COMPARISON OF VOLATILE ORGANIC COMPOUNDS IN A REGULATED AND A NONREGULATED CITY ATMOSPHERE

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ABSTRACT

Volatile organic compounds (VOC) are of concern due to their adverse effects on human health and tropospheric ozone formation. Nose level measurements of 109 speciated VOCs were performed for the first time along a busy urban street in Ankara, Turkey in the summer of 2003. The sampling was conducted at consecutive 4-hour intervals over a 24-hour period for one week. Samples were collected onto cartridges packed with Tenax TA and Carbopack B resins. Analysis was performed by thermal desorption, followed by gas chromatography coupled to a mass selective detector (GC/MSD). Time resolved data provided information on ambient levels of hydrocarbons ranging from C5 to C12. Toluene, m-, p- and o-xylene, benzene and ethyl benzene were the most abundant species followed by paraffins. Diurnal variation was observed with the highest concentrations in the morning and evening rush hours. Motor vehicle emissions, as expected, were the most important source affecting temporal variations in observed concentrations of VOCs. Preliminary results were also compared with those measured at Ottawa, Canada during the summer of 2000. Two cities had similar characteristic in emission sources. In both cities emissions associated with industrial sources were negligible and motor vehicles were the major sources for VOCs in summer. The comparison of the two cities demonstrated the influence of emission control strategies on the ambient levels of VOCs and differences in the vehicle fleet characteristics in the two cities. Regulatory emissions control has been well adopted in Ottawa for over a decade whereas Turkey currently lacks of emission control regulations for VOCs.
Key words: Volatile organic compounds, urban atmosphere, motor vehicle emissions, regulation.

INTRODUCTION

Volatile organic compounds (VOC) play an important role in tropospheric ozone formation. They are the precursors for or end products of photochemical reactions that create ozone in the troposphere (Atkinson, 2000). Tropospheric ozone has adverse impacts on human health and vegetation (Lipmann, 1991; Lefohn and Foley, 1992). Many VOCs have also been identified as toxic substances, and some of them are either known or suspected carcinogens (Axelrad *et al.*, 1999; US EPA, 1993). Motor vehicle emissions are generally the major source of VOC concentrations in urban atmosphere (CCME, 1997). It has been reported that motor vehicles cause approximately 54-58% of nationwide cancer cases associated with toxic air emissions in the U.S.A. (US EPA, 1990). Other sources of VOCs include but not limited to solvent use, architectural coatings, dry cleaning, printing and various consumer products.

In order to control and reduce VOC emissions from variety of sources regulatory actions were well adopted in Canada, the United States of America and Europe. In Canada, the national criteria air contaminants (CAC) inventory (1995) identifies a total of 2429 kilotonnes (kt) of VOC emissions with the most significant sources being transportation (31%), upstream oil and gas (28%), solvent use (19%), industrial sources (10%), residential/commercial fuel/wood combustion (6%) and fuel marketing (4%) (URL1, 2004). Measures developed jointly by the federal government, provinces, and territories to reduce VOC emissions from these source categories are in the form of environmental codes, guidelines, standards, and Memoranda of Understanding (MOUs) issued by the Canadian Council of Ministers of the Environment (CCME). These measures stemmed from the 1990 CCME Phase 1 NO_x/VOC Management Plan. There are 13 codes, guidelines, standards, or MOUs for solvent-use sub sectors that have been completed and endorsed by the CCME. Measures for reduction of VOC emissions from motor vehicles are also well adopted.

The distribution of VOC emissions among all contributing source sectors in the U.S. in 1999 indicates the solvent use sector as the second largest, contributing approximately 27% of the U.S. national VOC inventory compared to 47% from transportation, the largest contributing sector (URL1, 2004). A series of measures exist at the national (federal) level, in different regional contexts and within individual States. The primary driver for these measures is the U.S. National Ambient Air Quality Standard (NAAQS) for ground-level ozone. While most of the U.S. regulatory effort affecting the solvent sector has occurred since the 1990 Clean Air Amendments, a number of the solvent subsectors had applicable federal Control Technology Guideline (CTG) documents issued in the late 1970s or early 1980s.

In Europe, emissions of ozone precursors are generated mainly from the transport sector (EEA, 2003). In Western Europe (WE), the VOC reductions resulted mainly from the introduction of catalysts on new cars, and implementation of the solvents directive in industrial processes and other uses of solvents (EEA, 2003). The approach by the European Union (EU) to the limitation of VOC emissions from organic solvents is addressed under the EU Council Directive 1999/13/EC. The 20 activities targeted for control in the directive are consistent with ones identified in Canada and the U.S. The EU directive, while primarily intended to address problems associated with VOC acting as a precursor to ground-level ozone, also targets some specific VOC compounds for more stringent control as a consequence of the direct harm they pose to human health or to the environment (URL2, 2004).

