Characterization of volatile organic compound emission sources in Fort Saskatchewan, Alberta using principal component analysis

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Abstract Volatile organic compounds (VOCs) were measured at two sites in a highly industrialized zone in western Canada from September 2004 to March 2006. Principal component analysis (PCA) with varimax rotation was performed on 30 VOCs to identify the pollution sources. Aliphatics, aromatics, and halogenated aliphatics were studied. The two monitoring sites were 11 km apart, with site 1 closer to the city of Fort Saskatchewan and site 2 predominantly down wind from the industrial sources. PCA results provided the basis for interpreting the relationship between the ambient 24-h integrated VOC samples and the emission sources in the region. Challenges existed in interpreting the PCA results in such a highly industrialized region; however a unique feature to this study was the fact that the region was home to the only 1,2-dichloroethane emitting facility in Canada. Other specific industry related VOCs in the region were vinyl chloride, styrene and HCFC-22. Making use of these specific VOCs in the PCA allowed for easy identification of an industrial contribution. For factors that were not easily distinguishable, further PCA tests were conducted using carbon monoxide concentrations, wind direction data and seasonal splitting of the samples. The analysis found that five factors accounted for 82% of the variance at site 1 and five factors accounted for 81% of the variance at site 2. The factor accounting for the highest variability (~40%) at the two sites was the most difficult to interpret, but showed contributions from both industry and vehicle related emissions. Specific industrial sources were identified using 1,2-dichloroethane as a chemical tracer or by corroborating wind speed with known industry VOC emissions. Both sites had two factors identified as specific industry sources and these factors totaled to over 20% of the variance. Long range transport of stable halogenated compounds accounted for greater than 10% of the variance, and seasonal effects accounted for 5% of the variance.

Keywords Alberta, Canada · Fort Saskatchewan · Industry · Principal component analysis · Volatile organic compounds

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1 Introduction

Volatile organic compounds (VOCs) are recognized air pollutants that can react in the atmosphere to form ozone and secondary organic compounds. These secondary air contaminants are known to have adverse effects on human health, including reduced lung function, development of and increased symptoms of asthma, atherosclerosis, and reduced life expectancy (World Health Organization 2006). In addition to contributing to the formation of photochemical smog, a number of individual VOCs have been identified as important cancer risk factors in the urban environment (Hagerman et al. 1997).

Emission sources for VOCs include both anthropogenic and biogenic sources (Atkinson 2000). Ambient VOCs from anthropogenic sources are mainly attributed to vehicle emissions, fuel burning, evaporative loss of fuel and solvents and industrial sources, with vehicle emissions often being the primary emission source in urban areas (Ho et al. 2002; Fernandez-Villarrenaga et al. 2004; Guo et al. 2004a, b; Jorquera and Rappengluck 2004; Millet et al. 2005; Ohura et al. 2006; Buzcu and Fraser 2006). Biogenic emissions sources include biomass burning and vegetation. Emissions of isoprene and monoterpenes are primarily from vegetation sources, with a strong dependence on the plant species (Kesselmeier and Staudt 1999). Ambient VOC concentrations are the result of a combination of these two source categories.

This study examines VOCs in the Fort Saskatchewan region, a highly concentrated industrial area in western Canada with more than 30 major industrial facilities. Several of the industries in the area are categorized as downstream oil and gas or petrochemical production. Major anthropogenic point source emissions are reasonably well known due to requirements for industry to report emissions to the Government of Canada's National Pollutant Release Inventory. The study region is particularly unique since it lies between an urban centre and a national park. As well, there exists industrial activity in the region that does not occur elsewhere in Canada. At the time of the monitoring, the only facility emitting 1,2-dichloroethane in Canada was located in the heart of the industrial zone. Given the long atmospheric lifetime of 1,2-dichloroethane (43–111 days, Government of Canada 1994), the concentrations of 1,2-dichloroethane measured in this study can serve as an atmospheric chemical tracer. Other specific industry emissions in the region include vinyl chloride, styrene and HCFC-22. The blend of industrial, rural and urban sources affecting the region provides a unique setting for monitoring and studying air quality issues. The purpose of this study is to characterize the ambient VOC concentrations in the Fort Saskatchewan region.

VOC air monitoring studies measure a wide variety of compounds due to the abundance of different VOCs in the atmosphere and the ability to measure several different species using a single analytical method. Data obtained from a VOC study, therefore, can become onerous when there are several monitoring sites measuring hundreds of compounds. As such, data reduction techniques are often desirable. Principal component analysis (PCA) is a multivariate, statistical approach that is used to simplify a large data set. PCA acts to normalize and condense the large data set into factors that describe variance based on the assumption that all of the variance can be explained by an underlying set of factors (Shaw 2003). It should be noted that a factor does not necessarily represent a specific emission, but rather a pattern of association (Derwent et al. 1995). The PCA method is a natural choice for quantifying patterns of association between VOCs. Application of PCA to VOC data produces factors of correlated VOCs that describe the percentage of variance in the data and the factors can be used to identify emission sources or categories. Several researchers have used principal component analysis to characterize VOCs (Derwent et al. 1995; Fernandez-Villarrenaga et al. 2004; Guo et al. 2004a, b, 2006). PCA has also been used to study particulate matter and aerosols. Some research has been conducted using air quality

constituents and meteorological data as PCA inputs, specifically aerosols and wind direction (Jalkanen and Manninen 1996; Veltkamp et al. 1996; Wehner and Wiedensohler 2003).

For this study, PCA is used to examine the correlation factors for a sub-set of VOCs at two air monitoring sites in the Fort Saskatchewan region. This study combines data on emissions inventories, wind direction and ambient concentrations in order to characterize VOCs in the region. This paper characterizes the VOCs by examining the PCA factors and identifying the significant sources specific to the Fort Saskatchewan region based on an understanding of the facilities' reported emissions inventories. Since the only facility in Canada that produces 1,2-dichloroethane was located in the study region, the ambient concentrations of this VOC serve as a surrogate tracer gas in the PCA. To further refine the interpretation of the factors, PCA results are analyzed with wind direction, carbon monoxide concentrations and samples split by seasons at the two monitoring sites.

