

FACTORIZATION METHODS APPLIED TO CHARACTERIZE THE SOURCES OF VOLATILE ORGANIC COMPOUNDS IN MONTREAL, QUEBEC

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Abstract

Objectives: The study objective was to assemble emission characteristics of the sources of the ambient volatile organic compounds (VOCs) and to elaborate methods of organizing them into the sources' chemical profiles. **Material and Methods:** The UNMIX – sensor modeling method from the U.S. Environment Protection Agency (EPA) – was used to process the VOC concentration data acquired over the years 2000–2009 for 175 VOC species in 4 air quality monitoring stations in Montreal, Quebec. **Results:** The method enabled to assess VOC emissions from the typically distributed sources existing in urban environment and VOC occurrences characterizing the local, or point-like, sources. The distributed sources were inextricably associated with hydrocarbons from exhaust, heavier hydrocarbons from contaminated urban soil, fugitive evaporations of gasoline and liquefied petroleum gases (LPG), leakage from the industrial and commercial use of solvents, and the inert, ozone depleting gases permeating urban atmosphere. The sources' profiles were charted involving 60–120 VOC species per source. Spatial distribution of the sources was examined. **Conclusions:** The UNMIX application and the source profiling methods, by building robust chemical profiles of VOC sources, provided information that can be used to assign the measured VOC emissions to physical sources. This, in turn, provides means of assessing the impact of environmental policies, on one hand, and of industrial activities on the other hand on VOC air pollution.

Key words:

Volatile organic compound, UNMIX, Receptor modeling, Source profile, Pulp industry, Principal components

INTRODUCTION

Man-made volatile organic compounds (VOCs) contribute significantly to the urban air pollution. Widely occurring VOCs, such as e.g., benzene, ethylbenzene, xylenes, 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene, carbontetrachloride, chloroform, are toxic and/or carcinogenic substances [1–3]. In large cities, harmful effects of increasing ambient concentrations of pollutants are even more dangerous to the public health

due to the extent of exposure in the densely populated areas [1,4–10]. Atmospheric photochemistry converts the more reactive VOCs by oxygenation and through reactions with oxides of nitrogen to secondary VOCs, free radicals, ozone, and subsequently to smog organic aerosols [6,11,12].

Correlating VOC emissions from anthropogenic sources with public health indices allows to assess the impact of VOC pollution on human health. The research

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provides guidelines for planning emission control strategies. Achieving reduction in VOC concentrations in the ambient air comparable to the reduction of the “classic” pollutants (from 1970 to 2008 particulate matter concentration in the ambient air has decreased by over 50% [13,14]) seems feasible.

Source apportionment of numerous VOC species have already been examined [15–24]. The research presents the methods of modeling the ambient VOC multi-receptors operating in the air quality monitoring stations. The chief methods applied are the Principal Component methods – mainly the Positive Matrix Factorization (PMF). Also Chemical Mass Balance (CMB) system provides methods of modeling the receptors [25,26]. The methods consist in constructing sources’ chemical fingerprints – employing a menu of VOCs – in a form of sources’ emission profiles, relying on the user-specified inventory of the sources contributing to the measured totals.

The intricacies of organic air pollution and complex atmospheric chemistry make it challenging to build a reliable receptor model [26–29]. The VOC menu typically lists the most prominent VOCs, with high signal/noise ratio (SNR), which allow a clear-cut profiling of the sources. Thereby, some point sources, particularly the specialized industrial plants and the associated waste streams, which yield quite distinct chemical fingerprints of low-concentration VOCs, may stay unresolved.

This research addresses the issue by developing robust source discrimination routines, which also search for the low-emission sources that stay out in the usual hydrocarbon background in the urban air. This is achieved by applying principal component (PC) methods implemented by the U.S. Environmental Protection Agency (EPA): EPA UNMIX [30], which has the advantage over the other PC methods of telling the user which modeling attempt cannot be successful, thus, narrowing the output to the reliable receptor models.

MATERIAL AND METHODS

VOC measurements and data

As part of the National Air Pollution Surveillance (NAPS) federal program in Canada [31], air quality monitoring stations were installed across the country, several of them in Montreal, Quebec. The sensors operate basing on gas chromatography/flame ionization detector system (GC/FID) for quantification of light hydrocarbons in the C2 fraction, while a combined gas chromatography/mass selective detector (GC/MSD) system operating in selected ion monitoring (SIM) mode is used for quantification of heavier hydrocarbons, in the C3 to C12 fractions. The data used for this report consists of daily averages of VOC species concentrations in the ambient air. Measurements of 175 species were taken each 6th day in 4 monitoring stations located in the Great Montreal area (Figure 1). The concentrations are expressed in micrograms per cubic meter.

Stations 2 (No. 50104) and 3 (No. 50115) are located in downtown areas, close to a large body of water, one of them, i.e., station 2, is adjacent to a large multi-industrial park. Station 1 (No. 50103) is located in the East Montreal



Montreal-East (station 1) – petrochemical industry district; light grey (stations 2, 3) – densely populated urban area; dark grey – green terrains, suburbs, and semi-rural districts in the inner ring (station 4); white – body of water surrounding inner-ring Downtown Montreal.

Fig. 1. Demarcation of districts and localization of the National Air Pollution Surveillance (NAPS) monitoring stations in Montreal, Quebec

zone, formerly a borough of Montreal, a concentration of the petrochemical and chemical industries in the Great Montreal area. Station 4 (No. 50129) is located on the peripheries of Montreal, in a more countryside-like region, but crossed by highways. In the neighborhood there is also a pharmaceutical industry.

This report concerns VOC measurements taken over the years 2000–2009, during the period when effects of implementation of several international and federal clean-air programs [14,32,33] were already clearly visible. The number of all the measured VOC species in each station was 175, but many measurements bore errors. In this research, only the species that have 95% or more correct daily averages in the study period were considered. Therefore, the number of VOCs adequately measured and processed varies between 103 and 130, depending on the monitor.

U.S. EPA VOC data processing routines

The United States EPA makes 2 data processing applications based on the Principal Component method, i.e., EPA PMF and EPA UNMIX available. The methods perform linear modeling of many variables (VOC measurements) with a few expressly constructed predictors or factors – which are alleged apportionments of the measured emissions among putative sources. The applications impose restrictions on the factors they generate in order to make the claim that the factors represent physical sources (and not only one of the large number of mathematically correct solutions to the modeling problem) realistic. This study exploits mainly UNMIX.

The UNMIX applies stronger than PMF's requirements on the correlations between VOCs to consider them as coming from the same source, which makes successful models more reliable. UNMIX deduces the number of sources from the geometrical properties of the VOC concentration data – this number is more reliable than the user's estimates that PMF requires to supply. UNMIX does

not apply the “positive matrix” constraint; the emission profiles allow for negative values. Persistent negative values may signal VOC depletion in the atmosphere.

Finally, UNMIX possesses an important feature, which enables to make robust informed guesses regarding VOC sources: it fails to give results when the particular profiling cannot be made reliable. The success of profiling depends, in an essential way, on the collection of VOC species fed into the routine. By combining all the results from the successful run – thus, combining only partial reliable profiles defined in different limited VOC ranges – more reliable exhaustive chemical descriptions of VOC sources can be produced.

The method of combining partial emission profiles into the sources' extended profiles

Modeling the 175-VOC multi-receptor with UNMIX required applying the routine several hundred times in order to produce sufficiently exhaustive library of the reliable (according to UNMIX), but only partial (approximately 30 VOCs could be fed at a time into the routine), emission profiles. Thus, 500 to 700 (depending on the monitor) profiles were created to ensure that each of the 100 to 130 correctly measured VOCs participated in a successful profiling. A successful model featured 5 to 8 sources, depending on the VOC menu under scrutiny. Incidentally, a consistency in the UNMIX results was observed: adding a new VOC species to the menu never made the number of supposed sources decrease.

