Estimation of the Emission of Volatile Organic Compounds (VOCs) in Central Tokyo by the Dynamic Analysis of Their Temporally Increasing Atmospheric Concentrations in Calm Weather Afternoon Conditions

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The emissions of VOCs in central Tokyo were estimated by the dynamic analysis of their temporally increasing atmospheric concentrations in the afternoon of weekdays when anthropogenic emissions were most active and the mixing of the atmosphere was extremely small. The results agreed well with the emissions estimated from increments of the averaged atmospheric concentrations above the background concentrations.

The influences to atmospheric environment by anthropogenic trace gases emitted largely by human activities are seriously concerned in urban areas and air pollution has been often studied by using models (statistical model, dispersion model, etc.).[1–3]

We for the first time tried to estimate the emissions of nonreactive VOCs in central Tokyo by the dynamic analysis of their temporally increasing atmospheric concentrations.

Since Tokyo is one of the largest cities in the world and includes all kinds of human activities: i.e., industries, automobiles, facilities, houses, etc., most of anthropogenic emissions are involved on the average in the Tokyo area. Radioisotope Center of the University of Tokyo is just located at the center of Tokyo, and outdoor sample air was continuously drawn from the top of the building into the laboratory, where it was cryogenically preconcentrated and analyzed every 3 hours (in part 1.5 hours) with a GC-MS system.[4,5] The atmospheric concentrations of 21 volatile organic compounds (VOCs: hydrocarbons and halocarbons including CFC substitutes) were measured for more than 3 months from 15:00 on December 25, 1998 through 21:00 on April 1, 1999. Meteorological data were simultaneously measured at the top of the building.

Atmospheric concentration of anthropogenic VOCs in central Tokyo increases by the emission above the concentration coming into Tokyo from the outside and decreases by the diffusion and transport to the outside of assumed box. Besides them, there are effects by rain and photoreaction, while the rain effect can be excluded by selecting the period without rain and the photoreaction was not active because of winter.

Since all the compounds are emitted similarly into the box, the slope of the concentration increase by the accumulation is proportional to the emission of each compound when wind velocity becomes extremely small.

The data were selected when the horizontal mixing of atmosphere was nearly negligible. As the case for analysis, the best two periods from 12:00 to 21:00 on February 1 (Case 1) and from 15:00 to 22:30 on March 1 (Case 2) were chosen. Both the periods were afternoon of weekdays and the mixing of the atmosphere became extremely small (calm weather afternoon conditions). It was not raining. In Figure 1, the temporal changes of atmospheric concentrations of VOCs and meteorological parameters in Case 1 are shown. A low pressure center traveled along the south of Japan in this period. Decrease of atmospheric pressure was observed and wind direction changed southerly. In Case 2, a low pressure center traveled by Hokkaido and variations of meteorological parameters were observed similarly.

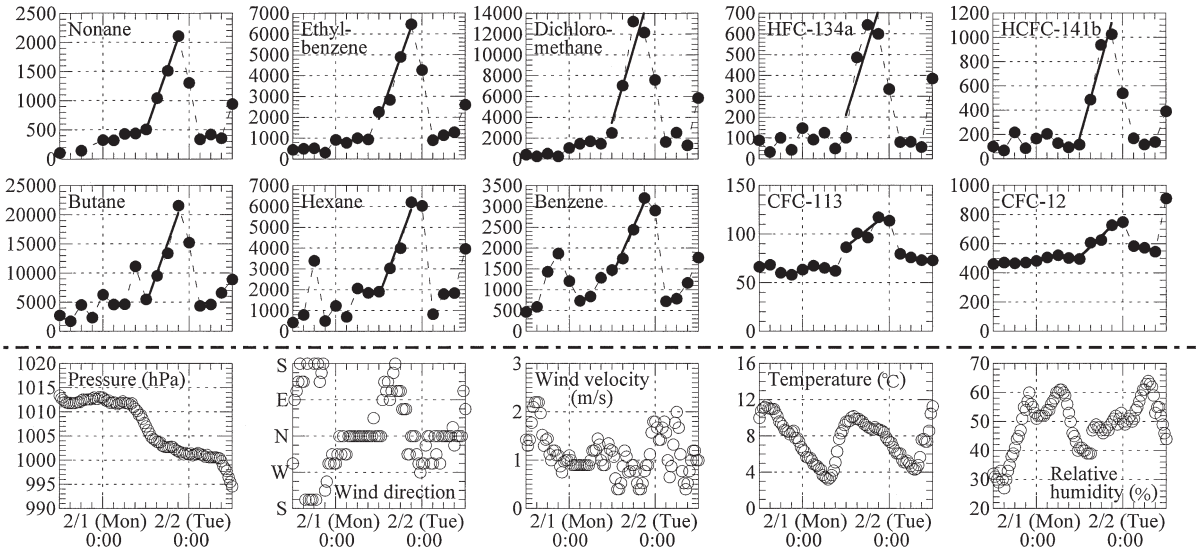

Figure 1. Variations of atmospheric concentrations of VOCs (in pptv) and meteorological parameters in Case 1 (February 1, 1999).