2 Experimental

2.1 Monitoring sites

Figure 1 shows the specific locations of the two air monitoring sites in the Fort Saskatchewan region. Figure 1 also shows the National Pollutant Release Inventory (NPRI) reporting industries in the area. The city of Fort Saskatchewan, home to 15,000 people (Statistics Canada 2006), is situated at the southwest corner of the Fort Saskatchewan region. Elk Island National Park, which protects approximately 190 km^2 of aspen parkland,
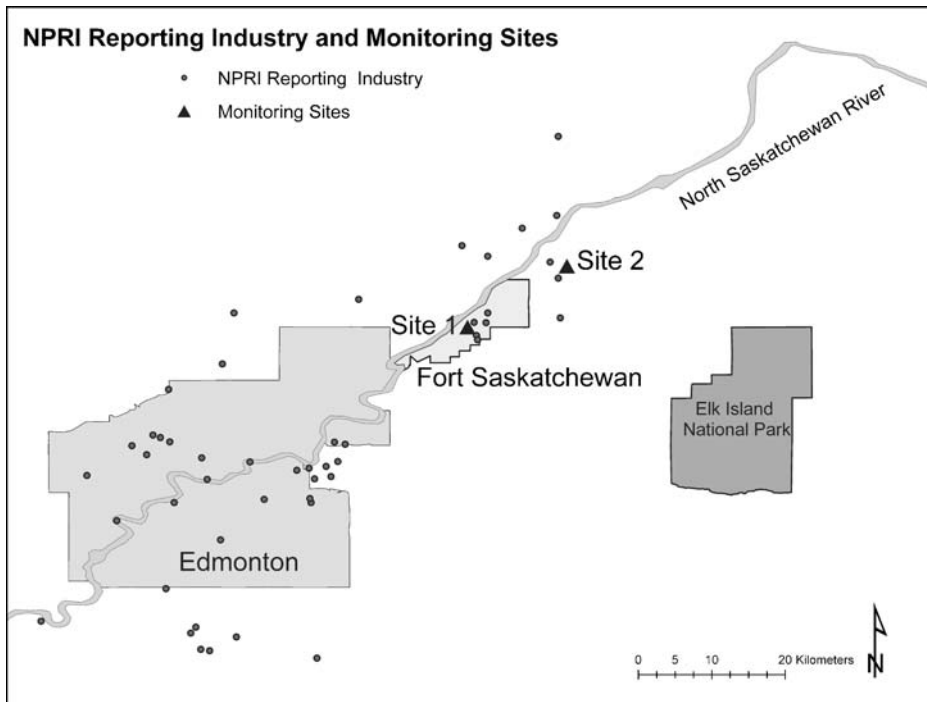

Fig. 1 City of Fort Saskatchewan and surrounding region

is located 20 km east of the Fort Saskatchewan industrial zone. The Fort Saskatchewan industrial zone covers 194 km[2] and is known as "Alberta's Industrial Heartland". As shown on Fig. 1, Sites 1 and 2 are 11 km apart. Figure 2 presents the wind rose for the city of Fort Saskatchewan from 1990 through 2006. The dominant wind direction is from the southwest; however, it is not uncommon for the area to receive winds from the northwest. As such, site 2 is predominantly downwind from a majority of the industrial facilities, and site 1 is closest to the city of Fort Saskatchewan. At the time of the study, the 1,2-dichloroethane emitting facility was located approximately 4 km northeast of site 1.

2.2 Sampling and analysis

Air samples were taken every 6 days for 24 h simultaneously at the two sites in the Fort Saskatchewan region. Sampling commenced September 12, 2004 and ended on March 30,
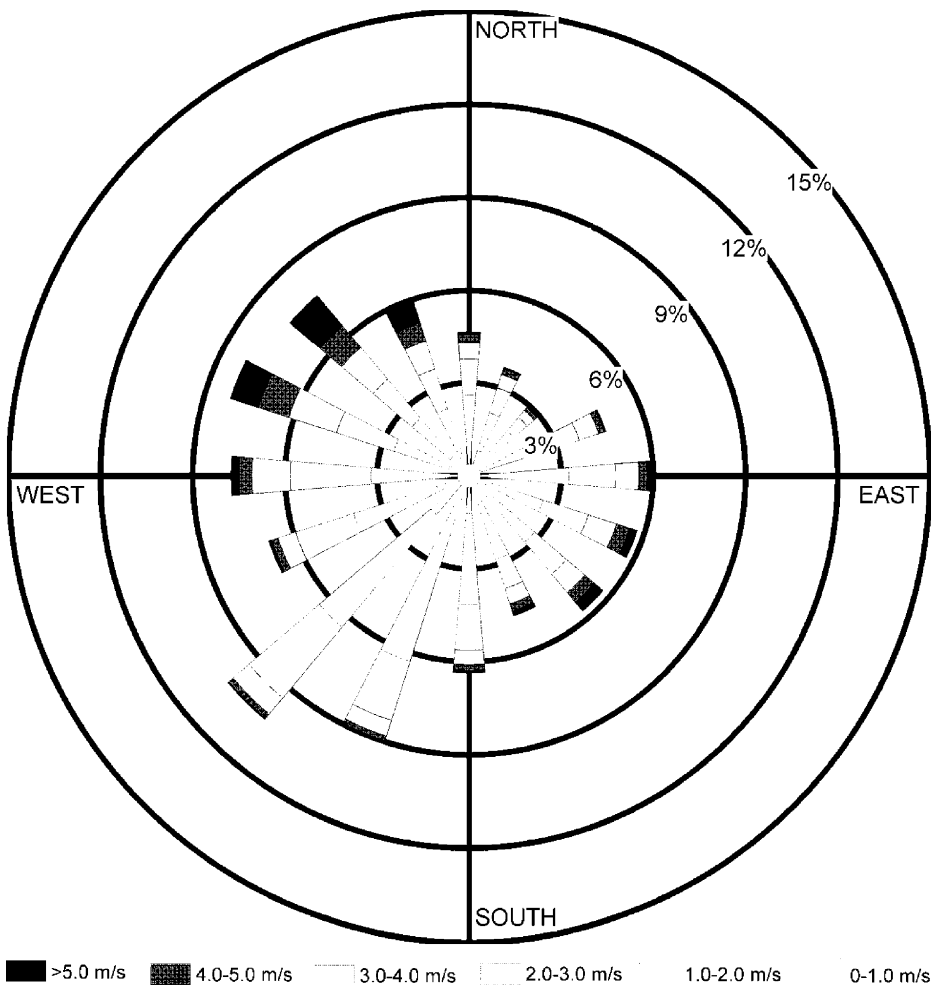
Fig. 2 Fort Saskatchewan wind rose. Hourly wind direction data were taken from the Fort Saskatchewan station from January 1990 through December 2006 (Clean Air Strategic Alliance 2007)

2006. A total of 91 and 94 samples were acquired from sites 1 and 2 respectively. Six litre evacuated SummaTM (Scientific Instrumental Specialists, Inc.) canisters were used to collect the air samples. These stainless steel canisters were specially passivated by a process that uses an electro-polishing step followed by chemical deactivation to produce a surface that is chemically inert (Wang and Austin 2006). In the field, samples were collected using whole air samplers (Xontech Inc., Model 910A).