Two partial profiles defined on different lists of VOC species may characterize the same source. If they do, they can be combined into one larger profile characterizing the source with VOCs from both lists. The criteria and the procedure of combining partial profiles (defined on short lists, circa 30 VOCs), into more exhaustive profiles (60–130 VOCs), are described below.

A profile describes a source of VOC emission in terms of the percentage of the measured total that is attributable

to this source. Question arises when 2 partial profiles are compatible, i.e., when they describe the same source. For the sake of this research, a heuristic measure of compatibility between the 2 profiles was elaborated.

Usually, the closeness of 2 numeric values a , b is defined in terms of the absolute value of their difference: $|a-b|$. However, for the percent values 0–100%, the distance between 0% and 40% (for example) would have more significance than the numerically same distance between 60% and 100%. Therefore, the distance between 2 percentage values was defined depending on their locations on the percent scale, and gauged using the following scale (in percent): -50, -20, -5, 8, 14, 21, 29, 40, 52, 70, 100, 140 (the values out of 0–100% appear in order to gauge the < 0 and > 100 UNMIX results). The distance between 2 values was set to the number of scale marks separating the values (a mark coinciding with a value was counted as 1/2), but only if that number was greater than 2, otherwise it was set to 0.

The distance between 2 profiles was defined as a normalized weighted sum of distances between the profiles' percentage values assumed on their common domain (on all shared VOCs). Average concentrations of VOC in the study period were taken for the weights. Normalization signified dividing the computed distance by the maximal possible distance, the latter being the number of marks on the scale (12 percentage values) times the sum of the VOC weights on the common domain. Two profiles were compatible (were considered as describing the same source) if, 1st, their distance was ≤ 0.05 and, 2nd, the overlap of their VOCs was large enough to cover at least 1/2 of the shorter profile. This usually signified at least 15 common VOCs, so incompatibility of 1 common VOC of an average concentration usually disqualified compatibility of the profiles.

Combining proceeded by taking a linear combination of the 2 profiles where they overlapped, and their own values where they did not. It is to be observed that combining

involves remembering, for each VOC, how many times it participated in the combining operations so far; if it appeared several times, its present value must be set to the average of all its appearances.

Combining was performed by a dedicated R program [34]. It has been verified that the collection of the final long profiles did not depend essentially on the way of selecting the "opening" partial profiles and the order of searching the profile libraries.

Two profiles generated by combining cycles were either strongly compatible ($> 95\%$, meaning distance < 0.05) or quite distant ($< 90\%$ compatible, distance 0.1). (The compatibility measure – the set-up for measuring the distance between 2 profiles – was tuned up to meet these criteria).

RESULTS AND DISCUSSION

UNMIX results, however in large part compatible with PMF results, offer a new picture. The profiles constructed by the combining procedure are of 2 kinds: long profiles with scarce, or none, negative values, reproducible with PMF to a satisfactory degree (compatibility of 90% or more), and short profiles featuring significantly more negative values. The number of the long profiles was limited to 6–8, while the short ones (and, basically, not-extendable profiles: the profiling with extended VOC menus fails) were as numerous as several dozen. It is argued in the discussion section that the appearance of "negative" sources in UNMIX profiles has a meaning different than "error."

Only the long profiles were tabulated and shown here. However, shorter profiles exhibiting "negative" emissions from unidentified sources are required to balance more than 100% values of contributions from the reported "positive" sources. A negative value may represent a deficit in the concentration of a species, which is more susceptible to photochemistry than its companions in a given partial profile; the species undergoes losses uncorrelated with emissions, thus, displaying a behavior suggesting

another source. Assuming that such a mechanism is at work, the percent values reported here would represent the initial, yet unaffected by the journey to the sensor, emissions.

The “traffic” source in Montreal, Quebec

The “traffic” profiles in Tables 1–4 are labeled T. In all the tables, CAS is the Chemical Abstracts Service registry number.

The center of the Montreal urban agglomeration shows abundant reactive species, which can be associated with exhaust, while in boroughs, where petrochemical industry is located, only more inert combustion products persist. The “traffic” source appears responsible for concentrations of a multitude of C4–C8 alkanes and alkenes, the most prominent being the unsaturated hydrocarbons used for gasoline blending and/or enhancing the octane content. The easiest way to recognize the “traffic” species is to observe their hourly pattern of ambient concentration [18,20–22,24]. When only daily averages are available, the following VOCs can be used as “traffic” source indicators:

- 2-methylpentane, a volatile but pervasive isomer of octane, a flag exhaust gas;
- 1-butene/isobutene, utilized for the production of gasoline blending components, also 2-methyl-2-butene, used in North American specialty blendings;
- hexane, constituting more than 1% in gasoline;
- pentane, its isomer 2,2-dimethylpropane in particular, constituting more than 1% in gasoline;
- cyclohexane, produced in exhaust from benzene reacting with hydrogen;
- heptane, and its isomers 2,4-dimethylpentane and 3-methylhexane, components of high-octane gasoline, up to 6%;
- 2,3,4-trimethylpentane, mainly used in aviation industry for production of specialty gasoline, wherein it constitutes circa 2%;

- ethylene, a C2 unsaturated hydrocarbon, which is an important natural plant hormone but also industrially recovered at a large scale from refinery gases, may have a loading in the “traffic” profiles – as a byproduct of gasoline combustion; however, its source appears to be the stationary combustion engines rather than the urban transit.

Heavier unsaturated hydrocarbons in paraffin series, nonane, decane, undecane, and dodecane, may occur in gasoline and in the exhausts – most often the nonane – but they have dominant sources in releases from consumer products (mainly from industrial synthetic building materials and housing equipment [35]), from the industrial waste streams and the contaminated urban soil [36–40], though environmental behavior of the vapors from the subsurface gasoline contamination of soil and groundwater is not a well understood phenomenon.

Industrial park in a downtown area

The National Air Pollution Surveillance stations 2 (No. 50104) and 3 (No. 50115) (Figure 1) are located symmetrically *vis-à-vis* pulp and paper industry sites, in a densely populated town center. The pulp and paper industry is represented by 2 large plants. Montreal is also an important administrative center for the pulp, paper, and wood industries in North America.

Figure 1 shows a large industrial park, Technopôle Angus, adjacent to the station No. 50104. Incidentally, this receptor captures VOCs typical of industrial sources. Table 1 shows models for receptors 2 and 3, employing the same set of VOCs and the same ordering of the set; this was the set of all the VOCs captured in station 3, located at a distance of 2.5 km from the industrial park. Some of the profiles for station 2 are quite compatible with profiles for station 3, but in the former, “industrial,” station 2 new sources appear. Moreover, every profile for the “industrial” station has an extension by up to 30 additional VOCs, which were invisible in station 3. Table 2 lists additional VOCs for station 2 and their allocation to their sources.

