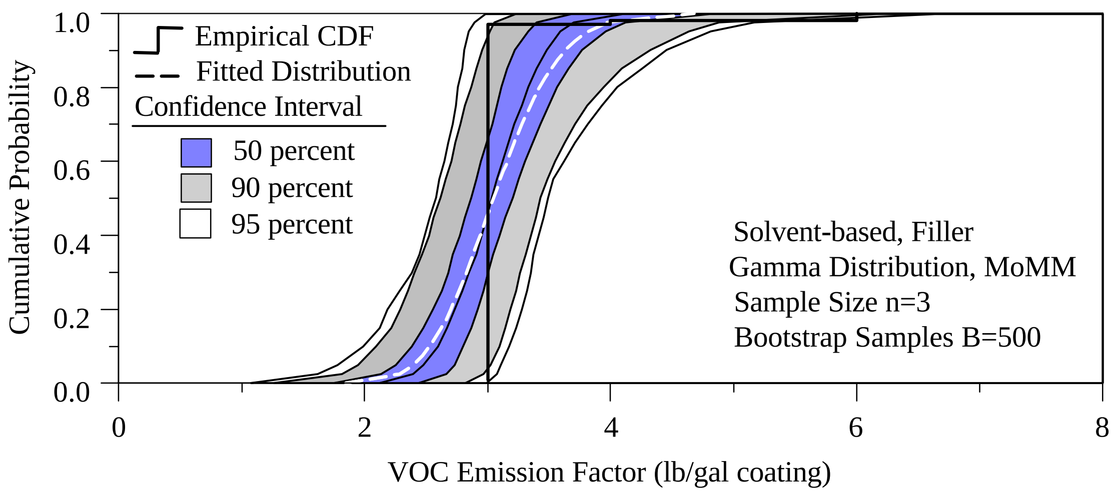




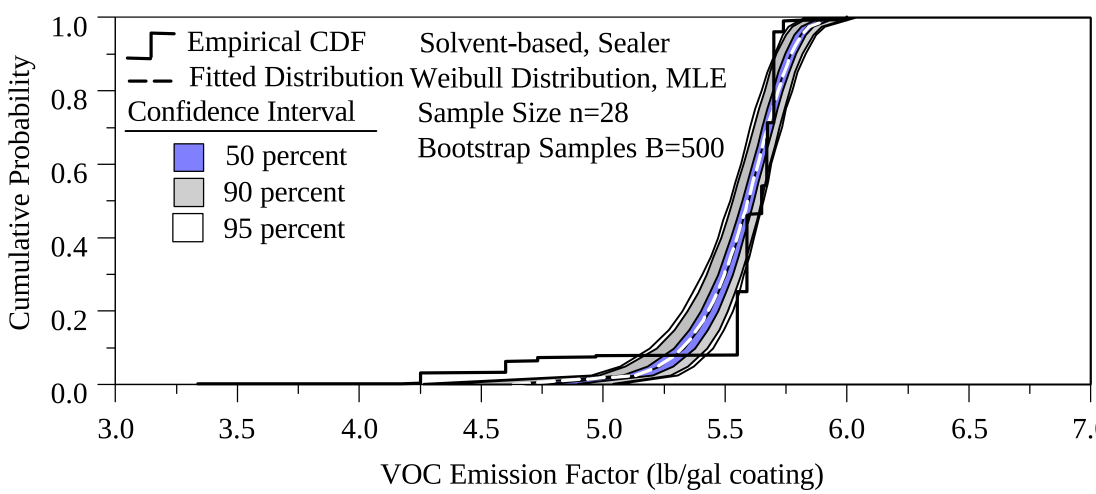
APPENDIX F. BOOTSTRAP SIMULATION GRAPHS FOR WOOD FURNITURE COATINGS



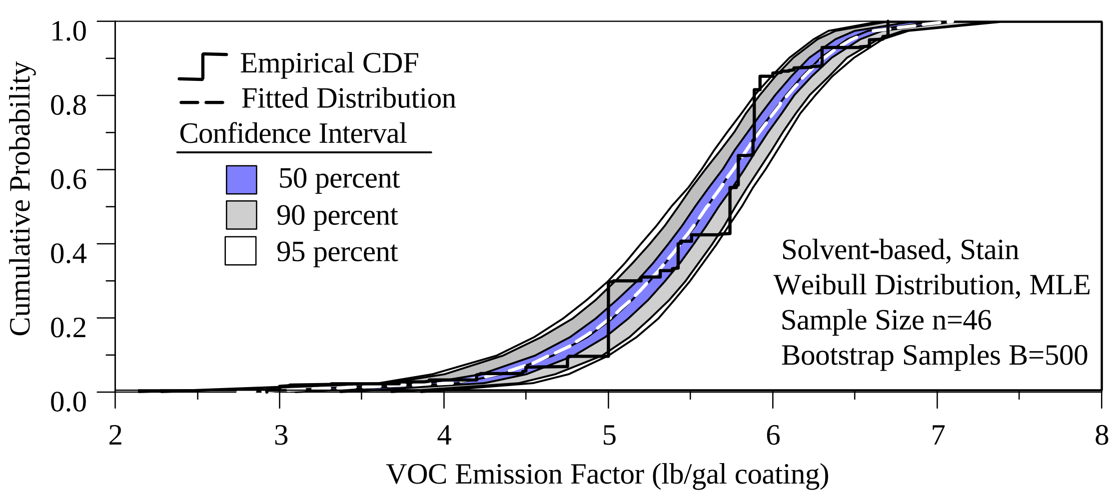




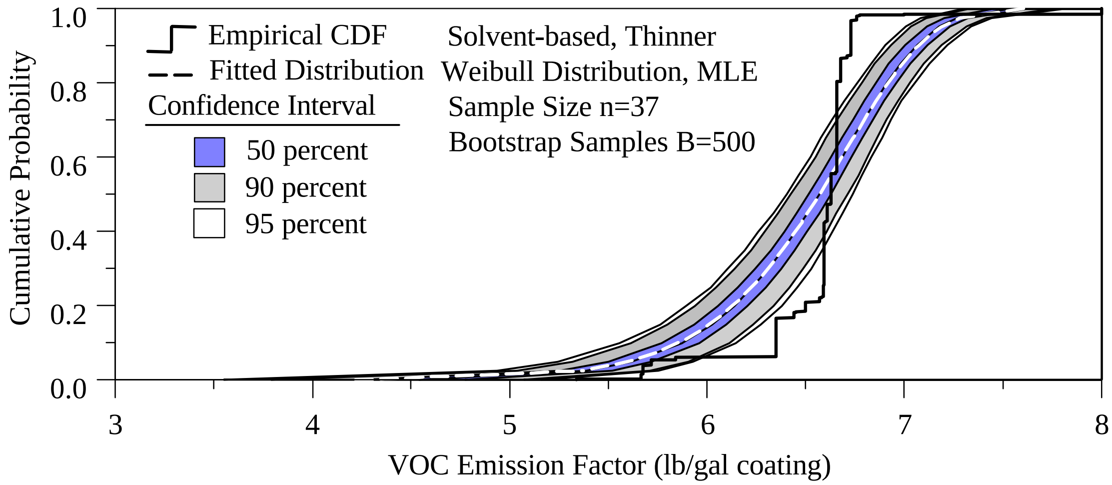
Empirical CDF
Fitted Distribution
Confidence Interval
50 percent
90 percent
95 percent
Solvent-based, Filler
Gamma Distribution, MoMM
Sample Size n=3
Bootstrap Samples B=500
Cumulative Probability
1.0
0.8
0.6
0.4
0.2
0.0
0
2
4
6
8
VOC Emission Factor (lb/gal coating)