Full canisters under pressure were sent to Environment Canada's Environmental Technology Centre (ETC) in Ottawa, Canada, where the samples were analyzed using a cryogenic preconcentration technique with a high resolution gas chromatograph and quadrupole mass-selective detector (GC-MSD), as described in Environmental Protection Agency Methods TO-14A and TO-15 (US EPA 1999). The canisters were sent to the lab and analyzed within 2–6 weeks of the sample being taken. An Entech Model 7100 preconcentrator with auto-sampler (Entech Instruments, Inc., Simi Valley, CA, USA) was used for sample preconcentration. The instruments used for species identification and quantification were an Agilent 6890 gas chromatograph and an Agilent 5973 MSD. The GC-MSD was operated in the selected ion monitoring mode (SIM). Identification of target analytes by SIM analysis is based on a combination of chromatographic retention time and relative abundance of selected monitored ions. The MSD acquires data for target ions only, and ignores all others. This detection technique is highly specific and sensitive.

An instrument calibration standard was prepared using stock gas standards prepared in the ETC laboratory from three multi-component liquid mixtures and gas mixture cylinders purchased from Scott Environmental Technology Inc. Quantification was based on daily five-point linear regression calibration curves obtained from analysis of this external standard mixture.

The Fort Saskatchewan VOC monitoring study measured 150 compounds, ranging from C_3–C_{12}. This is a common suite of VOCs that have been identified as ground-level ozone precursors, toxic chlorinated hydrocarbons and compounds found on the *Canadian Environmental Protection Act's* (CEPA's) Priority Substance List.

In the analysis of this study, carbon monoxide (CO) concentration from two urban sites, Edmonton Central and Fort Saskatchewan were used. Both sites are located in the downtowns of the two cities. CO is monitored continuously by gas filter correlation. Gas filter correlation uses infrared radiation and is operated by eliminating water vapour, CO_2 and other interferences.

3 Data analysis

3.1 Lower detection limits

Inaccuracies found at the lower concentrations due to detection limitations were dealt with by the method described in Hafner et al. (2004). Concentrations measured to be zero, and thus less than the lower detection limits, were replaced with a value equal to the detection limit divided by two. Values less than the lower detection limit but greater than zero were not altered. Of the 150 VOCs sampled, 25% of the compounds were measured above their lower detection limits in all samples and 5% of the compounds were never measured above their lower detection limits. Compounds that were above their detection limits for all samples included CFCs, BTEX (benzene, toluene, ethylbenzene and xylenes), 1,2-dichloroethane and most of the C_3–C_5 aliphatics. Tables 1 and 2 show the lower detection

limits, number of samples less than the lower detection limits and summary statistics for 30 of the VOCs measured at sites 1 and 2.

3.2 Principal component analysis

In order for PCA to be effective, there must be a large ratio of data points to number of variables; an excess of 25 to 50 samples is suggested for stable results (Guo et al. 2004b). With a suite of 150 VOCs per sample, and at least 91 samples per site, a subset of VOCs was selected for analysis. In the absence of a standard method to select compounds, the following criteria were used to select 30 compounds for analysis:

1. Compounds with more than 50% of samples registering below method detection limits were excluded from analysis. This criterion eliminated 46 substances. Substances eliminated included chlorinated alkanes (C_2+), chlorinated benzenes, butylbenzenes, and unsaturated straight-chained and branched C_6 and C_7.

Table 1 Site 1 VOC summary statistics

Compound	Arithmetic mean[a] ($\mu g/m^3$)	Standard deviation ($\mu g/m^3$)	Maximum[a] ($\mu g/m^3$)	Lower detection limits ($\mu g/m^3$)	# of samples below LDL
1,2,4-Trimethylbenzene	0.46	0.78	4.91	0.006	4
1,2-Dichloroethane	0.70	3.05	21.51	0.005	0
2-Methylbutane	3.15	3.86	20.49	0.009	0
2-Methylpentane	0.82	0.94	4.39	0.011	0
3-Methylhexane	3.13	25.68	245.32	0.005	2
3-Methylpentane	0.59	0.64	2.93	0.011	0
Benzene	0.73	0.74	4.12	0.008	0
n-Butane	6.71	9.49	67.34	0.06	0
Carbon tetrachloride	0.56	0.06	0.69	0.007	0
CFC-11	1.56	0.14	1.94	0.005	0
CFC-113	0.59	0.07	0.75	0.009	0
CFC-12	2.61	0.26	3.16	0.007	0
Chloromethane	1.06	0.14	1.39	0.006	0
Cyclohexane	0.19	0.21	1.18	0.007	1
Ethylbenzene	0.33	0.42	2.13	0.004	0
HCFC-22	3.00	3.41	17.46	0.008	0
n-Heptane	2.79	22.68	216.63	0.026	0
n-Hexane	0.94	1.46	12.35	0.019	0
Isobutane	3.14	4.08	24.24	0.005	0
Isoprene	0.17	0.30	1.41	0.01	10
m,p-Xylene	1.40	1.83	7.86	0.008	0
Methylcyclopentane	0.44	0.50	2.75	0.004	0
o-Xylene	0.50	0.68	3.30	0.003	0
n-Pentane	1.69	1.75	7.91	0.012	1
Propane	8.04	10.47	74.68	0.009	0
Propene	0.59	0.74	4.03	0.011	0
Styrene	0.08	0.14	0.91	0.001	2
Toluene	3.55	5.00	26.90	0.007	0
Vinyl chloride	0.09	0.32	2.14	0.004	4
α-Pinene	0.06	0.11	0.69	0.005	30

[a] 95% confidence levels: ±40% for concentrations ≤0.02 $\mu g/m^3$; ±30% for concentrations between 0.02–0.2 $\mu g/m^3$; ±15% for concentrations ≥0.2 $\mu g/m^3$

Table 2 Site 2 VOC summary statistics

Compound	Arithmetic mean[a] ($\mu g/m^3$)	Standard deviation ($\mu g/m^3$)	Maximum[a] ($\mu g/m^3$)	Lower detection limits ($\mu g/m^3$)	# of samples below LDL
1,2,4-Trimethylbenzene	0.09	0.14	1.03	0.006	1
1,2-Dichloroethane	0.44	1.22	10.19	0.005	0
2-Methylbutane	2.68	2.75	13.51	0.009	0
2-Methylpentane	0.70	0.72	3.97	0.011	0
3-Methylpentane	0.48	0.49	2.43	0.011	0
Benzene	1.03	1.89	16.41	0.008	0
n-Butane	4.74	5.09	28.13	0.06	0
Carbon tetrachloride	0.58	0.06	0.71	0.007	0
CFC-11	1.56	0.14	1.96	0.005	0
CFC-113	0.60	0.08	0.83	0.009	0
CFC-12	2.60	0.26	3.27	0.007	0
Chloromethane	1.09	0.13	1.46	0.006	0
Cyclohexane	0.17	0.18	0.85	0.007	0
Ethylbenzene	0.36	0.79	6.49	0.004	0
HCFC-22	0.55	0.06	0.74	0.008	0
n-Heptane	0.47	1.82	16.48	0.026	5
n-Hexane	0.73	0.77	3.96	0.019	1
Isobutane	2.66	2.74	13.92	0.005	0
Isoprene	0.15	0.39	2.79	0.01	34
m,p-Xylene	0.47	0.76	5.46	0.008	0
Methylcyclohexane	0.25	0.34	2.81	0.003	0
Methylcyclopentane	0.35	0.38	2.83	0.004	0
o-Xylene	0.16	0.25	1.80	0.003	0
n-Pentane	1.66	1.51	7.88	0.012	0
Propane	7.61	7.27	34.96	0.009	0
Propene	0.39	0.40	2.28	0.011	0
Styrene	0.37	1.51	14.06	0.001	0
Toluene	1.11	2.71	24.75	0.007	0
Vinyl chloride	0.27	0.53	2.61	0.004	2
α-Pinene	0.04	0.06	0.32	0.005	40

