Environmental Monitoring and Assessment (2005) **107:** 363–373
DOI: 10.1007/s10661-005-3546-8

VARIABILITY IN VOC CONCENTRATIONS IN AN URBAN AREA OF DELHI

ANJALI SRIVASTAVA
National Environmental Engineering Research Institute (NEERI), Mumbai Zonal Laboratory, 89/B, Dr. A. B. Road, Worli, Mumbai 400 018, India
(e-mail: srivastv@vsnl.com)

(Received 18 May 2004; accepted 20 September 2004)

Abstract. The variability of pollutants is an important factor in determining human exposure to the chemicals. This study presents the result of investigation of variability of Volatile organic compounds (VOCs) in urban area of Delhi, capital of India. Fifteen locations, in five categories namely residential, commercial, industrial, traffic intersections and petrol pump were monitored for one year every month during peak hours in morning and evening. Measurement focused on target VOCs as defined by USEPA. Variability was divided into measurement, spatial, temporal and temporal–spatial interaction components. Temporal component along with temporal–spatial interaction were found to be the major contributors to the variability of measured VOC concentrations. Need of continuous monitoring to capture short-term peak concentration and averages is evident.

Keywords: VOC, variability, ambient air, urban Delhi

1. Introduction

Volatile organic compounds (VOC) are known to be harmful to human health, ecosystem and atmosphere (Edgerton *et al*., 1989; Atkinson, 2000; Derwent, 1995; Kuran and Sojak, 1996; Dewulf and Langenhove, 1997). Some VOCs are highly toxic and mutagenic (Duce *et al*., 1983; Sweet and Vermette, 1992; Kostianen, 1995; Mukund *et al*., 1996). Considering the ill effects on human health there have been many studies to assess the concentrations of hazardous air pollutants including VOCs in the atmosphere of urban environment. (Singh *et al*., 1983; Hunt *et al*., 1998; Staten Island Report, 1997). In order to formulate effective VOC control policy, modeling studies leading to source apportionment and fate of observed VOC concentrations have been carried out (Fugita and Lu, 1998a, b; Fugita *et al*., 1994, 1995; Scheff and Wadden, 1993, 1996; Watson *et al*., 2001; Ying *et al*., 2003; Baldsano *et al*., 1998; Edwards *et al*., 2001; Jorquera and Rappengluck, 2004), but questions regarding spatial and temporal variability of VOCs still remain unanswered. Studies on spatial and temporal variability of concentrations of pollutants in urban areas are few. (Ding and Wang, 1998; Upmanis *et al*., 2001; Pleil *et al*., 1993) Such information is required to determine the optimum sampling period, frequency to capture short-term peak concentrations, optimum number and locations of monitoring sites for population exposure assessment.

Knowledge of variability of concentration within each microenvironment and between similar microenvironments is important in design of monitoring programmes and in the application of exposure models. Spatial and temporal variability of VOCs in urban areas for Indian cities is almost totally lacking. This paper deals with estimating spatial variability of VOCs between similar locations in urban areas of Delhi using statistical analysis procedures.

2. Study Design

Delhi is capital of India covering approximately 1500 sq. km and east west width approximately 51.9 km and northwest width approximately 48.48 km. The spread of Delhi is somewhat circular. Transportation network is predominately road-based with road length of 1248 km per 100 sq. km. The road network in the city is 22.487 km long. Spatial variability of VOCs in outdoor air was investigated through measurement at a network of fifteen locations in five category namely residential, industrial, commercial, traffic intersections and retail refueling stations (Figure 1). Three locations of each category were chosen and monitoring during peak activity hours twice a day (0800–1200 h, 1700–2100 h) every month during 2001 was carried out.