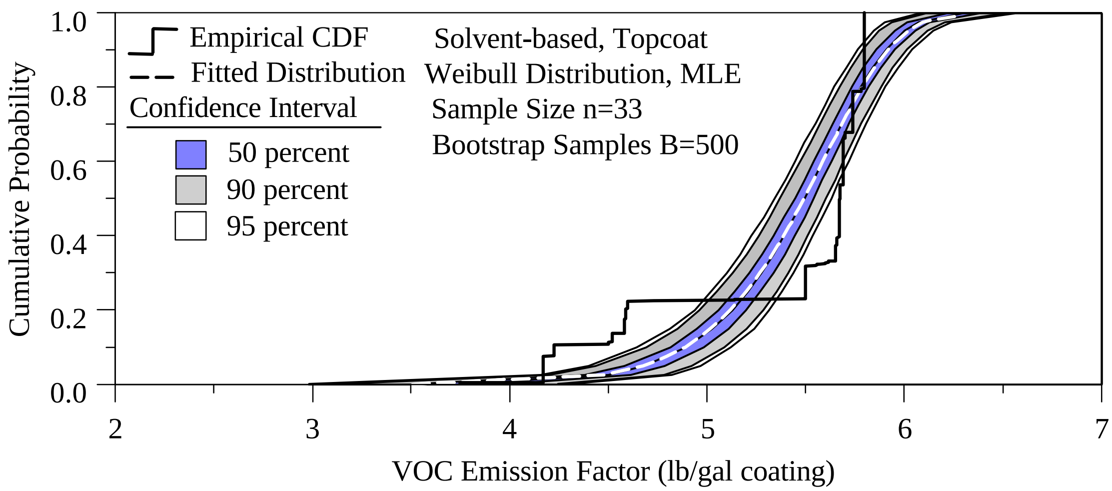


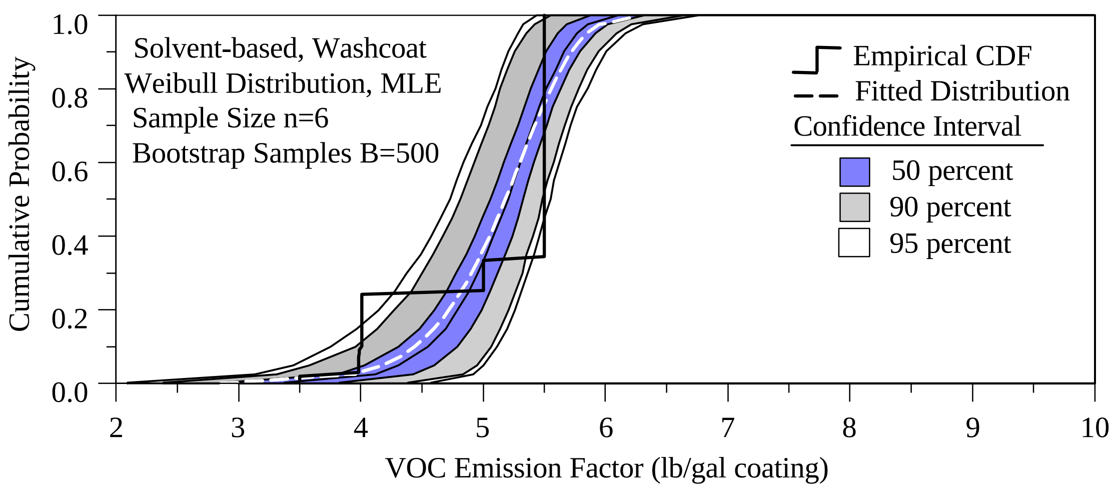
Empirical CDF
Fitted Distribution
Confidence Interval
50 percent
90 percent
95 percent
Solvent-based, Sealer
Weibull Distribution, MLE
Sample Size n=28
Bootstrap Samples B=500
Cumulative Probability
1.0
0.8
0.6
0.4
0.2
0.0
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
VOC Emission Factor (lb/gal coating)