[a] 95% confidence levels: ±40% for concentrations ≤0.02 $\mu g/m^3$; ±30% for concentrations between 0.02–0.2 $\mu g/m^3$; ±15% for concentrations ≥0.2 $\mu g/m^3$

2. Compounds reported to the 2004 reporting year of the National Pollutant Release Inventory (NPRI) in amounts greater than 2 tonnes were included in analysis. These compounds are listed in Table 3.
3. The predominantly biogenic compounds isoprene and α-pinene were included for analysis.
4. The remaining compounds were selected based on decreasing average ambient concentrations at each site.

PCA was carried out for each site using the software package XLSTAT. The multivariate analysis technique involves first normalizing the data such that each variable i has an average of zero and a standard deviation of one. This is accomplished by finding the z-score of each data point k using the formula $z_{ik} = \left(C_{ik} - C_{ik,avg} \right) / s_i$ (Guo et al. 2004b). In the context of the VOC data, C_{ik} refers to each individual concentration measured for compound i. $C_{ik,avg}$ and s_i are the arithmetic mean and the standard deviation of the ith compound.

Table 3 VOCs reported to the NPRI by Fort Saskatchewan facilities in total amounts greater than 2 tonnes for the 2004 reporting year (NPRI 2006)

VOCs reported in 2004
1,2,4-Trimethylbenzene
Ethylbenzene
Propene
1,2-Dichloroethane
n-Hexane
Styrene
Benzene
m,*p*-Xylene
Toluene
Cyclohexane
o-Xylene
Vinyl chloride

The correlation matrix of the normalized variables produces the resulting eigenvectors (identifying the factors) and the corresponding eigenvalues (identifying the fraction of total variance in the dataset described by the factor). The standard varimax rotation is applied to the correlation matrix to orthogonally rotate the axes (Hair et al. 1998).

Only a limited number of factors are significant enough to offer any explanation of the dataset. A common method to determine which factors are significant for analysis is to extract components with an eigenvalue greater than one (Thurston and Spengler 1985; Guo et al. 2004b). This ensures that each factor accounts for more variance within the dataset than does a single variable (Hair et al. 1998).

Outlier samples, where there are anomalous concentrations of certain subsets of VOCs, can interfere with PCA by showing up as extraneous factors that account for a large degree of variance within the dataset. As described by Guo et al. (2004b), these outliers are removed one at a time until successive removal of datum has little effect on the factors.

3.3 Principal component analysis—factor interpretation

There are challenges to analyzing 24-h integrated VOC samples with PCA analysis. As an aid to the PCA interpretation, additional tests were conducted to further understand the factors. Three corroborating tests were devised to help distinguish contributing sources. To test if a specific industrial facility with known emissions was a source, appropriate wind direction was included in the PCA and the factor re-analyzed. The wind data were expressed as the fraction of the 24 h period the hourly wind direction was either north, northeast, east, southeast, south, southwest, west or northwest. To test if VOCs varied with emissions from two nearby urban sites (Edmonton Central and Fort Saskatchewan), carbon monoxide concentrations, averaged over 24 h, were included in the PCA, and the factor was re-analyzed. Carbon monoxide (CO) was chosen for the corroborating test since it is known to be emitted from incomplete combustion of fossil fuels in urban areas (Guo et al. 2007). The downtown of Edmonton is strongly influenced by vehicle emissions (Cheng et al. 1997) and the monitoring site in Fort Saskatchewan is expected to have the same influence given its proximity to traffic sources. A third test to rule out the possibility that a factor was representative of a seasonal effect was to split the VOC samples into cold (November–April) and warm season (May–October) sub-sets based on when the sample

was taken. Splitting the VOC samples in this manner and running two PCA runs reduces the ratio of samples to variables and does not necessarily provide stable results. However, the results of the test can be used to understand the original PCA factors.

4 Results

The 30 compounds selected for analysis for sites 1 and 2 are listed in Tables 1 and 2, respectively. The summary statistics are shown for the raw data prior to the removal of outliers. Over the study period, the 30 compounds make up approximately 85% of the total measured VOC mass at site 1 and about 89% of the total VOC mass at site 2. Tables 4 and 5 show the PCA summary results. Five factors account for 82% of the variance at site 1 and five factors account for 81% of the variance at site 2. Tables 6 and 7 present the factor loadings for the 30 VOCs analyzed at each site. Factor loadings greater than 0.5 are bolded.

5 Discussion

5.1 Site 1—PCA results

Factor 1 (F1) loads with benzene, propane, propene, n-butane, n-pentane, alkyl substituted alkanes, n-hexane, n-heptane, ethylbenzene and xylenes. F1 accounts for 43% of the variability at site 1. With so many VOCs loading on this first factor, further tests are required to narrow down the contributing source. The additional PCA results from the three tests: wind direction, CO from Edmonton and Fort Saskatchewan, and seasonal data split are shown in Table 8.

Inclusion of wind direction in the PCA yields weak loadings of southwest winds on F1. Industry and the urban centers of Fort Saskatchewan and Edmonton lie to the southwest of both sites. The closest industry is to the northeast of site 1. No specific compounds load differently on the factor with different wind tests and no specific industry emissions can be identified on this factor. The weak loading of wind directions on F1 may be indicative of a ubiquitous source.

