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Source Characterization of Volatile Organic Compounds in Mashhad, Iran

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Abstract: Volatile organic compounds (VOCs) contribute to the formation of peroxyacetyl nitrate (PAN) and photochemical smog. The contributions of different sources of ambient VOC levels can be assessed using receptor models. A multivariate receptor model (Unmix) was used for determination of the VOCs sources in Mashhad, Iran. Concentrations of ambient VOCs were analyzed from December 2012 to March 2013 at the center of the Mashhad city. A high correlation coefficient between measured and predicted values (R^2= 0.96), indicated that the data were well modeled. Four possible VOCs source categories were identified and mobile sources such as vehicle exhaust (59%) and fuel evaporation (17%) were responded to more than half of the total VOC concentration. City gas and compressed natural gas (CNG) in line with biogenic sources were computed for 21% and 3% of the total VOC, respectively. Results of the source apportionment revealed that for decreasing the anthropogenic VOCs in the Mashhad atmosphere, the main strategy should point out the vehicle exhaust and fuel evaporations as the main sources of VOCs.

Key words: VOCs · Multivariate receptor model · Source apportionment · Unmix · Mashhad

INTRODUCTION

Many Volatile organic compounds (VOCs) species act as hazardous air pollutants. Exposure to VOCs can cause acute and chronic effects such as respiratory damage and can therefore, increase the risk of asthma. They can also affect the nervous, immune and reproductive systems. VOCs are pollutants that are often associated with human activities. In addition, VOCs play a significant role in the formation of oxidants such as ozone and PAN in the troposphere [1]. Thus, monitoring and modeling of the spatial and temporal distribution of those species, in particular in industrialized urban areas with high emission rates, is important for alleviation strategies concerning human health. The emission inventories for VOCs is an important factor to evaluate the effectiveness of strategies for reducing ground-level oxidants and hazardous organic compounds [2, 3]. VOCs are emitted from a variety of sources such as motor vehicle exhaust, gasoline evaporation, industrial emissions, solvent usage and vegetative burning [4-7]. Due to the variety and variability of sources involved, it may be more practical to estimate source contributions of toxic VOCs using receptor models, rather than emission-based models. Receptor modeling has been widely used for estimating source contributions for outdoor air

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pollution. Factor analysis models can extract source contributions from ambient samples without source profiles. UNMIX, multivariate receptor model, has undergone intense development and been applied in source apportionment of VOCs and particulate matter [8]. Unmix uses the ambient air measurement data alone to estimate the number of sources, the source compositions and the source contributions.

Mashhad as the biggest religious town is the second air polluted city in Iran due to the accelerated growth in urban population, industrial activity and attraction of more than 14 million pilgrims and tourists each year (second largest holy city in the world) [9]. Moreover, there are many polluting units like factories, compost plants, etc in Mashhad suburbs which are not compatible with dominant winds. Air pollution in Mashhad is responsible for a number of negative effects. It has been proved that air pollution can affect human health. These health effects include increased hospital admissions due to the exacerbation of cardiac and respiratory diseases, as well as increased mortality.

In response to this, the present study investigated, for the first time, the possible sources of VOCs using Unmix 6.0 (USEPA 2007), which was applied to data collected in the winter of 2013 in Mashhad.

MATERIALS AND METHODS

Receptor Models: Receptor models are focused on source contributions to pollution in the ambient environment from analysis of measurements at the point of impact. In mathematical terms, the general receptor modeling problem can be stated in terms of the contributions from independent sources to all chemical species in a given sample as follows [10]:

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij},$$

where x_{ij} is the jth species concentration measured in the ith sample, g_{ik} is the VOC mass concentration from the kth source contributing to the ith sample, f_{kj} is the jth species mass fraction from the kth source, e_{ij} is a residual associated with the jth species concentration measured in the ith sample and p is the total number of independent sources. Unmix has an advanced computationally intensive algorithm to estimate the number of sources that can be seen above the noise level in the data [11]. The final outputs of the UNMIX model are the estimates of the number of sources, the source composition, the average source contribution and source contribution to each sample.

UNMIX has been used in PAHs characterization studies in China [12], at a remote Vermont site [13]. For ambient VOC analysis, UNMIX has been applied at semi-urban area in the Belgrad [14], at Windsor, Canada [15] and for aircraft cabins [16]. In this study, the UNMIX version 6 receptor model developed by Henry was used to determine possible sources and source contributions to ambient concentrations of VOC. The UNMIX process starts with the normalization of data to a mean of one by dividing each measurement for a given species by the mean of all measurements of that species, in order to put all measurements on the same scale.

