Estimation of the Emission of Volatile Organic Compounds (VOCs) in Tokyo from Their Observed Increments of the Atmospheric Averaged Concentrations above the Background Concentrations

Takao Miyoshi and Yoshihiro Makide
Radioisotope Center, The University of Tokyo, Bunkyo-ku, Tokyo 113-0032

(Received August 17, 2001; CL-010802)

Emissions of 21 VOCs in the Tokyo area were estimated from the increments of the averaged concentrations on weekdays above the background concentrations. Their relative data were converted to actual emissions per capita based on statistical information of several compounds. The correlation with CFC substitutes was indicated to be most useful.

The influences on the atmospheric environment by anthropogenic trace gases emitted largely by human activities are seriously concerned in urban areas. The sources of some compounds have been estimated by several methods. The chemical mass balance model determines the contribution of major sources of a pollutant from an atmospheric measurement of the composition of the pollutant.[1–3] Emissions of hydrocarbons were estimated based on that of CO or benzene.[4,5]

We, on the other hand, analyzed our concentration measurement data[6] and estimated emissions of some compounds per capita in Japan by newly developed methods, which are different from those reported before.

Tokyo is one of the largest cities in the world constituting the Metropolitan area with surrounding cities on the Kanto plain and includes all kind human activities: i.e., industries, automobiles, facilities, houses, etc. Therefore, all kinds of anthropogenic emissions are involved on the average in the Tokyo area.

Radioisotope Center of the University of Tokyo is located precisely at the center of such Tokyo Metropolitan area.[6] Sample air was continuously drawn from the top of its building (19 m above the ground on the heights) into the laboratory, cryogenically preconcentrated (Entech 7000), and analyzed with a GC–MS system (Hewlett Packard 5972A).[6] The atmospheric concentrations of 21 volatile organic compounds (VOCs: hydrocarbons and halocarbons) were measured every 3 hours for more than 3 months from December 25, 1998 through April 1, 1999. Meteorological data were simultaneously measured at the top of the building.

Firstly, the relative emissions of non-reactive compounds in the Tokyo area were expected to be proportional to observed increments of the averaged atmospheric concentrations above the background concentrations.[6] For the estimation of emissions, we selected data on weekdays (from 9:00 on Monday through 6:00 on Saturday) when human activities were full excepting those when the atmospheric concentrations were extraordinarily high or wind velocity was more than 4 m/s which hardly reflected the emissions (Table 1, column "A"). The background concentration was determined as the averaged one when wind velocity was more than 6 m/s in Tokyo (column "B"). Their difference is proportional to the mole emission of each compound (column "C"). It was then multiplied by molecular weight and the relative emission was shown by weight (column "D").[6]

As the next step, the actual emissions of VOCs per capita were calculated based on those of some compounds shown in various statistical materials. Correlation between the relative emissions in the Tokyo area expressed by weight (X axis) and statistical emission estimates from several materials (Y axis; in g/y per capita) is shown in Figure 1. In the figure, three correlation lines were drawn as follows.

"Fitting I" is a correlation line corresponding to the smallest of the sales of CFC substitutes (1998) and halocarbons for solvent use (1997) per capita in Japan.[7,8] Therefore the emission of each compound cannot be more than the values estimated on this line.

"Fitting II" is a zone of the emissions of CFC substitutes (HFC-134a, HCFC-141b and HCFC-142b) in 1998 calculated by assuming that the ratios of their estimated emissions into the air to their sales in Japan[7] were same with those in the world estimated by AFEAS (Alternative Fluorocarbons Environmental Acceptability Study).[9]

"Fitting III" is a correlation line corresponding to the largest of the emissions of several VOCs in 1997 estimated by the investigation by Ministry of the Environment (which was conducted on the industrial companies in Kawasaki City, Kanagawa Prefecture),[10] by Japan Federation of Economic

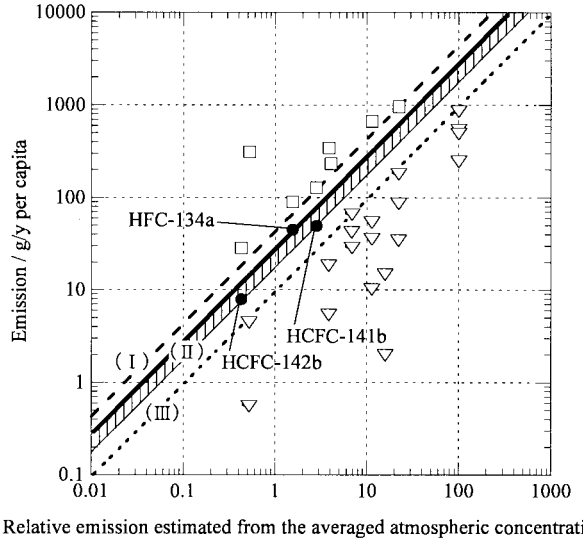

Figure 1. Correlation between relative emission of each compound estimated from the averaged atmospheric concentrations in the Tokyo area and annual emissions per capita based on several statistical materials. □ : Sales by chemical industries statistics[7,8]; ● : Emission estimation of CFC substitutes[7,9]; ▽ : Emission reported from industrial companies.[10–12]

Table 1. Relative emission of each compound obtained from its increment of the averaged atmospheric concentration, and estimated annual emission per capita

