



Source apportionment of stack emissions from research and development facilities using positive matrix factorization



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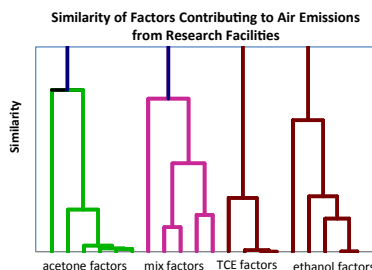
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HIGHLIGHTS

- Positive Matrix Factorization (PMF) was used for the first time on measured stack data.
- PMF was applied to air chemical emission sample data from research and development facilities.
- PMF identified between 9 and 11 sources contributing to the measured emissions.
- Some source profiles from the PMF application were common to all facilities, but others were unique.
- At least one source from each facility resembled the source profile of off-shift samples.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 20 May 2014

Received in revised form

14 August 2014

Accepted 19 August 2014

Available online 19 August 2014

Keywords:

Positive matrix factorization

Measured stack emissions

Bootstrapping

Volatile organic compounds

ABSTRACT

Research and development (R&D) facility emissions are difficult to characterize due to their variable processes, changing nature of research, and large number of chemicals. Positive matrix factorization (PMF) was applied to volatile organic compound (VOC) 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 stack emissions, depending on the building. Similar factors between buildings were major contributors to trichloroethylene (TCE), acetone, and ethanol emissions; other factors had similar profiles for two or more buildings but not 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 the factors to resemble more closely the off-shift concentration profiles. PMF accepted the constraints with little decrease in model fit.

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1. Introduction

Pacific Northwest National Laboratory (PNNL) operates a number of multidisciplinary laboratory research facilities for the U.S.

Department of Energy and sampled air chemical emissions from some of these facilities from 1998 to 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; this objective was addressed prior to the PMF analysis (Ballinger et al., 2013). Stack emission sampling also identifies and quantifies air toxics emitted

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to compare with compliance limits established by regulatory agencies (Ballinger et al., 2014). Results 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 et al., 2000). Conclusions reported in the paper were that none of the measurements of the target compounds exceeded an acceptable source impact level (WAC 173-460, 2009) and that an average release fraction calculated from the data provided reasonable validation of the factor used in compliance assessments. Additional analysis of the data included development of a metric to compare chemical signatures (Ballinger et al., 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 increase 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 detection limits 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 of missing measurements and data below detection limits.

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; Norris, 1998; Rose, 2006; Rizzo and Scheff, 2007; Jaeckels et al., 2007; Dogan et al., 2007; Paterson et al., 1999). PMF model applications have been broadened to other environmental media including soil contamination (Vaccaro et al., 2007) and off-shore sediments (Bzdusek et al., 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. PMF is also used in this unique application to identify and characterize off-shift contributions to emissions.

2. Materials and methods

2.1. Stack sampling

PNNL sampled air chemical emissions from the stacks of four facilities in Richland, WA from 1998 through 2008: a Life Sciences Laboratory (331 Building), a Chemical Sciences Laboratory (329 Building), a Radiochemical Processing Laboratory (325 Building), and the Environmental Molecular Sciences Laboratory (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., 0800–1500 h), but some were also 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. Data from lobby sampling was not used directly in the PMF analysis, but was used to compute ratios for the PMF constraint feature.

Table 1
Compounds analyzed in stack samples.

Compound ^a	All results	Building				PMF designation
		325	329	331	EMSL	
Percentage of results above detection limit						
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
Ethyl benzene	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-methylbenzene (group) ^b	39	24	21	33	95	Weak
1,4-Dichlorobenzene	33	53	17	39	12	Weak
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
Number of samples	344	77	72	141	54	–
Number of results ^c	683	154	140	281	108	–

^a Target compounds that met the >5% criteria of measurements greater than DLs for all emission points (and thus were included in the analysis).

^b Includes 1-methylethylbenzene, 1-ethyl-4-methylbenzene, and 1-ethyl-2-methylbenzene.

^c 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.

The sampling method used involved the collection of air samples onto triple sorbent traps which were subsequently analyzed for VOCs using gas chromatography/mass spectrometry (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 measurements were below detection limits. The target compounds were selected primarily from a standard containing the 39 compound mixtures specified in U.S. Environmental Protection Agency (EPA) Compendium Method TO-14 (EPA, 1999), plus a short list of supplementary analytes in a second standard (Ballinger et al., 2013, 2014).

2.2. Positive matrix factorization analysis

PMF is a form of factor analysis that decomposes response data (in this case stack emissions) into major contributing factors and provides a profile for each factor (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

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