Table 1. Percentage profiles of distributed sources: traffic (T), freon-22 (F), inert gases (I), and industrial sources A–F for 2 NAPS stations in Montreal center in 2000–2009

CAS	VOC	Industrial park station No. 50104						Downtown station No. 50115							
		T	F	I	A	B	C	D	concentration	T	F	I	E	F	concentration
75-45-6	freon-22	-1	83	14	15	4			4.59	10	62	-1	-1	-1	1.71
111-65-9	octane	30	4		7	22	14	28	0.27	24	27	21		20	0.32
75-09-2	dichloromethane	75	5	-6	33	7			1.19	25	31	9	-1	9	1.01
627-20-3	cis-2-pentene	45	4	25	19	1			0.19	30	8	-5	7	50	0.19
96-37-7	methylcyclopentane	40	1	42	11	-1			0.71	45	4	10	-6	41	0.85
100-41-4	ethylbenzene	33	4	20	6	8	22		1.14	29	8	16	-4	40	1.23
98-82-8	iso-propylbenzene	40	-2	17	8	10			0.07	22	6	9	6	51	0.08
103-65-1	n-propylbenzene	29	8	0	5	17			0.22	6	8	6	13	56	0.24
104-51-8	n-butylbenzene	25	9	-7	2	28			0.06	-7	8	4	19	60	0.06
105-05-5	1,4-diethylbenzene	47	11	-0	4	25			0.19	-6	8	4	14	65	0.20
111-84-2	nonane	12	5		9	44	9	51	0.32	19	20	20	-9	43	0.30
112-40-3	dodecane	-26	2		54	40	16	110	0.33	10	4	13		73	0.28
1120-21-4	undecane	-20	3		43	77	-1	31	0.56	6	0	16	14	76	0.44
124-18-5	decane	-12	4		28	74	-3	40	0.58	18	12	17	-1	56	0.43
111-66-0	1-octene	-16	7		33	19	67	29	0.03	18	4	21		36	0.03
108-67-8	1,3,5-trimethylbenzene	40	8	-3	8	22	12	55	0.31	33	7	23		25	0.36
108-87-2	methylcyclohexane	34	11	16	-5	7	21	8	0.34	27	13	17		37	0.38
108-88-3	toluene	43	7	23	5	7	19	14	6.47	42	7	14		34	7.73
287-92-3	cyclopentane	44	1		11	5	23	13	0.31	42	5	11	6	31	0.32
4050-45-7	trans-2-hexene	71	0		12	9	23	61	0.08	40	3	9	11	31	0.09
496-11-7	indane	42	3	0	-1	37	23	58	0.13	30	5	8	11	45	0.14
513-35-9	2-methyl-2-butene	68	0		7	-3	23	15	0.45	36	3	6	7	54	0.47
589-81-1	3-methylheptane	53	-1	24	6		20	16	0.25	24	4	13	14	55	0.32
526-73-8	1,2,3-trimethylbenzene	35	3		-3	49	25	78	0.26	23	7	7	9	56	0.28
100-42-5	styrene	20	24	-2	-4	16		103	0.22	11	8	10	1	41	0.22
108-38-3	m- and p-xylene	43	9		0	12	18	46	3.59	42	2	24			3.82
109-67-1	1-pentene	46	6	45	19	3	32	-9	0.18	32	5	17	18	17	0.19
110-54-3	hexane	59	7	48	-2	1	10	-10	1.09	46	1	19		22	1.16
107-83-5	2-methylpentane	55	5	32	12	3	17	5	1.73	41	-1	25			1.94

108-08-7	2,4-dimethylpentane	49	4	22	19	7	21	-2	0.13	40	3	24	0.17
110-82-7	cyclohexane	53	6		7	-4	29	-7	0.28	41	4	22	0.30
115-07-1	propylene	53	1		4	-7	45	-25	1.13	43	2	23	1.68
115-11-7	1-butene/isobutene	56	0		1	-6	50	-26	0.88	43	2	23	1.13
142-29-0	cyclopentene	54	2		23	-3	32	15	0.07	35	6	23	0.09
142-82-5	heptane	42	2		11	8	33	2	0.55	38	5	18	0.64
109-66-0	pentane	43	2	14	9	15	34	0	2.41	44	2	16	2.20
540-84-1	2,2,4-trimethylpentane	54	2		14	-3	39	-18	0.36	33	4	1	0.50
3522-94-9	2,2,5-trimethylhexane	16	2		8	6	59	-54	0.04	34	3	8	0.05
127-18-4	tetrachloroethylene	15	4		14	-8	74	-61	0.45	26	3	47	0.57
124-48-1	dibromochloromethane	6	6		41	15	31	12	0.03	6	13	36	0.02
135-01-3	1,2-diethylbenzene	8	3		25	35	6	26	0.02	14	10	28	0.02
135-98-8	sec-butylbenzene	10	6		11	35	10	17	0.03	13	10	25	0.03
15869-94-0	3,6-dimethyloctane	12	51		-3	27	8	-4	0.05	14	19	29	0.04
14686-13-6	trans-2-heptene	75	5		0	5	32	74	0.03	32	2	30	0.03
141-93-5	1,3-diethylbenzene	32	2		4	37	31	30	0.06	26	7	20	0.07
538-93-2	iso-butylbenzene	30	4		1	31	24	67	0.03	14	4	9	0.03
563-46-2	2-methyl-1-butene	46	0		18	-1	14	-4	0.30	41	1	2	0.34
590-18-1	cis-2-butene	38	10	67	18	-7	10	-8	0.31	42	3	6	0.32
589-34-4	3-methylhexane	57	3		12	8	21	13	0.70	27	4	8	0.88
463-82-1	2,2-dimethylpropane	40	8		27	-0	17	-20	0.03	33	7	12	0.03
565-59-3	2,3-dimethylpentane	64	6		16	5	18	5	0.24	31	3	6	0.31
591-49-1	1-methylcyclohexene	53	2	16	13	-3			0.03	16	6	3	0.03
693-89-0	1-methylcyclopentene	68	5	18	13	4			0.08	21	4	-3	0.10
590-35-2	2,2-dimethylpentane	52	3	41	3	-1	18		0.05	22	0	5	0.06
591-76-4	2-methylhexane	40	5	50	3	4			0.63	35	3	5	0.79
592-13-2	2,5-dimethylhexane	46	8	44	-5	19			0.09	31	5	4	0.12
592-27-8	2-methylheptane	40	7	41	-3	30	19	12	0.25	37	5	16	0.31
592-41-6	1-hexene	60	10	27	17	4	8	2	0.17	28	7	1	0.17
624-64-6	trans-2-butene	34	2	74	10	-3			0.38	67	4	7	0.39
646-04-8	trans-2-pentene	36	4	30	11	5			0.34	37	6	-2	0.34
75-83-2	2,2-dimethylbutane	36	7	42	23	8			0.38	25	8	10	0.40
565-75-3	2,3,4-trimethylpentane	63	-9		14	7	33	-5	0.14	28	3	2	0.17

Table 1. Percentage profiles of distributed sources: traffic (T), freon-22 (F), inert gases (I), and industrial sources A–F for 2 NAPS stations in Montreal center in 2000–2009 – cont.