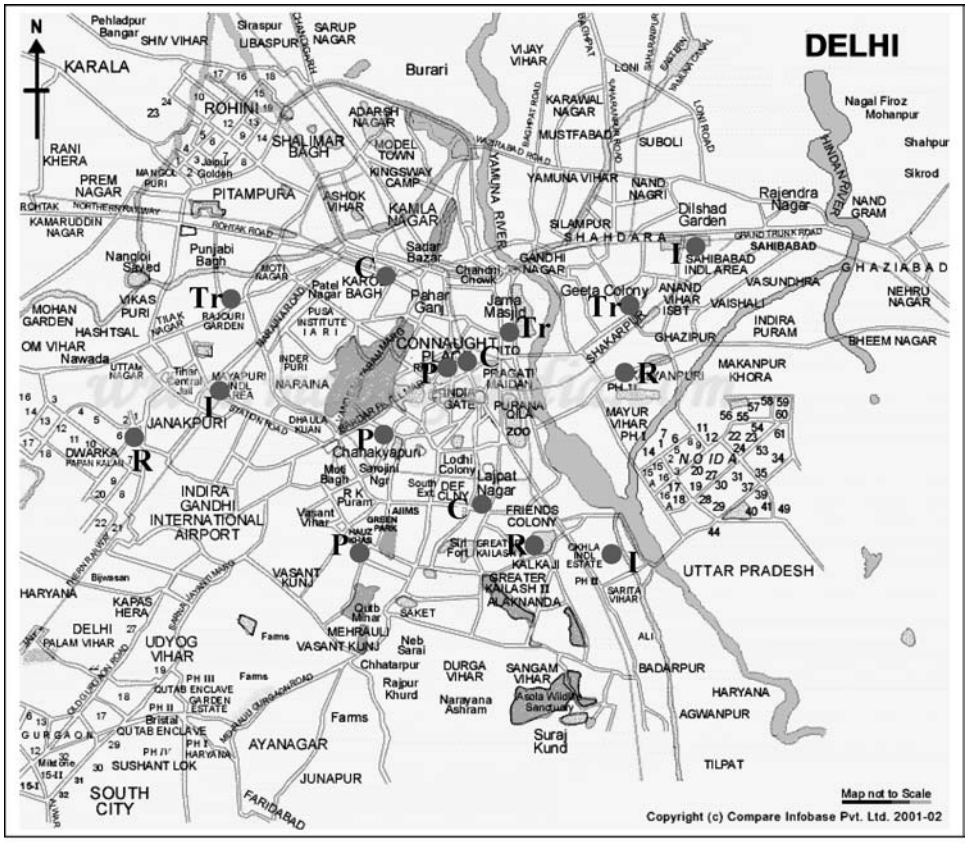
The sampling locations were selected on the basis of predominant activities in the area. All residential locations were typically residential and air quality is mainly influenced by domestic activities, vehicular movement, roadside eat outs and open burning of leaves, garbage etc. At the commercial locations air quality is influenced by restaurants, open eat outs, heavy (Truck, buses etc) and light duty vehicles (two wheelers, three wheelers and cars), generators, cinema halls and parking lots.

All the three industrial locations are purely industrial with no mixing of residential or commercial areas. Solvent use, degreasing, cable tire manufacturing, equipment manufacturing, vehicular combustion DG sets. Diesel internal combustion engines, air conditioning exhaust are major contributors to air pollution.

All the traffic intersections selected area busy intersections and witness frequent traffic jams during peak hours and average vehicular speed of 20–25 km/h. Monitoring was carried out at the kerb side of the intersections.

At the refueling stations monitoring was carried out at the centre of petrol pumps were vehicles halt for refueling. Degreasing activity is observed at these locations and they are about 500 m from the road.

Target VOCs specified in USEPA Compendium Method TO-14 (Table I) were monitored as four hourly averages using adsorption, thermal desorption and subsequent analysis on GC-MS. First three abundance were matched with NIST 98 library to identify the VOCs. Dr. Erhenstrofer standard VOC mix 15 was used to draw calibration curves for quantification of VOCs.



R= Residential, C=Commercial, I = Industrial, Tr = Traffic Intersection, P = Petrol Pump

Figure 1. Sampling locations in National Capital Region, Delhi.