The inclusion of CO concentrations from the Edmonton and Fort Saskatchewan downtown monitoring sites with the VOCs from site 1 results in loadings of CO on F1, with Fort Saskatchewan CO loading higher than the Edmonton CO (0.522 and 0.475 respectively). It is understood that vehicle exhaust is composed both of incomplete combustion products and unburned gasoline (McLaren et al. 1996) and that carbon monoxide (CO) is generally emitted from incomplete combustion (Guo et al. 2007). Therefore, the loading of the CO concentrations on F1 provides reason to believe there is some influence of vehicle related emissions on this factor. In particular, the aromatic VOCs of benzene, toluene, m,p-xylene, o-xylene and ethylbenzenes are known for emphasizing a contribution from vehicle exhaust

Table 4 Results summary for site 1 PCA with varimax rotation

	F1	F2	F3	F4	F5
Initial eigenvalue	14.06	4.13	3.40	1.61	1.28
% of variance	43.01	16.74	11.81	5.46	4.53
Cumulative %	43.01	59.75	71.56	77.02	81.54

Table 5 Results summary for site 2 PCA with varimax rotation

	F1	F2	F3	F4	F5
Initial eigenvalue	14.35	4.60	2.18	1.97	1.19
% of variance	38.73	14.72	6.41	7.13	13.99
Cumulative %	38.73	53.44	59.85	66.98	80.97

(Liu et al. 2008) and gasoline evaporation, also of vehicle origin, is associated with butanes and pentanes (Guo et al. 2007). The VOCs loading on F1 are associated with vehicle related emissions, although it should be noted that toluene does not load on this factor. Furthermore, the VOC loadings on F1 are identified as light-duty vehicle emissions based on a 1995 tunnel study in Vancouver, British Columbia (Rogak et al. 1998). Table 9 compares the VOCs that load on F1 to the mass percentage of VOCs identified in the Vancouver tunnel study. Since the Fort Saskatchewan study measures VOCs from a variety of sources under ambient conditions, the relative proportions of these VOCs do not align with those of the Vancouver

Table 6 Site 1 factor loadings from PCA with varimax rotation

Compound	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
1,2,4-Trimethylbenzene	0.209	**0.906**	−0.009	0.051	−0.078
1,2-Dichloroethane	0.146	0.022	0.020	**0.856**	−0.111
2-Methylbutane	**0.889**	0.251	−0.016	−0.048	−0.162
2-Methylpentane	**0.959**	0.220	−0.026	0.029	−0.005
3-Methylhexane	**0.853**	0.052	−0.111	0.059	0.134
3-Methylpentane	**0.936**	0.201	0.066	0.061	0.042
Benzene	**0.931**	0.145	0.031	−0.087	−0.111
n-Butane	**0.915**	0.186	0.065	−0.028	−0.220
Carbon tetrachloride	−0.017	0.154	**0.757**	0.343	−0.152
CFC-11	0.024	0.137	**0.912**	−0.015	−0.071
CFC-113	0.095	−0.164	**0.865**	−0.059	−0.019
CFC-12	−0.013	0.001	**0.932**	0.036	0.152
Chloromethane	−0.211	−0.011	**0.595**	−0.155	0.104
Cyclohexane	**0.797**	−0.136	−0.187	0.027	0.400
Ethylbenzene	**0.758**	**0.619**	−0.020	−0.019	−0.114
HCFC-22	−0.245	**0.655**	0.221	0.008	**0.516**
n-Heptane	**0.825**	−0.036	−0.112	−0.058	0.339
n-Hexane	**0.807**	−0.009	0.120	0.176	0.237
Isobutane	**0.891**	0.138	−0.020	−0.010	−0.226
Isoprene	−0.021	**0.648**	0.007	0.028	**0.538**
m,p-Xylene	**0.555**	**0.802**	0.028	−0.013	−0.118
Methylcyclopentane	**0.912**	0.136	−0.067	0.092	0.277
o-Xylene	**0.544**	**0.813**	0.014	0.009	−0.097
n-Pentane	**0.925**	0.154	0.019	0.138	−0.051
Propane	**0.861**	−0.101	0.052	0.165	−0.071
Propene	**0.872**	0.242	0.073	0.039	−0.178
Styrene	**0.611**	0.467	−0.067	−0.108	−0.018
Toluene	−0.001	**0.903**	0.029	0.076	0.182
Vinyl chloride	0.061	0.087	0.081	**0.765**	0.203
α-Pinene	0.452	0.440	−0.095	−0.203	0.079

Values greater than 0.5 are bolded

Table 7 Site 2 factor loadings from PCA with varimax rotation

Compound	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
1,2,4-Trimethylbenzene	**0.614**	0.025	0.054	0.105	**0.722**
1,2-Dichloroethane	0.289	0.146	0.213	−0.032	**0.651**
2-Methylbutane	**0.924**	−0.093	0.167	0.019	0.065
2-Methylpentane	**0.955**	−0.078	0.104	0.051	0.106
3-Methylpentane	**0.938**	−0.070	0.137	0.043	0.120
Benzene	0.316	0.036	−0.146	**0.814**	0.279
n-Butane	**0.869**	−0.031	−0.103	0.021	0.395
Carbon tetrachloride	−0.241	**0.816**	0.036	−0.035	−0.032
CFC-11	−0.146	**0.887**	−0.020	−0.063	−0.130
CFC-113	0.060	**0.905**	−0.063	0.080	0.011
CFC-12	−0.083	**0.949**	−0.029	0.056	−0.022
Chloromethane	−0.260	**0.608**	0.100	0.180	0.116
Cyclohexane	**0.751**	−0.018	−0.260	0.019	0.245
Ethylbenzene	0.206	0.164	0.018	**0.710**	0.018
HCFC-22	0.131	**0.854**	0.130	0.083	0.276
n-Heptane	**0.808**	−0.030	−0.132	0.066	**0.512**
n-Hexane	**0.940**	−0.049	0.021	0.056	0.191
Isobutane	**0.895**	−0.027	−0.111	0.042	0.313
Isoprene	−0.050	−0.009	**0.875**	−0.077	0.062
m,p-Xylene	**0.634**	−0.027	0.047	0.107	**0.714**
Methylcyclohexane	**0.737**	−0.083	−0.226	0.040	0.355
Methylcyclopentane	**0.951**	−0.072	0.008	0.034	0.174
o-Xylene	**0.633**	−0.007	0.058	0.103	**0.727**
n-Pentane	**0.956**	−0.013	−0.049	−0.011	0.194
Propane	**0.701**	0.057	−0.293	−0.061	0.334
Propene	0.485	0.192	−0.017	−0.005	**0.565**
Styrene	−0.190	0.037	−0.039	**0.893**	−0.022
Toluene	**0.646**	−0.069	0.105	0.063	**0.615**
Vinyl chloride	0.026	0.051	**0.798**	−0.097	0.162
α-Pinene	0.437	0.090	0.307	0.215	**0.593**

Values greater than 0.5 are bolded

study which measured isolated tunnel traffic. As shown in Table 3, many of the VOCs that load on F1 are also emitted by industry and therefore it is not expected that the same VOC ratios hold in the Fort Saskatchewan study. Another possible reason for different relative proportions is natural gas leakage and its influence on the lighter hydrocarbons propane, butane and isobutane (Na et al. 2004). Natural gas is a common fuel used in the region for industrial processes and residential heating. The concentrations of these lighter hydrocarbons in this study are higher with respect to toluene concentrations than predicted by the Vancouver vehicle emissions study (Rogak et al. 1998), indicating that gas leakage may also be affecting concentrations of these light hydrocarbons.

