

## A new approach for estimating VOC emissions from anthropogenic non-point sources in urban communities

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**Abstract**—In an attempt to estimate VOC emission from anthropogenic, non-point sources in an urban area, a new approach (SKYEM) was introduced as a part of the integrated environment management (IEM) project. SKYEM was developed for consulting user convenience on a basis of emission inventory methodologies developed in the USA, Europe, Australia, and Korea. The inventory was obtained from mobile and area sources resolved to census tract levels (Dong or village levels). SKYEM was used to provide an annual emission inventory for major volatile organic compounds, BTXS (benzene, toluene, xylene, and styrene), PCE, phenol, and MEK, from 13 sources in multimedia (air, water, and soil) for 151 villages in northeastern Seoul. Toluene (73%) and Xylene (16%) were largely emitted from important source categories, consumer solvents and mobiles, accounting for 60% and 26% of all estimated VOCs during the year 2002, respectively. BTXS were also measured at 10 sites located in the target area. Toluene presented the highest concentration (77%) with Xylene ranked second (15%). The similarity between concentration and emission may be explained by a model which describes scientific phenomena in or inter media. Therefore, a comparison of the prediction using the model with actual observations will be useful in examining uncertainties in, or the accuracy of the emission inventory from, non-point sources in an urban area.

Key words: Emission Inventory, Non-point Source, Area Source, Mobile Source, BTXS, Urban

### INTRODUCTION

Toxic air pollutants such as volatile organic compounds (VOCs) may contribute to, or exacerbate, hazards to human health and the environment, and also be a source of more serious problems such as the formation of ozone under sunlight in the atmosphere. Aromatic VOCs as a fraction of NMHC (non-methane hydrocarbons) have been proposed to be dominant components in the emission inventory of the EUROTRAC-2 project for the Lombardy region in Italy and of the EVA project [1,2]. In general, important emission source categories in emission inventories are comprised of natural (biogenic) sources, mobile sources, and stationary sources (point and non-point area sources) and mobile emission constitutes the major source of VOCs in urban areas that are not in close proximity to industrial sources.

Toxic air pollutants from area sources are also significant components of regional air pollution inventories. Several reviews of emission inventories have been conducted for the National Acid Precipitation Assessment Program, for the National Academy of Sciences study on tropospheric ozone in 1992, and for the Emission Inventory Improvement Program (EIIP) [3,4]. Those reviews emphasized difficulties in developing or compiling emission inventories and labor intensiveness due to the variety of area sources and the tremendous variability within classes of, or even a single, emission source. In addition, establishing an experimental plan or performing a field study is difficult in terms of investigating the emis-

sion characteristics of individual VOC compounds that are emitted from numerous area sources [4]. The above attempts to estimate the VOC emission inventories from area sources contain serious errors. Errors associated with an emission inventory could lead to inaccuracies in modeling results for photochemical processes [5-8].

The goals of the present study were to develop and to examine a new approach (SKYEM) for generating VOC emission inventories from anthropogenic sources in an urban area as a part of an integrated environment management (IEM) project supported by the Ministry of Environment in Korea and ECO-Technopia-21 (Core Environment Technology Development Project for Next Generation). The approach involves finding better ways to characterize uncertainties in, or the accuracy of, the emission estimates, such as providing specific information on emission sources, amounts of emissions, and the transfer of pollutants among the environmental multimedia into an emissions inventory based on previous studies [9-12]. A methodology for the emission estimates in SKYEM uses activity levels, emission factors, physico-chemical properties, and so on. Estimations using SKYEM are examined by using ambient concentrations collected at the same areas for emission estimates. More details of the emission inventory (SKYEM) will appear in following sections.

### EXPERIMENTAL

#### 1. Methodology of VOCs Emission Inventory

An emission inventory module, SKYEM, with an urban/industry option, was developed, based on the characteristics of the selected areas. In this paper, SKYEM is used for the urban cases because