3. Results and Discussions

Some VOCs were present in all the samples whereas some of them were present in some samples. Table II gives the percentage of samples from fifteen spatial locations that contained measured VOC during different seasons. These results shows that many of the VOCs are ubiquitous in Delhi's urban environment and point to the fact that exposure to these is likely to be extensive. This table shows that many of the chemicals monitored as target VOCs in compendium method TO-14 are rarely present in urban ambient air of Delhi. It is observed that percentage of samples in which VOCs are detected is higher during winter as compared to monsoon and summer. There is no national ambient air quality standard for VOCs and EPA does not list VOCs as criteria air pollutants. WHO has defined some guideline values for individual substances based on effects other than cancer and odour annoyance. A higher concentrations of benzene were observed in all the

TABLE I
Compendium method TO-14–target compound list (TCL)

1.	Dichlorodifluoromethane	22.	Trans-1,3-dichloropropene
2.	Methyl Chloride	23.	1,1,2-trichloroethane
3.	1,2-dichloro-1,1,2,2-tetrafluoroethane	24.	Toluene
4.	Vinyl Chloride	25.	1,2-dibromoethane
5.	Methyl Bromide	26.	Tetrachloroethane
6.	Ethyl Chloride	27.	Chlorobenzene
7.	Trichlorofluoromethane	28.	Ethyl Benzene
8.	1,1-dichloroethane	29.	M, p-xylene
9.	Dichloromethane	30.	Styrene
10.	3-Chloropropene	31.	1,1,2,2-tetrachloroehtane
11.	1,1,2-trichloro-1,2,2-trifluoroethane	32.	O-xylene
12.	1,1-dichloroethane	33.	4-ehtyl toluene
13.	Cis-1,2-dichloroethane	34.	1,3,5-trimethylbenzene
14.	Trichloromethane	35.	1,2,4-trimethylbenzene
15.	1,2-dichloroethanero	36.	M-dichlorobenzene
16.	1,1,1-trichloroethane	37.	Benzyl chloride
17.	Benzene	38.	P-dichlorobenzene
18.	Carbon tetrachloride	39.	O-dichlorobenzene
19.	1,2-dichloropropane	40.	1,2,4-trichlorobenzene
20.	Trichloroethene	41.	Hexachlorobutadiene
21.	Cis-1,3-dichloropropene		

samples and the values were much above WHO guideline concentration of 5–20 $\mu g/m^3$. Concentrations of other VOCs for which WHO guidelines is available like toluene, dichloromethane, 1,2-dichloroethane are well within the guideline values. Large fluctuation in concentrations of benzene, toluene, ethylbenzene, m-xylene and chloroform is shown by high standard deviation observed. Various components of variability for pollutants observed in more than 60% of the samples were examined.

The mean and standard deviations for the pollutants for each micro environment are mentioned in Table III. For each pollutants standard deviation (S.D.) shows total data variability. The standard deviation includes all sources of variability, which is measurement, temporal and spatial components.

Significance of variability can be measured in terms of relative standard deviation (R.S.D.), which is expressed as ratio of the standard deviation to the mean concentration.

Figure 2 shows the relative standard deviations for the pollutants measured in the present study. Many chemicals show low R.S.D. values. These can be expected to be uniformly distributed in space. Benzene, ethyl benzene, xylene, toluene, and

TABLE II
Seasonal variation of percentage of samples in which VOCs were measured

	Residential				Commercial				Industrial				Traffic intersection				Petrol pump			
	W	M	S	Ann	W	M	S	Ann	W	M	S	Ann	W	M	S	Ann	W	M	S	Ann
Toluene	100	100	100	100	100	100	100	100	100	100	75	92	100	89	100	96	100	89	100	96
Benzene	100	100	67	89	100	94	100	98	100	78	67	81	100	89	100	96	100	89	100	96
m-Xylene	72	56	54	61	100	78	33	70	98	78	25	67	100	67	25	64	100	83	41	75
Ethylbenzene	100	67	58	75	100	78	25	68	100	67	25	64	100	67	25	64	100	72	25	66
Naphthalene	100	89	25	71	100	78	25	68	67	67	21	51	100	67	25	64	100	67	25	64
Benzene, 1,3,5-trimethyl	10	50	4	21	97	61	21	60	90	67	21	59		50		17	100	61	25	62
Benzene, 1,2,4-trimethyl	10	17	4	10	47	39	13	33	80	67	21	56	28	20	8	19	97	50	21	56
p- Isopropyl toluene		6	4	3													97	50	17	54
Ethane, 1,2-dichloro-																	97	39	21	52
Isopropylbenzene	30	44	13	29	37	50	8	32	20	39		20		50		17	67	50	17	44
methylene chloride	43	11		18	20	11	17	16	47	39	29	38	23	11	21	18	57	28	42	42
Carbon Tetrachloride		6	21	9	33	22	17	24	33	44	17	31	50	22	17	30	67	22	25	38
Chloroform	20	22	42	28	23	44	38	35		56	33	30	43	39	50	44	60	44	8	38
n-Propylbenzene	33	33	8	25	63	44	17	41	53	39		31	67	11	17	31	63	33	13	36
sec-butylbenzene	10	6		5		11		4	33	17	8	19					33	22	8	21
Nbutylbenzene		6		2						6		2					33	17	8	19
Dichloromethane																	33	17	8	19