Splitting the VOC samples based on a cold and warm season and re-running the PCA results in a similar first factor for both seasons with some differences to 1,2,4-trimethylbenzene, toluene and m-, p-, and o-xylenes. It is important to note that the seasonally divided PCA results are not expected to be stable given the limited number of samples. The seasonal test provides inconclusive results since 1,2,4-trimethylbenzene, toluene and xylenes are all emitted by industry in the region (Table 3), as well as by vehicle related emissions (Table 9).

Table 8 Comparison of additional PCA tests conducted with wind direction, carbon monoxide concentrations and seasonal splitting for F1 at site 1

F1—site 1	F1—including SW wind	F1—including CO conc.	F1—cold season	F1—warm Season
1,2,4-Trimethylbenzene	0.218	0.177	**0.921**	−0.051
1,2-Dichloroethane	0.169	0.143	0.097	0.045
2-Methylbutane	**0.892**	**0.859**	**0.921**	**0.976**
2-Methylpentane	**0.961**	**0.946**	**0.879**	**0.990**
3-Methylhexane	**0.849**	**0.860**	**0.577**	**0.916**
3-Methylpentane	**0.938**	**0.929**	**0.842**	**0.967**
Benzene	**0.930**	**0.907**	**0.867**	**0.941**
n-Butane	**0.917**	**0.880**	**0.936**	**0.967**
Carbon tetrachloride	−0.008	−0.042	0.136	−0.179
CFC-11	0.023	0.005	0.146	0.076
CFC-113	0.093	0.092	−0.058	0.127
CFC-12	−0.016	0.002	−0.098	0.098
Chloromethane	−0.216	−0.194	−0.155	−0.355
Cyclohexane	**0.791**	**0.840**	0.320	**0.949**
Ethylbenzene	**0.764**	**0.723**	**0.948**	**0.710**
HCFC-22	−0.248	−0.201	−0.029	−0.292
n-Heptane	**0.818**	**0.858**	0.425	**0.898**
n-Hexane	**0.808**	**0.831**	0.528	**0.804**
Isobutane	**0.892**	**0.860**	**0.902**	**0.958**
Isoprene	−0.021	0.020	**0.716**	0.197
m,p-Xylene	**0.563**	**0.517**	**0.959**	0.361
Methylcyclopentane	**0.913**	**0.933**	**0.637**	**0.940**
o-Xylene	**0.551**	**0.508**	**0.947**	0.329
n-Pentane	**0.929**	**0.911**	**0.844**	**0.943**
Propane	**0.859**	**0.854**	**0.675**	**0.887**
Propene	**0.874**	**0.839**	**0.870**	**0.895**
Styrene	**0.615**	**0.581**	**0.801**	**0.689**
Toluene	0.008	−0.001	**0.837**	−0.173
Vinyl chloride	0.079	0.087	−0.044	0.200
α-Pinene	0.448	0.433	**0.560**	**0.594**
Edmonton CO		0.475		
Fort Saskatchewan CO		**0.522**		
SW WDR	0.422			

Values greater than 0.5 are bolded

Despite some agreement between F1 and vehicle related emissions, it is not possible to unambiguously determine whether F1 is vehicle dominated or industry dominated. The three tests used provide reason to believe that F1 is influenced by a mixture of industry and vehicle related emissions.

Factor 2 (F2) is specific to Site 1 and accounts for 17% of the variance. 1,2,4-Trimethylbenzene, ethylbenzene, HCFC-22, m-, p-, and o-xylene, isoprene and toluene load on this factor. Styrene loads more weakly on this factor with a value of 0.467. With the exception of isoprene, these compounds are reported emissions from one particular industrial site northeast of site 1 (NPRI 2006). However, low loading of northeast wind on F2 does not provide evidence in support of the theory that the NPRI reporting facility is the primary emission source. As well, studies have shown contributions of isoprene from vehicular exhaust (Guo et al. 2007). A time series plot (Fig. 3) of these F2 VOCs shows

Table 9 Comparison of VOCs with high F1 loadings with reported emission percentages from the Vancouver tunnel and traffic study (Rogak et al. 1998)

Compound	Site 1	Traffic VOC mass percent measured by Rogak et al. (1998)
Toluene		8.2
Propane	·	7.5
2-Methylbutane	·	7.0
Propene	·	5.1
m,p-Xylene	·	4.5
Benzene	·	4.5
n-Butane	·	4.4
n-Pentane	·	2.9
2-Methylpentane	·	2.6
3-Methylpentane	·	1.7
1,2,4-Trimethylbenzene		1.6
n-Hexane	·	1.5
Ethylbenzene	·	1.4
o-Xylene	·	1.7
Methylcyclopentane	·	1.0
3-Methylhexane	·	0.9
n-Heptane	·	0.6
Styrene	·	0.3
Methylcyclohexane	–	0.3
Cyclohexane	·	0.2
Isobutane	·	−0.1

· Denotes a compound that loads on factor F1

–Denotes a compound that did not meet selection criteria for PCA

that the concentrations peaked in spring and summer of 2005, then slowly declined. Figure 3 shows only some of the F2 VOCs in order to make the figure readable. Isoprene shows the seasonality typical to a VOC that depends on the growing season for vegetation (Hakola et al. 2003). Figure 3 also shows isoprene concentrations varying slightly throughout the winter months. The PCA test with a seasonal split removes isoprene from this factor in the warm season. The cold season PCA test causes F2 to change entirely by the VOCs loading on the first factor. Isoprene may be loading on this factor due to the coincidence of the other VOCs showing high concentrations over the spring and summer. The most plausible explanation is an unknown leak or equipment malfunction from one of the nearby industries; however verifying this hypothesis is not possible with the given data.