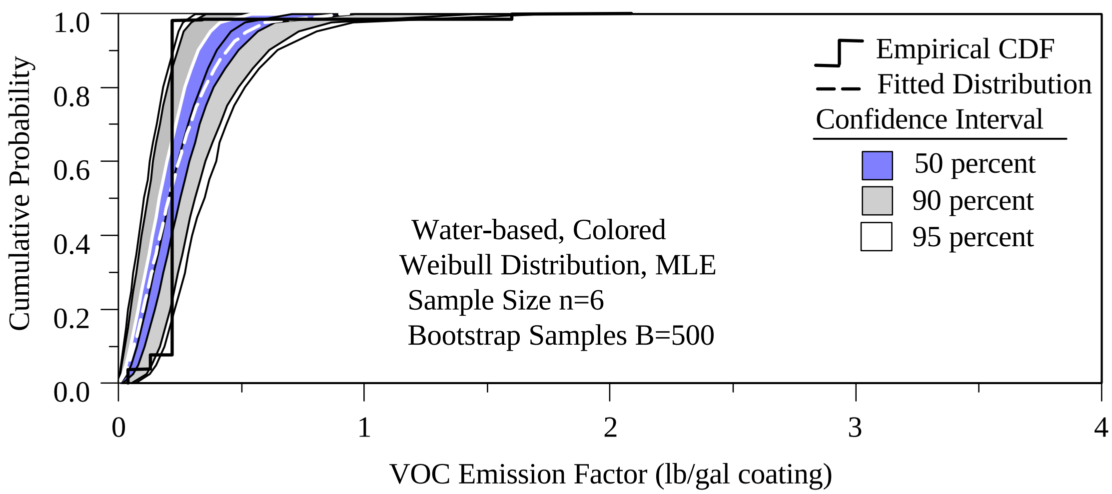


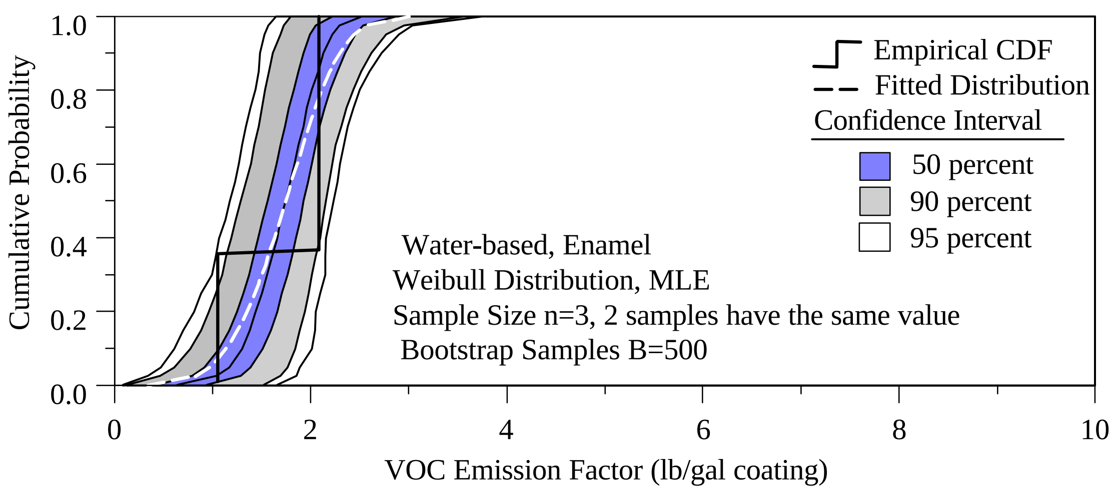
Empirical CDF
Fitted Distribution
Confidence Interval
50 percent
90 percent
95 percent
Solvent-based, Stain
Weibull Distribution, MLE
Sample Size n=46
Bootstrap Samples B=500
Cumulative Probability
1.0
0.8
0.6
0.4
0.2
0.0
2
3
4
5
6
7
8
VOC Emission Factor (lb/gal coating)

