Evaluation of Emissions from R&D Facilities Using Stack Measurements

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Abstract

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Research and development (R&D) facilities may be required to estimate air chemical emissions to demonstrate compliance with federal and state regulations, or to manage emissions to avoid nuisance impacts from their operations. These emissions are difficult to estimate because R&D facilities typically use a large number of chemicals in small quantities and engage in numerous and diverse activities which can change over time. Although not required for compliance, the Pacific Northwest National Laboratory (PNNL) sampled air chemical emissions from facility stacks during 1998–2008. The purpose of the sampling was to provide data to compare estimated release fractions to those used for emissions estimates and to verify that methods used to determine compliance with air regulations and permits conservatively predict actual emissions. This unique data set was analyzed to compare emissions with regulatory criteria; determine relationships with chemical inventories, use quantities, and properties; and identify signatures of sources contributing to the emissions.

For comparison with regulatory data, stack measurements were used as a basis to calculate 24-hr and annual average emissions and ambient air concentrations. The study included an extreme worst-case analysis maximizing emissions and alternate more realistic analyses using a Monte Carlo method that takes into account the full distribution of sampling results. The results from these analyses were then compared to emissions estimated from chemical inventories. Ambient air concentrations calculated from the measurement data were below acceptable source impact levels for almost all cases even under extreme worst-case assumptions. More realistic scenarios reduced the estimate significantly depending on the chemical and the mode of operation.

Release fractions were calculated by dividing emission estimates obtained using a Monte Carlo technique on the measured data by a building chemical inventory quantity. Release fraction values had a wide range among chemicals and among data sets for different buildings and/or years for a given chemical. Regressions of release fractions and of mean emissions to chemical inventory and properties gave weak correlations. These results highlight the difficulties in estimating emissions from R&D facilities using chemical inventory data.

Positive matrix factorization (PMF) was applied to stack measurements and, depending on the building, resulted in between 9 and 11 factors contributing to emissions. Some factors were similar between buildings, while others had similar profiles for two or more buildings but not for all four. At least one factor for each building was identified that contained a broad mix of many species, and constraints were used in PMF to modify these factors to resemble more closely the off-shift concentration profiles.

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1.0 INTRODUCTION

Emissions of hazardous air pollutants (HAPs) from research and development (R&D) facilities are difficult to estimate because these facilities typically use a large number of chemicals in small quantities and engage in numerous and diverse activities that can change over time. This investigation introduces methods using measured stack concentrations from R&D facilities to compare ambient concentrations and emissions with regulatory criteria, estimate release fractions of chemical inventories, evaluate relationships of emissions with chemical properties, and identify signatures of factors contributing to emissions.

1.1 Motivation and Specific Aims

Established in 1990, Title V of the Clean Air Act Amendments (CAAA; 42 U.S. Code [U.S.C.] 7661) creates an operating permit program for federal, state, and local authorities to regulate air pollution emissions from large sources. Title V requires the following sources of air pollution emissions to obtain operating permits (40 Code of Federal Regulations [CFR] 70):

- Sources that emit more than 100 tons per year (/yr) of a regulated air pollutant (e.g., carbon monoxide, nitrogen oxides, volatile organic compounds [VOCs], sulfur dioxide, and particulates).
- Sources located in nonattainment areas (areas that do not meet National Ambient Air Quality Standards) with emissions ranging between 10–100 tons per year depending on the pollutant and the seriousness of the nonattainment.
- Sources that emit more than 10 tons/yr of any single HAP or more than 25 tons per year of any combination of HAPs regulated under Title III of the 1990 CAAA.
- Any area (i.e., non-major) source for which a New Source Performance Standard (NSPS) or National Emission Standard for Hazardous Air Pollutant (NESHAP) is promulgated that the standard does not exempt from Title V.

In addition, permits are required for sources that are regulated under acid rain, ozone depleting substances, and other sections of the CAAA. Operating permits are issued by state and local permitting authorities, which may have additional or more stringent requirements than those mandated by federal regulations.

R&D facilities have the potential to be classified as a major source if emissions exceed HAP major source thresholds. These facilities may also need to be incorporated into a Title V permit if they are collocated with a manufacturing site that is a major source and if they cannot be excluded based on actual emission threshold rates, or based on individual size and production rate criteria. Thus, facilities conducting R&D will need to develop methods for estimating R&D emissions to establish compliance status with the regulation. In addition to federal regulations, some states have additional regulations that apply to air chemical emissions. Applicability to R&D facilities varies depending on the state and/or interpretation of the enforcing authority.

The U.S. Environmental Protection Agency (EPA) is responsible for enforcing the CAAA and has provided guidance on estimating airborne emissions from a number of regulated source categories (EPA 1995 and supplements) but not for R&D operations. Emissions of HAPs from R&D facilities are difficult to estimate because these facilities typically use a large number of chemicals in small quantities, engage in numerous and diverse activities, and chemicals and activities change over time. Estimation techniques typically assume upper-bound values especially for R&D operations conducted at multidisciplinary laboratories because of the breadth and evolving nature of research activities.

The unique nature of R&D has been recognized in Title III, Section 112(c)(7) of the CAAA of 1990 (42 U.S.C. § 7412(c)(7), 2011). The regulation requires establishing a “separate category covering research or laboratory facilities, as necessary to assure equitable treatment of such facilities” when establishing emission standards for HAPs. However, R&D facilities are not currently regulated as a unique category, and no guidance has been developed to estimate emissions from R&D activities. Although the EPA has not specifically listed R&D facilities as a source category of HAPs, they have considered doing so and submitted an Advance Notice of Proposed Rulemaking for the NESHAP: Source Category List to include R&D facilities on this list (62 Federal Register [FR] 25877–79, 1997). Public comments on the proposal noted the difficulties in estimating emissions from R&D activities that are highly variable in nature, with many small quantities of chemicals and a large number of often-changing processes (EPA, 1998). Comments also included a request for “guidance for clear, consistent potential to emit (PTE) calculation methodology for R&D operations.”

Pacific Northwest National Laboratory (PNNL) operates a number of multidisciplinary laboratory research facilities for the U.S. Department of Energy (DOE) and sampled air chemical emissions from some of these facilities during 1998–2008. The primary purpose of this sampling was to provide data to compare estimated release fractions to those used for emissions estimates, verifying that methods used to determine compliance with air regulations and permits conservatively predict actual emissions. Sampling also identifies and quantifies air toxics emitted to compare with compliance limits established by regulatory agencies. Results from initial sampling campaigns were evaluated and reported by Woodruff, Benar, and McCarthy (2000), who summarized the PNNL compliance approach and described sampling and analytical measurements for the first sampling campaigns. Conclusions reported in this paper were that none of the target compound measurements exceeded an acceptable source impact level (Washington Administrative Code [WAC], Chapter 173-460) and that an average release fraction calculated from the data provided reasonable validation of the factor used in compliance assessments. Recognizing that laboratory emissions are intermittent in nature and may change from one year to the next, additional sampling was conducted to estimate release fractions over a longer period and compare them to those typically used for emissions estimates to determine compliance with air regulations and permits.

The goal of this study was to use the comprehensive set of sampling data to test the following hypotheses:

1. Measurement data from R&D facilities can be used to compare air chemical emissions with regulatory criteria.
2. R&D emissions are related to chemical properties in addition to chemical use quantities.
3. Sources of air emissions from R&D facilities include activities that emit multiple compounds with a characteristic signature.

The following specific aims were set to address this goal.

Specific Aim 1: Evaluate emissions from R&D facilities against regulatory criteria using stack measurement data

One aim of this study was to calculate ambient air concentrations and total emissions (per year and per 24-hr) using measured stack concentrations in order to make the comparison to regulatory criteria. Calculations based on worst-case assumptions (maximizing estimated emissions or ambient concentrations) provide an initial basis for comparison, but alternative scenarios with more realistic assumptions are also investigated to quantify conservatism in worst-case assumptions.

Specific Aim 2: Estimate release fractions from measured stack concentrations and chemical inventory data and explore relationships with chemical properties

A Monte Carlo technique is used to estimate distributions of annual emissions from each data set, which consists of sampling data for a target compound for a given year and building. The emission distributions are combined with chemical inventory information to calculate distributions of release fractions. The relationship of release fractions and of emissions to chemical properties is investigated to seek improved methods of estimating emissions.

Specific Aim 3: Identify and characterize sources contributing to R&D stack emissions using source apportionment models

PMF is used to identify and characterize contributors to measured stack emissions from each building and from all buildings together. Results are compared among buildings to identify factors in common among all buildings and unique to individual buildings. Individual factors are considered to determine whether they indicate releases from specific activities or background concentrations.

1.2 Background

This section discusses background information pertinent to the analysis, including a description of regulatory criteria applicable to the compounds analyzed in the stack samples, a discussion of methods used to estimate emissions from R&D facilities, and applications of source apportionment.

Regulatory Criteria

This paper uses measured data to compare emissions with regulatory criteria and presents methods that take into consideration the variability of emissions over time. In addition to federal regulations, some states have regulations that apply to air chemical emissions. Applicability to R&D facilities varies depending on the state and/or interpretation of the enforcing authority. In Washington state, which is the location of R&D facilities known as PNNL, these regulations include *General Regulations for Air Pollution Sources* (WAC 173-400), *Operating Permit Regulation* (WAC 173-401), and *Controls for New Sources of Toxic Air Pollutants* (WAC 173-460), all of which contain requirements for control of a specific list of toxic air pollutants (TAPs) as well as address the criteria pollutants of particulate matter, carbon monoxide, nitrogen oxides, sulfur dioxide, lead, and ozone.

The list of TAPs includes carcinogens and non-carcinogens with nearly 400 compounds along with the following three associated levels for determining new source review requirements: acceptable source impact level (ASIL), small quantity emission rate (SQER), and de minimis emission threshold. ASILs are screening concentrations of the pollutants in the ambient air, SQERs are levels of emissions below which dispersion modeling is not required to demonstrate compliance with ASILs, and de minimis emission thresholds are trivial levels of emissions that do not pose a threat to human health or the environment. For carcinogenic compounds, the ASIL is an annual average concentration in micrograms per cubic meter ($\mu g/m^3$) based on an increased cancer risk of one in 1 million while for non-carcinogenic compounds, the 24-hr ASIL is a concentration ($\mu g/m^3$) based on a threshold concentration for toxic effects.

The Washington State Title V regulation allows emissions to be evaluated against a list of "thresholds for hazardous air pollutants" to determine whether an emission unit or activity within a permit can be considered insignificant. The list of threshold values is from WAC 173-401, while the list of TAPs and their associated ASIL, SQER, and de minimis values are from WAC 173-460. Not all of the same compounds are on both lists.

Methods Used to Estimate Emissions from R&D Facilities

A variety of methods are currently being used to estimate air chemical emissions from R&D facilities associated with national laboratories, and these are generally considered conservative in that they overestimate actual emissions. Although regulatory agencies have not established release fractions directly applicable to estimating air chemical emissions from R&D laboratories, many of the methods are based on applying a release fraction to chemical inventory and/or chemical usage. In at least one case, a release fraction of one (100%) has been applied to chemicals purchased for R&D activities in a given year to estimate emissions of VOCs and HAPs (North and Adelson, 1995). In another case, 5% was assumed based on input from research staff and applied to the subset of chemicals purchased for R&D activities and containing VOC or HAPs constituents (Skipper, 2000). Other methods vary depending on the requirements specified in a permit, agreements with regulatory agencies, or degree of conservatism required. However, the basis for the emission factors employed is not strongly tied to chemical or process characteristics, and the uncertainty in emissions estimates is unknown.

PNNL's approach was to adopt the method of 40 CFR 61 Appendix D, "National Emission Standards for Hazardous Air Pollutants" (2005) and WAC 246-247, "Radiation Protection – Air Emissions" (2005) for estimating emissions to the atmosphere. The regulation assigns a release fraction of 1 to gases, 10^{-3} to liquids and powders, and 10^{-6} to solids. The amount of material used by the facility for the period under consideration is multiplied by the release fraction to calculate emissions; thus, the release fraction is a type of emission factor applied to chemical inventory and/or usage data, which is a measure of activity rate. Additional factors are provided to take credit for filters or other control devices in reducing emissions. The basis for the 40 CFR 61 Appendix D release fraction applied to liquids and powders included a large number of materials and diverse activities but were limited with respect to volatile solutions (EPA, 1989a). Therefore, volatile liquids were identified by PNNL as a separate category with a release fraction of 0.1. In the cited regulations, the release fractions are applied to the “amount used at facilities for the period under consideration” (40 CFR 61, 2005) or to the annual possession quantity which is defined as “the sum of the quantity of a radionuclide on hand at the beginning of the calendar year and the quantity of that radionuclide received or produced during the calendar year” (WAC 246-247, 2005).

Source Apportionment

PMF is a widely applied receptor modeling technique that has been used extensively to assess sources contributing to ambient air particulate pollution since its introduction (Paatero and Tapper, 1994). For example, Norris (1998) used PMF to identify signatures of sources contributing to particulate matter in Spokane, WA; Rose (2006) studied fine particle data from National Parks to determine the impact of sources on visibility impairment; Rizzo and Scheff (2007) analyzed fine particle concentrations in Chicago, IL to identify contributing sources; Jaeckels, Bae, and Schauer (2007) looked for contributors to aerosols in St. Louis, MO using organic molecular markers as identifiers; and Dogan, Karakas, and Tuncel (2007) applied PMF to source apportionment of aerosols on the coast of Turkey. In addition to particulate matter, PMF has been applied to a wide range of air quality indicators such as particulate and gaseous species plus meteorological parameters in northern Michigan (Paterson et al., 1999). PMF model applications have been broadened to other environmental media, including soil contamination (Vaccaro et al., 2007) and offshore sediments (Bzdusek, Lu, and Christensen, 2006; Sundqvist et al., 2010). Applying PMF to determine contributions to stack emissions as presented in this paper is a unique use of the model.

1.3 Dissertation Framework

The following chapters provide a full description of the analyses performed for this dissertation. Section 2, “Sample Collection and Analysis,” provides details of the sampling and analysis conducted to obtain the stack measurement data. Sections 3, 4, and 5 are stand-alone journal articles that were either submitted for journal publication or, in the case of Section 4, were already published. Section 3, “Comparison of Stack Measurement Data from R&D Facilities to Regulatory Criteria: A Case Study from PNNL,” evaluates ambient air concentrations and total emissions derived from stack measurement data to regulatory criteria applicable to specific compounds. Section 4, “Estimating Air Chemical Emissions From Research Activities Using Stack Measurement Data,” uses a Monte Carlo technique to obtain a range of values for emission estimates which are used in conjunction with chemical inventory information to determine release fractions. Correlations between release fractions and total emissions with inventory data and chemical properties are investigated. Section 5, “Source Apportionment of Stack Emissions from Research and Development Facilities Using Positive Matrix Factorization,” uses source apportionment to identify and characterize factors contributing to measured stack emissions and explores the factors to determine whether they point to specific activities or processes. Finally, Section 6 contains a summary of the work, highlight of findings, and considerations for future sampling.

2.0 SAMPLE COLLECTION AND ANALYSIS

Samples of air emissions were collected during 1998–2008 from four PNNL-operated buildings: a Radiochemical Processing Laboratory (RPL; 325), a Chemical Sciences Laboratory (CSL; 329), a Life Sciences Laboratory (LSL; 331), and the Environmental Molecular Sciences Laboratory (EMSL) user facility. A single emission point was sampled from the first three buildings, and three emission points were sampled at EMSL. Sampling times were usually 100 minutes (min) taken within normal work day hours (i.e., 8 a.m.–5 p.m.). However, some longer and shorter sampling times were also used, and some samples were taken during a given sampling campaign to provide data on weekend and off-shift hours. Although samples were mostly obtained from exhaust stacks, early sampling campaigns included locations such as lobbies and corridors to represent background emissions (e.g., emissions from supply air, building components, or furniture). A total of 344 samples were obtained from building stacks with a range of 23–54 samples taken each year and 54–141 samples taken from each building over all years.

Air samples were collected from stack exhausts onto triple adsorbent tubes that were subsequently analyzed for VOCs using gas chromatography/mass spectrometry (GC/MS) analysis at a PNNL laboratory. Sampling was conducted by extracting a subsample of the effluent stream through a tube over a given time period so that volatiles and semi-volatiles in the stream were adsorbed onto graphitized sorbent beds within the tube. The sampler drew air simultaneously through two tubes in parallel flow paths with flow rates independently adjusted for each path as based on EPA Compendium Method TO-17 (EPA, 1999b). This method provides guidelines for collection of ambient air toxic organic compounds on a variety of different sorbent media.

All samples were collected on Supelco 300 triple-sorbent traps (TSTs), commercial products purchased from Supelco, Inc. in Bellefonte, PA. Each sampling device consists of a ground glass tube (115 millimeters [mm] long, 6 mm outside diameter, 4 mm inside diameter) containing a series of sorbent trapping beds arranged in order of increasing retentivity. Each tube contains 300 milligrams (mg) of Carbotrap™ C, 200 mg of Carbotrap™ B, and 125 mg of Carbosieve™ S-III.

The first two sorbents are forms of deactivated graphite with limited sorption power for less volatile organic compounds. The final trapping stage, Carbosieve™ S-III, is a graphetized molecular sieve capable of retaining the most volatile components, including the permanent gases such as propane, Freon-12, chloromethane, and vinyl chloride.

Prior to shipment to the field, all tubes were heated to a temperature of 380°C for at least 30 min with a reverse helium flow of 30 milliliters (ml)/min. Each tube was then transferred to Supelco plastic containers to avoid contamination during shipment and storage. Prior to sampling and during long-term storage prior to analysis, samples in the containers were kept in refrigerated storage at –20°C. Previous studies conducted at PNNL (Evans et al., 1998) spanning a wide range of analytes demonstrated that samples can be safely stored in that manner for prolonged periods without compromise of integrity.

The glass tubes were pre-marked with unique identification numbers. Each storage container was affixed with an identification label containing a separate unique sequential number associated with the sampling event as well as the tube number for the trap contained within. This information was also recorded on a field sampling log prepared at the same time to be used as a chain-of-custody record. Samples were transferred to the field and back to the lab at the conclusion of sampling under standard chain-of-custody protocol.

All samples were analyzed by thermal desorption and GC/MS using procedures consistent with the mass spectrometry and QA/QC guidelines set forth in EPA Compendium Method TO-15 (EPA, 1999a). A set of 49 compounds were targeted in the analysis, primarily from a standard containing the 39 compound mixtures specified in EPA Compendium Method TO-14 (EPA, 1989b) plus a short list of supplementary analytes in a second standard.[1]

At the completion of each daily batch run, all GC/MS data were copied to a disk for archiving and transferred to a remote chromatography data reduction system. Data reduction was performed using Environmental ChemStation G1701 CA Version C.00.00 analysis software.

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[1] Compendium Method TO-17 describes the method used to collect the samples onto sorbent tubes and references Method TO-15 for the GC/MS analytical procedure and Method TO-14 for a target compound list.

3.0 COMPARISON OF STACK MEASUREMENT DATA FROM R&D FACILITIES TO REGULATORY CRITERIA: A CASE STUDY FROM PNNL[2]

3.1 Abstract

Chemical emissions from R&D activities are difficult to estimate because of the large number of chemicals used and the potential for continual changes in processes. In this case study, stack measurements taken from R&D facilities at PNNL were examined, including extreme worst-case emissions estimates and alternate analyses using a Monte Carlo method that takes into account the full distribution of sampling results. The results from these analyses were then compared to emissions estimated from chemical inventories. Results showed that downwind ambient air concentrations calculated from the stack measurement data were below ASILs for almost all compounds, even under extreme worst-case analyses. However, for compounds with averaging periods of a year, the unrealistic but simplifying worst-case analysis often resulted in exceedances of lower level regulatory criteria used to determine modeling requirements or to define trivial releases. Compounds with 24-hr averaging periods were nearly all several orders of magnitude below all criteria, including the trivial release. The alternate analysis supplied a more realistic basis of comparison and an ability to explore effects under different operational modes.

3.2 Introduction

Established in 1990, Title V of the CAAA (42 U.S.C. 7661) creates an operating permit program for federal, state, and local authorities to regulate air pollution emissions from large sources. Operating permits are issued by state and local permitting authorities that may have additional or more stringent requirements than those mandated by federal regulations. The EPA is responsible for enforcing the CAAA and has provided guidance on estimating airborne emissions from a number of regulated source categories (EPA 1995, plus supplements).

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[2] This chapter was submitted for publication to the *Journal of the Air and Waste Management Association*, authors M. Ballinger (Battelle Seattle Research Center, Seattle, WA 98109); R. Woodruff and C. Duchsherer (Pacific Northwest National Laboratory, Richland, WA 99352); and T. Larson (Department of Civil and Environmental Engineering, University of Washington, Seattle, WA 98195).

R&D facilities are not currently regulated as a unique category, and no guidance has been developed to estimate emissions from R&D activities. However, these facilities may become stand-alone major sources (emissions exceed HAP major source thresholds), or they may need to be incorporated into a Title V permit if they are collocated with a manufacturing site that is considered to be a major source. The facilities can also be excluded based on either actual emission threshold rates or individual size and production rate criteria. Emissions of HAPs from R&D facilities are difficult to estimate because these facilities typically use a large number of chemicals in small quantities, engage in numerous and diverse activities, and chemicals and activities change over time.

In addition to federal regulations, some states have regulations that apply to air chemical emissions. Applicability to R&D facilities varies depending on the state and/or interpretation of the enforcing authority. In Washington State, these regulations include *General Regulations for Air Pollution Sources* (WAC 173-400), *Operating Permit Regulation* (WAC 173-401), and *Controls for New Sources of Toxic Air Pollutants* (WAC 173-460), all of which contain requirements for controlling the emissions of a specific list of TAPs as well as address the criteria pollutants of particulate matter, carbon monoxide, nitrogen dioxide, sulfur dioxide, lead, and ozone.

The list of TAPs includes carcinogens and non-carcinogens with nearly 400 compounds along with the following three associated levels for determining new source review requirements: ASIL, SQER, and de minimis emission threshold. ASILs are screening concentrations of the pollutants in the ambient air; SQERs are levels of emissions below which dispersion modeling is not required to demonstrate compliance with ASILs; and de minimis emission thresholds are trivial levels of emissions that do not pose a threat to human health or the environment. For carcinogenic compounds, ASIL is an annual average concentration ($\mu g/m^3$) based on an increased cancer risk of one in 1 million, while for non-carcinogenic compounds, the 24-hr ASIL is based on a threshold concentration for toxic effects.