Factor 3 (F3) for site 1 includes loadings of CFC-11 (trichlorofluoromethane), CFC-12 (dichlorodifluoromethane), CFC-113 (1,1,2-trichloro-1,2,2-trifluoroethane), chloromethane and carbon tetrachloride. These substances are relatively inert and as such take a long time to break down in the atmosphere. The atmospheric lifetimes of these substances are approximately 50, 185, 30, 1.0, and 40 years, respectively (Prinn et al. 2000; Tokarczyk et al. 2003). The long residence time in the atmosphere gives these substances the potential to travel great distances. Table 10 shows the average concentrations of CFC-11, CFC-12 and CFC-113 measured at sites 1 and 2 along with the halocarbons measured at a site in central Canada. The Boreal Ecosystem Research and Monitoring Site-Tall Tower (BERMS-TT) is chosen since it is at similar latitude to sites 1 and 2. BERMS-TT is part of the National Oceanographic and Atmospheric Association's Cooperative Air Sampling Network and the samples were analyzed by the ETC laboratory. BERMS-TT is recognized as a background
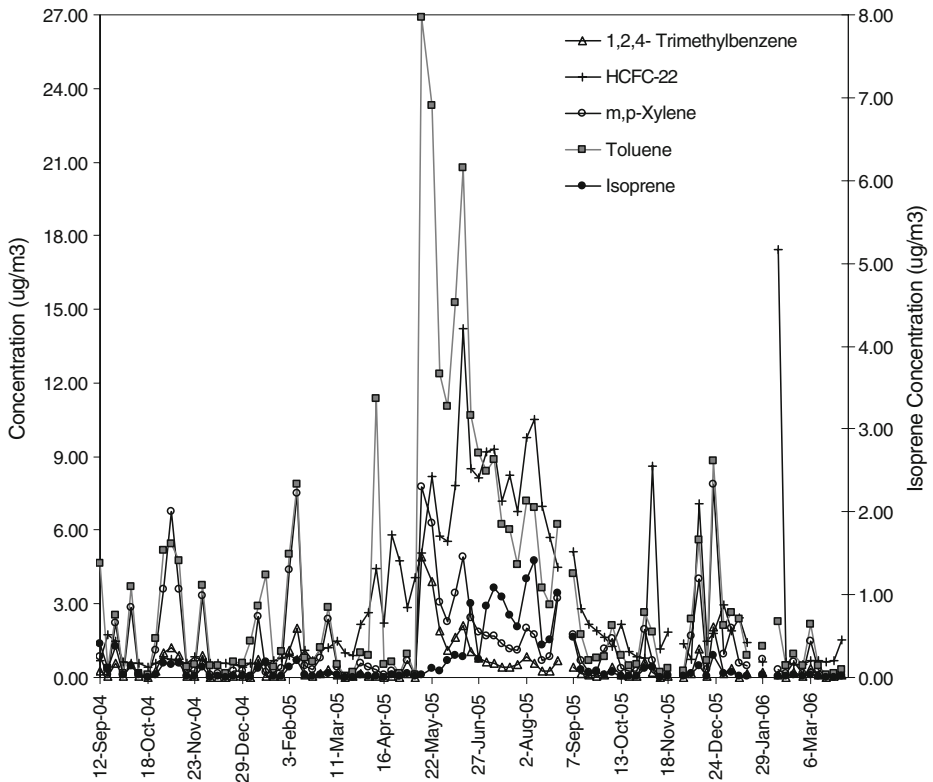
Fig. 3 Twenty-four-hour concentrations of VOCs loading on Factor F2 from Site 1. Isoprene concentrations are shown on the secondary y-axis

station. As shown in Table 10, the concentrations for the CFCs at site 1 and site 2 fall well within one standard deviation of the background site. There are no major differences between the concentrations at the BERMS-TT and the Fort Saskatchewan sites. These compounds are likely influenced by long range transport. Therefore, F3 for site 1 shows 12% of the variance in the Fort Saskatchewan VOCs and can be attributed to long range transport of the stable halogenated compounds.

Two chlorinated VOCs, 1,2-dichloroethane and vinyl chloride, were produced in the region during the period of study. Although 1,2-dichloroethane was produced primarily as an intermediate in vinyl chloride production (Government of Canada 1994), the two chemicals were released by two separate facilities in the region (NPRI 2006). At site 1,

Table 10 Average CFC concentrations and standard deviations (shown in brackets) for sites 1, 2 and BERMS-TT

Location	Lat. and long. coordinates	CFC-11 ($\mu g/m^3$)	CFC-113 ($\mu g/m^3$)	CFC-12 ($\mu g/m^3$)
Site 1	53.716, −113.20	1.56 (0.14)	0.59 (0.07)	2.61 (0.26)
Site 2	53.79, −113.078	1.56 (0.14)	0.60 (0.08)	2.60 (0.26)
BERMS-TT, Saskatchewan[a]	53.98, −105.117	1.54 (0.10)	0.6 (0.05)	2.64 (0.17)

[a] Data collected from April 2007–April 2008. Data obtained from Environment Canada

factor 4 (F4) consists of high loadings from both 1,2-dichloroethane and vinyl chloride and this factor accounts for 5% of the variance in VOCs. The facility producing 1,2-dichloroethane and the facility producing vinyl chloride both lie to the northeast of site 1 and inclusion of northeast wind extracts the factor with strong loadings of 1,2-dichloroethane, and vinyl chloride.

Isoprene and HCFC-22 load on F5 for site 1, which accounts for another 5% of the variance. The ambient concentrations for both VOCs show a strong seasonal pattern, with monthly average concentrations increasing during the summer months. This pattern is as expected for the biogenic VOC, isoprene. HCFC-22, on the other hand, has a long lifetime and is a potential candidate to load on F3. It is used as a refrigerant for air conditioners (McCulloch et al. 2006) and usage patterns may account for its seasonality. HCFC-22 is an NPRI reported emission in the region, where it is used as an industrial refrigerant. However, wind direction loads weakly on F5 and the test with the seasonal split results in α-pinene loading on this factor. This factor appears to be a product of seasonal effects and not a result of a specific source-to-receptor relationship.

5.2 Site 2—PCA results

Factor 1 (F1) for site 2 has loadings of 1,2,4-trimethylbenzene, propane, *n*-butane, *n*-pentane, alkyl substituted alkanes, *n*-hexane, *n*-heptane, xylenes and toluene. The factor accounts for 39% of the variability. Unlike site 1's F1, site 2 does not have strong loadings of benzene, ethylbenzene or propene. Also, unlike site 1, toluene loads on this site's F1. Three tests were conducted to further understand F1 and the results of these tests are shown in Table 11. Inclusion of southwest winds load weakly on F1 (0.3). Inclusion of CO concentrations from the Edmonton and Fort Saskatchewan downtown sites also load weakly on F1 (0.3 and 0.4, respectively). Splitting the VOC samples into a cold and warm season, and then re-running PCA for site 2 shows one significant change. In the cold season, 1,2-dichloroethane loads onto F1 with a factor loading of 0.62. In a similar vein to the discussion on Site 1, it is challenging to confidently determine whether F1 is dominated by vehicle emissions or by industry. In comparing the analysis on site 1 and site 2, it would appear F1 for site 2 has greater contribution from industrial emissions.