In Turkey, Air Quality Control Regulation (AQCR) that came into force in 1986 (Official Gazette numbered 19269 and dated 11.02.1986) includes limit values for air pollutants in ambient air and emission values from industrial facilities that must be complied. The regulation also sets emission limit values for BTEX compounds and olefins emitted from refineries and petrochemical plants. There are no other limit values or statements exist for VOC emissions from various sources or in ambient air in the AQQR. When the scientific background and regulatory actions in Turkey are compared with those of in Canada, the U.S. and Europe, it is seen that detailed investigations on the sources and control strategies of VOCs in Turkey should be accomplished. This research provides the preliminary data of the field measurements conducted in Ankara, Turkey and Ottawa, Canada to investigate levels and sources of VOCs in urban atmospheres and to compare differences.

METHODOLOGY

Ankara is the capital of Turkey and it is mainly occupied by the governmental institutions, universities and residential housing. Ankara lacks of heavy industrial facilities and thus the motor vehicle emissions are expected to be the major sources of VOCs in the city. Roadside sampling of VOCs were performed in the summer of the year 2003 for one week. Roadside sampling station was located at the downtown area, on a busy street namely the Atatürk Boulevard. This part of the city is mainly occupied by commercial buildings, foreign embassies, banks, and various government buildings. The sampling station was about 2 m from the curb and located on a junction. Sample inlet ports were approximately 1.5 m from ground level. Samples were collected at consecutive sessions of four hours and three times a day. The morning session was conducted between 8:00 and 12:00, the noon session was between 12:00 and 16:00 and the afternoon session was performed between 16:00 and 20:00. The morning and evening sampling sessions cover traffic rush hours.

Samples were collected onto cartridges packed with Tenax TA and Carbopack B resins via air sampling pump. The sampling flow rate was 20 mL min^{-1}. Breakthrough tests were conducted before starting the campaign and during the campaign. None of the target compounds were detected at the breakthrough tubes at a significant amount. Samples were brought to the laboratory immediately after collection for subsequent analysis. Analysis was performed by thermal desorption, followed by gas chromatography coupled to a mass selective detector (GC/MSD). Laboratory and field blanks were also analyzed. Analytical method validation was performed by investigation of method detection limit, linearity, precision and recovery.

An ambient sampling program was carried out on Slater Street in Ottawa, Canada during the summer of 2000 for one week. The ambient sampling stations were located beside a major public transit bus stop on a one-way artery so-called Slater Street, which is a major one-way artery running west to east through the downtown core and carrying approximately 750 vehicles per hour during the sampling periods. Nose-level samples were collected over 2-hour periods during the morning rush (7:30-9:30), mid-day (11:30-1:30) and evening rush (3:30-5:30. The roadside sampling station was set-up at pedestrian nose-level, approximately 1.5 m above the sidewalk, 60 cm from the curbside. Samples were collected in pre-cleaned, proofed and evacuated 6 L Summa canisters equipped with a flow controlling head assembly. Laboratory analyses were carried out for 165 VOCs at ERMD laboratories. The VOCs were determined using a Hewlett Packard 5890 Series II gas chromatograph with an Entech M7000 cryogenic concentrator for sample concentration and introduction. The quantification limits for this set of analytical conditions is approximately 0.2 to 0.5 ng/L.

RESULTS AND DISCUSSION

Results of the ambient samples collected at the roadside station during summer of 2003 in Ankara, Turkey are presented in Table 1 for selected compounds. The compounds given in the table are the dominating compounds in all sessions and they account for approximately 80% of the total concentrations measured at roadside station. Toluene was the most abundant compound having a median concentration value of 14.38 ng L^{-1}. Next abundant specie was the m,p-xylene followed by 2-methyl-butane and benzene. Diurnal variation of the data was

also investigated. Highest concentration values were observed during afternoon and morning sessions, coinciding with traffic rush hours. The results of the VOC measurements performed in the Ottawa roadside microenvironment are also presented in Table 1. Ankara and Ottawa had similar characteristic in emission sources. In both cities industrial emissions were negligible and motor vehicles were the major sources for VOCs in summer. Although meteorological conditions might influence the results, such a comparison between two cities may provide a broad view of the influence of emission control strategies on the ambient levels of VOCs and differences in the vehicle fleet characteristics in the two cities.