The Washington State Title V regulation allows emissions to be evaluated against a list of “thresholds for hazardous air pollutants” to determine whether an emission unit or activity within a permit can be considered insignificant. The list of threshold values is from WAC 173-401, while the list of TAPs and their associated ASIL, SQER, and de minimis values are from WAC 173-460. Many but not all of the same compounds are on both lists.

PNNL sampled for air chemical emissions from R&D laboratory buildings during 1998–2008 to obtain data to evaluate emission estimation methods and to identify and quantify air toxics emitted for comparison with compliance limits established by Washington state. Just as many different and changing processes in an R&D facility make it difficult to estimate emissions, the variability of measured emissions also make it difficult to compare with compliance limits for specific average periods. This study uses measured data to compare emissions with regulatory criteria and presents methods that consider the variability of emissions over time.

3.3 Methods

Stack Sampling

PNNL sampled air chemical emissions from the stacks of four buildings during 1998–2008: RPL (325), CSL (329), LSL (331), and EMSL. Sampling times were usually 100 min taken during normal work day hours (i.e., 8:00 a.m.–5:00 p.m.), except for the initial year of sampling, during which 300- and 50-min samples were obtained. A limited number of samples were acquired during nights and weekends to represent off-shift times when R&D activities are not likely to occur. Thus, sampling results are identified as on-shift and off-shift.

Although samples were mostly obtained from exhaust stacks, early sampling campaigns included locations such as lobbies and corridors to evaluate non-research related contributions to emissions. Data from these alternate locations were compared with off-shift samples to evaluate whether off-shift concentrations were similar to non-research emissions or whether they contained additional emissions from research being conducted in off-normal hours.

The sampling method was the collection of air samples from stack exhausts onto TSTs that were subsequently analyzed for VOCs using GC/MS analysis. The sampling apparatus had two parallel channels into which the air stream is drawn; each channel has its own flow rate, and one of the channels was programmed to collect a sample at double the flow rate of the other. Thus, each sample has a pseudo-duplicate to identify quality issues and to estimate uncertainty. Additional information on sampling and analysis procedures is provided in Woodruff, Benar, and McCarthy (2000).

Depending on the year, a total of 46–49 target compounds (Table 3.1) were analyzed by GC/MS. The compounds were selected primarily from a standard containing a mixture of 39 compounds specified in EPA Compendium Method TO-14 (EPA, 1989b), plus a short list of supplementary analytes in a second standard. Depending on the building, the number of stack samples taken varied from 54 to 141, with a total of 344 samples. Thirty-two compounds were listed as TAPs in WAC 173-460-150 with associated ASILs, SQERs, and de minimis criteria. Averaging periods were either 1 year (19 compounds) or 24-hr (13 compounds) representing carcinogenic and non-carcinogenic effects, respectively. Most of these compounds were also listed in the table of Title V Thresholds for hazardous air pollutants in WAC 173-401-531. The current list of TAPs has been in place since June 2009, at which time WAC 173-460 was revised to reflect current toxicology data, with some compounds previously listed as TAPs removed (Washington State Department of Ecology, 2008). For purposes of this evaluation, de-listed chemicals were assigned their previous ASIL as surrogate values for comparison and providing evaluation criteria for an additional nine compounds.

Table 3.1. Target Compounds and Associated Regulatory Criteria

		State TAPs*			**Title V†**
CAS#	**Compound Name**	**ASIL ($\mu g/m^3$)**	**SQER (lb/avg period)**	**De Minimis (lb/avg period)**	**Threshold (ton/yr)**
Target Compounds Listed as TAPs in WAC 173-460 with year averaging period					
79-34-5	1,1,2,2-Tetrachloroethane	0.0172	3.3	0.165	0.15
79-00-5	1,1,2-Trichloroethane	0.0625	12	0.6	0.5
75-34-3	1,1-Dichloroethane	0.625	120	6	0.5
106-93-4	1,2-Dibromoethane	0.0141	2.71	0.135	0.05
107-06-2	1,2-Dichloroethane	0.0385	7.39	0.369	0.4
106-99-0	1,3-Butadiene	0.00588	1.13	0.0564	0.035
106-46-7	1,4-Dichlorobenzene	0.0909	17.4	0.872	0.5
107-05-1	3-Chloropropene	0.167	32	1.6	0.5
75-05-8	Acetonitrile	60	1.15E+04	576	0.5
71-43-2	Benzene	0.0345	6.62	0.331	0.5
56-23-5	Carbon tetrachloride	0.0238	4.57	0.228	0.5
67-66-3	Chloroform	0.0435	8.35	0.417	0.45
100-41-4	Ethylbenzene	0.4	76.8	3.84	0.5

		State TAPs*			**Title V†**
CAS#	**Compound Name**	**ASIL ($\mu g/m^3$)**	**SQER (lb/avg period)**	**De Minimis (lb/avg period)**	**Threshold (ton/yr)**
87-68-3	Hexachloro-1,3-butadiene	0.0455	8.73	0.437	0.5
75-09-2	Methylene chloride	1	192	9.59	0.5
78-87-5	Propane, 1,2-dichloro-	0.1	19.2	0.959	0.5
127-18-4	Tetrachloroethylene	0.169	32.4	1.62	0.5
79-01-6	Trichloroethene	0.5	95.9	4.8	0.01
75-01-4	Vinyl chloride	0.0128	2.46	0.123	0.1
Target Compounds Listed as TAPs in WAC 173-460 with 24-hr averaging period					
71-55-6	1,1,1-Trichloroethane	1000	131	6.57	0.5
75-35-4	1,1-Dichloroethene	200	26.3	1.31	0.2
98-82-8	1-Methylethylbenzene	400	52.6	2.63	0.5
78-93-3	2-Butanone	5000	657	32.9	0.5
74-83-9	Bromomethane	5	0.657	0.0629	
108-90-7	Chlorobenzene	1000	131	6.57	0.5
75-00-3	Chloroethane	3.00E+04	3940	197	0.5
74-87-3	Chloromethane	90	11.8	0.591	0.5
67-56-1	Methanol	4000	526	26.3	0.5
95-47-6	o-Xylene	221	29	1.45	
106-42-3	p/m-Xylene	221	29	1.45	
100-42-5	Styrene	900	118	5.91	0.5
108-88-3	Toluene	5000	657	32.9	0.5
Target Compounds Previously Listed as TAPs in WAC 173-460 with 24-hr averaging period					
76-13-1	1,1,2-trichloro-1,2,2-trifluoroethane	2.7E+04	3547.8	177.39	
120-82-1	1,2,4-Trichlorobenzene	120	15.77	0.7884	0.5
76-14-2	1,2-dichloro-1,1,2,2-tetrafluoroethane	2.3E+04	3022.2	151.11	
95-50-1	1,2-Dichlorobenzene	1000	131.4	6.57	
67-64-1	Acetone	5900	775.26	38.763	
75-71-8	Dichlorodifluoromethane	1.6E+04	2102.4	105.12	
64-17-5	Ethanol	6300	827.82	41.391	
109-66-0	Pentane	6000	788.4	39.42	
75-69-4	Trichlorofluoromethane	1.9E+04	2496.6	124.83	
Target Compounds Not Currently or Previously Listed as TAPs in WAC 173-460					

CAS#	Compound Name	CAS#	Compound Name
541-73-1	1,3-Dichlorobenzene	108-67-8	1,3,5-Trimethylbenzene
10061-01-5	cis-1,3-Dichloropropene	611-14-3	1-Ethyl-2-Methyl-Benzene
10061-02-6	trans-1,3-Dichloropropene	622-96-8	1-Ethyl-4-methylbenzene
95-63-6	1,2,4-Trimethylbenzene	156-59-2	cis-1,2-Dichloroethene

* WAC 173-460-150; note that ASIL applies to ambient air concentration and the other criteria apply to stack emissions. Significant figures are the same as those given in the regulation.

† WAC 174-401-531

Calculation of Ambient Air Concentrations

Analytical results provided concentrations for each of the target compounds in the stack gases sampled, but ASILs are ambient air concentrations at locations in which there is no restriction or control of public access. Thus, a dispersion factor is needed to calculate ambient air concentrations from the measured data as shown in eq 3.1.

$$\text{Ambient Concentration} = \text{Stack Concentration} \times 1\text{E-3 g/mg} \times \text{Stack Flow Rate} \times \text{Dispersion Factor} \qquad (3.1)$$

Where Ambient Concentration = receptor concentration in $\mu g/m^3$

Stack Concentration = mg/m^3

Stack Flow Rate = m^3/s

Dispersion Factor = ambient air concentration at a specific location per unit of stack emission rate, calculated with units of $\mu g/m^3$ per g/s. The location is determined by the code as the maximum impact for the modeled emission point and meteorology.

Alternately, a stack concentration corresponding to the ASIL can be calculated by rearranging eq 3.1 as shown in eq 3.2.

$$C_{ASIL} = \frac{\text{ASIL}}{(1\text{E-3 g/mg} \times \text{Stack Flow Rate} \times \text{Dispersion Factor})} \qquad (3.2)$$

Where ASIL= $\mu g/m^3$

C_{ASIL} = stack concentration in mg/m^3 resulting in the air concentration equaling the ASIL at the specific location where the Dispersion Factor applies.

Dispersion factors were calculated for both annual and 24-hr average concentrations using the AERMOD atmospheric dispersion modeling system. Developed by a collaborative team of the American Meteorological Society and EPA, AERMOD has been adopted as the EPA's preferred regulatory model for both simple and complex terrain and is promulgated as the preferred regulatory model (EPA, 2012a).

BREEZE AERMOD version 7.3 was used in this application to calculate dispersion factors for each of the sampled buildings with inputs that included stack height and exit gas temperature as well as velocity, stack diameter, and building and emission point location/dimensions with respect to the surrounding area. All of these values were relatively constant over time for each emission point. Distances from the stacks to the nearest facility boundary ranged from 190 -

400m and AERMOD identified the location outside of these boundaries that resulted in the highest dispersion factor. Five years of meteorological data were used as input to AERMOD to provide the range of dispersion conditions with which to evaluate impacts. Data from local meteorological towers for 2004–2008 were chosen because those years corresponded with the most recent sampling campaigns.

Two operational scenarios were modeled with AERMOD, the first being theoretical in which operation occurs for “three shifts” daily for 365 days/yr and emissions are continuous at a constant rate. The second operational scenario was for the typical 8 a.m.–5 p.m. Monday through Friday “one shift” per day for a nominal 250 days/yr. The off-shift emissions were conservatively set at 10% of on-shift because maximum measured off-shift concentrations for the compounds closer to the ASIL values were almost all less than 10% of the maximum on-shift concentrations. Although R&D activities are not likely to be constant or continuous even during on-shift hours, the “one shift” AERMOD case quantifies some of the conservatism in operating mode assumptions.

Ambient air concentrations were calculated using the modeled highest 24-hr and annual average dispersion factors from the 5-year data set for each building coupled with the single highest 100-min concentration measured in the stack. While unrealistic, this approach provides bases for comparing scenarios and a screening comparison with corresponding ASIL values given in Table 3.1. In addition, the stack concentrations corresponding to ASIL values were calculated as shown in eq 3.2 and compared to the full set of sampling data, again using the single highest 24-hr and annual dispersion factor based on AERMOD modeling of the 5 years of meteorological data.

Calculation of Annual and 24-Hour Emissions

In addition to ASILs, which are screening concentrations of toxic air pollutants in the ambient air, other criteria (SQER, de minimis, and threshold values) in units of total emission for a given time period have regulatory significance. SQERs are levels of emissions below which dispersion modeling is not required to demonstrate compliance with ASILs; de minimis emission thresholds are trivial levels of emissions that are of no regulatory concern; and Title V thresholds can be used to determine whether an emission unit or activity can be considered insignificant for Title V permitting. Measured stack concentrations can be converted to emission rates by multiplying stack concentration by volumetric flow rate, which was relatively constant for the stacks sampled.[3] Although R&D emissions are highly variable as demonstrated by measurement data, an analysis is presented assuming continuous emissions at a constant rate equal to the single highest measured sample concentration for each compound. The stack concentrations that correspond to SQER and de minimis values can be back-calculated similarly to eq 3.2 for ASILs, except that no dispersion factor is needed and different conversion factors are required because SQER and de minimis are in units of pounds per averaging period. The stack concentrations corresponding to SQER and de minimis values for a three-shift scenario are presented for comparison to the sampling data.

Assumptions were made to simplify calculations that result in extreme maximum (over-estimated) estimates of emissions. The assumption of three operation shifts at the single maximum measured concentration carries a much higher degree of conservatism for the longer time frame of a year than for the shorter time frame of a day. For example, a 100-min sample time represents almost 7% of a day but only 0.02% of a year. A method that can be used to estimate annual emissions from all sampling data that takes into account the sporadic nature of R&D operations and variability of emissions is the Monte Carlo method described in Ballinger et al. (2013). Using the full set of sampling data allows incorporation of the different modes of operation such as on-shift and off-shift. Results are provided in the form of a distribution from which the user can choose the statistic with the desired degree of conservatism (e.g., maximum, 95th percentile, mean, or median values) to compare to regulatory values.

In this study, a Monte Carlo analysis was performed on measured data to calculate annual emissions under three modes of operation: (1) three full operating shifts, where R&D is assumed to occur around the clock and all samples (including those taken nights and weekends) are random estimates of emission concentrations at any time of the day, week, or year; (2) on-shift + off-shift, where samples taken during the normal workday ("on-shift") are random estimates of emissions from normal working hours (~2000 hrs/yr) and samples taken during nights and

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[3] Stack flow rates were measured using test methods in 40 CFR 60 Appendix A.

weekend (“off-shift”) are representative of reduced operations occurring the rest of the year; and (3) on-shift – off-shift, where on-shift samples are attributed to normal R&D work plus non-R&D sources (e.g., furniture, office equipment, building infrastructure) and off-shift samples are attributed to non-R&D sources alone. Off-shift is subtracted from on-shift in the third mode to represent emissions from R&D operations as a comparison to chemical inventory estimates.

Sampling data for each building were grouped into on-shift and off-shift. For the three shifts mode, the Monte Carlo simulation, performed using Crystal Ball (Oracle, 2012), involved randomly selecting a value from the distribution that included both on-shift and off-shift data for all sample years for a given building and multiplying that value by the stack volumetric flow and conversion factors to result in the units of lbs/yr. This calculation was executed 1000 times to result in a distribution of annual emission estimates. Calculations for the on-shift + off-shift mode were similar to the three shifts mode, except that random selections were taken separately from the on-shift and off-shift groups and weighted by the hours per year in that shift. On-shift was modeled as a normal distribution with a mean of 2000 hr/yr and sigma of 200 hr/yr, with off-shift occurring the remainder of the year. The on-shift – off-shift mode investigates the possibility that off-shift measurements represent emissions from non-research related operations, a concept supported by the similarity of off-shift concentrations to samples taken in hallways and corridors. Emissions were calculated by subtracting a randomly selected off-shift value from a randomly selected on-shift value before multiplying by the volumetric stack flow rate and the conversion factors. Negative values were set to zero for the final distribution in the on-shift – off-shift mode calculations.

An alternate approach to generating an annual emission estimate from an individual sampling result would be to treat each sample as an indicator of an individual 100-min segment of the year. The Monte Carlo simulation would then randomly select 5256 values (the number of 100-min segments in a year) to compute an emissions estimate and repeat that process 1000 times. This is more realistic than the original approach but more computationally demanding. The alternative approach was used on a limited number of compounds and compared to the original Monte Carlo simulations.

Sample measurements for many compounds were close to or below detection limits, prompting the question of whether detection limits provided sufficient resolution for a comparison with regulatory criteria. The analytical detection limit for each compound is based on the quantity of that compound collected on the sample tube. Thus, detection limits in terms of stack concentration varied with compound and with the volume of gases used to collect the sample. Annual emissions corresponding to detection limit concentrations were calculated by grouping all results below detection limits for each compound and building, and performing a Monte Carlo analysis to calculate a distribution assuming three full operating shifts. This is the same calculation as the three shifts mode described, except that only the concentrations flagged as below detection limit were included in the source distribution.

In addition to calculations performed using measured data, emissions were estimated from chemical inventory data for the years sampled. Data were obtained from a chemical inventory system that tracks chemicals currently in the buildings and also roughly estimates chemical usage based on inventory record changes. Usage quantities are calculated within the system by assuming that the contents of each container are used uniformly between the time a container is full when initially added to the inventory and the time it is removed from inventory. Inventory and usage data were obtained for the compounds with annual averaging periods and emissions calculated by applying a release fraction of 10% to the combination of usage plus one-half inventory quantities (Ballinger et al., 2013). The release fraction of 10% is consistent with that used by PNNL (Woodruff, Benar, and McCarthy, 2000). Chemical usage plus half of inventory was used because PNNL routinely uses this larger quantity to estimate emissions based on the following: in a population of many containers, it can be assumed that on average, the containers are half empty, and half the capacity has been used and was subject to emission processes.

3.4 Results

Ambient Air Concentrations

Ambient air concentrations calculated as shown in eq 3.1 were compared to ASILs and are displayed in Table 3.2 in terms of percent of ASIL. Results are provided for compounds with annual averaging periods (carcinogenic) arranged in order of highest to lowest percent. Compounds with 24-hr averaging periods (non-carcinogenic) are not shown in the table because they were several orders of magnitude less than ASILs with the highest result of 0.2% (p/m-xylene, 331 Building). As seen in Table 3.2, most calculated ambient air concentrations are less than 1% of the ASIL even under the maximally conservative assumptions of the single highest concentration emitted continuously from the stack over a year. Under these assumptions, only one measurement (chloroform in the 331 Building) exceeded the ASIL, and seven others exceed 1% of ASIL values for one or more emission points.

Table 3.2. Comparison of Calculated Concentrations to ASILs*

Compound	325 Building	329 Building	331 Building	EMSL
Chloroform	0.1%	7.0%	130.8%	1.8%
Carbon tetrachloride	0.7%	18.7%	1.8%	0.3%
Methylene chloride	0.9%	16.1%	0.4%	6.4%
Hexachloro-1,3-butadiene	1.7%	2.9%	10.4%	2.8%
Benzene	7.6%	1.4%	9.5%	1.0%
Trichloroethene	3.5%	4.8%	7.9%	5.0%
1,1,2,2-Tetrachloroethane	0.2%	0.2%	2.0%	0.2%
Ethylbenzene	0.0%	0.1%	2.0%	0.1%
1,3-Butadiene	0.2%	0.5%	0.7%	0.5%
1,4-Dichlorobenzene	0.2%	0.4%	0.5%	0.1%
Vinyl chloride	0.1%	0.3%	0.5%	0.4%
1,2-Dichloroethane	0.1%	0.2%	0.3%	0.5%
1,2-Dibromoethane	0.1%	0.2%	0.3%	0.2%
Tetrachloroethylene	0.0%	0.2%	0.0%	0.0%
Propane, 1,2-dichloro-	0.0%	0.1%	0.1%	0.1%
1,1-Dichloroethane	0.0%	0.1%	0.0%	0.0%
3-Chloropropene	0.0%	0.1%	0.1%	NM†
1,1,2-Trichloroethane	0.0%	0.0%	0.1%	0.0%
Acetonitrile	0.0%	0.0%	0.0%	0.0%

* Comparison of ambient air concentrations calculated from highest measured stack concentrations to acceptable source impact levels (target compounds with year averaging periods)

† Not measured: 3-Chloroprene was not part of the suite of target compounds analyzed during the time period that EMSL was sampled.

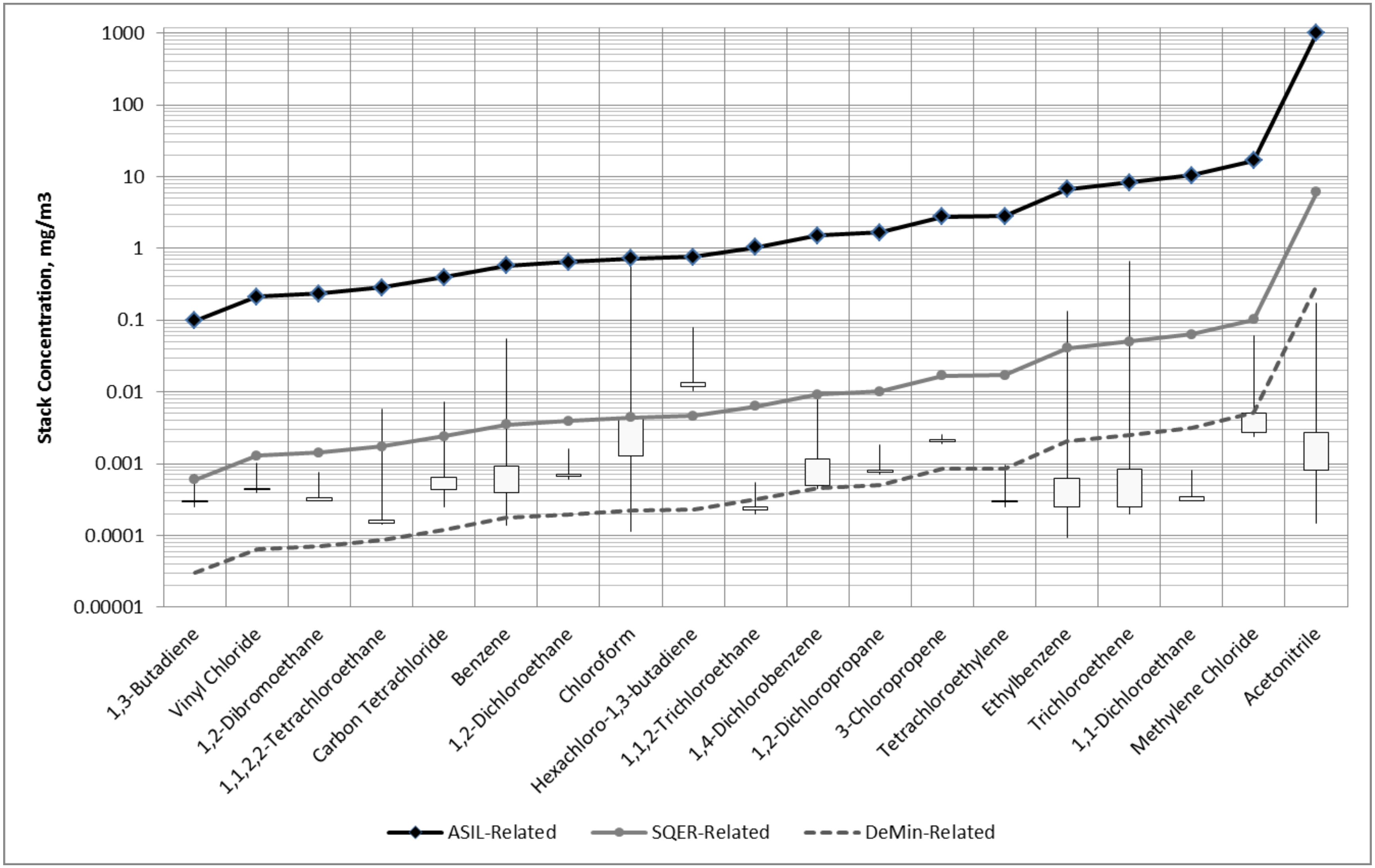
Sampling results from the 331 Building are used to demonstrate methods other than extreme worst-case analysis. This building was chosen because it had the greatest number of samples, most years sampled, and concentrations of interest in comparison to ASIL values as shown in Table 3.2. One of the worst-case analysis assumptions is computation of dispersion factor that assumes a constant, continuous emission for three full operational shifts and uses the highest value from 5 years of meteorological data. Alternative AERMOD scenarios were run to quantify some conservatism in these assumptions. Both annual and 24-hr dispersion factors were reduced by almost half for 331 Building if emissions during nights and weekends are 10% of emissions during normal on-shift working hours and were reduced by 45% if emissions during off-shifts are set to zero. Results from other emission points were similar to 331, with reductions ranging 16–65%.