Site Description: The holy city of Mashhad (Latitude 36°21'28" N, Longitude 59°33'20"E) is at an elevation of 985 m above sea level. Mashhad is a big populated city and located in north-east of Iran on a plain between Binalood and Hezar-Masjed heights; Furthermore, Mashhad has temperate climate and it has about 270-300 days of thermal inversion in year. This city is home to more than 2.5 million people. In addition to this, on religious ground, this city receives over 14 million pilgrims annually. In addition to thermal inversion, air stability and lack of rain, we should acknowledge that the most important factor of Mashhad air pollution is man-made pollutions like automobiles, factories and other pollutants. According to many physicians the reason of many diseases including gastrointestinal, heart, respiratory and vascular diseases in Mashhad is breathing polluted air. On this base environment office of Khorasan Razavi province in some periods of time recommends citizens having heart and respiratory diseases not to leave their homes.

The sampling site was located at the center of the city on the flat roof of hospital (10 m above the ground). The geographical location of the sampling site is shown in Fig. 1. In brief, the sampling location is surrounded by residential and commercial areas. Distance between this site and main street is about 200m. In addition, no significant local emission sources were found near the sampling location, suggesting that the sampling location in this study is adequate for representing the mixture of various VOC emission sources. During the sampling period the weather was average for that time of year (9–21°C).

Fig. 1: Geographical location of Mashhad and the measurement site.

Ambient Data: All ambient VOC concentrations were measured by continuous online gas chromatography (autoGC). Table 1 presents the exact value of limit of detection (LOD) for all investigated compounds (µg m^{-3}).The GC system was calibrated, both at the home lab and at the sites, with a certified 27 component hydrocarbon mixture calibration gas cylinder provided by the UK National Physical Laboratory (NPL, UK). This mixture contains aromatics, alkenes, alkanes in the ppbv range. Detailed description of the procedure for data collection and GC instrumentation can be found in Leuchner *et al*. (2010) and Sarkhosh *et al* (2012). Ambient samples were acquired at a flow rate of 15 mL/min for 40 min in the morning (from 07:00am), afternoon (12:30 p.m.) and evening (04:00 p.m.). Each sample VOCs concentrations were recorded in parts per billion by carbon (ppbC).

RESULTS AND DISCUSSION

Statistical summary of average VOC concentrations during winter that used as input to Unmix is presented in Table 1. Alkane group had the highest concentration of VOCs (isobutene,n-Decane and n-butane). This result are proved by other studies [17, 18]. For example, Rodolfo Sosa *et al*., reported alkane concentrations of 202-679 ppb C in the Mexico City (July 2000- February 2001).

Table 1: Statistical summary of VOC concentrations (µg m^3)

Species name	Median	SD	Maximum
Benzaldehyde	3.23	2.16	8.41
Isobutane	5.86	4.72	111.2
Isoprene	2.41	1.05	6.36
mixed -Xylene	1.91	0.98	3.65
o-Xylene	2.78	1.94	7.74
p-Xylene	2.17	1.01	6.12
Toluene	2.07	1.11	5.42
Cyclohexane	2.26	1.78	11.41
Benzene	2.82	1.76	5.43
1-Octane	3.26	1.79	8.32
MTBE	4.46	3.75	12.77
n-Butane	4.49	7.43	51.12
1-Butene	3.23	261	18.43
Ethylene	3.4	2.65	11.54
Mesitylene	1.13	1.22	4.07
n-Decane	4.32	3.21	16.14
Ethylbenzene	2.51	1.63	7.42

Table 2: Limit of detection (LOD) for all investigated compounds

Species name	LOD (micrograms per meter cubed)
Benzaldehyde	0.009
Isobutane	0.008
Isoprene	0.009
mixed -Xylene	0.02
o-Xylene	0.02
p-Xylene	0.02
Toluene	0.009
Cyclohexane	0.008
Benzene	0.009
1-Octane	0.02
MTBE	0.009
n-Butane	0.008
1-Butene	0.008
Ethylene	0.009
Mesitylene	0.02
n-Decane	0.02
Ethylbenzene	0.02

The model predicted element concentrations were correlated with field measured results (Fig. 2). The predicted plot of Vs measured VOCs concentrations showed that the Unmix model worked well and the measured and predicted VOCs mass concentrations are in good agreement (R^2 =98). For finding variability information, correlation between measured compounds and predicted, Pearson's correlation coefficients were calculated [19].