CAS	VOC	Industrial park station No. 50104						Downtown station No. 50115							
		T	F	I	A	B	C	D	concentration	T	F	I	E	F	concentration
67-66-3	chloroform	14	6	8	34				0.18	63	8	21	-3	14	0.21
74-84-0	ethane	14	2	62	17	3			2.92	72	0	50	-3	-4	4.04
106-97-8	butane	59	1	50	7	-1			4.57	61	2	31	-9	6	4.24
75-28-5	isobutane	60	11	42	-0	-5			3.91	83	-8	65	-5	23	3.83
74-85-1	ethylene	38	0	42	13	3			2.91	39	5	16	0	21	4.38
75-69-4	freon-11	0	6	62	32	7			1.76	43	8	36	5	0	1.87
75-71-8	freon-12	-7	3	75	43	10			2.90	34	10	16	4	-3	2.86
76-14-2	freon-114	-2	2	49	53	4			0.15	33	8	8	8	16	0.14
74-87-3	chloromethane	-2	6	74	32	6			1.18	26	9	13	3	13	1.19
76-13-1	freon-113	-5	4	58	52	9			0.77	29	6	12	8	9	0.77
106-46-7	1,4-dichlorobenzene	2	13	37	62	17			1.11	15	5	15	18	16	0.03
616-12-6	<i>trans</i> -3-methyl-2-pentene	68	8	20	4	3	31		0.05	6	10	14	32	19	0.46
611-14-3	2-ethyltoluene	44	7	15	1	12	48		0.26	6	7	1	18	43	0.06
620-14-4	3-ethyltoluene	45	5	17	1	11			0.61	15	5	5	17		0.29
78-79-5	isoprene	-6	1	20	27	72			0.29	15	5	5	17		0.73
74-95-3	dibromomethane	3	2		57	0			0.05	23	11	3	18	44	0.38
760-20-3	3-methyl-1-pentene	27	4	21	41	5			0.03	0	-1	24	20	37	0.05
74-98-6	propane	55	6	65	-2	9			3.43	18	1	-5	16	44	0.03
74-99-7	1-propyne	35	1	37	19	4			0.12	33	5	10	5	31	0.17
71-43-2	benzene	36	1	48	11	0			1.58	45	5	6	-1	34	2.01
78-78-4	isopentane	40	9	44	12	3			5.34	44	8	11	0	25	5.22
79-29-8	2,3-dimethylbutane	50	5	35	10	0			0.41	39	5	11	2	31	0.47
922-61-2	<i>cis</i> -3-methyl-2-pentene	44	6	28	-5	3			0.08	46	5	7	-3	42	0.09
96-14-0	3-methylpentane	50	3	34	8	-2			1.13	43	4	12	-6	30	1.30
95-47-6	<i>o</i> -xylene	47	4	14	8	7			1.16	37	6	11	0	36	1.26
7688-21-3	<i>cis</i> -2-hexene	42	9	5	4	8			0.07	30	7	7	5	32	0.07
106-99-0	1,3-butadiene	46	1	22	22	10			0.22	31	5	14	8	31	0.34
95-63-6	1,2,4-trimethylbenzene	55	9	-1	1	15			1.06	27	7	7	0	51	1.20
99-87-6	<i>p</i> -cymene	30	0	-9	7	19			0.09	-0	16	12	32	48	0.07

71-55-6	1,1,1-trichloroethane	12	4	14	38	12	0	4	14	38	-0	0.17	
75-00-3	chloroethane	-2	3	22	53	5	14	4	20	26	8	0.04	
74-83-9	bromomethane	10	19	11	41	-2	0.11	9	11	35	7	14	0.09

CAS – Chemical Abstracts Service registry number; VOC – volatile organic compound; NAPS – National Air Pollution Surveillance.
Values ≥ 25% are bolded, undetermined values are blank.

Table 2. Extensions of profiles for industrial park station No. 50104; volatile organic compounds (VOCs) not seen in a distant downtown station No. 50115

CAS	VOC	Industrial park NAPS station No. 50104											concentration
		T	F	I	A	B	C	D	E	F	G	H	
464-06-2	2,2,3-trimethylbutane	38	-1		22	12		22			22	11	0.02
4461-48-7	<i>cis</i> -4-methyl-2-pentene	58	1		13	-1		17			17	24	0.05
589-53-7	4-methylheptane	54	-2	22	5			22			22	15	0.10
622-96-8	4-ethyltoluene	45	4	15	6	10							0.32
75-01-4	vinylchloride	8	0	4	68	2							0.01
50-00-0	formaldehyde	1	3		36	5		20			20	-38	2.48
66-25-1	hexanal	-14	5	20	35	3							0.19
67-64-1	acetone	-4	5	15	32								3.76
107-06-2	1,2-dichloroethane	6	8	-5	44	23		-7			38		0.07
75-27-4	bromodichloromethane	24	2	12	45	13							0.07
91-20-3	naphthalene	36	1	-24	42	8							0.52
590-86-3	2-pentanone/isovaleraldehyde	20	1	40	26	5							0.13
100-52-7	benzaldehyde	16	2	64	31	14							0.17
75-25-2	bromoform	6	-2	29	55	2							0.03
108-90-7	chlorobenzene	-24	15	74	63	6		52					0.01
110-62-3	2-pentanal	-13	21	83	28	-4		57					0.13
110-83-8	cyclohexene	39	7		27	9		29			8		0.03
123-38-6	propionaldehyde	-3	4		29	-9		71			-49		0.42
107-02-8	acrolein	23	34		2	-10		32			-19		0.13
108-10-1	MIBK	-9	35	-10	10	-5		68			-20		0.15
2207-01-4	<i>cis</i> -1,2-dimethylcyclohexane	16	2		24	5		36			-9		0.04
2207-03-6	<i>cis</i> -1,4/ <i>trans</i> -1,3-dimethylcyclohexane	19	3		14	5		29			7		0.04

Table 2. Extensions of profiles for industrial park station No. 50104: volatile organic compounds (VOCs) not seen in a distant downtown station No. 50115 – cont.

CAS	VOC	Industrial park NAPS station No. 50104							concentration
		T	F	I	A	B	C	D	
2207-04-7	<i>trans</i> -1,4-dimethylcyclohexane	14	3		16	5	27	2	0.05
589-43-5	2,4-dimethylhexane	63	-2		12	6	29	3	0.12
590-73-8	2,2-dimethylhexane	44	3	44	2		40		0.03
75-07-0	acetaldehyde	36	-4	48	22	4			1.92
79-01-6	trichloroethylene	70	-3	24	8	6			0.15
78-93-3	MEK	-6	3	98	10	-1			1.42
638-04-0	<i>cis</i> -1,3-dimethylcyclohexane	29	5	11	2	49			0.11
13389-42-9	<i>trans</i> -2-octene	16	7		3	25	7	14	0.08

MIBK – methyl isobutyl ketone; MEK – methyl ethyl ketone.

Other abbreviations as in Table 1.

Values $\geq 25\%$ are bolded, undetermined values are blank.

Table 2 briefly presents the local VOC pollution features. And so, trichloroethylene, produced from ethylene (but banned from the food and pharmaceutical industries in the majority of the world due to concerns about its toxicity [41]), here supplements the usual occurrences of ethylene in the urban traffic and in the banks of inert gases. Acetaldehyde, another derivative of ethylene, used in an array of specialized industries manifests a similar behavior. It can be released to the environment during production, use, transportation, and storage. Also power plants, refineries, cement kilns, lumber mills and paper mills release acetaldehyde into the air.

Other aldehydes in Table 2, such as methyl ethyl ketone (MEK), 2-pentanal, and benzaldehyde, accompanied by chlorobenzene, have significant loadings in the “inert gases” profile due to their longer half-life of the reactions with hydroxyl radicals (several days, or months in the case of bromoform, or chloromethane) and/or slow volatilization rate [42,43].

Tables 2 and 3 show profiles labeled F. – for freon-22, which practically alone forms the profiles. This inert gas appears to be a separate source, as it has a different emission pattern from other freons: it supplements the formerly widely used ozone-depleting freon-11 and freon-12 and it escapes to the atmosphere from many of its uses such as: propellant, refrigerant, foaming agent, solvent and degreaser, fire extinguishing agent, and dry cleaning agent. Other freons may form the profile labeled I. – for “Inert,” as their longevity allows to detect them long after they were faded-out.