(*Continued on next page*)

TABLE II
(*Continued*)

	Residential				Commercial				Industrial				Traffic intersection				Petrol pump			
	W	M	S	Ann	W	M	S	Ann	W	M	S	Ann	W	M	S	Ann	W	M	S	Ann
Methane bromochloro	53	28	8	30		11		4	33	22	8	21	33	22	8	21	23	22	8	18
Propane 2 2 dichloro	3			1									57	22	13	30	33	11	8	18
o-Xylene	10	11	4	8	33	22	4	20	30	11		14	33	28	8	23	33	11	8	18
t-butylbenzene						6		2		6		2					30	17	4	17
Propane, 1,3-dichloro-																	30	11	8	16
Ethane 1 1 1 trichloro	3			1	10			3	100	67	25	64	17			6	30	11	8	16
Trichloroethylene																		6	4	3
sec-butylbenzene		6		2																
Propane, 1,2-dichloro-										11		4								
Ethene, 1,1-dichloro-		11		4																
Ethene, 1,1-dichloro-	10			3						11		4								
Ethane, 1,1,2,2-tetrachl						6		2												
Benzene, 1,4-dichloro-									30		8	13								
Benzene, 1,3-dichloro-													33	11	8	18				
Benzene, 1,2-dichloro-						6		2						6		2				

W – winter, M – monsoon, S – summer, Ann – annual.

TABLE III
Mean and standard deviation of measured VOCs

	Residential		Commercial		Industrial		Traffic intersection		Petrol pump	
	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.
Benzene	24.57	12.21	417.34	255.37	207.77	88.99	299.61	110.45	398.15	83.81
Benzene, 1,2,4-trimethyl	0.29	0.28	6.14	9.26	0.41	0.16	0.17	0.05	1.03	1.15
Benzene, 1,3,5-trimethyl	0.40	0.21	10.86	17.22	0.53	0.32	0.62	0.21	1.02	1.21
Carbon Tetrachloride	4.09	2.05	7.05	7.61	2.85	1.15	2.54	1.41	7.84	11.31
Chloroform	10.99	4.58	7.34	3.11	7.15	2.08	3.29	0.48	6.69	4.12
Ethane 1 1 1 trichloro	0.61	0.65	5.13	4.47	2.00	2.94	0.77	0.83	1.17	0.01
Ethylbenzene	2.57	1.79	28.77	26.07	30.07	22.34	33.85	12.11	2.31	0.80
iso-Propylbenzene	0.20	0.18	12.34	20.67	0.29	0.25	0.11	0.06	0.63	0.78
Methane bromochloro	5.35	4.29	7.67	4.10	13.20	9.23	4.08	2.57	2.77	0.01
Methylene chloride	13.63	8.11	12.65	4.64	12.11	7.39	20.72	6.36	9.73	4.45
m-Xylene	7.18	5.92	47.58	39.84	14.61	20.58	24.62	11.09	2.37	0.85
Naphthalene	0.39	0.30	0.62	0.53	0.72	1.19	1.04	1.48	0.14	0.14
n-Butylbenzene	0.76	0.00	14.19	19.37					1.23	0.71
n-Propylbenzene	1.03	0.93	8.41	11.77	1.81	2.29	0.51	0.47		
o-Xylene	0.96	0.91			0.47	0.36	1.05	1.21	3.99	0.01
p-Isopropyl toluene	0.14	0.01							0.25	0.37
Propane 2 2 dichloro	31.04	0.01					1.67	2.14	0.16	0.10
p-Xylene	0.26	0.16	1.07	0.96	1.53	2.23	0.90	0.21	0.80	1.05
sec-butylbenzene	0.04	0.01	0.09	0.12	0.11	0.00			0.02	0.01
Toluene	28.18	16.79	115.04	57.43	47.17	11.08	34.47	5.29	46.34	14.01
Trichloroethylene			0.35	0.01	0.77	0.59	1.99	0.01	33.33	0.01
Benzene, 1,4-dichloro-					0.20	0.01				
Benzene, n-butyl-					0.16	0.01				
Ethene, 1,1-dichloro-					0.06	0.01				
Propane, 1,2-dichloro-					0.06	0.01				
Benzene, 1,3-dichloro-							0.12	0.01		
Benzene, tert-butyl-									0.20	0.01
Ethane 1 1 dichloro									0.91	0.56