Calculated Stack Concentrations

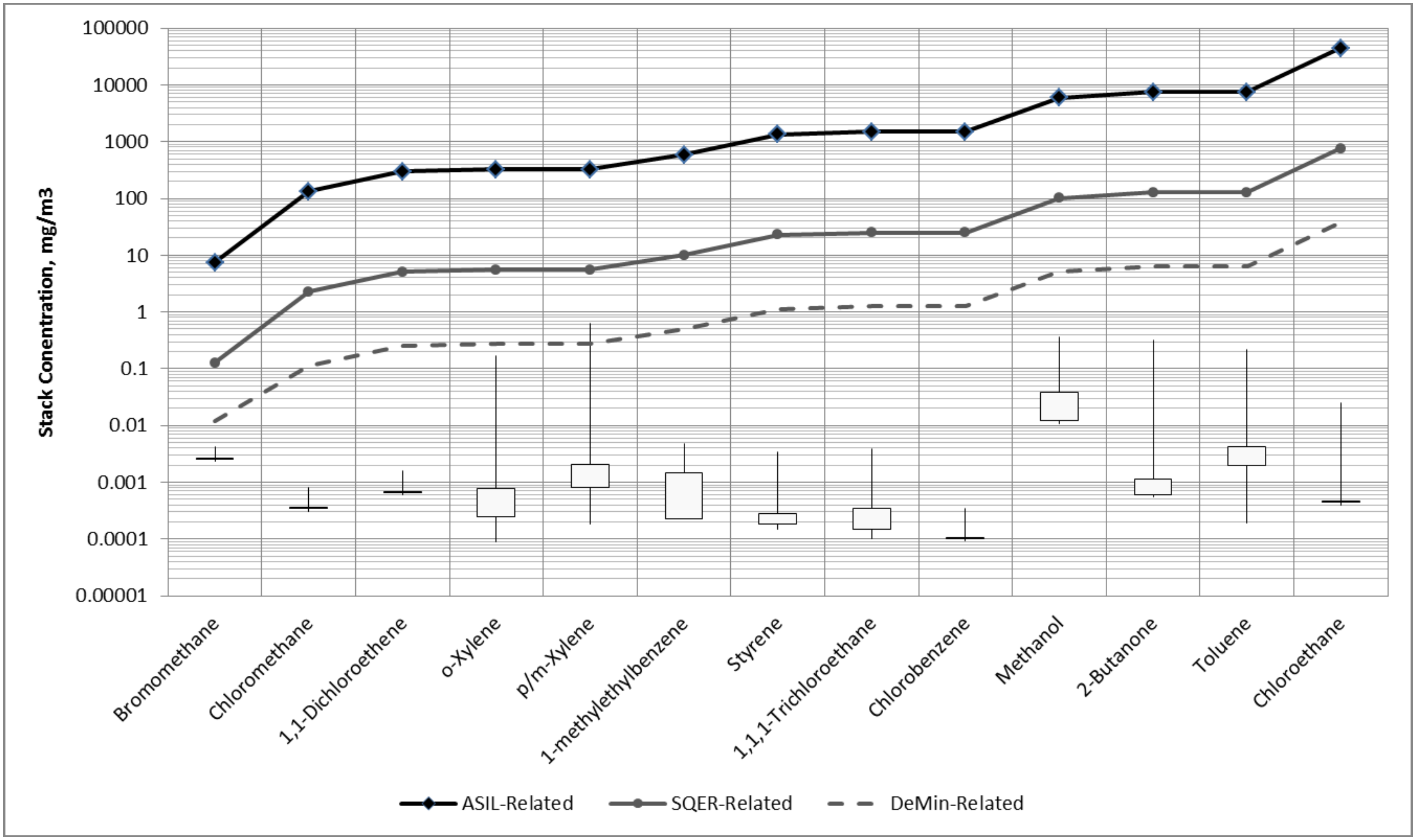
The stack concentration corresponding to regulatory criteria under extreme worst-case assumptions were calculated for each compound and are plotted as lines in Figure 3.1, along with distribution plots for each compound from the full set of sampling data. Common units of mg/m^3 are used for sampling results consistency. As shown in the figure, almost all sample distributions were orders of magnitude below the concentrations corresponding to the compounds' ASIL. Chloroform is the exception, with a single maximum measurement exceeding the calculated emission that would correspond to the ASIL; this agrees with the results shown in Table 3.2.

Figure 3.1 also displays calculated stack concentrations that correspond to the SQER and de minimis emission rates for comparison to sample distribution plots for the full set of sampling data. Several compounds with year averaging periods had sample results above SQER-related stack concentrations, but almost all were above de minimis-related criteria.

For compounds with 24-hr averaging periods, all measured concentrations were also below SQER- and de minimis-related values, except for one p/m-xylene value that was above de minimis. Results for compounds that were previously listed as TAPs were similar to those shown in Figure 3.1b; all measured concentrations were below regulatory criteria formerly assigned to those compounds.



a. Compounds with Year Averaging Period



b. Compounds with 24-hr Averaging Period

Figure 3.1. Calculated Stack Concentrations Corresponding to ASILs Compared to Stack Sampling Distributions (3331 Building)

Probabilistic Emission Estimates

The simplifying extreme worst-case assumptions are unrealistic for the comparison of compounds that have year averaging periods with levels of regulatory significance. Consequently, Monte Carlo simulations were used to reduce the level of conservatism in the emission estimate for comparison with the SQER and de minimis criteria by obtaining estimates of annual emissions based on the full set of measured data. These simulations are also used to evaluate the three alternate modes of operation. Figure 3.2 shows the results for the 331 Building when the Monte Carlo simulation is run using the three full operating shift mode (Mode 1). In this process, a randomly selected measurement is treated as a constant, continuous source and is used to calculate one estimate of annual emissions. The process is repeated 1000 times, creating a distribution curve. The maximum from the curve is the same as the extreme maximum case, but less extreme estimates such as the 95th percentile and median values are also generated (Figure 3.2). Results are normalized by each compound's SQER criteria to show the differences compared to the SQER criteria.

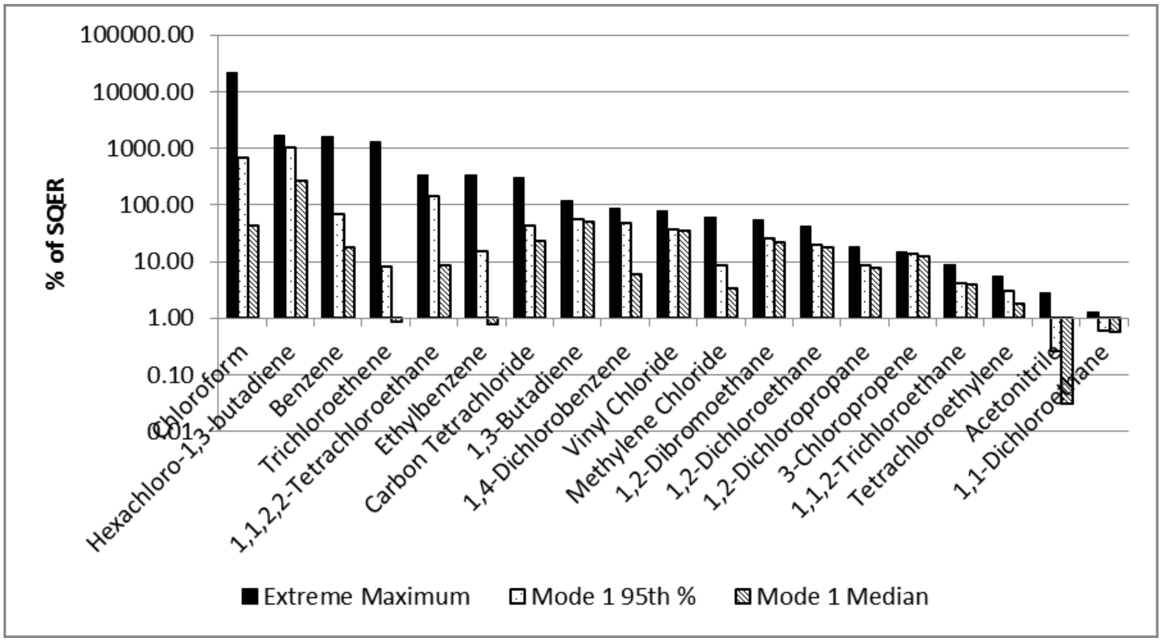


Figure 3.2. Comparison of 95th Percentile Annual Emission Estimates (331 Building)

Many of the compounds that exceed the SQER using the extreme maximum concentration are below the SQER with the three shifts mode 95th percentile value, and only hexachloro-3-

butadiene exceeds the SQER using the median of the distribution. This agrees with Figure 3.1a, which shows that all hexachloro-3-butadiene sample results were above the SQER-related concentration for that compound. The reduction is generally greater for the compounds that are a higher percentage of the SQER. Reductions in shifting from assumptions of extreme maximum to 95th percentile ranged from over two orders of magnitude (trichloroethene) to 60% (hexachloro-3-butadiene).

A more rigorous alternate approach was used in which 5256 random samples were selected to represent each 100-min segment of the year and then used to calculate an annual emission. The process was repeated 1000 times to generate a distribution of emission estimates for three selected compounds: chloroform, hexachloro-1,3-butadiene, and benzene. The alternate calculations were performed for both the three shifts and the on-shift + off-shift modes. As would be expected, the alternate approach produced almost the same mean but with a much narrower distribution than the original Monte Carlo simulation. For the compounds studied, the range of the distribution using the alternate more rigorous calculations was similar to the 95% confidence interval of the mean using the original process. In almost all cases, the maximum from the alternate calculations was less than the upper bound on the mean (using a 95% confidence interval) from the original Monte Carlo simulations. The range of the mean appears to be a reasonable substitute for the more rigorous alternate calculations, and the upper bound on the mean represents a realistic yet still conservative estimate of annual emissions for a given operational mode.

Changing the assumptions about the modes of operations also made a significant difference in estimating emissions for many of the compounds. Figure 3.3 shows the changes in estimated emissions for the four compounds with emissions closest to their SQER based on the three full operating shift model. Results using the upper mean of the distributions produced from the Monte Carlo simulations under the different modes are displayed. Chloroform is above the SQER under all operational mode assumptions, and hexachloro-1,3-butadiene is above the SQER under the three shifts and the on-shift + off-shift modes but not the on-shift – off-shift mode. All other compounds are below their SQER criteria under all operational modes.

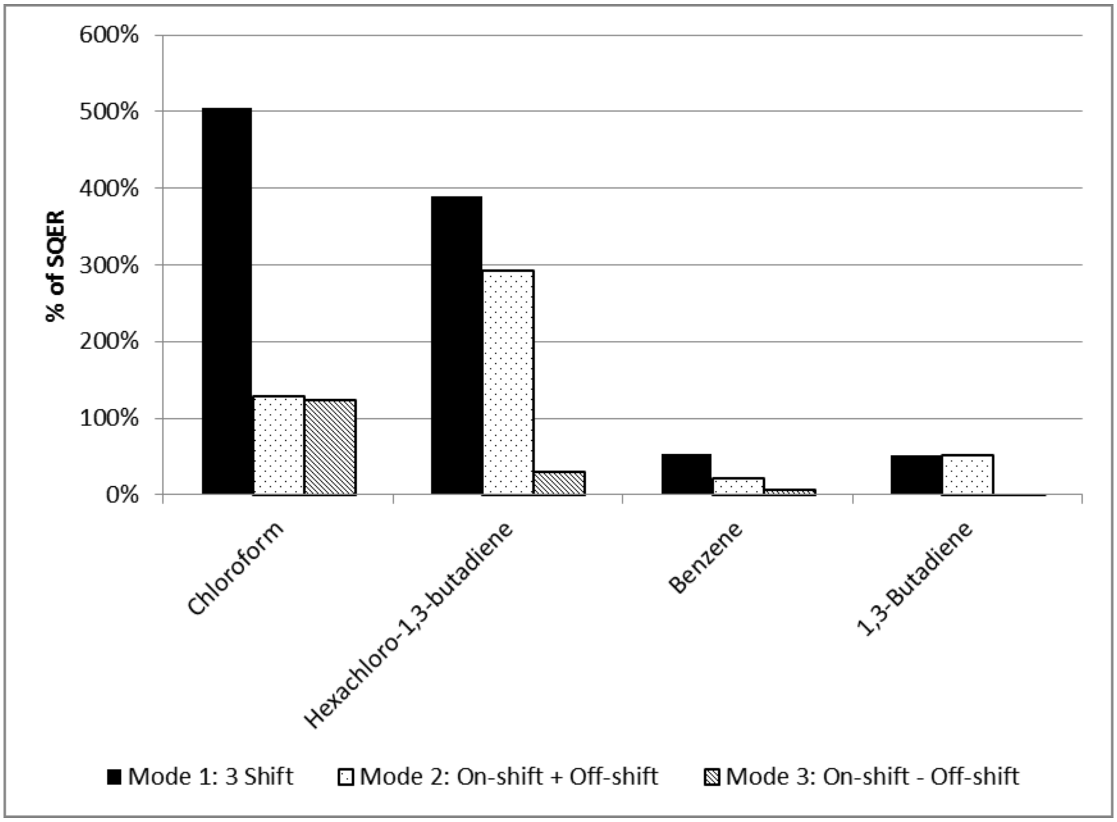


Figure 3.3. Comparison of Annual Emission Estimates Under Different Operational Modes (331 Building; Using Upper Bound of Mean from Monte Carlo Distribution)

For a number of compounds, the difference between three shifts and on-shift + off-shift mode is small, but between on-shift + off-shift and on-shift – off-shift is significant. These are compounds where the on-shift and off-shift concentrations are similar, with many less than the detection limit so that subtracting off-shift from on-shift gives a result close to zero. For example, a high percentage of sampling results for hexachloro-1,3-butadiene and 1,3-butadiene shown in figure 3.3 were below analytical detection limits and resulted in zero or near zero values for the on-shift – off-shift calculation. In addition, the inventory for many compounds was found to be low or zero, granting credibility to the on-shift – off-shift mode, which assumes off-shift sample results represent underlying background contributions from sources other than R&D operations.

A similar evaluation was made comparing calculated emissions to de minimis values, which are established at 5% of SQER values. All of the compounds except for 1,1-dichloroethane and acetonitrile exceeded de minimis values under extreme maximum assumptions. The Monte Carlo simulation results allow for more realistic emission estimates to compare with de minimis criteria. The upper bound on the mean from distributions generated for each operating mode were compared to de minimis values, and Table 3.3 indicates those compounds that exceeded de minimis using these values. The list in Table 3.3 identifies the compounds that remain above the de minimis criteria, as levels of conservatism are reduced from extreme maximum to more realistic estimates of emissions. Only four compounds have estimated emissions above de minimis criteria under on-shift – off-shift mode assumptions. However, this may be an artifact of detection limits that are not sensitive enough to detect concentration levels for the comparison.

Table 3.3. Calculated Emissions Above De Minimis Criteria (331 Building)

		Upper 95% Confidence Interval of the Mean			**Mean of Distribution Using < Detection Limits (DL) Sampling Results**
Compound	**Extreme Maximum**	**Mode 1: Three Shift**	**Mode 2: On-shift + Off-Shift**	**Mode 3: On-shift - Off-Shift**	
Hexachloro-1,3-butadiene	X	X	X	X	X
Chloroform	X	X	X	X	
1,1,2,2-Tetrachloroethane	X	X	X	X	X
Benzene	X	X	X	X	X
1,3-Butadiene	X	X	X		X
1,4-Dichlorobenzene	X	X	X		X
Carbon tetrachloride	X	X	X		X
Vinyl chloride	X	X	X		X
1,2-Dibromoethane	X	X	X		X
1,2-Dichloroethane	X	X	X		X
Ethylbenzene	X	X			
3-Chloropropene	X	X	X		X
Methylene chloride	X				
1,2-Dichloropropane	X	X	X		X
Trichloroethene	X	X			
1,1,2-Trichloroethane	X				
Tetrachloroethylene	X				
1,1-Dichloroethane					
Acetonitrile					

Some of the compounds listed in Table 3.3 had a high percentage of sampling results that were flagged as “U” or under the detection limit. These results are assigned detection limit concentrations. A Monte Carlo analysis was applied to the sample results that were under detection limit concentrations to obtain a distribution that represents the lowest quantity of emissions that could be detected. Three shifts operating assumptions were used for the simulation. The mean of this distribution for each compound was compared to de minimis criteria. As shown in Table 3.3, the outcome of this detection limit analysis was that over half of the compounds with annual averaging periods were above de minimis using detection limit concentrations. For these compounds, sampling did not provide sufficient resolution to compare annual emissions with de minimis criteria. Similarly, the detection level does not provide sufficient resolution for the on-shift – off-shift mode calculations for those compounds.

Title V threshold values are given in tons/yr of emission and are generally much higher than SQER values, although two compounds, trichloroethene and acetonitrile, have threshold values that are less than SQER criteria. Comparing estimated emissions based on the highest measured concentrations from the 331 Building resulted in two compounds with extreme maximums above threshold values: chloroform and trichloroethene. Calculated emissions using upper bound on the mean of the distribution under three shifts operational assumptions reduces the estimates so that both of these compounds are below threshold criteria.

Chemical inventory data were used as an alternate method to estimate annual emissions. This included chemical inventory at the beginning of the year corresponding to the years sampled for each building and usage data for those years. Some compounds did not have corresponding inventory data for specific buildings or years. For example, only 11 of the 19 compounds with year averaging periods had inventory data for the 331 Building during the 7 years sampled, and three of those 11 did not have inventory data for all years. Figure 3.4 shows the highest estimated annual emissions from the inventory calculations for the six compounds with the highest percent of SQER. Inventory-based emission estimates are compared to upper bound of the mean values from the Monte Carlo-generated distributions under the different operational modes. In all cases, only chloroform was shown to exceed SQER criteria. The inventory-based value for chloroform exceeded the SQER for 2 of the 7 years sampled, but the average was just under the SQER. In general, the inventory-based emission estimates are most similar to the upper bound of the mean from the on-shift + off-shift calculated distributions for this data set.

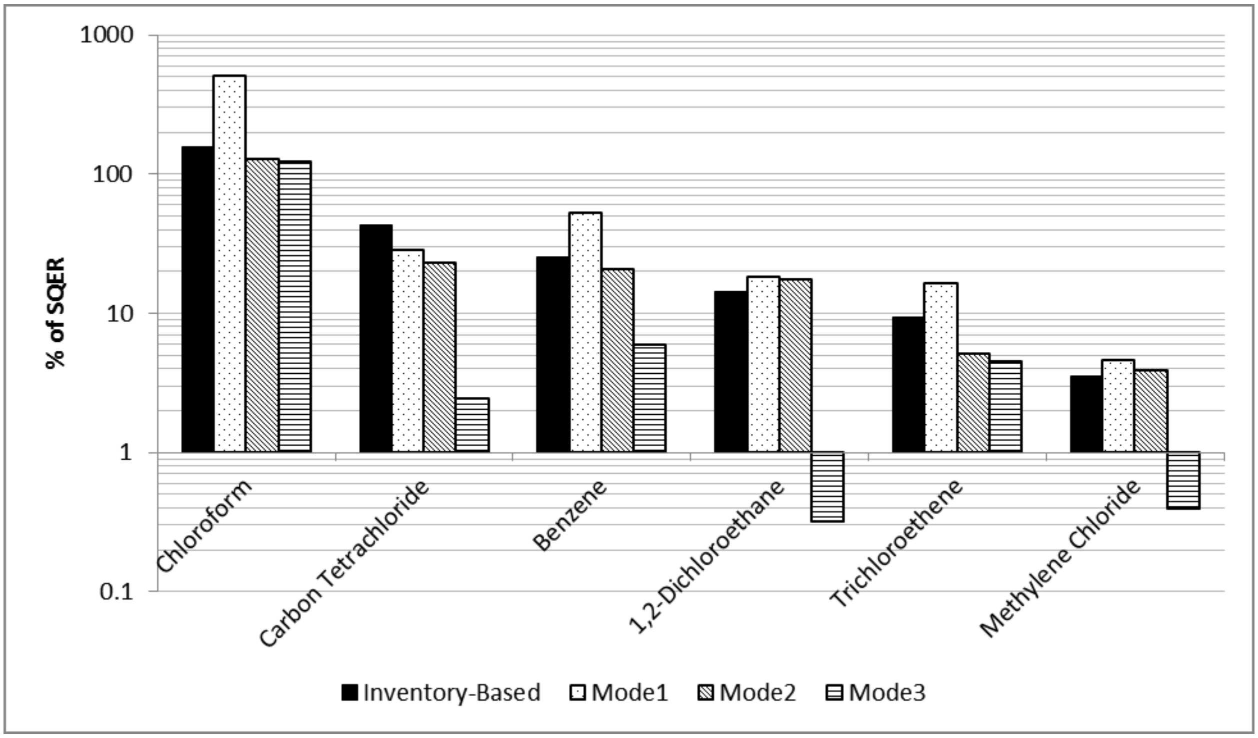


Figure 3.4. Comparison of Emission Estimates Based on Inventory vs. Measurements (331 Building; Using Upper Bound of Mean for Modes)

3.5 Discussion

Comparing stack measurements to regulatory criteria for air emissions requires assumptions about the temporal variability of the emissions. Even though stack measurements show a wide range of concentrations, using an extreme worst-case approach that maximizes emissions estimates simplifies the analysis. This approach revealed that almost all of the target compounds measured in the four R&D buildings sampled over a 10-year time frame were below ASILs, even using the single highest 24-hr and annual dispersion factors based on 5 years of meteorological data and continuous release plus the single highest concentration measured for each compound. Only one compound, chloroform, was above its ASIL using these assumptions, and seven others were greater than 1% of their ASIL.