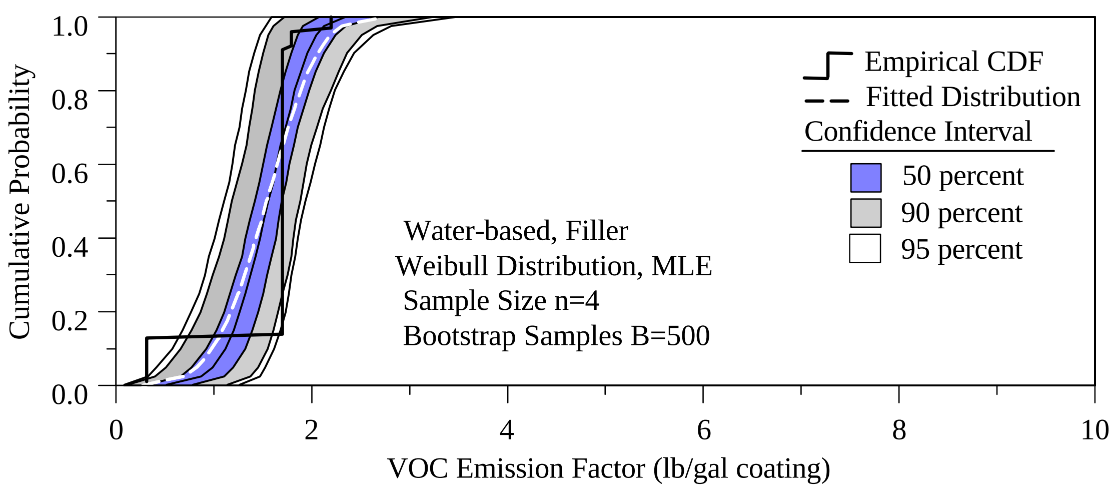

Empirical CDF
Fitted Distribution
Confidence Interval
50 percent
90 percent
95 percent
Solvent-based, Thinner
Weibull Distribution, MLE
Sample Size n=37
Bootstrap Samples B=500
Cumulative Probability
VOC Emission Factor (lb/gal coating)

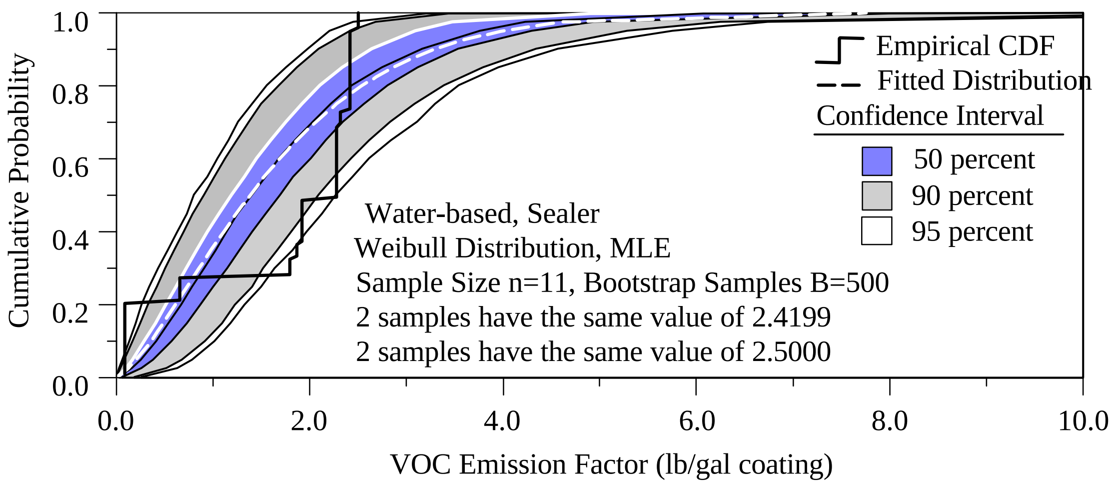

Empirical CDF
Fitted Distribution
Confidence Interval
50 percent
90 percent
95 percent
Solvent-based, Topcoat
Weibull Distribution, MLE
Sample Size n=33
Bootstrap Samples B=500
Cumulative Probability
VOC Emission Factor (lb/gal coating)


Solvent-based, Washcoat
Weibull Distribution, MLE
Sample Size n=6
Bootstrap Samples B=500
Empirical CDF
Fitted Distribution
Confidence Interval
50 percent
90 percent
95 percent
Cumulative Probability
VOC Emission Factor (lb/gal coating)