Factor 2 (F2) for site 2 contributes to 15% of the variance and has high loadings of CFC-11, CFC-12, CFC-113, chloromethane, carbon tetrachloride and HCFC-22. This factor is similar to site 1's F3 and is identified as contribution from long range transport. It is noted that the difference between the two sites for this factor is that site 2 has a loading from HCFC-22, whereas site 1 did not. Unlike the other halocarbons that load onto this factor, the difference in loading between sites 1 and 2 for HCFC-22 suggests that source influences on HCFC-22 may be local rather than due to long range transport.

Factor 3 (F3) at site 2 has significant loadings of vinyl chloride and isoprene. On further investigation, it is found that both of these compounds exhibited maximum concentrations during the summer of 2005. As stated above, isoprene is predominantly a biogenic substance and emissions are directly linked to the growing season (Hakola et al. 2003). In contrast with isoprene, the observed summer peak in vinyl chloride concentrations is most likely associated with fugitive emissions from industry. Incorporation of wind data into PCA more accurately depicts the different sources. With south wind included, vinyl chloride loads on a factor with wind direction, as the vinyl chloride facility lies south of site 2. With northeast winds included, isoprene loads on a separate factor as expected since the area to the northeast of site 2 is less industrialized and is more heavily treed.

Table 11 Comparison of additional PCA tests conducted with wind direction, carbon monoxide concentrations and seasonal splitting for F1 at site 2

F1—site 2	F1—including SW wind	F1—including CO conc.	F1—cold season	F1—warm season
1,2,4-Trimethylbenzene	**0.672**	**0.740**	**0.862**	**0.591**
1,2-Dichloroethane	0.302	0.396	**0.628**	0.234
2-Methylbutane	**0.892**	**0.936**	**0.883**	**0.910**
2-Methylpentane	**0.937**	**0.970**	**0.914**	**0.971**
3-Methylpentane	**0.915**	**0.964**	**0.928**	**0.973**
Benzene	0.340	0.352	0.364	0.371
n-Butane	**0.892**	**0.901**	**0.943**	**0.860**
Carbon tetrachloride	−0.259	−0.254	−0.283	−0.119
CFC-11	−0.164	−0.165	−0.357	0.060
CFC-113	0.061	0.043	−0.045	0.210
CFC−12	−0.084	−0.082	−0.161	0.088
Chloromethane	−0.235	−0.205	−0.198	−0.233
Cyclohexane	**0.819**	**0.719**	**0.650**	**0.744**
Ethylbenzene	0.206	0.196	0.006	0.434
HCFC-22	0.156	0.183	0.237	0.195
n-Heptane	**0.872**	**0.856**	**0.882**	**0.829**
n-Hexane	**0.934**	**0.960**	**0.957**	**0.946**
Isobutane	**0.913**	**0.910**	**0.938**	**0.905**
Isoprene	−0.066	−0.054	**0.702**	0.024
m,p-Xylene	**0.696**	**0.746**	**0.813**	**0.620**
Methylcyclohexane	**0.818**	**0.729**	**0.664**	**0.709**
Methylcyclopentane	**0.966**	**0.945**	**0.864**	**0.941**
o-Xylene	**0.691**	**0.752**	**0.861**	**0.583**
n-Pentane	**0.966**	**0.960**	**0.920**	**0.953**
Propane	**0.744**	**0.682**	**0.745**	**0.619**
Propene	**0.518**	**0.629**	**0.788**	0.474
Styrene	−0.182	−0.191	−0.214	−0.185
Toluene	**0.700**	**0.745**	**0.705**	**0.759**
Vinyl chloride	0.040	0.023	0.164	0.049
α-Pinene	0.465	**0.535**	**0.759**	0.398
Edmonton CO		0.326		
Fort Saskatchewan CO		0.452		
SW WDR	0.301			

Values greater than 0.5 are bolded

Factor 4 (F4) of site 2 has loadings of benzene, ethylbenzene, and styrene, and accounts for 7% of the variance. These three compounds are released from the chemical plant producing styrene that is located north of the monitoring station (NPRI 2006). North wind loads on this factor when wind direction is incorporated into PCA, providing good indication that F4 is an industry factor.

For site 2, 1,2-dichloroethane loads on F5 along with 1,2,4-trimethylbenzene, *m*- and *p*-xylene, *o*-xylene, propene, heptane, toluene and *α*-pinene. Southwest winds and load on this factor when included in PCA. When CO concentrations are included, the factor changes significantly with only CO loading and an absence of VOCs loading. 1,2,4-Trimethylbenzene, 1,2-dichloroethane, *m*-, *p*-, and *o*-xylene and toluene are among emissions reported to the NPRI by facilities lying west and southwest of site 2 (NPRI

2006). This factor appears to represent a strong influence from industry and accounts for 14% of the variance at site 2.

Based on the interpretations at sites 1 and 2 for the five factors, it is noticed that 1,2,4-trimethylbenzene and toluene pattern together. This is the case for site 1 for F2 (Table 6), site 2 for F1 (Table 7), site 2 for F5 (Table 7) and the seasonal test for F1 at site 1 (Table 8). The pattern may indicate that the variance in ambient concentrations for these two substances is dominated by industrial emissions.

6 Conclusion

This study characterized the VOCs in an industrialized region in western Canada by conducting principal component analysis (PCA) on ambient concentrations and examining these results in conjunction with emission inventories and wind direction frequency. Two air monitoring sites in the Fort Saskatchewan region were used to collect the VOC data, and PCA with varimax rotation was performed on 30 VOCs at each site. The analysis found five factors accounted for 82% of the variance at site 1 and five factors accounted for 81% of the variance at site 2. For both sites, the factor accounting for the highest variability was the most difficult to interpret. PCA tests with wind direction, carbon monoxide concentrations from two other monitoring stations in downtown cores and a seasonal split to the VOC samples were conducted as an aid to the interpretation. For site 1, 43% of the variability showed influence from vehicles and industry. The PCA test with carbon monoxide suggested the factor was influenced more from vehicles than industry. For site 2, 39% of the variability was also attributed to a combination of vehicle and industry. The seasonal test suggested the factor was influenced more from industry than vehicles. Factors were attributed to specific industrial sources by either the presence of 1,2-dichloroethane or by corroboration with reported emissions and wind direction. For sites 1 and 2, two factors were identified as specific industry contribution with variability totaling 21 and 22%, respectively. The other sources identified by PCA were long range transport of stable halogenated compounds, accounting for 12–15% of the variability, and seasonal contribution including fugitive emission sources accounting for 5–6% of the variability. An apparent pattern found in the PCA analysis was that 1,2,4-trimethylbenzene and toluene consistently loaded together on industry identified factors, indicating the variance for these two substances is dominated by industrial sources as opposed to vehicle emissions. The interpretation of 24-h integrated VOC samples with PCA was possible due to the region's unique emissions, in particular 1,2-dichloroethane. Hourly VOC concentrations would be necessary to further understand the relationships between the vehicle and industry emissions in the region.

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