Part of the conservatism is due to assumptions in calculating dispersion factors that convert stack emissions to ambient air concentrations. AERMOD was used to calculate dispersion under worst-case conditions and alternative cases representing different operational modes. Actual dispersion factors may be 50% or less compared to model predictions if the model assumes continuous emissions over time, but the source actually only emits during the day and is greatly reduced or eliminated during nights and weekends.

Measured chloroform concentrations ranged over nearly four orders of magnitude. An assumption of continuous emissions over a year at the highest concentration measured may simplify the calculation but is not realistic. This becomes evident by visualizing the sampling data compared to regulatory criteria under extreme maximum assumptions as presented in Figure 3.1 for the 331 Building. The figure shows that compounds with 24-hr average regulatory limits were several orders of magnitude below the corresponding ASILs and SQER values and were also well below de minimis-related values except for maximum values of p/m-xylene. However, several compounds with yearly average regulatory limits have some measured values higher than SQER-related concentrations, and almost all have measurements higher than de minimis-related values.

Monte Carlo techniques were used to calculate emissions for compounds with annual average limits to compare with criteria used by regulators to determine modeling requirements or define trivial emissions. This technique allows consideration of the full range of data and the investigation of different modes of operation. Results vary depending on the compound, the statistical value selected from the resulting distribution, and operational mode (Figures 3.2 and 3.3). Applying the analysis to the 331 Building measurements indicated that eight compounds exceeded SQER criteria under extreme maximum assumptions, but only three exceeded SQER criteria compared to the 95th percentile value from the distributions generated by Monte Carlo simulations and only two, hexachloro-1,3-butadiene and chloroform, exceeded SQER criteria compared to the upper 95% confidence interval of the mean of the distributions.

Comparisons of extreme maximum and Monte Carlo generated emission estimates to the more restrictive de minimis criteria were made for the compounds with annual average regulatory limits. All but two of these compounds (1,1-dichloroethane and acetonitrile) exceeded de minimis criteria under extreme maximum conditions. Results from the Monte Carlo analysis showed some additional compounds below these criteria, but many remained above, including those for which the analysis showed most samples to be below DL. To address whether DL provided sufficient resolution for this comparison, an analysis similar to three shifts was performed on sample results flagged as less than the detection limit. The median of the resulting distribution was then compared to de minimis and SQER values.

Hexachloro-1,3-butadiene was the only compound that exceeded SQER values using detection limit results, but ten others exceeded de minimis, as shown in Table 3.3. Eight compounds had DL that allowed for comparison with de minimis criteria, as indicated by no X in the right-most column of Table 3.3. The de minimis comparison for these compounds shows that acetonitrile and 1,1-dichloroethane are below de minimis under all scenarios, chloroform is above de minimis under all scenarios, and five other compounds (ethylbenzene; methylene chloride; trichloroethene; 1,1,2-trichloroethane; and tetrachloroethylene) may or may not be above de minimis, depending on the operational mode assumed.

Chemical inventory data was used as an alternate method to calculate annual emissions for compounds with averaging period of a year and with sufficient inventory. Eight of the compounds met these conditions in the case of the 331 Building. Inventory-based estimates were similar to estimates based on measurements using the Monte Carlo techniques in that they made similar predictions with respect to whether a chemical was above or below SQER and de minimis criteria.

3.6 Conclusions

Measurements from R&D facilities were evaluated against regulatory criteria using simplifying conservative assumptions, and the bases for these assumptions were explored to quantify degrees of conservatism. Predicted downwind concentrations were below ASILs for almost all compounds, even under extreme maximum analyses. Chloroform was the only compound for which the extreme maximum assumptions resulted in a predicted ambient annual average concentration above the ASIL. Concentrations of compounds in the measured data ranged over several orders of magnitude, so using maximum measured concentrations to calculate annual emissions or ambient concentrations based on annual averaging periods is unrealistic. Using Monte Carlo techniques allows emissions to be estimated based on the full range of measured concentrations, and a comparison value can be selected from the resulting distribution that corresponds to the desired degree of conservatism (e.g., upper bound of the mean, 95th percentile). The methods shown also provide a means to incorporate different operational modes.

Applying Monte Carlo techniques to measured data from one of the PNNL facilities was helpful in comparing estimated emissions to regulatory criteria used to determine modeling requirements or define trivial levels of emissions. Although extreme maximum analysis indicated that eight compounds with annual averaging periods exceeded SQER values, most of these were shown to be below SQER values using Monte Carlo analysis. Only one compound exceeded SQER values under all methods. DL were problematic for many of the compounds when comparing estimated emissions to the lower de minimis criteria. Of the eight compounds with sufficient detection for the comparison, two were below de minimis even under extreme maximum conditions, one was above de minimis under all operating mode assumptions, and the other five had mixed results depending on the mode of operation assumed.

Chemical inventory methods provide an alternate method of estimating annual emissions and produced similar results with respect to determining which compounds exceeded SQER and de minimis values. Of the three operational modes investigated, inventory-based estimates were the most similar to the mode that assumes off-shift samples represent a reduced level of operations during nights and weekends.

3.7 Acknowledgements

The authors thank Jeremy Rishel for his assistance in the AERMOD calculations and Professor Christopher Simpson for his careful review of the manuscript and suggestions for improvements.

4.0 ESTIMATING AIR CHEMICAL EMISSIONS FROM RESEARCH ACTIVITIES USING STACK MEASUREMENT DATA[4]

4.1 Abstract

Current methods of estimating air emissions from R&D activities use a wide range of release fractions or emission factors with bases ranging from empirical to semi-empirical. Although considered conservative, the uncertainties and confidence levels of the existing methods have not been reported.

Chemical emissions were estimated from sampling data taken from four research facilities over 10 years. The approach was to use a Monte Carlo technique to create distributions of annual emission estimates for target compounds detected in source test samples. Distributions were created for each year and building sampled for compounds with sufficient detection frequency to qualify for the analysis. The results using the Monte Carlo technique without applying a filter to remove negative emission values showed almost all distributions spanning zero and 40% of the distributions having a negative mean. This indicates that emissions are so low as to be indistinguishable from building background. Application of a filter to allow only positive values in the distribution provided a more realistic value for emissions and increased the distribution mean by an average of 16%.

Release fractions were calculated by dividing the emission estimates by a building chemical inventory quantity. Two variations were used for this quantity: chemical usage, and chemical usage plus one-half standing inventory. Filters were applied so that only release fraction values from zero to one were included in the resulting distributions. Release fractions had a wide range among chemicals and among data sets for different buildings and/or years for a given chemical. Regressions of release fractions to molecular weight and vapor pressure showed weak correlations. Similarly, regressions of mean emissions to chemical usage, chemical inventory,

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molecular weight and vapor pressure also gave weak correlations. These results highlight the difficulties in estimating emissions from R&D facilities using chemical inventory data.

4.2 Introduction

Emissions of HAPs from R&D operations are difficult to assess due to their inherent variability in duration and rate; thus, emissions are typically estimated assuming upper-bound values. This is especially true of R&D operations conducted at multidisciplinary laboratories because of the breadth and evolving nature of research activities. The unique nature of R&D has been recognized in Title III, Section 112(c)(7) of the CAAA of 1990 (42 U.S.C. § 7412(c)(7), 2011). The regulation requires establishing a "separate category covering research or laboratory facilities, as necessary to assure equitable treatment of such facilities" when establishing emission standards for HAPs. However, R&D facilities are not currently regulated as a unique category, and no guidance has been developed to estimate emissions from R&D activities. Although the EPA has not specifically listed R&D facilities as a source category of HAPs, they have considered doing so and submitted an Advance Notice of Proposed Rulemaking for the NESHAP: Source Category List to include R&D facilities on this list (62 FR 25877–79, 1997). Public comments on the proposal noted the difficulties in estimating emissions from R&D activities that are highly variable in nature with many small quantities of chemicals and a large number of often-changing processes (EPA, 1998). Comments also included a request for "guidance for clear, consistent PTE calculation methodology for R&D operations."

If emissions exceed HAP major source thresholds, R&D facilities have potential to be classified as such. They may also need to be incorporated into a Title V permit if they are collocated with a manufacturing site that is a major source, and they cannot be excluded based on actual emission threshold rates or based on individual size and production rate criteria. Thus, facilities conducting R&D will need to develop methods for estimating R&D emissions to establish compliance status with the regulation. In addition to federal regulations, some states have additional regulations that apply to air chemical emissions. Applicability to R&D facilities varies depending on the state and/or interpretation of the enforcing authority.

A variety of methods are currently being used to estimate air chemical emissions from R&D facilities associated with national laboratories, and these are generally considered conservative in that they overestimate actual emissions. Although release fractions directly applicable to estimating air chemical emissions from R&D laboratories have not been established by regulatory agencies, many of the methods are based on applying a release fraction to chemical inventory and/or chemical usage. In at least one case, a release fraction of one (100%) has been applied to chemicals purchased for R&D activities during a given year to estimate emissions of VOCs and HAPs (North and Adelson, 1995). In another case, 5% was assumed, based on input from research staff, and applied to the subset of chemicals purchased for R&D activities and containing VOC or HAPs constituents (Skipper, 2000). Other methods vary depending on the requirements specified in a permit, agreements with regulatory agencies, or degree of conservatism required. However, the basis for the emission factors employed is not strongly tied to chemical or process characteristics, and the uncertainty in emissions estimates is unknown.

PNNL's approach was to adopt the method of 40 CFR 61, "National Emission Standards for Hazardous Air Pollutants" Appendix D (2005) and WAC 246-247 "Radiation Protection – Air Emissions" (2005) for estimating emissions to the atmosphere instead of measuring emissions. The regulation assigns a release fraction of 1 to gases, 10^{-3} to liquids and powders, and 10^{-6} to solids. The amount of material used by the facility for the period under consideration is multiplied by the release fraction to calculate emissions; thus, the release fraction is a type of emission factor applied to chemical inventory, which is a measure of activity rate. Additional factors are provided to take credit for filters or other control devices in reducing emissions. The basis for liquids and powders included a large number of materials and diverse activities but were limited with respect to volatile solutions (EPA, 1989a). Therefore, PNNL identified volatile liquids as a separate category with a release fraction of 0.1. In the cited regulations, the release fractions are applied to the "amount used at facilities for the period under consideration" (40 CFR 61, 2005) or to the annual possession quantity which is defined as "the sum of the quantity of a radionuclide on hand at the beginning of the calendar year and the quantity of that radionuclide received or produced during the calendar year" (WAC 246-247, 2005).

Release fractions for R&D facilities have not been measured and emissions from these activities are normally too low to require sampling. Although not required for compliance, PNNL sampled air chemical emissions from facility stacks during 1998–2008. Results from initial sampling campaigns were evaluated and reported by Woodruff, Benar, and McCarthy (2000). Conclusions reported in this paper were that none of the measurements of the target compounds exceeded state ASILs even using significant overestimation factors, and that an average release fraction calculated from the data provided reasonable validation of the factor used in compliance assessments. Recognizing that laboratory emissions are intermittent in nature and may change from one year to the next, additional sampling was conducted to estimate release fractions over a longer period and compare them to those typically used for emissions estimates to determine compliance with air regulations and permits.

An in-depth analysis is performed in this paper on the comprehensive set of sampling data. A Monte Carlo technique is used to estimate distributions of annual emissions from each data set, which consists of sampling data for a target compound for a given year and building. In addition, the emission distributions are used with chemical inventory information to calculate distributions of release fractions. The relationship of release fractions and of emissions to chemical properties is investigated.

4.3 Methods

Stack Sampling

PNNL sampled air chemical emissions from the stacks of four facilities during 1998–2008: RPL (325), CSL (329), LSL (331), and EMSL. These buildings were chosen based on their considerable size, large chemical inventories, and diverse nature of research. The 325 Building operations involve evaluation, analysis, and testing of radioactive, radiochemical, chemical, and physical material properties. This building has bench-scale testing capabilities in addition to fume hoods, glove boxes, and hot cells for work with high-level radioactive material. Operations in the 329 Building at the time of sampling involved wet chemistry laboratories for organic and inorganic radiochemical and chemical analysis. The building has subsequently been vacated and is no longer operational. The 331 Building provides research capabilities to study the interactions of chemicals and radionuclides with plants, animals, and microorganisms and the fate of chemicals and radionuclides in the environment. Biological, microbiological, geochemical, and aquaculture research is performed in this building. EMSL is a user facility that provides experimental resources to engineers and scientists from other organizations in addition to PNNL. These resources include mass spectrometers, nuclear magnetic-resonance spectrometers, surface science tools to study atomic and molecular scales, flow cells, and high-precision analytical instruments. Table 4.1 compares the buildings in terms of relative size and number of laboratories and also identifies the stack sampling locations.

Table 4.1. Buildings Sampled for Chemical Air Emissions

Building	# Labs	Lab Space, 1000 ft^2	Sampling Location(s)
325 RPL	100	45	Main Stack
329 CSL	32	15	Main Stack
331 LSL	84	39	Main Stack
EMSL	168	70	Stacks 3, 4, and 5

Sampling times were usually 100 min taken within normal work day hours (i.e., 8:00 a.m.–5:00 p.m.) except for the initial year of sampling in which 300- and 50-min samples were taken. Samples taken during normal working hours are referred to as on-shift samples. Samples were also taken on weekends, holidays, or other times when research activities would not be expected to occur and are referred to as off-shift. Because laboratory experiments can be sporadic and very short in duration, efforts were made to choose on-shift sample times that were more likely to include research activities covering mid-morning and mid-afternoon equally and spread evenly over Monday through Friday. Sampling was more heavily concentrated on the summer months to coincide with increased periods of activity.

Although samples were mostly obtained from exhaust stacks, early sampling campaigns also included other locations such as lobbies and corridors to evaluate non-research related contributions to emissions. Data from these alternate locations are believed to indicate background concentrations of chemicals and were used for comparison to off-shift samples to verify the presence of background concentrations of some compounds. The results from the non-stack sampling locations showed similar concentrations to off-shift samples, with both non-stack and off-shift concentrations less than on-shift concentrations. A visual comparison is shown in Figure 4.1 for toluene detected in samples taken from the 329 Building. Other buildings and other compounds provided similar results with respect to similarity of non-stack and off-shift concentrations and with almost no detection in trip blanks. Table 4.2 summarizes the number of sampling events representing on-shift and off-shift activities for each building and year sampled.

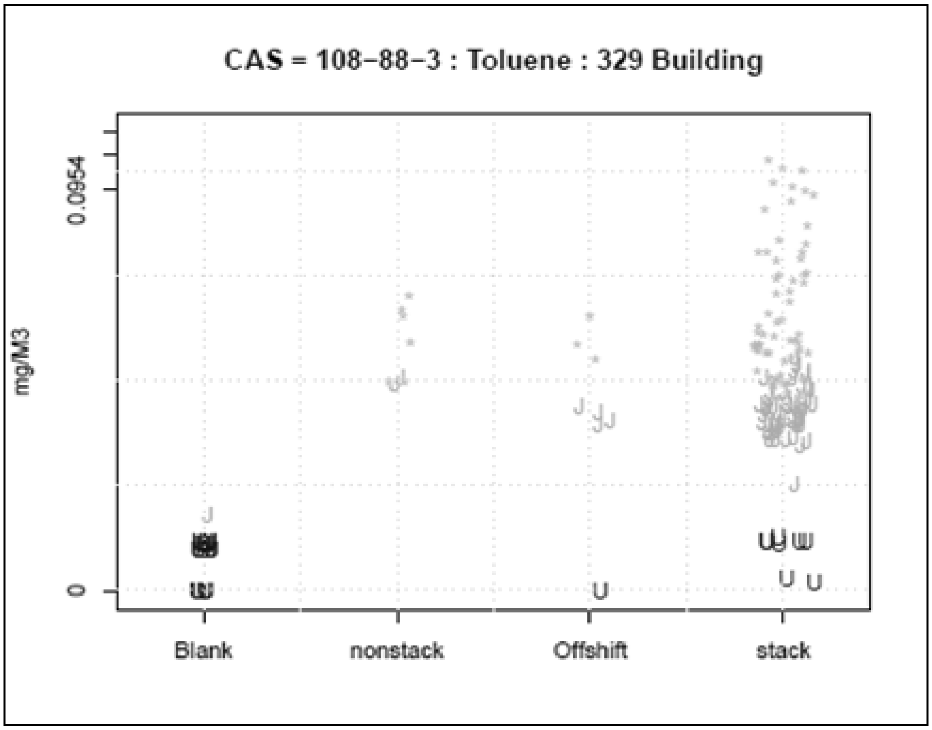


Figure 4.1. Concentrations of Toluene in Samples from 329 Building (U = below detection limit; J = between MDL and estimated quantitation limit). Note that units are in log scale.

Table 4.2. Number of Sampling Events

Year(s)	**325**		**329**		**331**		**EMSL**	
Sampled	**Off-shift**	**On-shift**	**Off-shift**	**On-shift**	**Off-shift**	**On-shift**	**Off-shift**	**On-shift**
1998	1	3	3	9		8		
1999–2000		24		18		22		
2001							3 (Stack 3) 1 (Stack 4) 2 (Stack 5)	17 (Stack 3) 18 (Stack 4) 13 (Stack 5)
2002	1	12	1	14	1	16		
2003						23		
2005				27				
2006					3	33		
2007	1	35						
2008					1	34		
Total	3	74	4	68	5	136	6	48

The sampling method used was the collection of air samples from stack exhausts onto TSTs that were subsequently analyzed for VOCs using GC/MS analysis. Each trap contained 300 mg of Carbotrap™ C, 200 mg of Carbotrap™ B, and 125 mg of Carbosieve™ S-III. The first two sorbents were deactivated graphite with limited sorption power for less volatile compounds. The final trapping stage was a graphitized molecular sieve used to retain the most volatile components including dichlorodifluoromethane, which has the highest vapor pressure of the target compounds. Instrument detection limits (IDLs) that represent method detection at the 99% confidence level were established from quality control data. Most of the results above the detection limit were also above the IDL for compounds reported in this study. The standard error for recovery of concentrations of standards at the detection limit ranged from 9–102%, with chloroform having the lowest standard errors and 1,1,2,2-tetrachloroethane having the highest.

The sampling apparatus had two parallel channels into which the air stream is drawn; each channel has its own flow rate, and one of the channels was programmed to collect a sample at double the flow rate of the other. Thus, each sample has a pseudo-duplicate to identify quality issues. Additional information on sampling and analysis procedures is provided in Woodruff, Benar, and McCarthy (2000).

Depending on the year, between 46 and 49 target compounds were analyzed by GC/MS. Many compounds were present in such low concentrations that results were below the DL. Table 4.3 shows the number of results (unpaired) and the percent of the total above the detection limit for on-shift and off-shift samples for each of the target compounds. Data sets with 10% or fewer of the stack concentration sampling results above the detection limit were screened out for this analysis. Although detection frequencies are similar for off-shift and on-shift samples, off-shift concentrations are lower. As previously mentioned, off-shift concentrations were found to be similar to those from samples taken from corridors and hallways. In these facilities, ventilation systems are designed to supply air to clean areas or areas of limited hazards (e.g., corridors) and move air in the direction of progressively more hazardous/contaminated areas. This design places the laboratories at a negative air pressure with respect to the corridors and hoods, gloveboxes, and hot cells at a negative air pressures with respect to the laboratories. The non-stack (corridor and hallway) concentrations are higher than background concentrations reported for the state of

Washington in the Technology Transfer Network 2002 National-Scale Air Toxics Assessment (EPA, 2012b), indicating that non-laboratory sources are contributing to these concentrations. These sources could be from building or office components. The objective of this study is to estimate emissions from laboratory operations and evaluate the relationship with chemical inventories used for R&D activities. Therefore, the non-laboratory contributions are subtracted from the stack sampling data. Concentrations from off-shift samples were used to represent non-laboratory contributions to emissions because they were similar to non-stack sample results.