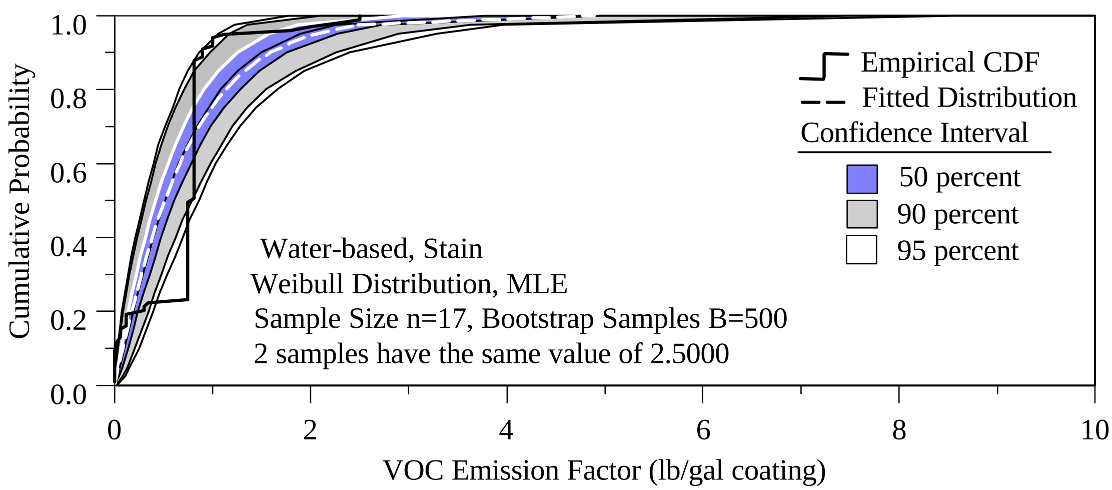

1.0
0.8
0.6
0.4
0.2
0.0
Cumulative Probability
0
1
2
3
4
VOC Emission Factor (lb/gal coating)
Empirical CDF
Fitted Distribution
Confidence Interval
50 percent
90 percent
95 percent
Water-based, Colored
Weibull Distribution, MLE
Sample Size n=6
Bootstrap Samples B=500


1.0
0.8
0.6
0.4
0.2
0.0
Cumulative Probability
0
2
4
6
8
10
VOC Emission Factor (lb/gal coating)
Empirical CDF
Fitted Distribution
Confidence Interval
50 percent
90 percent
95 percent
Water-based, Enamel
Weibull Distribution, MLE
Sample Size n=3, 2 samples have the same value
Bootstrap Samples B=500

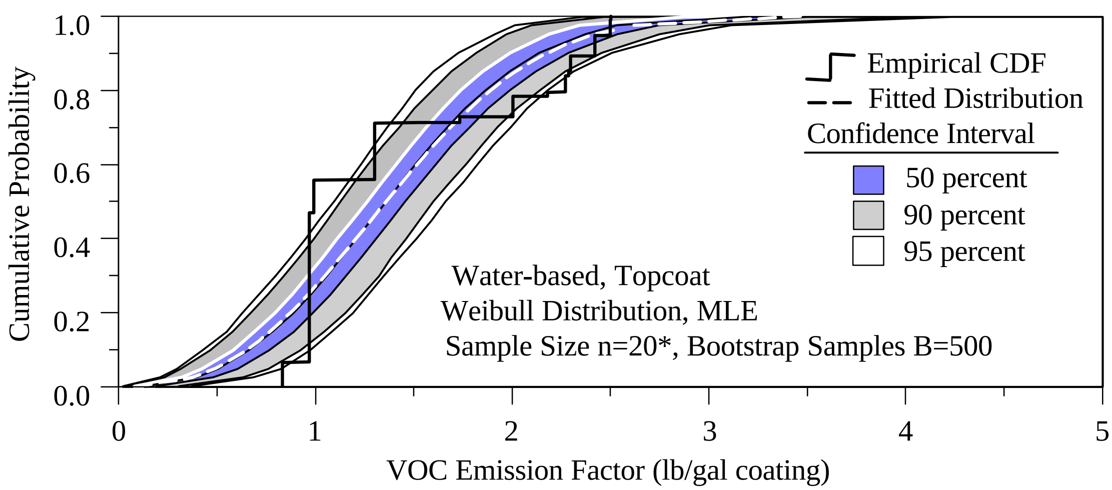

1.0
0.8
0.6
0.4
0.2
0.0
Cumulative Probability
0
2
4
6
8
10
VOC Emission Factor (lb/gal coating)
Empirical CDF
Fitted Distribution
Confidence Interval
50 percent
90 percent
95 percent
Water-based, Filler
Weibull Distribution, MLE
Sample Size n=4
Bootstrap Samples B=500