Profiles A, B, and C in Table 1 (industrial park station 2) and their extensions in Table 2 describe industrial sources located in the nearby industrial zone. The presence of the non-traffic hydrocarbons in paraffin series C9–C12, nonane to dodecane are suggestive of industrial sites. Particularly decane, which is universally used in petroleum, gasoline, plastics, rubber, and paper-processing industries, participates widely in organic synthesis, in jet

Table 3. Percentage profiles of traffic source (T) and 6 other sources (G–L) for NAPS station No. 50103 located in the petrochemical industry zone of Montreal-East in 2000–2009

CAS	VOC	Petrochemical industry zone NAPS station No. 50103										
		T	G	H	I	J	K	L	concentration			
75-83-2	2,2-dimethylbutane	-12	1	-1	15	13	0	77	4.71			
99-87-6	<i>p</i> -cymene	6	13	13	10	7	5	46	0.07			
10061-02-6	<i>trans</i> -1,3-dichloropropene	10	17	7	9	6	5	48	0.19			
104-51-8	<i>n</i> -butylbenzene	-4	17	9	8	7	6	47	0.14			
106-99-0	1,3-butadiene	10	16	14	5	9	7	39	0.04			
108-67-8	1,3,5-trimethylbenzene	14	10	6	24	16	24	37	0.03			
2207-03-6	<i>cis</i> -1,4/ <i>t</i> -1,3-dimethylcyclohexane	20	6	18	7	20	9	54	0.02			
100-44-7	benzylchloride		-4	1	52	20	7	32	1.02			
541-73-1	1,3-dichlorobenzene	22	6	9	40	16	9	37	0.11			
124-48-1	dibromochloromethane	7	7	-1	29	21	18	28	0.06			
3522-94-9	2,2,5-trimethylhexane	9	-2	23	28	-4	11	62	0.10			
5779-94-2	2,5-dimethylbenzaldehyde	16	-22	3	80		6	76	6.50			
111-84-2	nonane	14	0	6	71	3	9	68	0.10			
538-93-2	iso-butylbenzene	11	3	19	40	10	7	44	0.05			
590-18-1	<i>cis</i> -2-butene	21	-14	4	79	26	3	78	8.85			
590-73-8	2,2-dimethylhexane	24	17	3	33	40	1	30	0.53			
4050-45-7	<i>trans</i> -2-hexene	1	0	-4	83	8	4	-11	2.12			
78-87-5	1,2-dichloropropane		2	3	54	6	12	14	0.14			
79-01-6	trichloroethylene		-2	8	68	-9	6	6	0.29			
79-29-8	2,3-dimethylbutane	-1	-2	-2	98	3	3	1	0.84			
80-56-8	<i>a</i> -pinene		1	1	62	17	17	8	1.25			
110-82-7	cyclohexane	13	8	-1	76	2	8	17	0.45			
111-65-9	octane	4	1	-5	69	6	8	22	0.97			
922-61-2	<i>cis</i> -3-methyl-2-pentene	18	59	0	77	8	9	5	0.63			
95-47-6	<i>o</i> -xylene	10	56	5	65	-2	4	20	0.06			
108-08-7	2,4-dimethylpentane	24	56	-3	88	1	1	9	0.49			
106-46-7	1,4-dichlorobenzene	24	54	2	66	6	5	14	0.35			
107-06-2	1,2-dichloroethane	29	28	2	40	19	14	19	0.33			
624-64-6	<i>trans</i> -2-butene	28	31	16	7	2	6	19	0.10			

Table 3. Percentage profiles of traffic source (T) and 6 other sources (G–L) for NAPS station No. 50103 located in the petrochemical industry zone of Montreal-East in 2000–2009 – cont.

CAS	VOC	Petrochemical industry zone NAPS station No. 50103										L	concentration
		T	G	H	I	J	K	L					
638-04-0	<i>cis</i> -1,3-dimethylcyclohexane	25	25	15	10	3	5	22	0.04				
115-11-7	1-butene/isobutene	53	2	12	17	8	15	22	0.15				
71-55-6	1,1,1-trichloroethane	54	10	1	21	10	5	30	0.15				
108-90-7	chlorobenzene	32	24	32	-2	16	14	27	0.03				
674-76-0	<i>trans</i> -4-methyl-2-pentene	97	17	33	3	2	10	6	0.04				
1120-21-4	undecane	48	8	34	8	14	14	7	0.02				
109-66-0	pentane	13	8	29	4	-2	6	20	0.05				
111-66-0	1-octene	10	6	38	4	-2	6	21	0.13				
590-35-2	2,2-dimethylpentane	4	2	54	2		7	3	0.93				
620-23-5	<i>m</i> -tolualdehyde	12	17	33	9	3	15	12	0.03				
74-96-4	ethylbromide		11	47	3	4	3	4	0.28				
760-20-3	3-methyl-1-pentene		2	64	6		1	-1	0.08				
78-78-4	isopentane		4	46	12	-8	8	9	0.14				
79-92-5	camphene		24	30	5	4	1	13	0.04				
464-06-2	2,2,3-trimethylbutane	11	9	63	-6	11	11	14	0.04				
2207-04-7	<i>trans</i> -1,4-dimethylcyclohexane	14	11	33	2	11	10	9	0.63				
75-69-4	freon-11		0	34	15	11	7	36	0.59				
78-93-3	MEK		4	33	12	7	3	35	0.14				
2097503	<i>cis</i> -3-heptene		0	48	10	35	4	36	2.68				
75-34-3	1,1-dichloroethane		4	2	17	66	69	7	0.11				
6876-23-9	<i>trans</i> -1,2-dimethylcyclohexane	14	5	12	13	58	51	13	0.03				
87-68-3	hexachlorobutadiene	-2	6	4	10	47	60	4	0.27				
79-34-5	1,1,2,2-tetrachloroethane	20	1	3	18	29	63	6	0.66				
110-54-3	hexane	4	17	6	16	68	43	4	0.25				
124-18-5	decane	4	18	1	8	63	32	16	0.06				
529-20-4	<i>o</i> -tolualdehyde	64	3	7	5	65	31	12	0.73				
611-14-3	2-ethyltoluene	26	11	4	19	57	31	24	0.09				
67-66-3	chloroform	5	3	5	11	69	59	11	0.47				

75-35-4	1,1-dichloroethylene	1	7	26	57	59	6	0.05
78-79-5	isoprene	3	4	47	30	25	10	2.80
872-05-9	1-decene	4	1	28	42	37	8	10.03
105-05-5	1,4-diethylbenzene	8	1	37	80	65	2	0.64
540-84-1	2,2,4-trimethylpentane	24	0	44	27	27	62	1.09
112-40-3	dodecane	7	3	-5	8	92	88	0.51
75-09-2	dichloromethane	-9	4	22	61	61	16	0.52
79-00-5	1,1,2-trichloroethane	0	3	14	-3	65	3	0.53
589-34-4	3-methylhexane	0	4	1	0	71	6	1.22
287-92-3	cyclopentane	66	0	9	38	15	26	0.18
463-82-1	2,2-dimethylpropane	64	5	-6	44	22	10	0.11
156-60-5	<i>trans</i> -1,2-dichloroethylene	67	2	9	31	17		0.35
821-95-4	1-undecene	5	7	42	27	23	12	1.77
156-59-2	<i>cis</i> -1,2-dichloroethylene	10	2	25	27	22	29	0.62
1077-16-3	hexylbenzene	46	13	34	4	3	5	5.52
563-45-1	3-methyl-1-butene	44	6	6	-2	15	6	0.57
565-59-3	2,3-dimethylpentane	26	4	10	15	1	4	0.27
565-75-3	2,3,4-trimethylpentane	39	4	17	17	11	19	0.38
107-83-5	2-methylpentane	78	12	22	9	5	51	6.56
592-41-6	1-hexene	18	-15	69	24	-4	68	4.51
622-96-8	4-ethyltoluene	16	-6	57	22	7	53	0.60
625-27-4	2-methyl-2-pentene	13	-10	70	2	-3	62	0.20
627-20-3	<i>cis</i> -2-pentene	24	-2	41	21	12	42	0.20
74-84-0	ethane	17	6	33	5	2	40	1.38
74-95-3	dibromomethane		-1	50	16	11	46	0.92
75-25-2	bromoform		-1	53	17	14	44	0.88
75-27-4	bromodichloromethane		-2	67	13	6	45	0.12
5989-27-5	limonene	15	31	21	2	6	27	0.07
142-82-5	heptane	1	62	0	-4	6	2	0.03
591-76-4	2-methylhexane	21	54	-4	1	3	-4	0.17
592-13-2	2,5-dimethylhexane	18	30	22	-3	1	23	0.33
4170-30-3	crotonaldehyde	5	65	16	5	10	4	3.65
74-85-1	ethylene	-6	36	-2	-1	1	2	0.31

Table 3. Percentage profiles of traffic source (T) and 6 other sources (G–L) for NAPS station No. 50103 located in the petrochemical industry zone of Montreal-East in 2000–2009 – cont.