Table 4.3. Frequency of Detection for Target Compounds

Compound Name	CAS#	Off-shift Samples		On-shift Samples	
		# Results	**% > DL**	**# Results**	**% > DL**
1,1,1-Trichloroethane	71-55-6	36	67%	647	65%
1,1,2,2-Tetrachloroethane	79-34-5	36	8%	647	14%
1,1,2-trichloro-1,2,2-trifluoroethane	76-13-1	36	83%	647	73%
1,1,2-Trichloroethane	79-00-5	36	0%	647	0%
1,1-Dichloroethane	75-34-3	36	8%	647	4%
1,1-Dichloroethene	75-35-4	36	8%	647	4%
1,2,4-Trichlorobenzene	120-82-1	36	31%	647	28%
1,2,4-Trimethylbenzene	95-63-6	36	53%	647	57%
1,2-Dibromoethane	106-93-4	36	0%	647	1%
1,2-dichloro-1,1,2,2-tetrafluoroethane	76-14-2	36	0%	647	3%
1,2-Dichlorobenzene	95-50-1	36	8%	647	13%
1,2-Dichloroethane	107-06-2	36	0%	647	2%
1,2-Dichloropropane	78-87-5	36	0%	647	0%
1,3,5-Trimethylbenzene	108-67-8	36	33%	647	48%
1,3-Butadiene	106-99-0	36	0%	647	0%
1,3-Dichlorobenzene	541-73-1	36	22%	647	27%
1,4-Dichlorobenzene	106-46-7	36	25%	647	34%
1-Ethyl-2-Methyl-Benzene	611-14-3			128	37%
1-Ethyl-4-methylbenzene	622-96-8	28	46%	484	41%
1-methylethylbenzene	98-82-8	8	13%	35	11%
2-Butanone	78-93-3	36	50%	647	40%
3-Chloropropene	107-05-1	16	0%	388	0%
Acetone	67-64-1	36	92%	647	98%
Acetonitrile	75-05-8	36	78%	647	61%
Benzene	71-43-2	36	92%	647	89%
Bromomethane	74-83-9	36	0%	519	0%
Carbon Tetrachloride	56-23-5	36	83%	647	77%
Chlorobenzene	108-90-7	36	17%	647	16%
Chloroethane	75-00-3	36	0%	647	2%
Chloroform	67-66-3	36	86%	647	90%
Chloromethane	74-87-3	28	4%	612	2%
cis-1,2-Dichloroethene	156-59-2	36	8%	647	3%
cis-1,3-Dichloropropene	10061-01-5	36	14%	647	10%

Compound Name	CAS#	Off-shift Samples		On-shift Samples	
		# Results	% > DL	# Results	% > DL
Dichlorodifluoromethane	75-71-8	36	89%	647	93%
Ethanol	64-17-5	36	53%	647	73%
Ethylbenzene	100-41-4	36	83%	647	89%
Hexachloro-1,3-butadiene	87-68-3	36	25%	647	18%
Methanol	67-56-1	28	43%	596	40%
Methylene Chloride	75-09-2	36	75%	647	83%
o-Xylene	95-47-6	36	83%	647	80%
p/m-Xylene	106-42-3	36	92%	647	92%
Pentane	109-66-0	36	67%	647	69%
Styrene	100-42-5	36	39%	647	40%
Tetrachloroethylene	127-18-4	36	0%	647	8%
Toluene	108-88-3	36	94%	647	97%
trans-1,3-Dichloropropene	10061-02-6	36	8%	647	9%
Trichloroethene	79-01-6	36	78%	647	74%
Trichlorofluoromethane	75-69-4	36	97%	647	95%
Vinyl Chloride	75-01-4	36	0%	647	0%

In addition to screening for low detection frequency, data sets (buildings and years) with little or no inventory of the target compounds were also removed from analysis because a primary objective was to determine the relationship between chemical inventory and emissions. Data from 1998 (the first year sampled) were not used in the analysis due to the difference in sampling time (a 300-min sample time was used in 1998 compared to 100 min for all subsequent sampling), the small number of samples taken, and concerns about the accuracy of the sample flow measurements.

Sampling results include chemical name, Chemical Abstract Service number (CAS#), molecular weight, quantity extracted from the sample, sample time, sample flow rate, calculated sample concentration, and any quality flags associated with the sample (e.g., below analytical detection limit, present in laboratory blanks, above or below range of concentrations used in calibration of instrument).

In addition to the sampling data, PNNL maintains a Chemical Management System (CMS) that contains inventory information on chemicals used in each laboratory space. This web-based tracking system tracks chemicals currently in the buildings and also roughly estimates chemical usage based on changes in CMS inventory records. Usage quantities are calculated by assuming the contents of each container are used uniformly between the time a container is full when initially added to the inventory and the time it is removed from inventory. Data that can be obtained from CMS include chemical name, CAS#, location (building and room), and quantity. These data were collected for the target compounds and for chemicals that have the target compounds as constituents, along with the constituent percentage. The CMS data provide an estimate of inventory usage quantities over relatively long periods of time; the uncertainty of the usage is considered greater when considering a shorter period (e.g., chemical usage over a year using this data is better estimated than chemical usage over a month).

Estimating Emissions

Annual emissions of target compounds were estimated from the stack sampling data for each year and building. The following equation was used for the calculations:

$$E_{ib} = (C_{stack} - C_{background})_{ib} (Q_{stack})_b (t) (CF) \tag{4.1}$$

Where E_{ib} = emissions of compound i from building b, lb/yr

C_{stack} = concentration of compound i measured in stack samples from building b taken during hours when research activities are expected to occur (on-shift), $\mu g/m^3$

$C_{background}$ = concentration of compound i measured in stack samples from building b taken during weekends, holidays or other times when research activities are not expected to occur (off-shift), $\mu g/m^3$

Q_{stack} = volumetric flow rate of stack from building b, m^3/hr

t = hours per year of on-shift operations

CF = lbs/µg conversion factor.

The average of the two duplicates was used as the measured concentration. As shown in eq 4.1, emission concentrations from research operations were calculated by subtracting the off-shift concentration distribution from the on-shift concentration distribution. This was done by using a Monte Carlo simulation in Crystal Ball (Oracle, 2012) in which the software randomly selects from the distribution of measured on-shift concentrations then subtracts a second randomly selected value from the distribution of measured off-shift concentrations for the same compound and building. These distributions contained the full set of sampling data, including concentrations that were less than the detection limit which were assigned detection limit values. The result was multiplied by the individual stack flow rate, which did not vary significantly for the years sampled, and by the hours per year on-shift. Although research operations are allowed around the clock, most research activities are believed to occur during a normal 8:00 a.m.–5:00 p.m. workday Mondays through Fridays and not on holidays. In this analysis, on-shift time was modeled as a normal distribution with a mean of 2000 hrs/yr and a standard deviation of 200 hrs/yr. The result of eq 4.1 is a distribution of emissions E_{ib} for each compound and each data set. One thousand simulations were generated for each distribution, and simulations were run in triplicate for a few of the chemicals (acetone, carbon tetrachloride, and ethanol) to determine repeatability of the results. The replications indicated that results were stable with differences of less than 10% in the means for almost all of the distributions tested.

The Crystal Ball software has several options for characterizing the input data as a distribution, and two of these were evaluated to determine which should be used in the analysis:

1. With this option, identified as best fit within the software, the user reads in the set of data. A mathematical fit determines the set of parameters for each distribution that best describe the characteristics of the data. Then, the closeness of each fit is judged using one of several standard goodness of fit tests (i.e., Anderson-Darling, Kolmogorov-Smirnov, and Chi-Square). In this analysis, Chi-Square was used for goodness of fit criteria. The highest ranking fit is chosen to represent the data. The user can choose from among all distributions supported by the software.
2. A user reads in the set of data, and the Custom Fit option draws on this distribution of data in calculations.

A comparison was made evaluating the two options for three of the more common compounds. Distributions were created using eq 4.1 for acetone, carbon tetrachloride, and methanol for each year and building sampled using both options, and the results were compared.

Estimates of annual emissions using eq 4.1 may result in unrealistic negative values when the random selection from the on-shift concentration distribution is less than that for off-shift. This is more likely to occur with data sets containing many results close to the detection limit or close to background concentrations. Filters can be applied within the software so that only positive values are included in the resulting distribution. The unfiltered model provides the least restrictions on the data and aids in identifying the frequency in which on-shift concentrations are equal to or below off-shift concentrations, but the filtered model is helpful in limiting the data to positive emission values. Results from both filtered and unfiltered models are presented; the filtered case allows only values above zero in the resulting distribution of emissions, and the unfiltered case allows all values, positive and negative. A third method would be to allow subtraction only if the on-shift concentration is greater than the off-shift concentration. This is more difficult to do in Crystal Ball in that it requires manipulation of individual trial data. Results from this third method are provided for a few selected compounds.

Existing models for estimating releases were examined to assist in interpretation of the results. Model equations provided insight into the chemical- and process-specific properties influencing emissions. One of the methods used to calculate transport of contaminants in the environment is Fick’s first law, which relates the emission flux to the concentration gradient (Hemond and Fechner-Levy, 2000):

$$J = -D \times dC/dx \tag{4.2}$$

Where J = flux density in $g/cm^2/s$
D = diffusion coefficient in cm^2/s
dC/dx = concentration gradient in g/cm^4

Fick’s first law could be applied to open containers of chemicals used in R&D activities where the concentration gradient is a result of a relatively high vapor concentration of the chemical at the liquid/gas interface and essentially zero concentration in the air stream flowing over it. The vapor concentration at the surface can be estimated using the ideal gas law: $n/V = P/RT$, with P as the partial pressure of the compound and equal to its vapor pressure at equilibrium. The molar concentration n/V is multiplied by molecular weight to obtain mass concentration so that the gradient term in eq 4.2 is directly related to vapor pressure and chemical molecular weight.

The diffusion coefficient in eq 4.2 depends on properties of the air stream and of the compound. For molecular diffusion, the coefficient is a function of temperature and pressure of the air stream, molecular weight, and size of the molecules that are diffusing into the air. The flux density J is applied to the flux area, which could be represented by the open area of a beaker or flask for R&D operations.

Evaporation rate equations used to estimate emissions from spilled liquids present emission rate as a function of the vapor pressure and molecular weight of the material spilled in addition to spill area and wind speed transporting evaporated material. An equation developed by Clancey (1974) and used by Powell (1984) to estimate evaporation rates from spills/leaking equipment is:

$$W = 79.6\,((P_{vap} \times MW)/T) \times u^{0.78} \times r^{1.89} \tag{4.3}$$

Where W = evaporation rate in g/s
P_{vap} = liquid vapor pressure in atmospheres
MW = molecular weight in g/g mol
T = temperature in Kelvin
u = wind speed in m/s
r = radius of spilled material in m.

A similar equation is provided estimating releases from spilled pools of hazardous materials (EPA, 1999c):

$$QR = 0.284 \times u^{0.78} \times A \times (P_{vap} * MW^{2/3})/(82.05{*}T) \tag{4.4}$$

Where QR = evaporation rate in lbs/min
P_{vap} = Liquid vapor pressure in mmHg
MW = molecular weight in g/g mol

T = temperature in Kelvin
u = wind speed in m/s
A = area of spilled material in ft^2.

Although emissions appear to be inversely related to temperature in all these equations (via the ideal gas law for eq 4.2), vapor pressure increases logarithmically with temperature according to the Antoine equation, so the overall effect is an increase in mass emissions with temperature.

Wind speed is also an important factor, but for laboratories, this velocity is controlled by requirements for air flow across the face of hoods where chemical work is performed and thus would not be a factor to explain differences in emissions between compounds. Flux area and area of spilled material in these equations represent the interface over which the emission occurs and are directly related to the quantity of chemical used if containers are similar in size (i.e., 2 liters [L] of a chemical would have double the flux area of 1 liter, given that both are processed in 1-L beakers because the larger quantity would require double the number of beakers).

Estimating Release Fractions

Release fractions are often used in estimating emissions from research facilities. The following equation explains the term release fraction as discussed in this report:

$$\text{Release Fraction (RF)} = \text{mass emitted per year/mass used per year} \qquad (4.5)$$

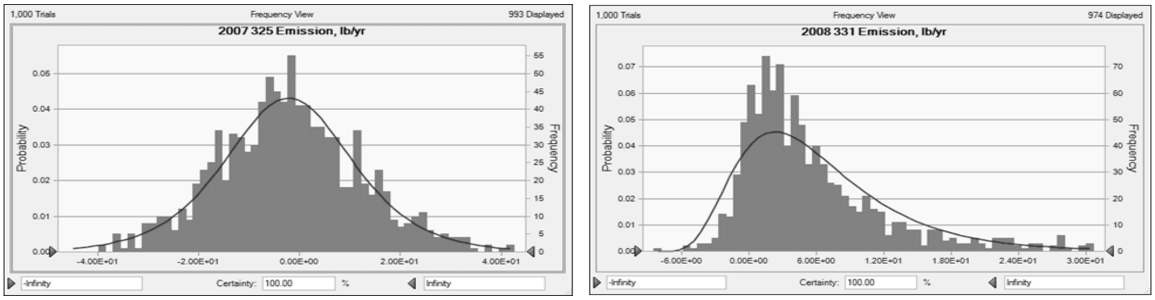
The mass emitted per year is calculated as discussed in the previous section. For the denominator, inventory data was obtained from CMS. For each building and year sampled, CMS provided the inventory of chemicals with the target compounds at a single point in time (January 1 of the given sampling year) and chemical usage for the year. The chemical usage data are obtained by assuming a chemical is used uniformly from the time it is brought into a building until the empty container is removed. Two variations were used for the RF denominator: usage, and usage plus half the capacity of the containers shown in inventory. Chemical usage was used because theoretically, this quantity should be a more direct measure of experimental activity and thus total emissions. Chemical usage plus half of inventory was used because PNNL routinely uses this larger quantity to estimate emissions based on the following: in a population of many containers, it can be assumed that on average the containers are half empty, and half the capacity has been used and was subject to emission processes.

A filter was applied to the calculations, limiting RF values from 0 to 1 because a release fraction by definition falls within this range. Negative values result when the random selection from the on-shift concentration distribution is less than that for off-shift (data sets with many results close to the background or the detection limit); values over 1 result when the estimated annual emission is greater than the amount shown in chemical inventory (data sets with low chemical inventory or high emission estimate in comparison to inventory). In this analysis, filters were applied to obtain distribution results within a realistic range. In addition to the previous screening criteria, the number of filtered values was evaluated in determining RF results for further analysis. Where more than 90% of values were filtered, data sets were omitted from evaluation.

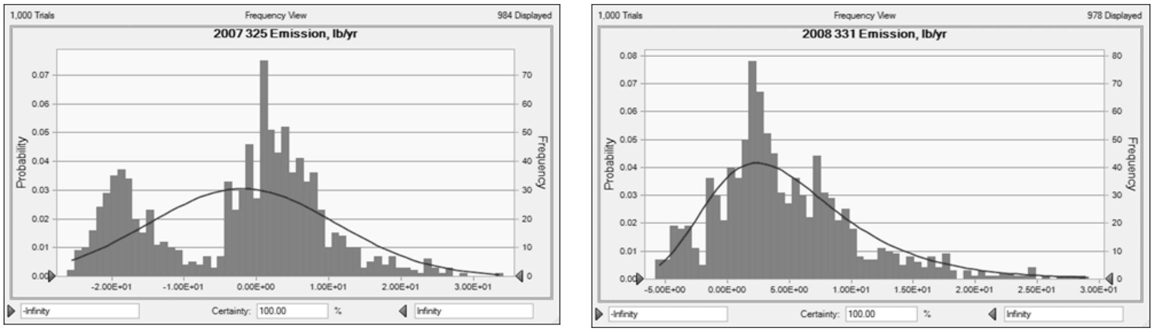
4.4 Results

Modeling Input Data

A comparison was made evaluating the difference between modeling input data as a best fit curve versus no curve fitting. The difference in the Monte Carlo analysis is that a value is randomly chosen either from a curve or the input data value group. Distributions were created using eq 4.1 for acetone, carbon tetrachloride, and methanol for each year and building sampled for both input data options. The top graphs in Figure 4.2 show eq 4.1 results for two of the acetone data sets with C_{stack} and $C_{background}$ modeled as curves (Option 1), while the bottom graphs show eq 4.1 results for these same data sets but with C_{stack} and $C_{background}$ selected from the discrete data (Option 2). Option 1 provides smoother results but may conceal potentially important features like the bimodal characteristics shown in the distribution of Figure 4.2 (lower left graph). Note that the curves shown in the graphs are best fit curves of the results, and the Crystal Ball gallery does not contain a bimodal curve.



a. Emission Estimates with Input Concentrations Modeled as Curves (Option 1)



b. Emission Estimates with Input Concentrations Supplied as Discrete Values (Option 2)

Figure 4.2. Monte Carlo Simulation of Annual Emissions with Input Data Modeled as Best Fit Curve and Input Data Supplied as Discrete Values (Acetone/325 Building/2007 on left; Acetone/331 Building/2008 on right; no filters was applied to the simulations)

Using the best fit curve option for input to eq 4.1 also appears to overestimate emissions, as indicated by a comparison of the mean of eq 4.1 results using both options. The curve-fitted input data (Option 1) gave mean results over 4 times greater than that of inputting discrete data. Other factors considered in the comparison of the options were the mixed success at fitting curves to the data sets (i.e., for some data sets the probability that the data followed a distribution curve was <90%; for others, this probability was >5%) and the recognition that entering the sampling data directly is likely to generate fewer errors associated with curve fitting. As a result of this evaluation, Option 2 was used in the remainder of the analysis.

Annual Emissions

Distributions of emissions were estimated for 24 of the 49 target compounds after removing compounds with low detection frequency and low inventory. However, not all of these compounds had sufficient sample detection or inventory for all data sets. Table 4.4 identifies the compounds and data sets for which estimates could be made. Each X in Table 4.4 represents a distribution of emission estimates generated for the compound, year, and building (Figure 4.2, bottom row graphs show examples of acetone results from 325 Building in 2007 and 331 Building in 2008). As noted in the previous section, sampling data were directly entered as discrete values using the Custom Fit option in the software, and calculations were made both with and without filtering negative emissions. As it is difficult to compare entire distributions, the mean was obtained for each distribution, and these values are shown in box plots in Figures 4.3 and 4.4. Figure 4.3 shows the range of values for distribution means for 16 of the compounds when negative values are not filtered out of the distribution. Figure 4.4 shows results for an additional six compounds – those with the highest estimated emissions– and displays results both with and without filtering out negative values.

Table 4.4. Data Sets with Estimates of Emissions

	325 Building			**329 Building**			**331 Building**					**EMSL**
Compound Name	**1999**	**2002**	**2007**	**1999**	**2002**	**2005**	**1999**	**2002**	**2003**	**2006**	**2008**	**2001**
1,1,1-Trichloroethane	X	X	X	X	X	X	X	X	X	X	X	X
1,1,2,2-Tetrachloroethane											X	X
1,1,2-trichloro-1,2,2-trifluoroethane	X	X	X	X	X	X	X	X	X	X	X	X
1,2,4-Trimethylbenzene	X	X	X	X	X			X	X	X	X	X
1,3,5-Trimethylbenzene	X	X	X	X	X			X	X	X	X	X
2-Butanone	X	X		X	X			X	X	X	X	X
Acetone	X	X	X	X	X	X	X	X	X	X	X	X
Acetonitrile		X	X	X	X	X	X	X	X	X	X	X
Benzene	X	X	X	X	X	X	X	X	X	X	X	X
Carbon Tetrachloride	X	X	X	X	X	X	X	X	X	X	X	X
Chloroform	X	X	X	X	X	X	X	X	X	X	X	X
Dichlorodifluoromethane	X	X	X	X	X	X	X	X	X	X	X	X
Ethanol	X	X	X	X	X	X	X	X	X	X	X	X
Ethylbenzene	X	X	X	X	X	X	X	X	X	X	X	X
Methanol	X		X	X	X	X	X		X	X	X	X
Methylene Chloride	X	X	X	X	X	X	X	X	X	X	X	X
o-Xylene	X	X	X	X	X	X	X	X	X	X	X	X
p/m-Xylene	X	X	X	X	X	X	X	X	X	X	X	X
Pentane	X	X	X	X	X	X	X		X	X	X	X
Styrene			X		X	X			X	X	X	X
Tetrachloroethylene										X		
Toluene	X	X	X	X	X	X	X	X	X	X	X	X
Trichloroethene	X	X	X	X	X	X	X	X	X	X	X	X
Trichlorofluoromethane	X	X	X	X	X	X	X	X	X	X	X	X

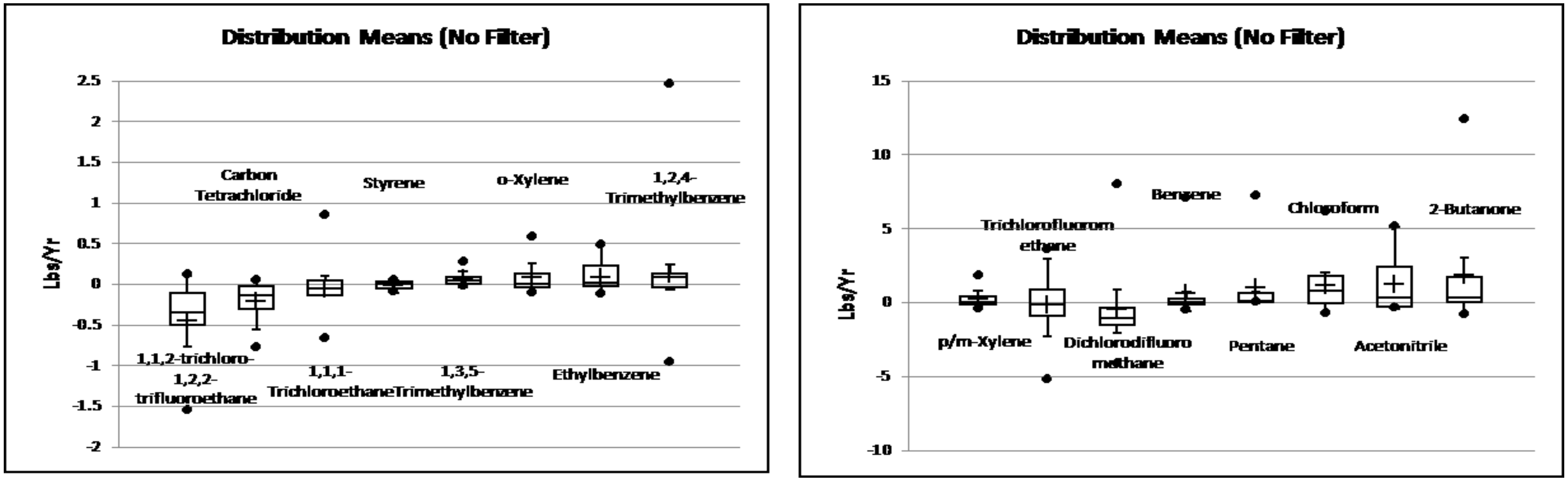


Figure 4.3. Box Plots of Means from Emission Distributions Calculated Using Monte Carlo Model (without filtering negative values from distributions)

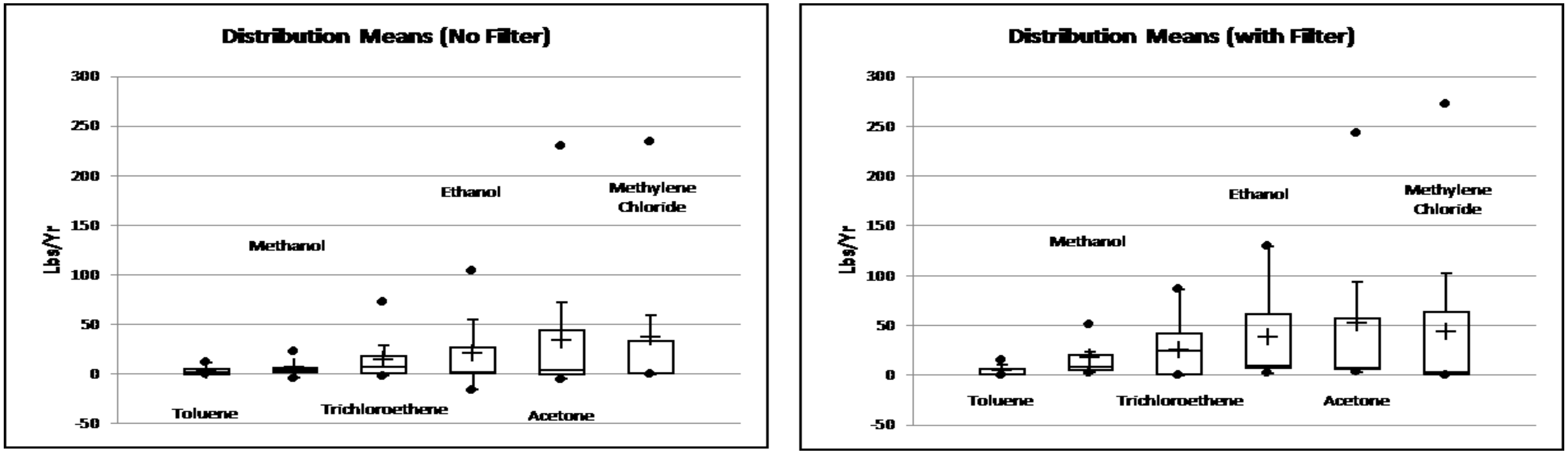


Figure 4.4. Comparing Emission Results Using Filter vs. No Filter for Compounds with Highest Calculated Emissions

If no filter is applied, almost all of the compounds have at least one negative value (i.e., the mean of the distribution is negative for at least one data set), and almost one-third of the compounds have a negative when averaging the means for all of the data sets. On an individual data set basis, the means are negative for about 40% of the 251 distributions generated (one distribution for each X in Table 4.4). The 95% confidence interval of the distribution was also evaluated, and this interval included zero for most cases. Table 4.5 lists the few data sets where the lower 95% confidence interval of the distribution was greater than zero. Even though negative emissions are not realistic, the unfiltered model is believed to provide a truer sense of whether measured emissions were signficantly above background; data sets with negative means indicated essentially zero emissions.