Table 1. Comparison of Roadside VOC Values Measured in Two Cities

	Ankara	**Ottawa**
	Median (ng L^{-1})	**Median (ng L^{-1})**
Olefins		
n-Pentane	3.61	2.56
2-methylbutane	7.53	7.97
2,2-dimethylbutane	2.05	0.51
n-Hexane	2.16	1.21
2,3-dimethylbutane	1.26	0.84
Methylcyclopentane	1	1.26
2-methylpentane	4.36	2.63
n-Heptane	1.28	0.66
3-methylpentane	3.55	2.25
2-methylhexane	1.52	0.9
n-Octane	0.5	0.45
3-methylhexane	1.58	1.3
n-Nonane	0.54	0.19
n-Decane	1.02	0.38
Aromatics		
Toluene	14.38 (8.79-57.13)	7.23 (2.21-12.08)
m,p-Xylene	12.57 (4.11-29.84)	3.24 (BDL-5.27)
Benzene	5.50 (3.16-13.53)	2.18 (0.72-3.26)
o-Xylene	4.39 (0.85-10.75)	1.19 (BDL-2.25)
Ethylbenzene	3.89 (2.19-9.22)	1.48 (BDL-3.18)

Ranges are given in parenthesis for aromatic VOCs.

As can be seen from Table 1, VOC concentrations measured in Ankara were about twice higher than that were measured at Ottawa roadside station. The variability of the data collected in Ottawa was also less than that was observed in Ankara. For instance, toluene had maximum and minimum concentration values of 57.13 and 8.79 ng L^{-1}, respectively, for the Ankara sampling campaign. These values were 12.08 and 2.21 ng L^{-1} for Ottawa sampling campaign. Although median concentration value of toluene measured in Ankara was only two times higher than that was measured in Ottawa, minimum and maximum values measured in Ankara were about four to five times more than that were measured in Ottawa. Higher variability in the Ankara data might be due to different emission characteristic or partly due to meteorological conditions.

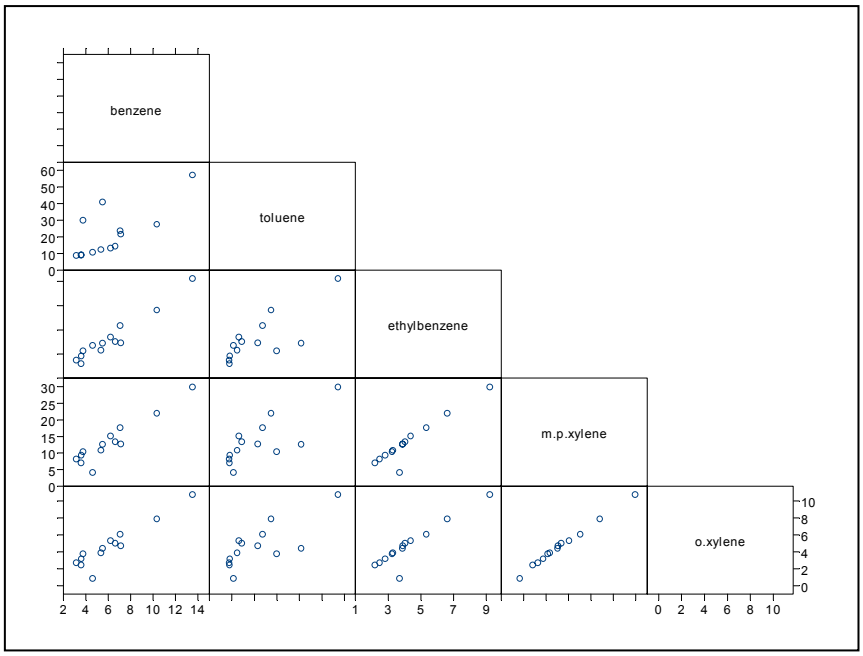

Figure 1. BTEX correlation matrix of Ankara data.

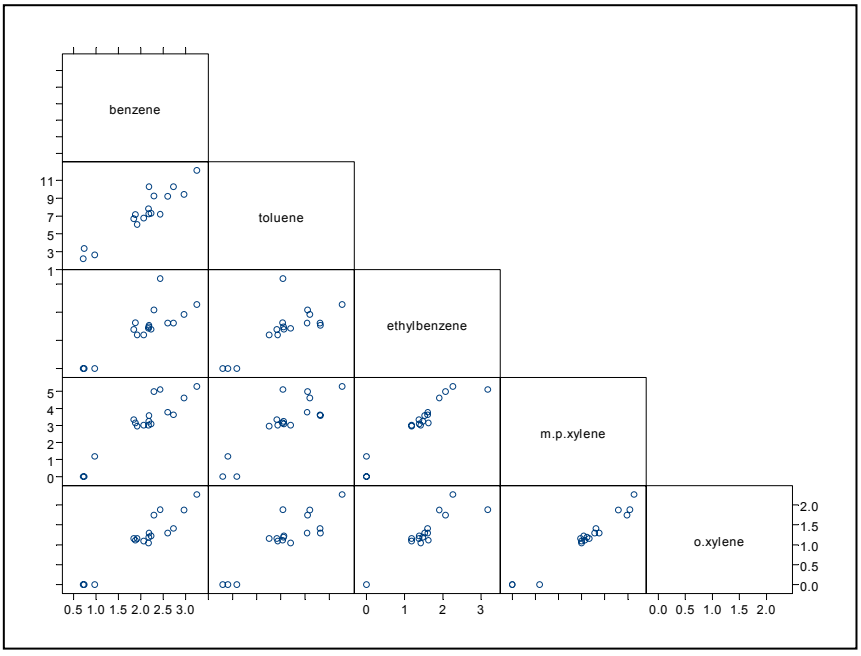

Figure 2. BTEX correlation matrix of Ottawa data.