CAS	VOC	Petrochemical industry zone NAPS station No. 50103								L	concentration
		T	G	H	I	J	K	L			
75-71-8	freon-12		31	5	-2	2	3	8	0.25		
76-13-1	freon-113		51	2	4	4	2	3	0.02		
76-14-2	freon-114		6	19	23		5	20	0.15		
123-38-6	propionaldehyde	11	10	14	1	72	6	-23	0.07		
50-00-0	formaldehyde	23	13	23	-5	4	7	-17	0.15		
95-50-1	1,2-dichlorobenzene	1	9	15	10	12	17	7	0.24		
98-06-6	tert-butylbenzene	-12	5	24	3	2	8	9	0.21		
589-53-7	4-methylheptane	15	16	21	3		18	5	0.01		
589-81-1	3-methylheptane	17	20	16	14	-9	8	16	0.03		

Abbreviations as in Table 1 and 2.

Values $\geq 25\%$ are bolded, undetermined values are blank.

fuel research, and in the manufacturing of paraffin products. It is also used in cleaning agents.

Vinylchloride (highly toxic, flammable, and carcinogenic organochloride, important monomer) and its precursor, 1,2-dichloroethane, as well as naphthalene, chloroethane, and 1,4-dichlorobenzene appearing in source A, suggest local manufacturing of polymer materials, including the polyvinyl chloride (PVC), specialty polymers such as synthetic textile fibers, dyes, and possibly organoaluminum compounds [1,44].

The source corresponding to profile B is characterized by high participation of isoprene in the emission. This hydrocarbon released into the atmosphere by hundreds of million tons by trees, is also a chemical raw material used to make polymeric materials and synthetic versions of the natural rubber.

Profile C shows numerous compounds used in the research laboratories, in the synthesis of fine organic chemicals, and in the biomanufacturing: 2-pentanal, 1,2-dimethylcyclohexane, *cis*-1,4/*t*-1,3-dimethylcyclohexane, and *trans*-1,4-dimethylcyclohexane. The tetrachloroethylene present here is an excellent solvent for organic materials and degreaser. Methyl isobutyl ketone (MIBK) is used as a solvent for nitrocellulose, lacquers and certain polymers, and resins. Alkene 1-butene/isobutene, besides being used in the production of octanes, is also used to manufacture other chemical products, such as polyethylene, polypropylene resins, polybutene, butylene oxide, and MEK.

Profile D is distinguished by styrene, a precursor to polystyrene and several copolymers. Approximately 7 million tons are produced worldwide annually from ethylbenzene, which in turn is prepared on a large scale by alkylation of benzene with ethylene. Styrene is employed in preparing materials such as rubber, plastic, insulation, fiberglass, pipes, automobile and boat parts, food containers, and carpet backing [45]. Compound 1,3,5-trimethylbenzene, which has shorter half-life time (12 h) than styrene, is still present in the vicinity of petrochemical and

chemical industrial sites; it is an important solvent used in coatings, cleaners, pesticides, and inks. Alkene *trans*-2-hexene occurs in similar circumstances; however, it is used in smaller quantities and most often in the research facilities.

Columns under “Downtown station No. 50115” in Table 1 show profiles for the station at some distance (2.5 km) from the industrial park. The T, F, and I. profiles have their versions here, still reminiscent of the corresponding profiles for the “industrial” station 2. Profile E is characterized by strong presence of dibromochloromethane, which is a quite stable trihalomethane (half-life counted in months) appearing in the atmosphere as a by-product of the water treatment and disinfection procedures. The compound may be present nearby a drinking water treatment plant. Profile F is an agglomeration of the “industrial” profiles seen in station 2, which escape a closer analysis. It appears to be the image of the industrial pollution already scrambled by the atmospheric chemistry – due to 2.5 km distance from the pollution sources.

Petrochemical industrial suburb (Montreal-East)

Montreal-East, formerly a borough, the precincts where petrochemical industry was located, is the East-North extremity of the city of Montreal, Quebec. Three important refineries operated here during the time period for which this analysis was performed. Also the chief petrochemical plants are located in this region.

Table 3 shows the source profiles produced in NAPS station 1 (No. 50103) situated in the Montreal-East industrial zone (time period: 2000–2009). Here, the “traffic” profile is characterized by the “lingering exhaust” fingerprints, consisting of a strong presence of volatile 2-methylpentane in the air, but also of low-volatility cyclopentane. The specialty gasoline component, 2,3,4-trimethylpentane, is also present. Yet the traffic’s typical emissions of hexanes, pentanes, heptanes, and octanes are detected only in their most lingering forms and must be

assigned to the industrial sources. On the other hand, organochlorides such as 1,1,1-trichloroethane, 1,2-dichloroethylene, and specialty compounds such as 4-methyl-2-pentene (which tends to appear in the “traffic” profiles), are arguably the fairly persistent remains of discharges from industrial factories (textile processing and dyeing) rather than from fuel combustion in motor vehicles.

Another characteristic of the petrochemical industry profiles is the absence of emissions of liquefied petroleum gases (LPG): propane, butane, propylene, butadiene, butylene, and isobutylene. Therefore, these emissions, occurring in other regions, appear to be escapes from the consumer widespread usage of LPG.

Petrochemical industry involves petroleum refining processes, creating point-like sources of fugitive organic pollutants and more dispersed sources in a form of effluents and waste streams. The refining processes and operations are of several basic types [46–49]. The 3 predominant ones are: fractionation (distillation into fractions of hydrocarbon compounds of differing boiling-point ranges), dividing molecules by thermal and catalytic cracking, and rearranging molecules with isomerization and catalytic reforming. Combining molecules through alkylation (introducing alkyl groups, such as methyl, $-\text{CH}_3$, or ethyl, $-\text{C}_2\text{H}_5$, group, into organic compound [50,51]), polymerization (converting light olefin gases including ethylene, propylene, and butylene into hydrocarbons of higher molecular weight and higher octane number that can be used as gasoline blending stocks), hydrogenation (addition of hydrogen atoms to the molecule [52,53]), dehydrogenation (catalytic elimination of hydrogen atoms from molecules), gas-phase photochemical reactions, coal carbonization, and many other reactions most often involving ethylene or benzene [54–56] also has great technological importance.

It appears that the processes result in releasing a plethora of compounds that usually are reported to us as “solvents” [47,57] into the environment. Specialty solvents and useful intermediates such as 2-methyl-2-pentene,

cis-3-methyl-2-pentene, 2,4-dimethylpentane, *trans*-4-methyl-2-pentene, *trans*-2-hexene, *cis*-1,4/*t*-1,3-dimethylcyclohexane, *cis*-2-pentene, iso-butylbenzene, 2-ethyltoluene, or 4-ethyltoluene can be observed. It is not known to the authors if the compounds are targeted in the refinery operations, or if they are by-products.