Table 4.5. Data Sets with 95% CI Above Zero

Compound Name	Year(s) Sampled	Building Sampled
Acetone	2001	EMSL
2-Butanone	2002, 2006, 2008	331
Chloroform	2008	331
Ethylbenzene	2003	331
o-Xylene	2003	331
p/m-Xylene	2003	331
Tetrachloroethylene	2002	331
Toluene	2008	331

Comparison of the box plots in Figure 4.3 between no filter versus filter models also shows that using a filtered model tends to shift the results upward, which is as expected because the lowest (negative) values are screened out. Considering all compounds and all data sets, the filter model increases estimated emissions by about 16%, as shown by the slope of the regression equation in Figure 4.5. This figure compares the mean of each of the 251 distributions generated with and without a filter.

A third method in which individual trials were evaluated and subtraction of background was only allowed if the result was positive was applied to a limited number of compounds. Evaluation of the distribution means for the three compounds methanol, acetone, and trichloroethene using this third method showed results very similar to the no filter results. For these three compounds (34 data sets), the filter model increased mean emissions by 12% compared to no filter, but the third method only increased the mean by 2% compared to no filter.

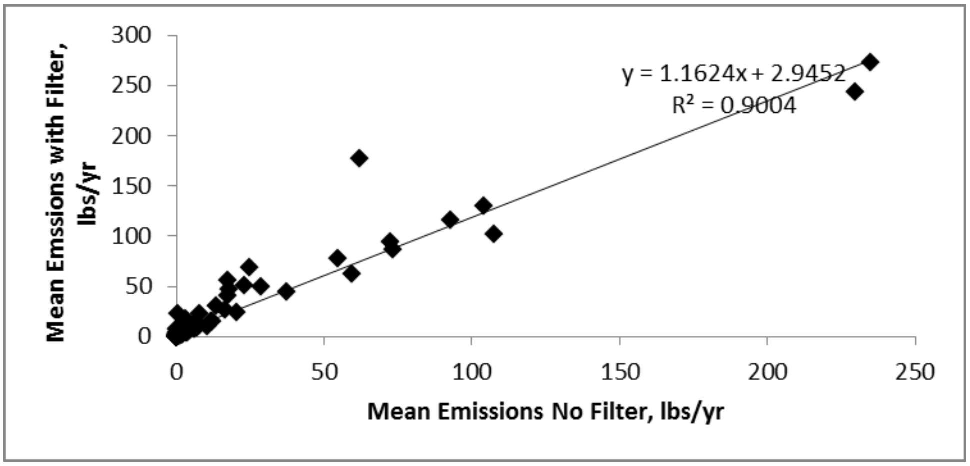


Figure 4.5. Comparing Mean Emissions from Distributions Calculated Using a Filter vs. No Filter

Release Fractions

Distributions of release fractions were generated for a subset of the data sets in Table 4.4. Compounds with little or no inventory for a given year and building were not included. A screening of a 0.5 lb inventory was used as a cutoff for RF calculations following evaluation of amounts needed to obtain measured emissions, and RF values are not presented for data sets where the involved inventory (either usage or usage plus half capacity of containers in inventory) was less than 0.5 lb. This reduced the number of distributions from 251 to 201 for RF based on usage plus half inventory and 132 for RF based on usage alone. Results are shown in Figure 4.6 as box plots of the distribution mean.

These graphs show the quartiles, average, minimum, and maximum values for each target compound that had enough detectable stack concentrations and sufficient inventory data for the calculations. The top graph in Figure 4.6 shows the results for RF calculations based on chemical usage alone, and the bottom graph shows the results for RF calculations based on chemical usage plus half inventory. The usage data for some of the compounds was above 0.5 lbs for only one year so that the box plot is represented by a single line in the upper group of boxplots.

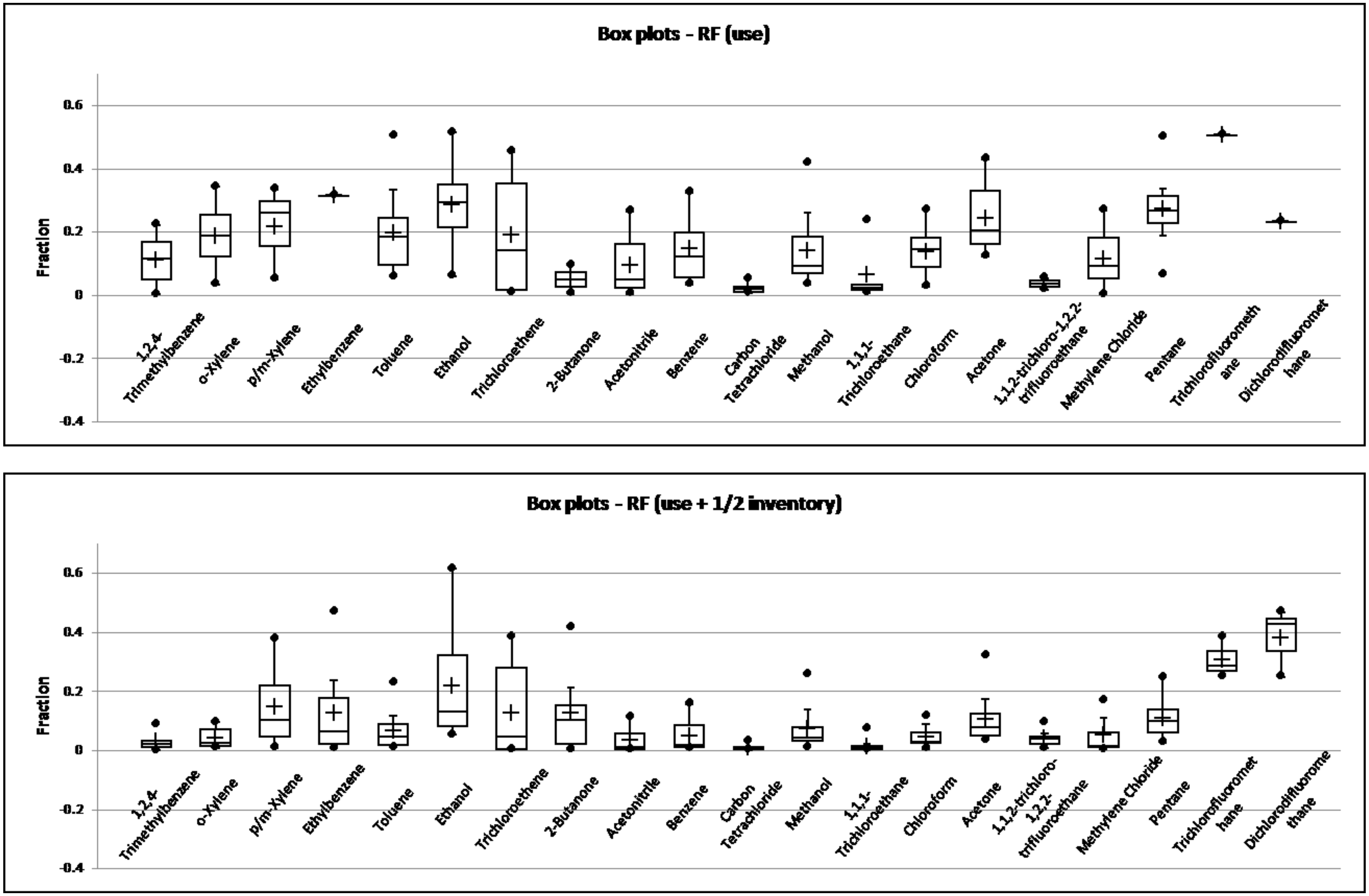


Figure 4.6. Box Plots of Means from RF Distributions Calculated Based on Chemical Usage and Chemical Usage + ½ Inventory (in order from least to highest vapor pressure)

Compounds are shown in order from lowest to highest vapor pressure. The mean RF based on chemical usage + half inventory for about two-thirds of the compounds is below 10%. Many additional compounds have average RFs (e.g., average of the means from several distributions) above 10% when RF is calculated based on chemical usage alone. The average and the range of the mean RFs for all distributions are provided in Table 4.6 for each compound.

Table 4.6. Average of Mean Release Fractions from Distributions Calculated Using Monte Carlo Model

Compound Name	RF (Use + ½ Inv), Distribution Mean		RF (Use), Distribution Mean	
	Average	Range	Average	Range
Tetrachloroethylene	0.1%			
1,1,2,2-Tetrachloroethane	0.1%		0.9%	
Carbon Tetrachloride	0.9%	0.3–3.0%	2.3%	0.9–5.2%
1,1,1-Trichloroethane	1.5%	0.2–7.3%	6.4%	0.9–23.7%
1,2,4-Trimethylbenzene	3.0%	0.05–8.8%	11.3%	0.3–22.3%
Styrene	3.0%	0.3–8.7%		
Acetonitrile	3.6%	0.2–11.3%	9.4%	0.5–26.5%
1,1,2-trichloro-1,2,2-trifluoroethane	4.0%	0.7–9.3%	3.7%	1.8–5.5%
o-Xylene	4.3%	0.9–9.6%	18.9%	3.5–34.3%
Chloroform	4.5%	0.6–11.5%	13.7%	2.8–27.1%
Benzene	5.0%	0.7–15.7%	14.7%	3.4–32.5%
Methylene Chloride	5.1%	0.3–17.0%	11.4%	0.4–26.9%
Toluene	6.5%	1.1–23.0%	19.8%	6.0–50.3%
Methanol	7.3%	1.1–25.8%	14.2%	3.4–41.9%
Acetone	10.4%	3.6–32.1%	24.3%	12.4–43.0%
Pentane	10.8%	2.6–24.8%	27.3%	6.4–49.9%
Ethylbenzene	12.6%	0.8–47.1%	31.5%	
2-Butanone	12.6%	0.2–41.5%	5.0%	0.5–9.5%
Trichloroethene	12.6%	0.3–38.5%	19.1%	1.0–45.3%
p/m-Xylene	14.6%	0.9–37.9%	21.7%	5.2–33.6%
1,3,5-Trimethylbenzene	18.2%	2.1–34.2%		
Ethanol	22.0%	5.3–61.6%	28.7%	6.2–51.4%
Trichlorofluoromethane	30.8%	25.1–38.5%	50.7%	
Dichlorodifluoromethane	38.2%	24.9–46.8%	23.2%	

Although it is difficult to compare distributions, the means from each of the RF distributions were obtained and the relationship between RF (Use + ½ Inv) and RF (Use) investigated (Figure 4.7). Although there does not appear to be any statistically significant correlation, RF (Use) is several times higher than the RF (Use + ½ Inv).

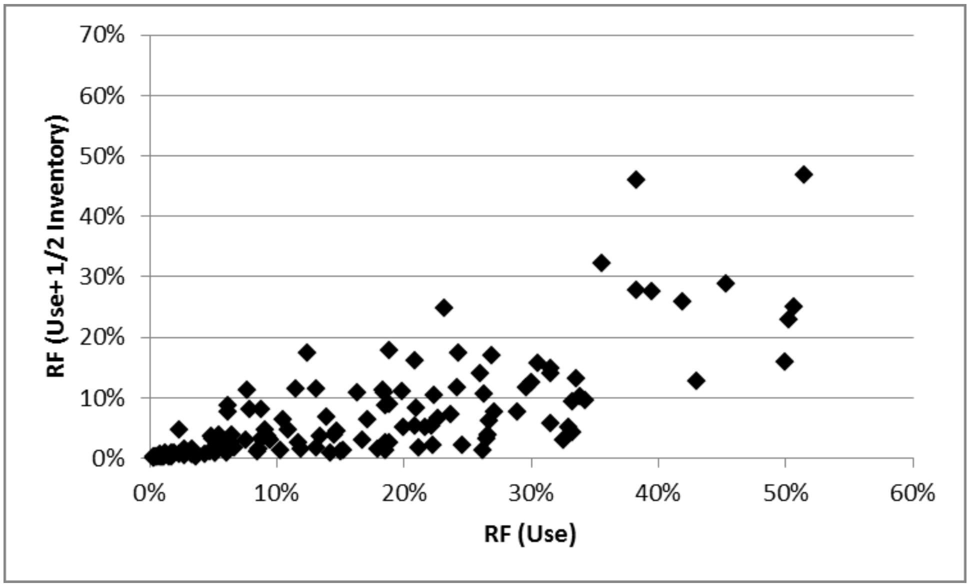


Figure 4.7. Comparison of the Mean from RF distributions Calculated Using Two Variations (Usage + ½ Inventory vs. Usage alone; data from all chemicals/buildings/years for which both RF variations could be calculated)

4.5 Discussion

A distribution of annual emission estimates was created for each of the data sets in Table 4.4. When no filter was applied restricting the results to positive values, the distributions almost always encompassed the value zero and frequently had a negative mean. These results occur because stack concentrations randomly selected from among the samples taken during normal working hours are low enough to be at or below background concentrations for a large number of the 1000 trials run in the Monte Carlo simulations. Although negative emissions are not a realistic outcome, this technique highlights how often the zero or negative values occur, lending credence to the perception of low R&D emissions. Applying a filter to the emissions estimates provides a more realistic distribution of values because all estimates within these distributions are by definition above zero. The mean and 95 percentiles for the filtered distributions are greater than non-filtered and provide a conservative estimate of releases while still incorporating subtraction of background values.

The premise of the release fraction is that emissions are directly proportional to the quantity of chemical used. In this analysis, chemical quantities were represented by CMS usage and inventory data. The results of the RF calculations show a wide range of RFs with differences between compounds but also between data sets for the same compounds. Factors that could contribute to this variation include potentially large errors in estimating emissions with source concentrations so close to background levels, challenges in obtaining data that accurately represents chemical usage, chemical and process parameters likely to influence emissions in addition to chemical quantities, and emissions from sources other than chemical inventories. Although RF provides a relatively simple method to calculate emissions from facilities that employ a wide variety of chemicals and processes, evaluation of other methods of emission calculations can provide insight into the properties that could explain RF variations.

As described by eqs 4.2, 4.3, and 4.4, the difference in release fractions between chemicals may be partially explained by their vapor pressure and molecular weight. To explore this relationship, the average was taken of the RF distribution means for each compound and regressed against the compound vapor pressure and molecular weight. Room temperature (or 20°C) was used as vapor pressure reference temperature, recognizing that this is not likely to represent all processes in the laboratory but provides a baseline for the analysis. Vapor pressure data from the SRC chemical property database (2012) was used to obtain vapor pressures at 25°C, and the Clausius-Clapeyron equation (General Chemistry Online, 2012) was used to adjust these values to 20°C. The SRC database was used because data on vapor pressure and enthalpy of vaporization (used in the Clausius-Clapeyron equation) was available for all of the compounds of interest.

Linear regressions were performed between the average RF for each compound and the corresponding parameters for molecular weight, vapor pressure at 20°C, and MW × Pvap. Regression coefficients were low (below 0.5) for all combinations, including linear regressions of the log values. RFs based on Usage + ½ Inventory had higher correlations to vapor pressure and molecular weight than RFs based on usage alone. Also, correlations to vapor pressure were higher than for molecular weight; adding molecular weight to the RF versus vapor pressure regression did not significantly improve the regression coefficient. Figure 4.8 is a plot of the data with the highest correlation: RF (Use + ½ Inv) versus vapor pressure. In Figure 4.6, the individual mean RF (Use + ½ Inv) are displayed for each compound with the compounds sorted by vapor pressure. Figure 4.6 illustrates the lack of RF and vapor pressure correlation and also shows a wide range of RFs at each vapor pressure.

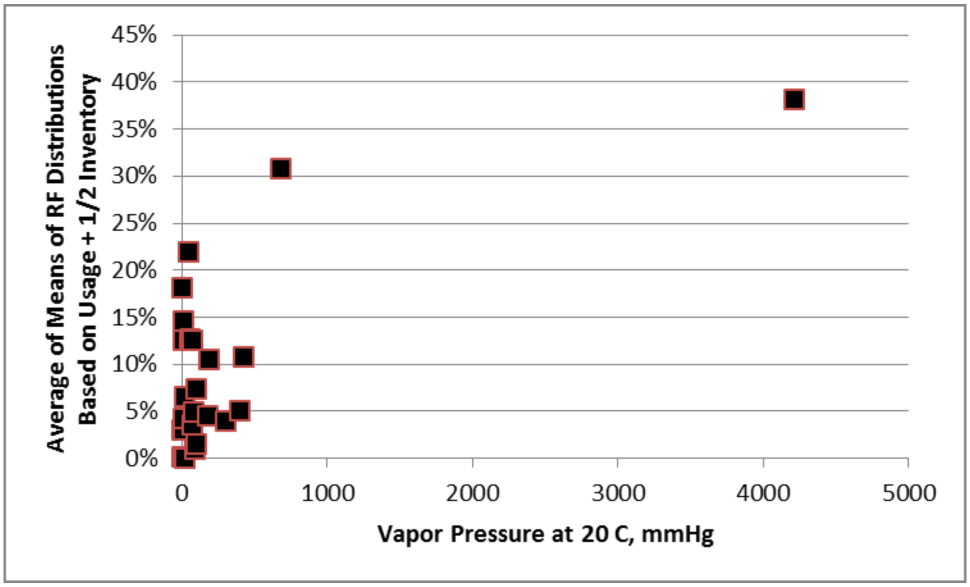


Figure 4.8. RF (Usage + ½ Inv) vs. Compound Vapor Pressure

Results from the regression indicated that a step back was needed in evaluating factors affecting emissions, and that emissions may not be directly related to chemical usage or inventory. Additional regressions were performed with the estimated emission quantity as the dependent variable instead of the release fraction, and with the following independent variables: chemical usage, chemical inventory, vapor pressure at 20°C, and molecular weight. The y variable was the mean of the distribution for annual emissions using the filtered model. Chemical usage and inventory data with less than 0.5 lb/year were removed. All parameters were converted to log values in the analysis to allow for power relationships like those in eqs 4.3 and 4.4. Individual correlations of the mean emissions to each of the independent variables indicated that chemical usage and chemical inventory were equal indicators for estimating emissions, although both had low regression coefficients. These two variables appear to be weakly collinear with a tolerance of 0.32; a tolerance of less than 0.1 indicates a collinearity issue. Adding inventory in addition to useage as a variable only slightly increases the goodnessoffit for the equation. Molecular weight and vapor pressure had even fewer significant correlations to emissions. The optimimum correlation for all four factors gave the following empirical relationship with a regression coefficient of less than 0.5: $E = f(use^{0.4}, inv^{0.4}, MW^{-0.7}, Pvap^{0.2})$. Figure 4.9 shows predictions using the correlation equation versus the input data on emissions; the lack of agreement illustrates the difficulties in modeling emissions from R&D facilities using chemical inventory data given the variety of processes.

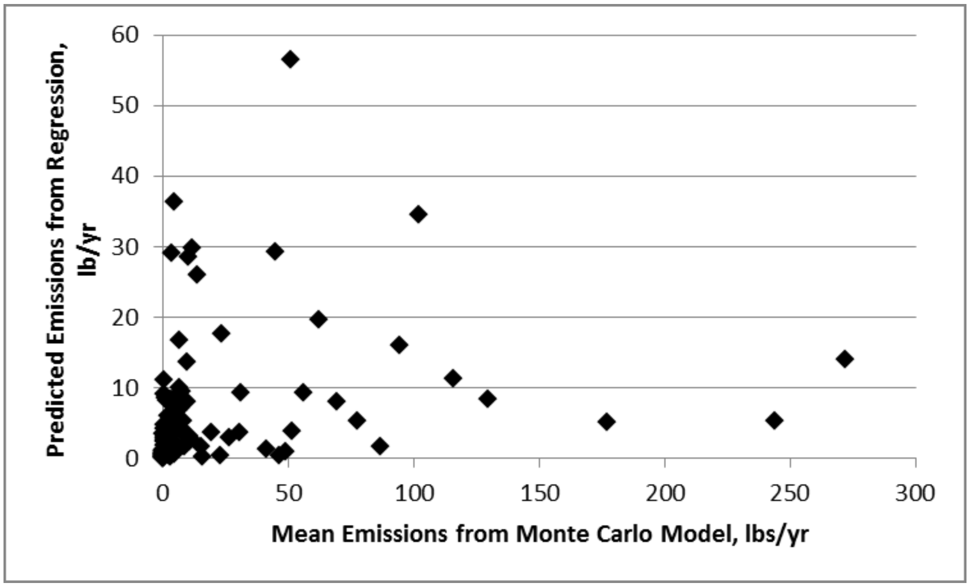


Figure 4.9. Predicted Emissions from Regression vs. Emission Estimates Input to Regression

4.6 Conclusions

A Monte Carlo technique can be used on stack sampling data to give a distribution of emission estimates. For R&D facilities with low emissions, the sampling data may contain many results near or below the detection limit, which can result in negative net emissions (stack sampling – background) estimates in the Monte Carlo results. Calculations can be filtered so that only positive emission values are included in the results, but this will upwardly shift the mean estimated emissions. The unfiltered calculations can be used to provide a confidence level in determining whether emissions are above background concentrations, and the filtered calculations can provide realistic conservative emission estimates. Application of the unfiltered technique to the PNNL measurement data showed close to background emissions for almost all data sets. The filtered technique provided a positive estimate of these emissions, which was somewhat conservative but still allowed for background adjustment.