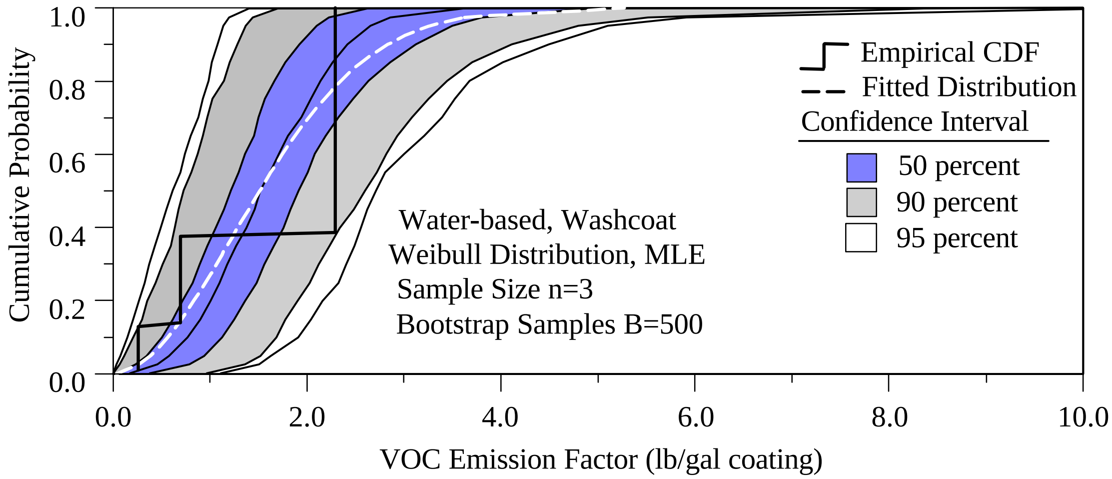
Empirical CDF
Fitted Distribution
Confidence Interval
50 percent
90 percent
95 percent
Water-based, Sealer
Weibull Distribution, MLE
Sample Size n=11, Bootstrap Samples B=500
2 samples have the same value of 2.4199
2 samples have the same value of 2.5000
Cumulative Probability
0.0
0.2
0.4
0.6
0.8
1.0
0.0
2.0
4.0
6.0
8.0
10.0
VOC Emission Factor (lb/gal coating)



Empirical CDF
Fitted Distribution
Confidence Interval
50 percent
90 percent
95 percent
Water-based, Stain
Weibull Distribution, MLE
Sample Size n=17, Bootstrap Samples B=500
2 samples have the same value of 2.5000
Cumulative Probability
0.0
0.2
0.4
0.6
0.8
1.0
0
2
4
6
8
10
VOC Emission Factor (lb/gal coating)



Empirical CDF
Fitted Distribution
Confidence Interval
50 percent
90 percent
95 percent
Water-based, Topcoat
Weibull Distribution, MLE
Sample Size n=20*, Bootstrap Samples B=500
Cumulative Probability
0.0
0.2
0.4
0.6
0.8
1.0
0
1
2
3
4
5
VOC Emission Factor (lb/gal coating)


1.0
0.8
0.6
0.4
0.2
0.0
Cumulative Probability
0.0
2.0
4.0
6.0
8.0
10.0
VOC Emission Factor (lb/gal coating)
Empirical CDF
Fitted Distribution
Confidence Interval
50 percent
90 percent
95 percent
Water-based, Washcoat
Weibull Distribution, MLE
Sample Size n=3
Bootstrap Samples B=500