The high correlation coefficient (r^2=0.98) was observed for all of the VOCs, e.g. mixed -Xylene (Fig.2) ($p<0.05$). This data also indicated that there was a strong control over data collection during the sampling and

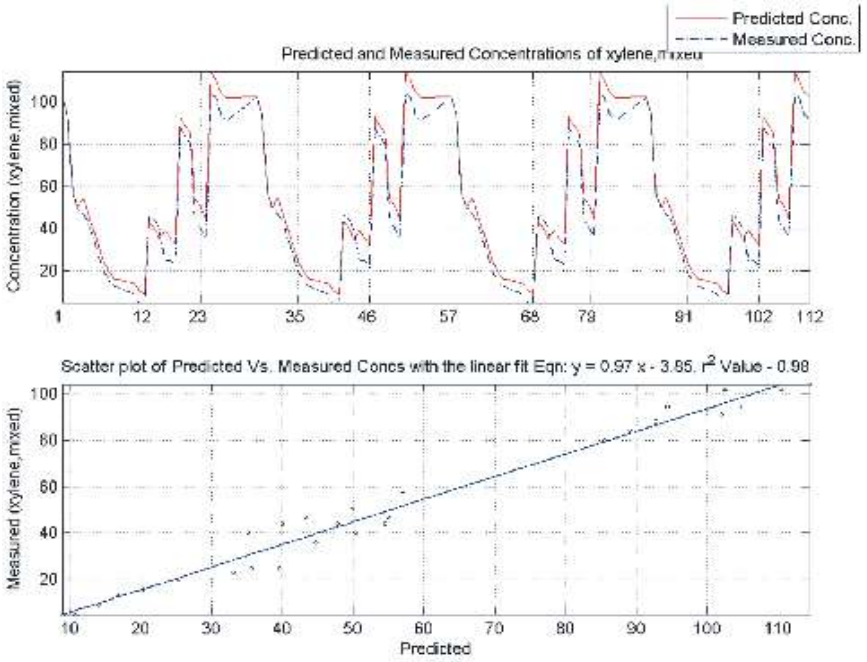

Fig. 2: Predicted versus observed concentrations of mixed -Xylene

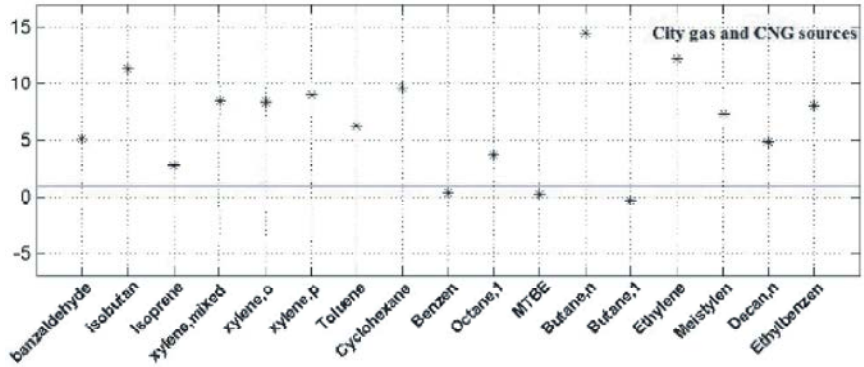

Fig. 3: signal-to-noise ratio species for City gas and CNG sources sources

analytical period. The model was frequently run applying different number of factors, minimum signal-to-noise ratio (Min. S/N), minimum R^2 and optimized% mass in order to resolve the most physically profiles of reasonable source. It was found five-factor solution via evaluating different source profiles resolved by each run. The minimum R^2 value of 0.96 and Min. S/N ratio of 2.47 are below the recommended values of 0.80 and 2.0, respectively.

Fig. 3. indicate the high SNR (signal to noise ratio) of each species for the three source. This fig indicates a High correlation between species and profile sources and verifies that Unmix model worked very well. The species profile for each of the Sources resolved by the Unmix model is showed in Fig. 4. It should be noted that bars represent relative fractions of a species to the overall mass of the respective species.

The first Source is mainly dominated by benzene, MTBE (methyl tertiary butyl ether), a gasoline additive, C8-aromatics (xylenes and ethylbenzene) and toluene. Buzcu and Fraser study (2006) [20]is proved that these elements are good markers of ‘‘vehicle exhaust’’. It should be noted that this factor had the highest contribution (59%) to the total mass of TVOC among the other factors. According to the Fig. 4 the second source profile, contributes approximately 17% to VOC mass and it is enriched with contain benzene, isobutene, MTBE, 1-butane, o-xylene, etc. [21]proved that the main origin of this source category can be gasoline vapor (fuel evaporation).