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Table 1. Relative emission of each compound in central Tokyo estimated by two methods

Category	Compound	Case 1*	Case 2*	Mean of Cases 1&2	Emission A**	Emission B**
Compounds for solvent use	Nonane	176	97.8	131	4.4	3.7
	Toluene	2170	2620	2380	57	65
	Ethylbenzene	490	305	387	11	10
	Dichloromethane	1180	707	913	20	14
	Trichloroethylene	304	229	264	9.0	7.3
	Tetrachloroethylene	94.5	66.4	79.2	3.4	2.5
CFC substitutes; HFC (hydrofluorocarbon) and HCFCs (hydrochlorofluorocarbons)	HFC-134a (CH_2FCF_3)	55.0	25.7	37.6	1.0	1.0
	HCFC-141b (CH_3CCl_2F)	106	42.3	67.0	2.0	1.8
	HCFC-142b (CH_3CClF_2)	6.49	27.7	13.4	0.35	0.27
	HCFC-22 ($CHClF_2$)	162	74.2	110	2.5	2.6
Compounds from automobile emission	Butane	1740	1440	1580	24	19
	Pentane	408	460	433	8.1	7.4
	Hexane	461	319	383	8.6	9.1
	Isoprene	39.8	40.3	40.0	0.71	0.65
	Benzene	195	197	196	4.0	4.4
	Acetone	135	187	159	2.4	4.5
CFCs and halocarbons already regulated by the "Montreal Protocol on the Substances Depleting Stratospheric Ozone"	1,1,1-Trichloroethane	25.5	5.97	12.3	0.43	0.34
	CFC-113 (CCl_2FCClF_2)	2.93	4.30	3.55	0.17	0.14
	CFC-11 (CCl_3F)	7.84	2.56	4.48	0.16	0.32
	CFC-12 (CCl_2F_2)	23.9	28.1	25.9	0.82	0.50
	Tetrachloromethane	0.340	0.313	0.326	0.013	0.058

* Case 1 is the slope of increasing concentration of each compound (pptv/hour) in the period 12:00–21:00 on February 1, 1999, and Case 2 in the period 15:00–22:30 on March 1, 1999.

** Emission A is the relative emission (this work) in central Tokyo obtained from the geometrical mean of the slopes of increasing concentrations; the mean was multiplied by molecular weight. Emission B is the relative emission estimated from the increment of the averaged atmospheric concentration of weekdays for 3 months above the background concentration.[5] Both emissions are shown by weight and normalized to HFC-134a.

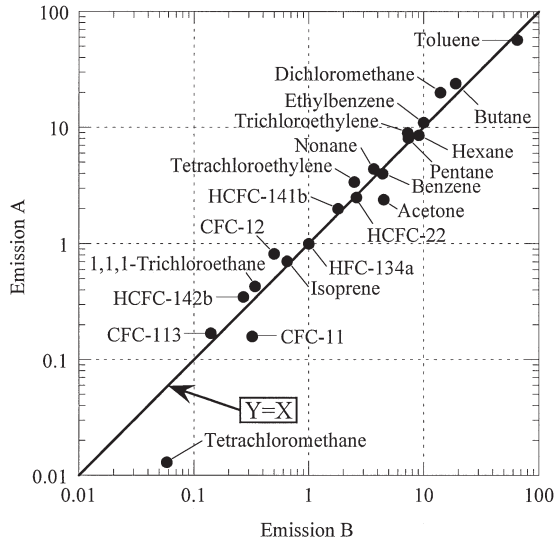

Figure 2. Correlation between the relative emissions of each compound in central Tokyo estimated by the two methods A and B (see the footnote of Table 1).

Table 1 shows the slopes of the increasing concentration of each compound in both periods (pptv/hour, which is proportional to the relative emission shown by mole), their geometrical means, and the relative emissions in central Tokyo estimated by two methods. The first one (Emission A) is by the present work: the temporal slope of concentrations was multiplied by molecular weight and the relative emission of each compound was shown by weight and normalized to HFC-134a. The other (Emission B: we reported previously)[5] is the relative emission estimated by the increment of the averaged atmospheric concentration of weekdays for 3 months above the background concentration which is the average when wind velocity was more than 6 m/s. The actual annual emission was calculated using the emission of CFC substitutes (typically of HFC-134a) in 1998 based on statistical materials[5] (sales of CFC substitutes in Japan[6] and ratios of their emissions into the air to sales in the world[7] estimated by AFEAS (Alternative Fluorocarbons Environmental Acceptability Study)).

Correlation between the emissions estimated by the two methods is shown in Figure 2. The result showed a very close correlation and most compounds were located near the line of Y=X. Though the analytical methods of data were completely different, the relative emission estimates obtained by the two methods based on the different duration agreed well. It was effective to select the observation period in the calm weekday afternoon when anthropogenic emissions were most active. Although at dawn the atmospheric mixing usually becomes small in a day, the correlation was worse because the emissions by human activities were also little and anthropogenic emissions were not properly reflected by the dynamic method. The more detailed comparison of many cases will clarify the pattern of emission and sources; e.g., continuously released compounds gave smaller values by the method A than by B.

This unique and dynamic analysis method will be promising for the release estimation of more reactive compounds with shorter lifetimes down to several hours in the atmosphere.

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