Note. All mean concentrations values are in $\mu g/m^3$.

Naphthalene show R.S.D. values between 1 and 2 while all other VOCs measured shows a R.S.D. value of greater than 4 with a maximum of 9 for secondry Butylbenzene.

To apportion the variability observed for each pollutant into measured, spatial, temporal and temporal–spatial interaction components analysis of variance was performed. SPSS package was used for analysis. The results are presented in Table IV for the pollutants detected in more than 60% of the samples. In this analysis total variance is broken down into four parts namely a measured component, spatial

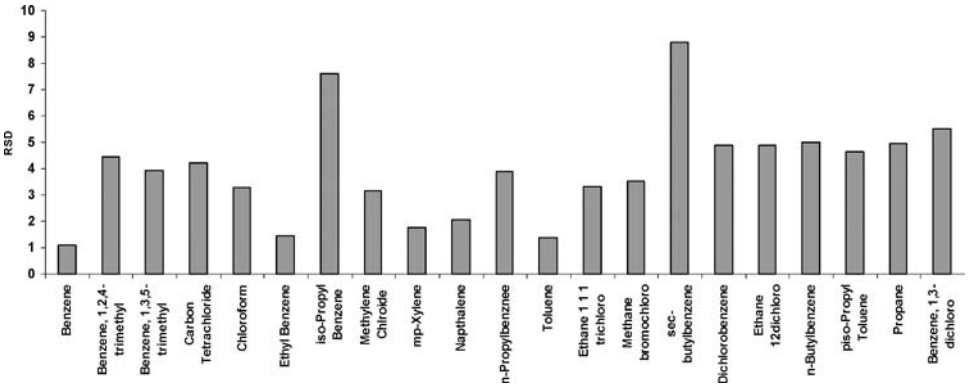


Figure 2. Relative standard deviation for frequently detected VOCs.

component, temporal and temporal–spatial interaction component. Each measured concentration can be represented in terms of these components as follows:

$$a_{\mathrm{ijk}} = \mu + \varepsilon_{\mathrm{ijk}} + \alpha_{\mathrm{i}} + \beta_{\mathrm{j}} + \alpha\beta_{\mathrm{ij}} \tag{1}$$

where a_{ijk} is the concentrations of kth sample measured at the jth time period at the ith spatial site; μ is the overall mean concentration in all samples, $\varepsilon_{\mathrm{ikj}}$ is the effect of measurement error on the kth sample, measured at the jth time period of the ith spatial site. α_{i} is the effect of site i, which accounts for difference between the mean concentrations measured at site i and the mean concentrations in all samples. β_{j} is the effect of time j, which accounts for difference between the mean concentrations at time j and the mean concentration in all samples.

$$\alpha\beta_{\mathrm{ij}} = \mu_{\mathrm{ij}} - (\mu + \alpha_i + \beta_i) \quad \text{is the interaction affect of site } i \text{ and time } j \tag{2}$$

where μ_{ij} is the mean concentrations for site i and time j. Thus the measurement, spatial, temporal and spatial–temporal interaction variance components represent the variability in pollutant concentrations due to effects $\varepsilon_{\mathrm{ijk}}$, α_{i}, β_{j} and $\alpha\beta_{\mathrm{ij}}$, respectively.