Other compounds, such as octane, heptane, 2,4-dimethylpentane, 2,2-dimethylpentane, 1,4-diethylbenzene, 2-methylhexane, 3-methylhexane, 1-hexene are clearly targeted in operations of distillation, while nonane, dodecane, *cis*-2-butene may come from the cracking, distillation, and/or catalytic dehydrogenation operations. Also 2,2-dimethylbutane, 2,3-dimethylbutane, 2,2,4-trimethylpentane are targeted in the operations of alkylation of ethylene. Benzylchloride is targeted in photochemical reaction of toluene with chlorine. Cyclohexane is produced by hydrogenation of benzene, and xylenes are targeted in the processes of catalytic reforming and coal carbonization.

Table 3 exhibits a number of species occurring only in this zone. Apart from *p*-cymene, there also appear monoterpenes camphene and α -pinene, however, indicating separate sources. They are probably sequels of wood pulping and traditional timber industry, or the naturally occurring wood terpenes.

Aldehydes such as propionaldehyde, tolualdehydes, and MEK come from those sources, rather than from traffic or petrochemical plants. On the other hand, other aldehydes, crotonaldehyde and 2,5-dimethylbenzaldehyde – important building blocks in the organic chemistry – are probably produced in refinery operations.

Refineries also produce important intermediates in the manufacture of chlorinated pesticides and solvents, chloroform, bromoform, dichloromethane, bromodichloromethane, dibromomethane, 1,1-dichloroethane, 1,1,2,2-tetrachloroethane, 1,2-dichloropropane, and *trans*-1,3-dichloropropene [1], while hexachlorobutadiene is released as a by-product in the manufacture of

the chlorinated solvents. Occurrence of trichloroethylene, 1,1,2-trichloroethane, and 1,1-dichloroethylene, which arise in some refinery processes, here, most likely, are results of operations of a textile industrial unit.

Suburban district

Table 4 presents a model for the peripheral station 4 (No. 50129), located in a suburban district surrounded by agglomerations of pharmaceutical companies and research laboratories (almost 200 pharmaceutical companies are located in and around Montreal). The model shows typical distributed sources: T. (traffic), F. (freon-22), I. (inert), but also a local source of emissions characteristic for organic synthesis in the pharmaceutical industry, labeled Pha. Indeed, the manufacture of pharmaceutical products involves mainly species such as: decane, 2-, 3-, 4-ethyltoluene, 1,2,3-trimethylbenzene, iso-butylbenzene, indane, and also chloroform – a common solvent used in a laboratory.

A separate source, labeled Ch. for “Chemical manufacturing” is distinguished by the compounds such as 3-methyl-1-pentene, bromoform, dibromomethane, freons, and 1,2-dichloropropane, which are important intermediates in the production of many chlorinated chemicals, mainly solvents, degreasers and pesticides.

Finally, source X cannot be easily qualified. It is distinguished by a massive emission of ethylene, simple unsaturated hydrocarbon (C_2H_4) widely used in the petrochemical and chemical industries, and 1-propyne (C_3H_4) – a specialty fuel for not-industrial application, extremely flammable unsaturated aliphatic alkyne.

Citywide features of the hydrocarbon pollution

Short chain haloalkanes such as dichloromethane and dibromomethane, very common solvents and reagents, formerly widely used in preparation of pesticides and fumigants – but toxic when released to the atmosphere – appear in all the 4 stations in Montreal and have manifold

Table 4. Percentage profiles of distributed sources: traffic (T), freon-22 (F), inert gases (I), and industrial sources pharmaceutical (Pha.), chemical manufacturing (Ch.), and unknown (X) for NAPS station No. 50129 located at Montreal periphery in 2000–2009

CAS	VOC	Peripheral NAPS station No. 50129							concentration
		T	F	I	Pha.	Ch.	X		
75-45-6	freon-22	-5	73	9		10	18	1.51	
100-42-5	styrene	10	36	-4		-1	1	0.21	
111-66-0	1-octene	6	25	8		10		0.03	
3522-94-9	2,2,5-trimethylhexane	13	31	4	4	-1		0.04	
592-41-6	1-hexene	13	40	17	12	-5		0.09	
611-14-3	2-ethyltoluene	16	4	10	61	1		0.11	
620-14-4	3-ethyltoluene	16	9	17	62	-2		0.26	
622-96-8	4-ethyltoluene	14	4	10	61	3		0.14	
135-98-8	sec-butylbenzene	23	13	-5	55		20	0.02	
15869-94-0	3,6-dimethyloctane	24	8	11	50	4		0.02	
526-73-8	1,2,3-trimethylbenzene	24	1	22	67	-2		0.10	
538-93-2	iso-butylbenzene	8	9	0	48	14	30	0.01	
75-09-2	dichloromethane	-1	0	13		6	57	0.63	
74-85-1	ethylene	3	2	76		-4	73	1.98	
74-99-7	1-propyne	18	0	68		0	61	0.08	
71-43-2	benzene	18	2	68		4		1.06	
115-07-1	propylene	12	1	77		0		0.72	
106-99-0	1,3-butadiene	9	2	76		2		0.12	
589-34-4	3-methylhexane	24	5	28	22	14		0.39	
496-11-7	indane	27	3	22	63	-7		0.05	
141-93-5	1,3-diethylbenzene	27	7	3	55	11	55	0.03	
124-18-5	decane	29	7	-2	78	36	60	0.19	
1120-21-4	undecane	24	11	-8		50		0.19	
112-40-3	dodecane	26	8	-18		-5		0.12	
75-83-2	2,2-dimethylbutane	71	3	13		8	1	0.20	
78-78-4	isopentane	79	4	14		11	2	3.29	
79-29-8	2,3-dimethylbutane	66	1	12		8	9	0.21	

Table 4. Percentage profiles of distributed sources: traffic (T), freon-22 (F), inert gases (I), and industrial sources pharmaceutical (Pha.), chemical manufacturing (Ch.), and unknown (X) for NAPS station No. 50129 located at Montreal periphery in 2000–2009 – cont.

CAS	VOC	Peripheral NAPS station No. 50129							concentration
		T	F	I	Pha.	Ch.	X		
95-47-6	<i>o</i> -xylene	50	-3	2		-1	22	0.59	
922-61-2	<i>cis</i> -3-methyl-2-pentene	65	1	6		3	15	0.03	
96-14-0	3-methylpentane	59	1	7		8	14	0.64	
96-37-7	methylcyclopentane	64	-1	2		2	13	0.40	
98-82-8	iso-propylbenzene	28	2			10	21	0.04	
108-67-8	1,3,5-trimethylbenzene	31	5	15		-4		0.12	
100-41-4	ethylbenzene	34	5	22		1	19	0.62	
103-65-1	<i>n</i> -propylbenzene	37	1	9		2		0.10	
107-83-5	2-methylpentane	58	3	22		-5		0.94	
95-63-6	1,2,4-trimethylbenzene	33	-1	-2		-3	28	0.43	
74-98-6	propane	39	0	36		7	45	3.51	
75-28-5	isobutane	78	-2	47		2	24	2.33	
106-97-8	butane	64	2	28		0		2.95	
108-08-7	2,4-dimethylpentane	48	4	27		-14		0.07	
115-11-7	1-butene/isobutene	39	1	56		-3		0.51	
108-88-3	toluene	40	3	25		1		3.59	
108-38-3	<i>m</i> and <i>p</i> -xylene	44	5	22		3		1.98	
108-87-2	methylcyclohexane	66	5	6		3		0.19	
109-66-0	pentane	61	2	18		-6		1.41	
109-67-1	1-pentene	49	9	16	4	-3	4	0.10	
110-54-3	hexane	48	4	11		-24		0.65	
110-82-7	cyclohexane	60	1	22		0		0.16	
111-65-9	octane	50	4	11	8	-3	33	0.14	
111-84-2	nonane	51	3	7		-4		0.14	
142-29-0	cyclopentene	58	6	12	16		10	0.03	
142-82-5	heptane	44	3	18	20	16		0.32	
127-18-4	tetrachloroethylene	49	4	3	15	17	33	0.26	