The Monte Carlo technique can also be used to calculate distributions of release fractions from stack sampling measurements in combination with chemical usage and inventory data. In these calculations, a filter is required to confine the results composing the distribution from zero to one. Release fractions had a wide range among different chemicals and among data sets for the same chemical. The variation in release fractions among chemicals did not correlate well with molecular weight or vapor pressure at 20°C. Also, no statistically significant correlation was found between the mean emission estimates and the independent variables investigated (chemical usage, chemical inventory, molecular weight, and vapor pressure). The lack of correlation could be due to inaccuracies in estimating emissions that are so close to background levels, difficulties in tracking precise data on chemical usage, or challenges in determining and incorporating other factors such as processes requiring heating , chilling, and varying levels of mechanical agitation (e.g., bubbling) that impact emissions in the highly variable R&D environment. This work substantiates the difficulties in estimating emissions from R&D facilities based on chemical inventory data.

4.7 Acknowledgments

The authors thank Professor Christopher Simpson for his careful review of the manuscript and suggestions for improvements.

5.0 SOURCE APPORTIONMENT OF STACK EMISSIONS FROM RESEARCH AND DEVELOPMENT FACILITIES USING POSITIVE MATRIX FACTORIZATION[5]

5.1 Abstract

Emissions from R&D facilities are difficult to characterize due to the wide variety of processes used, changing nature of research, and large number of chemicals. PMF was applied to VOCs concentrations measured in the main exhaust stacks of four different R&D buildings to identify the number and composition of major contributing sources.

PMF identified between 9 and 11 source-related factors contributing to the stack emissions, depending on the building. The factors that were similar between buildings were major contributors to trichloroethylene (TCE), acetone, and ethanol emissions. Several other factors had similar profiles for two or more buildings but not for all four. One factor for each building was a combination of p/m-xylene, o-xylene and ethylbenzene. At least one factor for each building was identified that contained a broad mix of many species, and constraints were used in PMF to modify the factors to resemble more closely the off-shift concentration profiles. PMF accepted the constraints with little decrease in model fit. Although the PMF model predicted the profiles of the off-shift samples, the percent of total emissions was under-predicted by the model versus the measured data.

5.2 Introduction

PNNL operates a number of multidisciplinary laboratory research facilities for DOE and sampled air chemical emissions from some of these facilities during 1998–2008. The primary purpose of this sampling was to provide data to compare estimated release fractions to those used for emissions estimates, verifying that methods used to determine compliance with air regulations and permits conservatively predict actual emissions. Sampling also identifies and quantifies air toxics emitted to compare with compliance limits established by regulatory agencies. Results

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[5] As of February 2013, this chapter was submitted for publication to *Environmental Science and Technology*, authors M. Ballinger (Battelle Seattle Research Center, Seattle, WA 98109) and T. Larson (Department of Civil and Environmental Engineering, University of Washington, Seattle, WA 98195).

from initial sampling campaigns were evaluated and a paper was published that summarized the PNNL compliance approach and described sampling and analytical measurements for the first sampling campaigns (Woodruff, Benar, and McCarthy, 2000). Conclusions reported in the paper were that none of the measurements of the target compounds exceeded an acceptable source impact level (WAC Chapter 173-460) and that an average release fraction calculated from the data provided reasonable validation of that used in compliance assessments. Additional analysis of the data included development of a metric to compare chemical signatures (Ballinger, Duchsherer, and Metoyer, 2009), ranking of compounds according to risk to potential downstream receptors (Ballinger and Duchsherer, 2010), use of a Monte Carlo technique to estimate emissions (Ballinger and Duchsherer, 2012), and preliminary use of PMF on a subset of the data (Ballinger and Duchsherer, 2011).

The wide range of chemicals and processes used in R&D laboratories increases the complexity of estimating air chemical emissions from R&D facilities. In addition, the laboratory-scale quantities of chemicals results in emissions that may be close to or below analytical DL using standard sampling techniques. PMF was chosen to analyze the sources of variability of this stack emission data because it can incorporate measurement uncertainty information, including consideration for missing measurements and data below DL.

PMF is a widely applied receptor modeling technique that has been used extensively to assess sources contributing to ambient air particulate pollution since its introduction (Paatero and Tapper, 1994). For example, PMF was used to identify signatures of sources contributing to particulate matter in Spokane, WA (Norris, 1998); another study recorded fine particle data from National Parks to determine the impact of sources on visibility impairment (Rose, 2006); fine particle concentrations were analyzed in Chicago, IL to identify contributing sources (Rizzo and Scheff, 2007); contributors to aerosols were sought in St. Louis, MO using organic molecular markers as identifiers (Jaeckels, Bae, and Schauer, 2007); and PMF was applied to source apportionment of aerosols on the coast of Turkey (Dogan, Karakas, and Tuncel, 2007). In addition to particulate matter, PMF has been applied to a wide range of air quality indicators such as particulate and gaseous species plus meteorological parameters in northern Michigan (Paterson et al., 1999). PMF model applications have been broadened to other environmental media including soil contamination (Vaccaro et al., 2007) and offshore sediments (Bzdusek, Lu, and Christensen, 2006; Sundqvist et al., 2010). Applying PMF to determine contributions to stack emissions as presented in this paper is a unique use of the model.

In this application, PMF is used to identify multivariate features contributing to measured emissions from several R&D facilities with an objective of determining chemical combinations that point to processes or activities important to emissions and also to evaluate how these source-related features vary over time within a building and between buildings.

5.3 Experimental

Stack Sampling

PNNL sampled air chemical emissions from the stacks of four facilities in Richland, WA during 1998–2008: RPL (325), CSL (329), LSL (331), and EMSL. Sampling times were usually 100 min, except for the initial year of sampling, which included 300- and 50-min samples. Most of the samples were obtained during normal working hours (i.e., 8:00 a.m.–5:00 p.m.), but some were taken on weekends, holidays, or other off-shift times when research activities would not be expected to occur. Although samples were mostly obtained from exhaust stacks, early sampling campaigns also included other locations such as lobbies and corridors to evaluate non research-related contributions to emissions from activities such as office and building operations.

The sampling method used involved the collection of air samples onto TSTs that were subsequently analyzed for VOCs using GC/MS analysis. The sampling apparatus had two parallel channels into which the air stream is drawn; each channel has its own flow rate and one of the channels was programmed to collect a sample at approximately double the flow rate of the other. Thus, each sample has a pseudo-duplicate to identify quality issues and to estimate uncertainty. Depending on the year, GC/MS analyzed a total of 46–49 target compounds, many of which were present in such low concentrations that results were below DL. The target compounds were selected primarily from a standard containing the 39 compound mixtures specified in the Compendium Method TO-14 (EPA, 1989b), plus a short list of supplementary analytes in a second standard.

Positive Matrix Factorization Analysis

PMF is a form of factor analysis that decomposes response data (measured concentrations of VOCs in stack emissions) into major contributing factors and provides a profile for each (Paatero and Tapper, 1994). In this application, PMF based on the ME-2 algorithm (Norris et al., 2008) is used to determine the number and relative abundance of significant contributors to the stack emissions from each laboratory. PMF has an advantage in that the solution is constrained so that no contributor can be negative; all sources contribute either zero or positive input to the total emissions. The PMF model is described by eq 5.1 in which sampling data are attributed to a number of independent sources, each of which is a chemical fingerprint f and contributing a mass g to the sample.

$$x_{ij} = \sum_{k=1}^{p} \left(f_{kj} \times g_{ik} + e_{ij}\right) \tag{5.1}$$

Where x_{ij} = concentration of species *j* in sample *i*

f_{kj} = fraction of species *j* in factor *k*

g_{ik} = mass of factor *k* contributing to sample *i*

e_{ij} = residual of species *j* in sample *i* not explained by the model.

PMF finds a best fit for a specified number of factors by minimizing an object function Q, as shown in eq 5.2.

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left(\frac{x_{ij} - \sum_{k=1}^{p} f_{kj} \times g_{ik}}{u_{ij}} \right) \tag{5.2}$$

Where u*ij* = the uncertainty associated with x_{ij}.

As a result of eq 5.2, each data point is individually weighted depending on its uncertainty, allowing the solution to emphasize the data with higher confidence while still using data that are at or below detection level.

In addition to using EPA PMF 4.1 for this analysis, the PMF User Guide (Norris et al., 2008) and a technical paper (Reff, Eberly, and Bhave, 2007) were used to obtain information on how to set up and run PMF, including preparation of input files and recommendations on input parameters. The technical paper states that some works advocate dropping species that have a large number (>95%) of measurements smaller than DLs. Table 5.1 lists the target compounds that were analyzed in the samples sorted by overall detection frequency. As seen in the table, most compounds had similar detection frequencies for all buildings. Others such as acetonitrile and 2-butanone, had much higher detection frequencies in some buildings.

Table 5.1. Compounds Analyzed in Stack Samples

Compound*	All Results†	Building†				PMF Designation
		325	329	331	EMSL	
Acetone	98%	98%	98%	97%	99%	Strong
Toluene	97%	95%	94%	98%	99%	Weak
Trichlorofluoromethane	95%	90%	99%	94%	100%	Weak
Dichlorodifluoromethane	92%	90%	86%	94%	100%	Weak
p/m-Xylene	92%	95%	81%	94%	95%	Strong
Chloroform	90%	68%	96%	96%	95%	Strong
Benzene	89%	88%	87%	88%	99%	Bad
Ethylbenzene	88%	88%	80%	91%	94%	Strong
Methylene Chloride	82%	73%	96%	75%	96%	Strong
o-Xylene	81%	71%	71%	85%	94%	Strong
Carbon Tetrachloride	77%	73%	74%	78%	87%	Strong
Trichloroethene	74%	94%	66%	58%	98%	Strong
1,1,2-trichloro-1,2,2-trifluoroethane	74%	65%	66%	75%	92%	Weak
Ethanol	72%	41%	56%	95%	74%	Strong
Pentane	69%	55%	67%	68%	93%	Strong
1,1,1-Trichloroethane	65%	57%	59%	62%	96%	Weak
Acetonitrile	62%	17%	64%	72%	98%	Strong
1,2,4-Trimethylbenzene	57%	47%	19%	68%	91%	Weak
1,3,5-Trimethylbenzene	47%	25%	24%	57%	83%	Weak
2-Butanone	40%	18%	22%	40%	97%	Strong
Styrene	40%	34%	29%	48%	41%	Weak
Methanol	40%	22%	19%	60%	39%	Weak
1-Ethyl-Methyl-Benzene (group)‡	39%	24%	21%	33%	95%	Weak
1,4-Dichlorobenzene	33%	53%	17%	39%	12%	Weak

Compound*	All Results†	Building†				PMF Designation
		325	329	331	EMSL	
1,3-Dichlorobenzene	27%	12%	14%	36%	37%	Weak
1,2,4-Trichlorobenzene	28%	28%	7%	33%	40%	Weak
Hexachloro-1,3-butadiene	18%	19%	7%	24%	16%	Weak
Chlorobenzene	16%	3%	8%	33%	2%	
1,1,2,2-Tetrachloroethane	13%	2%	4%	18%	31%	
1,2-Dichlorobenzene	13%	6%	8%	23%	2%	
cis-1,3-Dichloropropene	10%	9%	10%	14%	0%	
trans-1,3-Dichloropropene	8%	8%	9%	11%	0%	
Tetrachloroethylene	7%	5%	6%	11%	3%	
1,1-Dichloroethane	5%	0%	6%	0%	20%	
1,1-Dichloroethene	4%	1%	3%	0%	21%	
cis-1,2-Dichloroethene	3%	0%	0%	0%	21%	
1,2-dichloro-1,1,2,2-tetrafluoroethane	3%	2%	1%	4%	2%	
Chloromethane	2%	0%	2%	1%	6%	
Chloroethane	2%	0%	1%	3%	0%	
1,2-Dichloroethane	1%	0%	1%	0%	7%	
1,2-Dibromoethane	1%	1%	1%	0%	0%	
Bromomethane	0%	1%	0%	0%	0%	
1,1,2-Trichloroethane	0%	0%	1%	0%	0%	
1,3-Butadiene	0%	0%	1%	0%	0%	
1,2-Dichloropropane	0%	0%	0%	0%	0%	
3-Chloropropene	0%	0%	0%	0%		
Vinyl Chloride	0%	0%	0%	0%	0%	
Number of Samples	344	77	72	141	54	
Number of Results§	683	154	140	281	108	

* Target compounds in shading met the >5% criteria of measurements greater than DLs for all emission points and thus were included in the analysis.

† Percent of results above detection limit

‡ Includes 1-methylethylbenzene, 1-ethyl-4-methylbenzne, and 1-ethyl-2-methylbenzene.

§ Samples were taken in pairs so that there were two results per sample except for a limited few taken during the first year of sampling.

PMF requires two data input files: a file with sampling dates and chemical concentrations for each of the samples and a corresponding file with uncertainty values “to give the model an estimate of the confidence the user has in each value” (Norris et al., 2008). Uncertainties should include sampling and analytical errors, and guidance (Reff, Eberly, and Bhave 2007) suggests that using the analytical or method uncertainties that correspond with each species concentration value is the simplest method for creating the uncertainty matrix. However, the duplicates taken in this sample set can be used to quantify a wider range of uncertainties than analytical or method uncertainties. To determine uncertainty for PMF input, the average and standard deviation of the stack concentration for each pair was computed for all pairs where both measurements were above the detection limit. Standard deviation was then plotted as a function of concentration for each compound. Where one or two of the highest concentrations for a given compound had a significant effect on the regression, these values were removed. Uncertainties were then calculated from the regression equation.

Uncertainties obtained using this method were higher than the recovery precision reported by the analytical laboratory, as would be expected, and ranged from 5% for 2-butanone to 107% for benzene with many compounds in the 30–40% range. An uncertainty of 5/6 of the DL was assigned to results below detection limit as recommended by the PMF User Guide (Norris et al., 2008).

Input data can be evaluated in PMF 4.1 to determine suitability for further analysis. For example, the concentration/uncertainty tab in PMF gives the signal-to-noise ratio (S/N) that "indicates whether the variability in the measurements is real or within the noise of the data" (Norris et al., 2008). In PMF 4.1, S/N is calculated as shown in eq 5.3.

$$\left(\frac{S}{N}\right) = \sqrt{\frac{\sum_{i=1}^{n}\left(x_{ij} - s_{ij}\right)^{2}}{\sum_{i=1}^{n}\left(s_{ij}\right)^{2}}} \tag{5.3}$$

The PMF User Guide suggests changing the categorization of a species to "bad" if the S/N is <0.2 and "weak" if the S/N is >0.2 but <2. Categorization as weak triples the provided uncertainty and categorization as bad excludes the species from the rest of the analysis. For the stack data, categorization of species following this recommendation is shown in the results section.

Parameters required to run the PMF base code are number of runs, number of factors, and seed. The number of runs is the number of times the code analyzes the data using the specified number of factors; the default value of 20 was used in these applications. The number of factors is the estimated number of sources contributing to the stack emissions, and this was varied. PMF decomposes the data into optimal source profiles (concentration or percent of each species that make up a factor) and contributions (amount each factor contributes to the individual samples). For this analysis, the number of factors started at six and was increased or reduced depending on the resulting goodness of fit values that are output by the code. Seed is the starting point for each iteration and the default of random seed was used for all of the runs.

PMF produces goodness of fit or Q values that reflect how well the factors fit the actual data with low Q values indicating a better fit. Two goodness of fit parameters are produced; Q_{true} is based on all the data, and Q_{robust} is calculated excluding outliers. Q_{robust} values were compared to theoretical Q values that were calculated using the following equation (Norris et al., 2008):

$$Q_{theory} = nm - p(n+m) \tag{5.4}$$

Where n is the number of species
m is the number of samples
p is the number of factors.

The number of species, n, is adjusted for signal-to-noise ratio as follows: n=1 for each strong species; n= 1/3 for each weak species; n = 0 for each bad species. This corresponds to the PMF treatment of tripling the uncertainty for species marked as weak and excluding species marked as bad.

The number of factors that best fit a data set can be initially chosen based on the PMF Q_{robust} or Q_{true} value closest to Q_{theory} (Reff, Eberly, and Bhave, 2007). Alternatively, the change in Q with increase or decrease in number of factors can be used to determine the optimal number of factors (Camero, Capitani, and Gawlik, 2009). Both methods are employed in this analysis and the number of factors that result in a reduction in Q_{robust} values closest to the reduction in Q_{theory} was used to select the initial number of factors. This factor number was obtained for each of the individual facilities and for all the data grouped as a whole.

PMF identifies outliers (not well modeled results) by species and sampling date and shows their scaled residual value which indicates inadequacy of the model to predict that species for individual sampling results. Residuals above three standard deviations from a normal distribution for that species are listed by PMF. The reduction in number of factors generally increases the number of scaled residuals. Thus, the lower the Q and the lower the number of residuals, the better the model fit.

Bootstrapping within PMF was then used to determine the stability of the initially identified factors (noted as base factors in PMF). Bootstrapping resamples from the original data set and determines whether randomly selected blocks of the original data would produce factors similar to the base factors. The fit is indicated by mapping the new factors to the base factors, and bootstrap results with many unmapped or mis-mapped factors may indicate too many factors in the base model. In addition to minimization of Q and residuals while evaluating factor mapping, a coefficient of determination (COD) was used as a diagnostic tool to quantify the ability of the model to reproduce the original data (Sundqvist et al., 2010). The COD is similar to a regression coefficient in that a value of 1 implies a perfect fit.

Displacement analysis was also used to evaluate the number of factors. Displacement analysis in PMF checks for rotational ambiguity of the model by changing the fit of each species in a factor within a specified incremental change in Q. Four levels of displacement are evaluated corresponding to four allowed incremental changes in Q. A key output identifies the extent of factor swapping, with more swapping indicating factors that are not well defined and a possible need to decrease the number of factors.

A unique feature is provided in PMF 4.1 that allows users to specify constraints to modify one or more factors by incorporating known or suspected relationships for species within the factor. This feature was used to investigate the contributions from suspected underlying sources from non-research processes such as building operations and office activities. Samples taken during off-shift times were analyzed for each building to evaluate similarity among the off-shift group and similarity to factor profiles generated by PMF. Ratios of compounds were obtained from the off-shift data to represent a building signature for these sources, and these ratios were applied to modify the PMF factor with the most similar profile. The results from this adjustment were evaluated to determine the difference in model fit compared to the unconstrained model.

5.4 Results and Discussion

The PMF code was run on stack sampling data from each of four R&D facilities sampled over 10 years. In addition, PMF was run on the data from all buildings grouped together. The S/N ratio for the compounds was similar for each data set, except for 2-butanone which has a significantly higher S/N for EMSL than for other individual buildings. This is consistent with the higher detection frequency for 2-butanone at EMSL versus the other buildings. Twelve compounds had S/N ratios above 2 and were labeled as strong in PMF (Table 5.1). Fourteen compounds with ratios between 0.2 and 2 were labeled as weak, which effectively triples the uncertainties assigned. Benzene was the only compound with a ratio below 0.2 and was labeled as bad, causing benzene results to be removed from the PMF analysis.

Factor Identification

Factors chosen for the runs ranged from 6-12 and goodness of fit (Q) values were evaluated for each of the runs (Figure 5.1). The number of factors initially chosen where the drop in Q_{robust} was approximately equal to the drop in Q_{theory} varied between 9 and11 for individual buildings and was 12 for all buildings together. Table 5.2 shows the summary results from these runs including the number of measured results that are not well represented by the model, as identified by scaled residuals above 3.

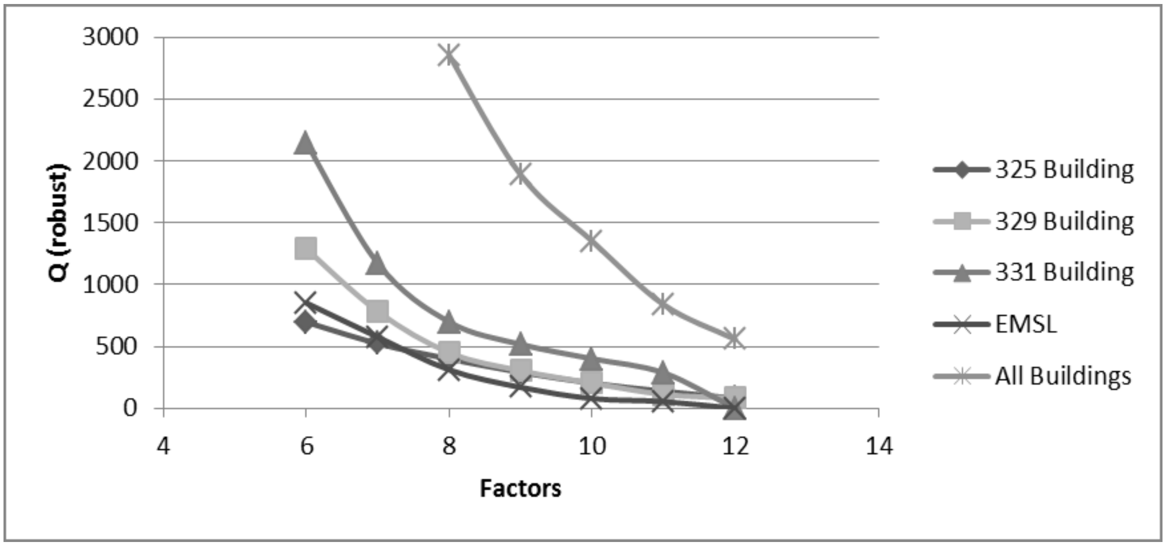

Figure 5.1. Change in Q Values with Number of Factors

Table 5.2. Summary of PMF Results

Building	**325**	**329**	**331**	**EMSL**	**All Bldgs**
# Factors $\Delta Q_{robust} = \Delta Q_{theory}$	10	11	9	10	12
# Residuals > 3	4	1	2	0	3
% Bootstrap mapping issues	15%	16%	12%	1%	6%
# Displacement Swaps	4 at top level	None at top level	None at top 3 levels	None at all 4 levels	None at top 2 levels
COD	0.800	0.996	0.986	0.971	0.990

Bootstrapping and displacement analysis was performed on the initially identified number of factors and these results also varied with the data set as shown in Table 5.2. EMSL factors appeared to be well formed with no scaled residuals above 3, few unmapped or mis-mapped factors from bootstrapping, and no swapping of factors from displacement analysis at all four levels of allowable increase in Q. The 329 and 331 Building factors were the next most stable with few outlying scaled residuals and relatively few mapping and swapping issues. The 325 Building 10-factor model had factor swapping at the first level of allowable incremental change in Q which indicates that the solution should not be used (Norris et al., 2008). A 9-factor model corrected this issue, with no swapping at the highest level and a slight decrease in bootstrapping mapping issues. The number of outlying residuals was increased from 4 to 5, and the COD decreased to 0.697 with the 9-factor model, both of which were indicators of a reduced fit to the original data.