Measurement variability can arise from variability introduced by the sampling and analysis methods and from actual atmospheric concentrations variability. To uncouple the two sources information on precession of sampling and analysis method under actual field conditions is required. Information on sampling and analysis variability was obtained by collection of duplicate samples. The differences between parallel measurements were attributed to measurement variability.

The concentrations difference measured from one site to the other averaged across all time periods is given by spatial component. The differences in concentrations measured from one time period to the other averaged across all sampling

TABLE IV
Analysis of variance results – factors contributing to variability

	Components of variability (%)			
	Measured	Spatial	Temporal	Spatial-temporal interaction
Residential				
Benzene	3	1	12	84
Toluene	5	3	10	82
Naphthalene	15	3	15	67
Ethylbenzene	10	5	15	70
mp-Xylene	10	6	19	65
Commercial				
Toluene	5	2	35	58
Benzene	3	2	36	59
Ethylbenzene	10	5	26	59
mp -Xylene	10	4	18	68
Naphthalene	15	10	25	50
Benzene, 1,3,5-trimethyl	20	18	25	37
Industrial				
Toluene	5	3	32	60
Benzene	3	2	29	66
mp-Xylene	10	5	40	45
Benzene, 1,2,4-trimethyl	7	15	31	47
Benzene, 1,3,5-trimethyl	20	13	25	42
Ethane 1 1 1 trichloro	5	20	41	34
Ethylbenzene	10	7	25	58
Traffic intersection				
Benzene	3	5	15	77
Toluene	5	6	18	71
Ethylbenzene	10	5	16	69
mp-Xylene	10	8	17	65
Naphthalene	15	10	28	47
Petrol pump				
Benzene	3	2	20	75
Toluene	5	2	18	75
mp-Xylene	10	5	24	61
Ethylbenzene	10	5	25	60
Naphthalene	15	8	31	46
Benzene, 1,3,5-trimethyl	20	10	25	45
All category locations				
Toluene	5	15	28	52
Benzene	3	10	30	57
Naphthalene	7	22	30	41
Ethylbenzene	10	18	32	40
mp -Xylene	10	26	31	33

sites is quantified by temporal component. Concentration differences systematically observed from one time period to other, but for which the magnitude of these systematic differences varied from one sampling site to other is represented by temporal–spatial interaction. This component also includes random differences observed among the sites and hence would also account for the variability caused by local emissions and wind direction.

Variance contribution from the four-variance component were calculated with an expected mean square analysis (Neter and Wasserman, 1974).

The results for analysis of variance shows that maximum variability is introduced due to spatial and temporal interactions. The measurement variability varied from 3 to 20 and spatial variability from 1 to 20 amongst same category of locations and from 10 to 26 amongst all the locations of different categories. Temporal variability is the second major component contributing to variability in concentrations of VOCs in Delhi. Complexities are introduced by diurnal variations in local sources, local effects of wind, other meteorological conditions, and local factors. Mean concentrations at a particular site and time may thus vary significantly from what would be predicted from observed site and time effects. These complexities in pollutant concentrations, which vary both by site and time result in, joint temporal–spatial variability. Large temporal spatial interaction in attributed to high concentrations measured at few time periods at one or more sites.

4. Conclusion

The factors contributing to variability of VOC concentration in urban area of Delhi was studied in the present work. Fifteen locations covering five categories namely residential, commercial, industrial, traffic intersections and petrol pumps were monitored for a period of one year during morning and evening hours. The results shows that variability in VOC concentrations are mainly introduced by temporal component that is diurnal variations – local sources, meteorology etc. at the time of monitoring and temporal and spatial interactions and complexities arising due to time factor and site locations both. The results stress the need of continuous monitoring at sensitive sites to capture realistic short-term peak concentrations and averages. The knowledge of these concentrations are necessary to formulate policies to avoid undesirable health impacts due to exposure.

Acknowledgments

The author wishes to acknowledge Scientist and Head, Delhi Zonal Centre, Dr. R. C. Dixit, Dr. M. Prakash, Scientist, Delhi Zonal Centre and project assistant Ms. A. E. Joseph, Mr. S. Patil, Mr. A. More, for their contribution during the field measurements. The author also wishes to thank Director NEERI, Dr. S. Devotta for his encouragement and Central Pollution Control Board for funding the study.

References

Atkinson, R.: 2000, *Atmos. Environ.* **34**, 2063–2101.