2207-03-6	<i>cis</i> -1,4/ <i>trans</i> -1,3-dimethylcyclohexane	48	2	6	12	12	12	0.02
2207-04-7	<i>trans</i> -1,4-dimethylcyclohexane	55	1	0	11	21	21	0.03
287-92-3	cyclopentane	66	1	16	4	4	4	0.18
4050-45-7	<i>trans</i> -2-hexene	54	3	23	16	-11	-11	0.03
463-82-1	2,2-dimethylpropane	37	6	14	4	23	23	0.02
513-35-9	2-methyl-2-butene	81	2	16	4	-16	-16	0.16
563-46-2	2-methyl-1-butene	66	4	15	1	7	7	0.14
540-84-1	2,2,4-trimethylpentane	36	2	23	22			0.21
565-59-3	2,3-dimethylpentane	25	5	27	19	12	12	0.14
590-18-1	<i>cis</i> -2-butene	55	2	35	-9			0.15
624-64-6	<i>trans</i> -2-butene	84	0	39	5	-4	4	0.18
7688-21-3	<i>cis</i> -2-hexene	49	5	28		10	6	0.03
591-76-4	2-methylhexane	27	4	29	19	8	8	0.35
592-27-8	2-methylheptane	28	3	23	19	-6	43	0.12
627-20-3	<i>cis</i> -2-pentene	70	5	4	12	-9	-9	0.08
638-04-0	<i>cis</i> -1,3-dimethylcyclohexane	33	2	0	3	2	2	0.06
646-04-8	<i>trans</i> -2-pentene	72	2	7	16	-17	-17	0.15
760-20-3	3-methyl-1-pentene	26	3	11		52	7	0.02
56-23-5	carbontetrachloride	-9	6	40	16	43	52	0.59
107-06-2	1,2-dichloroethane	-16	11	26		56	56	0.05
71-55-6	1,1,1-trichloroethane	-15	7	26		53	55	0.19
74-84-0	ethane	-5	3	50		26	67	2.62
75-25-2	bromoform	-28	7	29		55	41	0.03
75-69-4	freon-11	-20	7	30		41	62	1.72
76-13-1	freon-113	-23	6	32		48	65	0.63
76-14-2	freon-114	-13	5	44		50	53	0.13
75-71-8	freon-12	-17	7	0		41	65	2.70
74-87-3	chloromethane	-16	6	22		35	65	1.16
74-83-9	bromomethane	-13	18	20		46	40	0.08
74-95-3	dibromomethane	-26	14	12		54	35	0.04
75-00-3	chloroethane	-13	13	18		30	23	0.03

Table 4. Percentage profiles of distributed sources: traffic (T.), freon-22 (F.), inert gases (I.), and industrial sources pharmaceutical (Pha.), chemical manufacturing (Ch.), and unknown (X) for NAPS station No. 50129 located at Montreal periphery in 2000–2009 – cont.

CAS	VOC	Peripheral NAPS station No. 50129							concentration
		T.	F.	I.	Pha.	Ch.	X		
67-66-3	chloroform	-5	3	0	74	26			0.15
78-87-5	1,2-dichloropropane	-24	5	3		93	20		0.02
590-35-2	2,2-dimethylpentane	20	6	18	20	10			0.02
592-13-2	2,5-dimethylhexane	22	7	16	11	-5	24		0.06
589-43-5	2,4-dimethylhexane	18	4		20				0.07
589-53-7	4-methylheptane	20	2		24				0.05
589-81-1	3-methylheptane	17	3		23				0.12
693-89-0	1-methylcyclopentene	20	8	16	5	-3			0.03

Abbreviations as in Table 1 and 2.

Values $\geq 25\%$ are bolded, undetermined values are blank.

sources. This happens regardless of the efforts to curb their release into the environment [32,58,59]. Their presence in the environment is still a result of different product/waste streams coalescing in evaporations into atmosphere. The toxicity of trihalomethanes (chloroform, bromodichloromethane, dibromochloromethane, and bromoform) is widely discussed [60–67], but their usage as water disinfectant persists. They form in the atmosphere as a quite stable byproduct when chlorine is added to water to kill bacteria and, therefore, appear in each monitoring station. They are also used on a smaller scale in laboratories in chemical manufacturing [67,68].

Trichlorobenzenes are hardly detectable in the urban atmosphere in Montreal (they have a relatively short half-life in the atmosphere), and their possible source: volatilization from sediments and soils [63,69–73] is not detected. Dichlorobenzenes (1,2-, 1,3-, 1,4-) appear in emissions from petrochemical factories and from manufacture of polymers, while chlorobenzene, the production of which in the U.S. declined considerably in the 2nd half of last century, is still detectable in emissions from automotive industries, where it is used as a solvent to degrease automobile parts [1].

Great restrictions on the use of chlorofluorocarbons (freons: 11, 12, 113, 114) as refrigerants and propellants have been imposed since 1980 [14]. They have now been largely replaced by hydrochlorofluorocarbon freon-22. The chlorofluorocarbons, as very inert gases, still persist in the atmosphere accompanied by the abundant chlorinated hydrocarbons, chloroform and chloromethane, however, never in a company of freon-22. This suggests that sources of freon-22 and the ozone-depleting freons are different: the former has a source in the industry and in the consumer goods, while the latter ones are inert atmospheric vestiges of formerly massive releases from the wide industrial and consumer usage.

The Montreal “traffic” source, in comparison to the traffic in Mexico City [24] and locations in China [21–23], is more

loaded with species related to octane content in the gasoline and to gasoline combustion products, such as ethylene. It is not clear whether the distinction reflects differences in urban transit technologies and/or in fuel additives or results of the methodology applied. The chloroethane used in leaded gasoline, but banned in Canada since 1980, disappeared from the traffic source. Its counterpart in the unleaded gasoline, methyl tert-butyl ether (MTBE), is also absent.

Methodological aspects

Factorization methods as PMF, but also UNMIX, preferentially treat the variables with higher average values. Therefore, the highest-concentration VOC species are given priority in emission profiles. The highest concentrations should be the 1st to divulge their sources, however, the UNMIX application also makes it possible to discern some lower-concentrations VOCs that persistently accompany the high-concentration species, providing chemical data, which facilitate identification of the sources.

The lowest-concentration VOCs are the most problematic, particularly when dealing with point sources: environmental influence of VOCs destroys the relationship between the source emission pattern and the measurements performed by a distant receptor. In the case of the distributed sources, the lowest-concentration VOCs tend to form noise-like background for the more prominent VOCs. UNMIX would refuse to produce results when the measurements cannot be reliably “unmixed” even when assuming “negative” sources, i.e., taking into account an environmental depletion of VOCs.

But, when with some VOC menu UNMIX achieves success, the measured VOC concentration becomes a sum of the positive inputs from VOC emissions by physical sources – reduced by VOC depletion due to reactions in the atmosphere. The removal of VOC, largely depending on the weather and not necessarily correlated with an input from a physical source, is represented as separate “negative” sources.

The “negative” sources present a complex picture and they require further investigation: preliminary seasonal analysis of the ambient concentrations of VOCs suggested that specific air masses could be responsible for affluence of some species, at the same time causing depletion of other species. If confirmed, this would explain the heterogeneous nature of sensor models generated with EPA UNMIX.

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