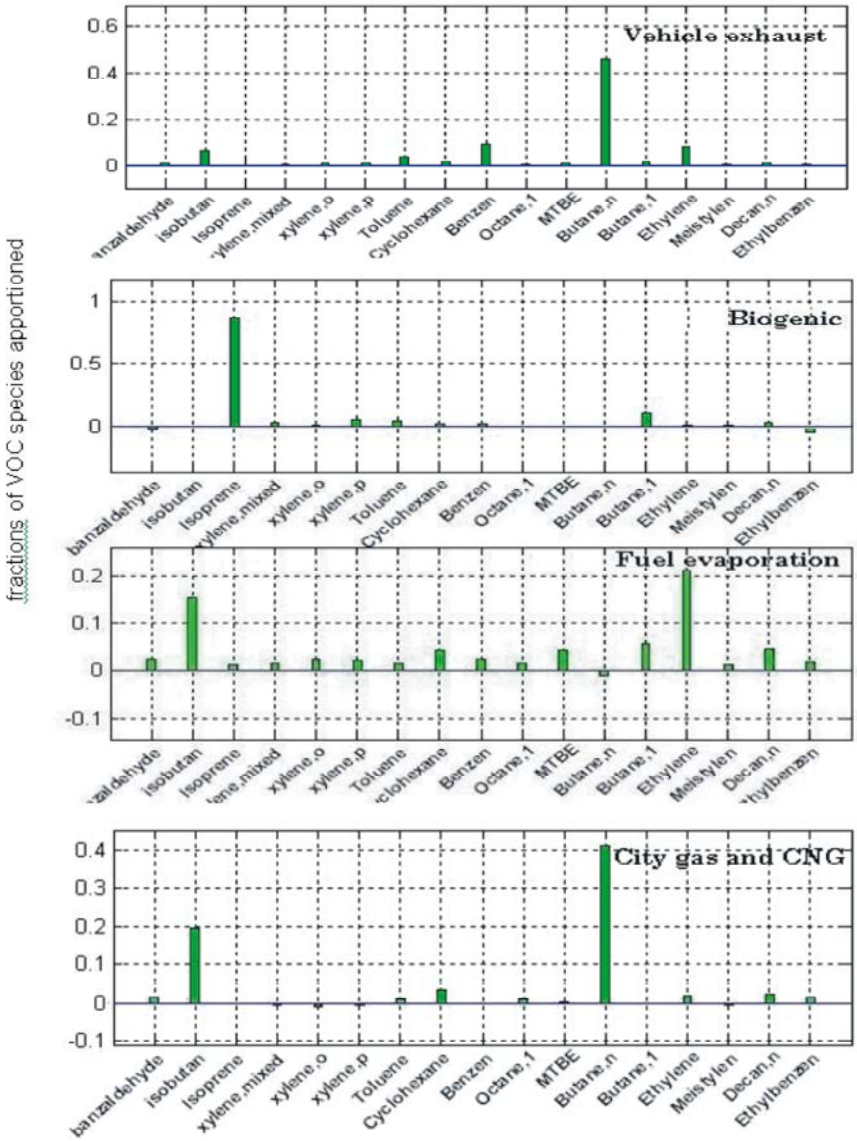

Fig. 4: Representative factor profiles by the Unmix analysis

The results of this study showed that in Mashhad city the large contribution of vehicular is not unique. We even found 39% contribution fraction from vehicle sources at traffic of China [12] and 57% in Windsor [15].

Source 3 was primarily assembled by the different compounds including isobutane and n-butane. The combination of these species is typically found in city gas and also condensed natural gas (CNG). The city gas and CNG mainly are used for cooking and heating in residential and commercial areas [15]and also instead of diesel for heavy-duty natural gas engines.

As Fig. 4 shows, source 4 was dominated by isoprene, which is an indicator of a biogenic source [21]. Biogenic VOC emissions from shrubs and trees can be determined by isoprene, which is commonly used as the marker of biogenic emissions despite its high reactivity [22]. However, due to the high reactivity of isoprene, the biogenics factor contributions should be reported with caution and viewed as a lower limit. It should be considered that Isoprene can also be characterized by industrial emissions when emitted with other industrial VOCs such as 3-methyl pentane, xylene and n-butane.

By comparison of our results with a metropolitan area that frequently experience intense smog like Los Angeles, Santiago and Mexico City, it can be concluded that the dominant sources of VOCs in this study and in other cities were motor vehicle related sources. The contribution percentage of vehicle-related

sources to ambient VOC in Mashhad city was higher than Windsor (58%) and Houston (30%)[17]. In general, the relative contribution from evaporative source for the Mashhad city was relatively lower than in Los Angeles (31%)[23]. Because evaporative emission is reduced in Mashhad fuel rationing due to recently increase of fuel prices.

CONCLUSIONS

Source apportionment was determined for the VOC samples collected by using the Unmix ver. 6.0 model of EPA in Mashhad city during the winter of 2013. A high correlation coefficient between measured and predicted values (R^2= 0.96), indicates that the data were well modeled. Unmix estimates the major source for VOCs was traffic (vehicle exhaust 59% and fuel evaporation 17%). Other sources such as City gas and CNG (21%) and biogenic source (3%) were also an important contribution.

This knowledge would be very useful in formulating effective VOC control strategies to control pollution of secondary species.

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