Baldsano, J. M., Delgado, R. and Calbo, J.: 1998, *Environ. Sci. Tehcnol.* **32**, 405–412.

Derwent, R. G.: 1995, *Environ. Sci. Technol.* **4**, 1–15

Dewulf, J. and Langenhove, H. Van: 1997, *Atoms. Environ.* **31**, 3291–3307.

Ding, W. H., Wang, J. L.: 1998, 'Spatial concentration profiles of C_2-C_6 hydrocarbons in the atmosphere of Taipei', *Chemosphere* **37**, 1187–1195.

Duce, R. A., Mohnen, V. A., Zimmerman, P. R., Grosjean, D., Cautreels, W. J., Chatfield, R., Jaenicke, R., Ogren, J. A., Pellizzari, E. D. and Wallace, G. T.: 1983, *Rev. Geophys. Space Phys.* **21**, 921–952.

Edgerton, S. A., Holdren, M. W. and Smith, D. L.: 1989, *JAPCA* **39**, 729–732.

Edwards, R. D., Jurvelin, J., Korstinen, K., Saarela, K. and Jantunen, M.: 2001, *Atmos. Environ.* **35**, 4829–4841.

Fujita, E. M. Watson, J. G., Chow, J. C. and Lu, Z.: 1994, *Environ. Sci.Technol.* **28**, 1633–1649.

Fujita, E. M., Watson, J. G., Chow, J. C. and Magliano, K. L.: 1995, *Atmos. Environ.* **29**, 3019–3035.

Fujita, E. M. and Lu, Z.: 1998a, *Prepared for ENSR Corporation*, Camarillo, CA, Desert Research Institute, Reno NV.

Fujita, E. M. and Lu, Z.: 1998b, *Prepared for Coordinating Research Council*, Atlanta, GA, Desert Research Institute, Reno, NV.

Hunt, W. F. Jr., Faoro, R. B. and Treas, W.: 1998, *Report on the Interim Database for State and Local Air Toxic Volatile Organic Chemical Measurements*. EPA-450/4-86-012, US Environmental Protection Agency Research Triangle Park, North Carolina.

Jorquera, H. and Rappengluck, B.: 2004, *Atmos. Environ.* **38**, 4243–4263.

Kostianen, R.: 1995, *Atmos. Environ*. **29**(6), 696–702.

Kuran, P. and Sojak, L.: 1996, *J. Chromatogr. A*. **733**, 119–141.

Mukund, R., Kelly, T. J. and Spicer, C. W.: 1996, *Atmos. Environ*. **30**(20), 3457–3470.

Netter, J. and Wasserman, W.: 1974, *Applied Linear Statistical Models*, Richard D. Irwin, Homewood, pp. 842.

Pleil, J. D., McClenny, W. A., Holdern, M. W., Pollack, J. A. and Oliver, K. D.: 1993, *Atmos. Environ.* **27**A, 739–747.

Scheff, P. A. and Wadden, R. A.: 1993, *Environ. Sci. Technol*. **27**, 617–625.

Scheff, P. A., Wadden, R. A., Kenski, D. M., Chung, J. and Wolff, G.: 1996, *JAWMA* **46**, 1048–1057.

Singh, H. B., Salas, L. J., Sites, R. and Shigeishi, H.: 1983, Measurement of Hazardous Organic Chemicals in the Ambient Atmosphere. EPA-600/3-83-002, US Environmental Protection Agency, Research Triangle Park, North Carolina.

Staten Island Report: 1997, Staten Island /New Jersey Urban Air Toxic Assessment Project Report, Vol. I Summary. EPA/902/R-93-001a, US Environmental Protection Agency Research Triangle Park, North Carolina.

Sweet, C. W. and Vermette, S. J.: 1992, *Environ. Sci. Technol.* **26**, 165.

Upmanis, H. E. and Anderson-Skold, Y.: 2001, *Water Air Soil Pollut.* **129**, 61–81.

Watson, J. G., Chow, C. Judith and Fujita, E. M.: 2001, *Atmos. Environ.* **35**, 1537–1584.

Xu, Ying and Zhang, Y.: 2003, *Atmos. Environ.* **37**, 2497–2505.