Correlation matrices drawn for the BTEX compounds were presented for Ankara and Ottawa data in Figure 1 and 2, respectively. Linear regression was used to assess the preliminary source identification in both cities. Benzene has been used as the reference compound of motor vehicle source (Derwent et al., 2000). Investigation of Figure 1 for correlation of compounds with benzene yields that concentrations of all compounds showed a good correlation with benzene except toluene concentrations. Toluene concentrations also showed poor correlation with ethylbenzene, m,p-xylene and o-xylene concentrations. This indicates

that BEX compounds were mainly associated with motor vehicle sources whereas toluene might have other additional sources. Paint and solvent use might be other sources of toluene measured in Ankara. Further detailed investigation are planned to be performed.

Figure 2 showed that concentration of TEX compounds were correlated with that of benzene. Correlation between individual species was similar. Thus, the main source of the BTEX concentrations measured in Ottawa during summer was motor vehicle. Detailed investigation of source contribution will be performed by receptor modeling. Differences in the type of sources in two cities might be due to different emission control regulations. Canada had adopted measures to regulate VOC emissions from various sources whereas Turkey lacks of emission control regulations for VOCs.

CONCLUSIONS

Roadside measurements of speciated VOCs were performed along busy urban streets at a regulated (Ottawa, Canada) and a non-regulated (Ankara, Turkey) city atmosphere. VOC concentrations measured in Ankara roadside environment during summer were about two times more than that were measured in Ottawa. The variability of the data recorded in Ankara was also higher than the Ottawa data. Poor toluene to benzene correlation observed in Ankara indicated additional VOC sources to motor vehicles in this city. Although the differences in meteorological conditions might have and influence in the observed differences, regulatory actions play more critical role in the differences observed in two cities. It is necessary to prepare and implement a proper VOC management plan and regulatory actions in Turkey.

REFERENCES

Atkinson, R., 2000. "Atmospheric Chemistry of VOCs and NOx", *Atmospheric Environment*, 34, 2063-2101.

Axelrad, D.A., Morello-Frosch, R.A., Woodruff, T.J., and Caldwell, J.C., 1999. "Assessment of estimated 1990 air toxics concentrations in urban areas in the United States", *Environmental Science and Policy*, Vol. 2., pp. 397-411.

CCME-Canadian Council of Ministers of the Environment, 1997. "Canadian 1996 NOx/VOC Science Assessment, Ground-level ozone and its precursors, 1980-1993", ISBN 1-896997-00-7, February.

Derwent, R.G., Davies, T.J., Delaney, M., Dollard, G.J., Field, R.A., Dumitrean, P., Nason, P.D., Jones, B.M.R., Pepler, S.A., 2000. "Analysis and interpretation of the continuous hourly monitoring data for 26 C2-C8 hydrovarbons at 12 United Kingdom sites during 1996", *Atmospheric Environment*, 34, 297-312.

EEA, 2003. "Europe's environment: the 3rd assessment", European Environment Agency, Copenhagen, p 122.

Lefohn, A.S., and Foley, J.K., 1992. "NCLAN results and their application to the standard-setting process: protecting vegetation from surface ozone exposures", *Air & Waste Management Association*, Vol. 42, pp. 1042

Lippmann, M., 1991. "Health effects of tropospheric ozone", *Environmental Science and Technology*, Vol. 25, pp. 1925

URL1, 2004. "Future Canadian Measures for Reducing Emissions of Volatile Organic Compounds (VOC) from Consumer and Commercial Products", Environment Canada, http://www.ec.gc.ca/nopp/DOCS/consult/voc-cov/cons-2003/en/dp3.cfm

URL2, 2004. "A Federal Agenda for Reduction of Emissions of Volatile Organic Compounds from Consumer and Commercial Products", Environment Canada, http://www.ec.gc.ca/nopp/DOCS/notices/voc/en/supportDoc_p4.cfm

US EPA, 1990. "Cancer Risk from Outdoor Exposure to Air Toxics", Vol. 1, Final Report, EPA, 450/1-90-004a. Office of Air Quality Planning Standards, Research Triangle Park, NC, USA.

US EPA, 1993. "Motor Vehicle Related Air Toxics Study", U.S. Environmental Protection Agency, Office of mobile sources, Office of Air and Radiation: Ann Arbor, MI.