The better fit of the PMF model to the EMSL data compared to the other buildings may be partially attributed to the single year of sampling at EMSL versus multiple years at the other buildings. However, EMSL is unique compared to the other buildings in a number of different aspects: the laboratory is relatively new with start-up of research in 1998 compared to 1950s and 1960s for other buildings; EMSL is built in five pods with a central emission stack from each pod, where the other buildings have one central stack; and the EMSL sampling campaign was conducted in one year from three of the five stacks compared to multi-year sampling from the single stack at the other buildings. All EMSL stacks were grouped together in this analysis to provide sufficient data points for the PMF analysis, just as all the years of sampling were combined for the other buildings. Given the differences between EMSL and the other facilities, it is surprising that the differences in the PMF factors are not more noticeable.

The 325 Building had the least well-defined fit to the PMF model. The 10-factor model was decreased to 9 to reduce factor swapping and was successful at eliminating swapping at the first incremental change in Q. However, the 9-factor model had a higher number of residuals above 3, and low COD compared to other buildings. The 325 Building has a much higher stack flow rate than other buildings because this emission point serves a larger laboratory area that contains hot cells and glove boxes for work with high activity radioactive material, which requires higher ventilation flows to reduce potential for personnel contamination. This may contribute to overall lower concentrations of compounds with increased uncertainties close to the detection limit.

Comparison of Factors

PMF factors were labeled with the building and compound for which the factor contributed a high percent to total emissions. For many factors, this was a single compound, but for others it was a group of species (i.e., xylenes) or named “mix” if the group was a mix of many species. The comparison of factor profiles from the different buildings is shown in the dendogram in Figure 5.2. Factors that modeled a high percentage of emissions of acetone, TCE, and ethanol had similar profiles in all buildings. These profiles were characterized by predominating concentrations of the single chemical and minor contributions from a few other chemicals. The acetone content was high enough in the 329 2-butanone factor, 331 mix factor, and EMSL chloroform factor that they appeared similar to the acetone factors.

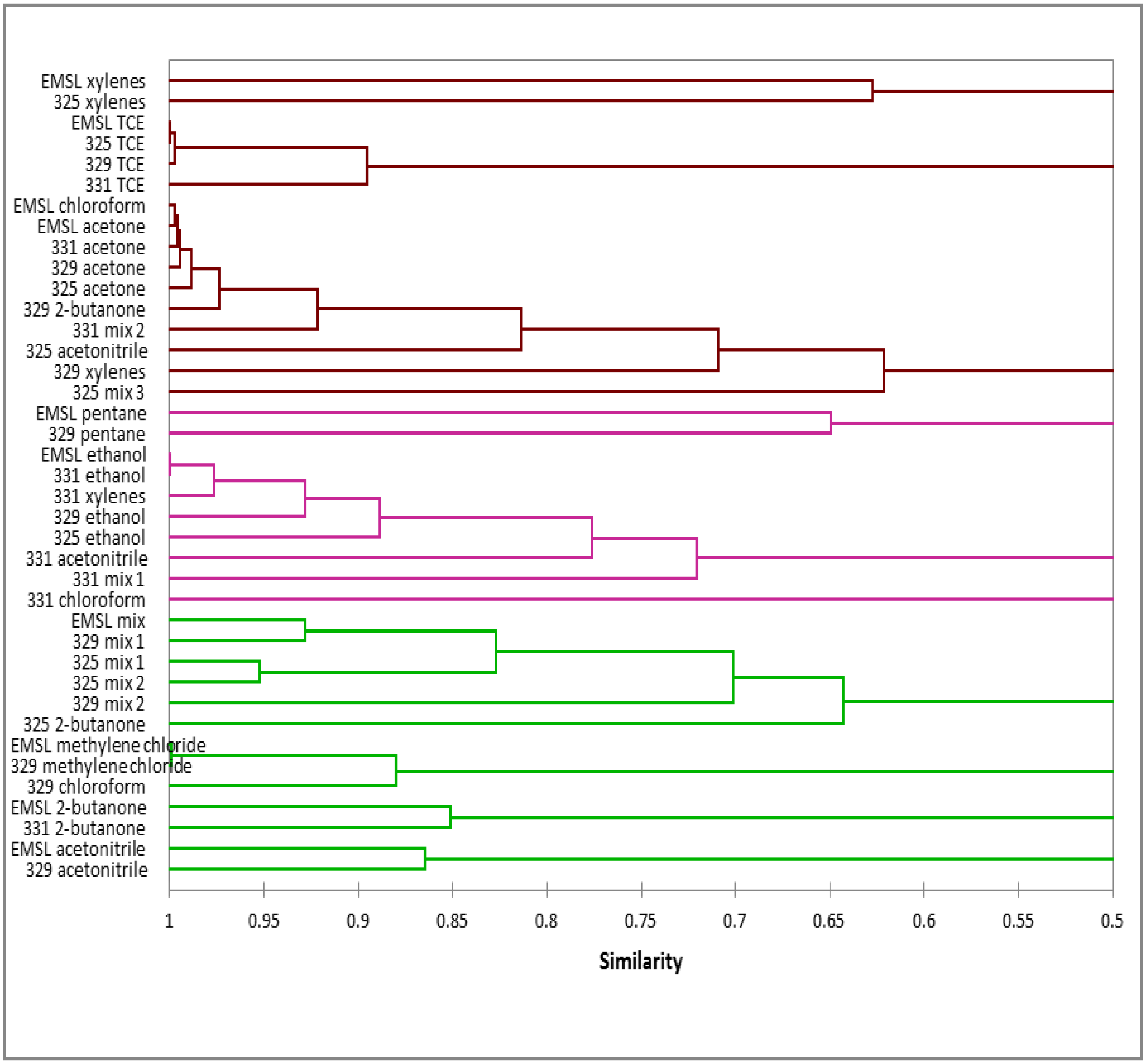

Figure 5.2. Similarity Dendogram for PMF Factors

All buildings also had single factors that contributed a high species percent of acetonitrile, 2-butanone, and xylenes, the latter a combination of o-xylene, p/m-xylene and ethyl benzene. However, the profiles of these factors were not similar among buildings (Table 5.3). The three compounds o-xylene, p/m-xylene, and ethyl benzene are used in stains and fixatives in microbiology laboratories that are prevalent in the 331 and EMSL buildings. A review of chemical inventory data for the years sampled verifies the presence of these compounds primarily in 331 and EMSL, to a lesser extent in the later sampling years for 325, and in very minor quantities in 329. The dendogram shows that profiles for the xylene factors differ between buildings with the most similarity between the EMSL and 325 xylene factors. For these two buildings, the concentration of p/m-xylene is approximately double that of o-xylene and ethyl benzene. The 331 xylene factor also has this ratio but additionally has a high concentration of ethanol increasing its similarity to the ethanol factors.

Table 5.3. Similarity of PMF Factors

Factor Identifier	**% Species Accounted for in Emissions**	**325**	**329**	**331**	**EMSL**
TCE	80–90	Similar to other TCE factors			
Ethanol	60–99	Similar to other ethanol factors			
Acetone	60–85	Similar to other acetone factors			
Acetonitrile	62–86	Similar to acetone factors	Similar to EMSL factor (Pearson 0.865)	Similar to EMSL & 329 ethanol factors (Pearson > 0.8)	Similar to 329 factor (Pearson 0.865)
Xylenes: o-xylene p/m-xylene ethylbenzene	 47–81 49–85 16–82	No close similarities	No close similarities	Similar to ethanol factors	No close similarities
2-butanone	51–90	No close similarities	Similar to acetone factors	Similar to EMSL (Pearson 0.851)	Similar to 331 (Pearson 0.851)
Chloroform	63–86		Similar to methylene chloride factors (Pearson 0.88)	No close similarities	Similar to acetone factors
Methylene Chloride	87–89		Similar to EMSL factor		Similar to 329 factor
Pentane	80		No close similarities		No close similarities
Mix 1		Similar to EMSL and 329	Similar to EMSL and 325	No close similarities	Similar to 325 and 329
Mix 2		Similar to Mix 1	Similar to 325 Mix 1 (Pearson 0.801)	Similar to acetone factors	
Mix 3		No close similarities			

The three compounds chloroform, methylene chloride, and pentane had factors that contributed a high percent of species emissions for multiple but not all buildings. Chloroform is used in a variety of organic extraction processes, activities that are common in all buildings except 325. This explains the presence of chloroform factors for 329, 331, and EMSL but not 325. Methylene chloride factors for 329 and EMSL correspond to the compound's use for regulatory organic analysis, an activity primarily in these two buildings. Pentane is used as an organic solvent and is equally present in chemical inventories. Pentane emissions are predominately explained by a single factor in the 329 and EMSL facilities but are incorporated into multiple mix factors for 325 and 331.

Each building had one or more factors that accounted for a broad mix of compounds. As shown in the dendogram, mixes from three of the four buildings (325, 329, and EMSL) had similar profiles. The factors for each building are summarized in Table 5.3, along with the percentage of the compound emissions attributed to the factor and a description of profile similarities to other factors. For the 325 Building, three of the nine factors were a mix of compounds as opposed to centered on one or two species. Models for the other buildings only required one (EMSL) or two (329 and 331) mix factors to fit the data. As mentioned previously, the 325 Building has a much higher stack flow rate than the other buildings, which may contribute to overall lower concentrations of compounds and less differentiation between factors.

Constraints to Model Off-shift Measurements

Profiles for the mix factors were compared to profiles from the samples collected during off-shift hours to determine whether one or more of the factors could be attributed to off-shift concentrations of chemicals in the building. Off-shift samples are believed to be representative of emissions when little or no research activities are being conducted in the building and may be present as an underlying contribution to all samples. This contribution could constitute 15–50% of the mass of emissions as calculated using the median off-shift sample concentrations (Table 5.4).

Table 5.4. Constrained Model Summary Results

Factor	Building			
	325	329	331	EMSL
All Compounds Pearson's r* – no constraints	0.908	0.393	0.860	0.665
All Compounds Pearson's r* – with constraints	0.987	0.913	0.990	0.927
Compounds with no Ratio Applied: Pearson's r*– no constraints	0.431	0.239	0.416	0.687
Compounds with no Ratio Applied: Pearson's r*– with constraints	0.448	0.259	0.309	0.027
Increase in Q (dQ)	1.4%	1.2%	1.6%	8.6%
% Emissions represented by off-shift sampling data†	54%	22%	15%	38%
% Emissions from Mix Factor	8%	3%	15%	14%
% Emissions from Mix Factor with Constraints	17%	1%	8%	7%
% Emissions all Mix Factors with Constraints	40%	5%	10%	7%

*Mix factor compared to off-shift median

† Off-shift median concentrations assumed to be a subcomponent of every sample

Although only a limited number of off-shift samples were taken (3–6, depending on the building), the relative concentration of the 27 compounds were similar for most of the off-shift samples for a given building. In addition, the off-shift profiles for the 325 and 331 Buildings were similar to each other. Ratios were computed for each building to characterize off-shift sample profiles using hexachloro-1,3-butadiene as the denominator because it had the least variation in concentration. Ratios from the compounds contributing the most to the off-shift concentrations were applied as constraints in PMF to adjust the mix factor with the profile most similar to off-shift samples (Table 5.5).

Table 5.5. Ratios* Applied to Mix Factor in Constrained Model

Compound	Building			
	325	329	331	EMSL
1,2,4-Trichlorobenzene	1.05	0.71	0.72	0.73
Acetone	0.40	2.51	0.29	1.43
Dichlorodifluoromethane	0.41	0.54	0.19	0.27
Ethanol	0.15	1.04	0.73	0.19
Methanol	0.77	0.96	1.00	3.12
Methylene Chloride	0.19	0.46	0.20	0.54
Trichloroethene	0.36	0.33	0.02	0.16
Trichlorofluoromethane	0.24	1.22	0.20	1.54

* Ratio of the identified compound to hexachloro-1,3-butadiene

The constrained PMF model improved the similarity of the mix factor profiles to the profiles of off-shift samples (as intended) with little reduction in model fit as quantified by increase in Q if all compounds are considered (Table 5.4). However, if the compounds used in the ratio application are removed, the similarity to the off-shift median profiles may be increased or reduced depending on the building.

A second evaluation was performed to determine whether the PMF model verified contributions of this factor in terms of percent emissions. If off-shift sampling data represents underlying emissions that occur continually from a building, then off-shift concentrations are a subcomponent of every sample, and the fraction of total emissions from these contributions can be calculated and compared to the fraction contributed by the PMF mix factor. The percent of emissions of each building due to underlying emissions was calculated using median off-shift concentrations. As shown in Table 5.4, these emissions are significant for all buildings and could be as much as half of the emission concentrations for the 325 Building. The percent of emissions from the mix factor that was most similar in profile to the off-shift sample profiles was calculated from the PMF output and is also presented in Table 5.4.

For all buildings except 331, the PMF mix factor represented a much smaller percent of emission concentrations than estimated using off-shift sampling data. The PMF model attributes at least some of the off-shift concentrations to other factors. Applying constraints increased mix factor percent contribution for the 325 Building but decreased for other buildings. All buildings except EMSL have multiple mix factors, and the percent contribution from all mix factors using the constrained model is also shown in Table 5.4. This percent is still below that estimated from the sampling data, indicating that mix factors are not the only contributions to off-shift samples.

This analysis is the first to apply source apportionment to stack emissions to gain insight into the processes contributing to those emissions, particularly when the processes are highly variable over time. PMF was useful in identifying the single compounds that tended to dominate factor modeling and a combination of three chemicals commonly emitted together. PMF was also valuable in identifying factors from each building with a broad mix of compounds, constraining the factor to resemble more closely off-shift measurements for the compounds used in the ratio and evaluating whether this factor represents an underlying contribution to emissions.

5.5 Acknowledgements

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6.0 SUMMARY AND FINDINGS

6.1 Summary

This dissertation used measured stack concentrations from R&D facilities to compare emissions to regulatory criteria, calculate release fractions, evaluate relationships with chemical properties, and identify contributors to emissions through source apportionment. The comparison with regulatory criteria showed that downwind ambient air concentrations calculated from the stack measurement data were below ASILs for almost all cases, even under extreme worst-case analyses. However, for compounds with averaging periods of a year, the worst-case analysis was too extreme to evaluate emissions with lower levels of regulatory criteria used to determine modeling requirements or to define trivial releases. Compounds with 24-hr averaging periods were almost all several orders of magnitude below all criteria including the trivial release criteria. An alternate analysis using the full range of sampling data supplied more realistic emissions estimates and an ability to explore effects under different operational modes. This alternative analysis involved use of a Monte Carlo technique to generate a distribution of emissions from random selections of the measurement data.

A similar Monte Carlo technique was used to calculate release fractions from the stack measurement data and building chemical inventory data. The calculations allowed application of filters so that only release fraction values from zero to one were included in the resulting distributions. Release fractions had a wide range among chemicals and among data sets for different buildings and/or years for a given chemical. Regressions of release fractions to molecular weight and vapor pressure showed weak correlations. Similarly, regressions of mean emissions to chemical usage, chemical inventory, molecular weight and vapor pressure also gave weak correlations. These results highlight the difficulties in estimating emissions from R&D facilities using chemical inventory data.

The use of factor analysis on measured stack emissions from R&D facilities identified between 9 and 11 factors depending on the building. The majority of these factors were focused on explaining emissions from a single dominating chemical. Although 49 target compounds were analyzed, only 27 of these were above the detection limit frequently enough to be included in the analysis. Factors for TCE, acetone, and ethanol were identified and were similar between buildings. Other factors dominated by explaining a high percentage of a single species were acetonitrile, 2-butanone, chloroform, methylene chloride, and pentane. Some of these factors were identified for multiple (but not all) buildings, and factor profiles between buildings were dissimilar. A factor was identified for all the buildings that combined high percentages of o-xylene, p/m-xylene, and ethyl benzene in a consistent ratio, and one or more factors were identified for a broad mix of compounds.

This analysis is the first to apply source apportionment to stack emissions to gain insight into the processes contributing to those emissions, particularly when the processes are highly variable over time. PMF was useful in identifying the single compounds that tended to dominate factor modeling and a combination of three chemicals commonly emitted together. PMF was also valuable in identifying factors from each building with a broad mix of compounds, constraining the factor to more closely resemble off-shift measurements and evaluating whether this factor represents an underlying contribution to emissions.

6.2 Conclusions

Chemical air emissions from R&D facilities are difficult to estimate because of the wide variety and changing nature of processes. Chemical inventory-based methods are often applied but seldom verified with actual emission measurement data. The data set from PNNL offered a unique opportunity to evaluate actual emissions from several buildings over a 10-year time period. Although the data set included a small fraction of the thousands of chemicals used, it included target compounds with a wide range of chemical properties, use within the laboratories, and regulatory significance. The measurement data allowed for an overall evaluation of R&D emissions compared to regulatory data, an assessment of the adequacy of inventory-based estimation methods considering potential improvements to these methods, and an identification of multi-component sources.

Emissions from R&D facilities were determined to be low with many results below detection limit concentrations which were sufficient to compare emission concentrations to ASIL values but are not always sufficient to compare with the lower level criteria of SQER and de minimis values. An extreme worst-case analysis can be used to evaluate compliance, but this method is not realistic particularly in applications of annual emissions for sources that have a large temporal variability. An analysis using Monte Carlo methods is helpful in obtaining a conservative yet realistic emissions estimate and investigating the impacts of operational variability. Application of both of these methods showed that non-carcinogenic compounds were orders of magnitude below their regulatory criteria including the de minimis quantity defining quantities below regulatory concern. It was more difficult to evaluate compliance with lower level criteria for the carcinogenic compounds because many of these were above de minimis, even with results that were below DL.

The Monte Carlo method was also useful in assessing release fractions which are applied to chemical inventories to estimate emissions. A mean release fraction value of 10% was obtained for two-thirds of the compounds when applied to chemical usage plus one-half inventory, but the value was higher for the other third. The range of release fraction values ranged considerable for most compounds both between buildings and between years for a given building. The suspected relationship between release fractions and chemical properties such as molecular weight or vapor pressure could not be established, which may be due to inaccuracies in estimating emissions that are so close to background levels, difficulties in tracking precise data on chemical usage, or challenges in determining and incorporating other process parameters that can impact emissions.

Source apportionment was applied to the stack measurement data in an additional effort to gain insight into the identification of processes contributing to emissions from R&D facilities. The source apportionment attributes useful for this application are the ability to extract multivariate features from data with multi-component analysis of many samples while weighing individual uncertainty of the data. In this application, the source apportionment model identified some factors that were similar among the four buildings studied and a few that were unique. All buildings had a low level multi-compound “mix” factor that could be adjusted to resemble more closely the chemical profile of off-shift samples with little loss of model fit.

6.3 Suggested Future Research

The PNNL data set taken from four facilities over a 10-year time frame demonstrates the difficulty in estimating air emissions and a wide range/high uncertainty in current estimation methods based on chemical inventories. If additional sampling at this facility is conducted to verify actual emissions further, the following paragraphs describe considerations for these sampling campaigns.

Characterization of Non-R&D Sources

The current sampling data indicate that concentrations of many compounds in off-shift samples were similar in concentration to samples taken in locations with no R&D emissions such as hallways and corridors. This similarity has implications on assumptions about operational modes and can make a significant difference in calculating emissions. Only a limited number of off-shift samples were collected, yet they are assumed to represent a large portion of the year. Future work should combine collection of additional off-shift samples, along with observational data on operational practices from researchers or building managers.

Focus on Carcinogenic Compounds

Small laboratory-scale quantities of chemicals are used in R&D facilities and result in low emissions that are more of a concern for carcinogenic compounds than non-carcinogenic compounds. An evaluation of R&D chemical inventory and usage data weighted by regulatory or hazard criteria should assist in identifying compounds of interest. Combined with feasibility and cost of analysis for the compounds, this evaluation would provide a more directed suite of target compounds.

Evaluate Analytical Detection Limits

As discussed in Section 3, detection limit concentrations for some compounds may be insufficient to compare stack emissions to regulatory values of interest. An evaluation should be performed for the compounds to be analyzed in future sampling campaigns to verify that sampling parameters (such as sampling time discussed below) are sufficient in combination with the DL to meet the objective.

Evaluate Sampling Times

The sampling objective is to maximize the mass collected without exceeding the time at which contaminants could migrate through the column of the sample tube and exit the downstream side, thereby underestimating the amount in the air volume sampled. Sample times of 100 min were sufficient for the compounds analyzed in the current data but may not be appropriate for the compounds to be analyzed in future sampling.

Actual measurements of stack emissions from R&D facilities are rare and the data set from PNNL provides a unique opportunity to characterize these releases. This dissertation presented methods that took into account the wide range of compounds and the temporal variability of emissions to compare emissions to regulatory criteria, assess current methods used to estimate releases, and identify the number and composition of major contributing sources.

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