Compound	Category	A / pptv=10^{-12}v/v	B	C =A−B	D=C×M /10000	E / g/y per capita
Nonane	Compounds for solvent use	580	132	448	5.75	170
Toluene		13400	2540	10900	100	2900
Ethylbenzene		1910	428	1480	15.7	460
Dichloromethane		3110	487	2620	22.3	650
Trichloroethylene		986	124	862	11.3	330
Tetrachloroethylene		293	61.0	232	3.85	110
HFC-134a (CH_2FCF_3)	CFC substitutes; HFC (hydrofluorocarbon) and HCFCs (hydrochlorofluorocarbons)	202	50.4	152	1.55	45
HCFC-141b (CH_3CCl_2F)		301	58.4	243	2.82	82
HCFC-142b (CH_3CClF_2)		67.8	25.4	42.4	0.426	12
HCFC-22 ($CHClF_2$)		752	286	466	4.03	120
Butane	Compounds from automobile emission	7110	1960	5150	29.9	870
Pentane		2190	600	1590	11.5	330
Hexane		1990	357	1630	14.0	410
Isoprene		169	20.5	149	1.01	29
Benzene		1250	378	870	6.8	200
Acetone		2170	984	1190	6.91	200
1,1,1-Trichloroethane	CFCs and halocarbons already regulated by the "Montreal Protocol on the Substances Depleting Stratospheric Ozone"	106	66.6	39	0.52	15
CFC-113 (CCl_2FCClF_2)		83.4	71.8	11.6	0.217	6.3
CFC-11 (CCl_3F)		279	243	36	0.49	14
CFC-12 (CCl_2F_2)		558	494	64	0.77	22
Tetrachloromethane		97.0	91.2	5.8	0.089	2.6

A: weekday's averaged concentration. B: background concentration. Their difference C is multiplied by molecular weight M, and the relative emission D is shown by weight. E: estimated annual emission per capita in the early months of 1999.

Organizations (in all prefectures of Japan),[11] and by the Tokyo Metropolitan Government and the Tokyo Metropolitan Research Institute for Environmental Protection (in Tokyo Metropolis).[12] The largest values were selected because the aggregate amounts of emissions were incomplete by the reports from industrial companies; the emissions of the chemical substances were not necessarily reported accurately from all companies in addition to the incompleteness of coverage of the investigation. For example, in the investigation of Japan Federation of Economic Organizations,[11] 75.5% industrial companies answered the investigation. The actual emissions should be much larger than the values estimated by the Fitting III.

Therefore, the emission based on the Fitting II which is between the Fittings I and III seems most possible. Furthermore in the Fitting II, the release estimation of HCFCs (mainly used as blowing agent for closed-cell foams) by AFEAS[9] has been suggested to be underestimated.[13] The upper line of the Fitting II corresponding to HFC-134a (mainly used as refrigerant) was finally shown to be most reliable.

The annual emissions of all the compounds per capita in the Tokyo area calculated by the correlation "the upper line of the Fitting II" in Figure 1 are shown in Table 1 (column "E"). The largest among them is about 2900 g/y of toluene while the value contains large uncertainty. The compounds for solvent use and from automobile emission are exhausted by some hundreds g/y, the CFC substitutes by some tens g/y, and the CFCs and halocarbons already regulated by the "Montreal Protocol on the Substances Depleting Stratospheric Ozone" by some g/y.

From these values per capita, the total emissions of VOCs in Tokyo or in the Metropolitan area are given by multiplication of the population, 11 million or about 30 million, respectively.

The law concerning PRTR (Pollutant Release and Transfer Register) was enforced in 2001 in Japan. By this enforcement, more reliable statistical values of the emissions of some chemical substances will be available in the future and more accurate estimation of the emissions of all the substances will be obtained based on those revised statistics.

References and Notes

1 R. A. Wadden, I. Uno, and S. Wakamatsu, *Environ. Sci. Technol.*, **20**, 473 (1986).
2 C. W. Sweet and S. J. Vermette, *Environ. Sci. Technol.*, **26**, 165 (1992).
3 R. McLaren, D. L. Singleton, J. Y. K. Lai, B. Khouw, E. Singer, Z. Wu, and H. Niki, *Atmos. Environ.*, **30**, 2219 (1996).
4 E. Grosjean, D. Grosjean, and R. A. Rasmussen, *Environ. Sci. Technol.*, **32**, 2061 (1998).
5 R. G. Derwent, T. J. Davies, M. Delaney, G. J. Dollard, R. A. Field, P. Dumitrean, P. D. Nason, B. M. R. Jones, and S. A. Pepler, *Atmos. Environ.*, **34**, 297 (2000).
6 T. Miyoshi and Y. Makide, *Nippon Kagaku Kaishi*, **2001**, 223.
7 "Annual Report on the Monitoring of the Stratospheric Ozone Layer," Ministry of the Environment, Tokyo (2001).
8 "Yearbook of Chemical Industries Statistics 1997," Compiled by Research and Statistics Department, Minister's Secretariat, Ministry of International Trade and Industry, Tokyo (1998).
9 AFEAS; http://afeas.org/prodsales_download.html (2001).
10 Ministry of the Environment; http://www.env.go.jp/chemi/prtr/h10pilot/hokoku10.html (1999).
11 Japan Federation of Economic Organizations (Keidanren); http://www.keidanren.or.jp/japanese/policy/pol232/index.html (1999).
12 The Tokyo Metropolitan Research Institute for Environmental Protection; http://www.kankyoken.metro.tokyo.jp/japanese/news/news19/news19.htm (1999).
13 T. Shirai and Y. Makide, *Chem. Lett.*, **1998**, 357.