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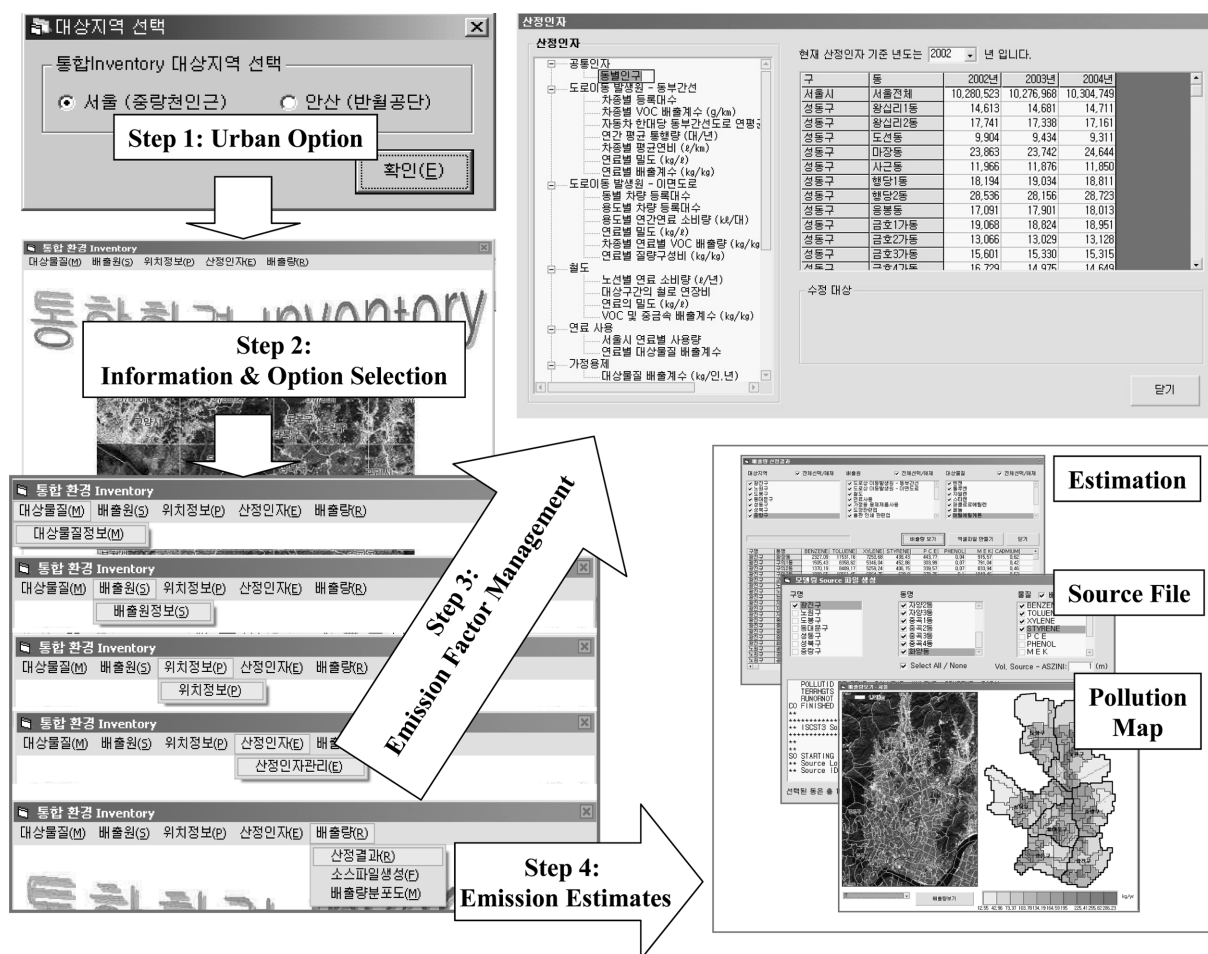


Fig. 1. SKYEM operating steps for user's convenience.

urban areas have more serious pollution problems, in which non-point sources, rather than point sources, are the sources of emission. In general, the anthropogenic non-point area source collected similar emission units within a geographic area at the county level in previous studies. In SKYEM, however, small specific areas (i.e., village level or division level) can be selected as well as the city level or the county level. SKYEM was developed for consulting user convenience; the user can obtain information of compounds, emission source types and positions, emission factors, and so on. Fig. 1 shows SKYEM operating steps for user convenience. Users select the region (the city and the individual or several or entire divisions in the city), the year, the emission source type (point, line, or area), and the chemical component (the individual VOC or VOCs, the heavy metal, or all components), SKYEM produces emission data for all villages in the selected divisions. When an urban area and the year are selected in step 1 and 2 of Fig. 1, SKYEM automatically utilizes data (e.g., populations, societal concerns, geological significance, vehicle registration data, distribution systems, and so on) collected from emission sources as shown in step 3. In step 4, users can obtain a map for emission distribution and two types of data files, an excel file for analyzing data and a source file for the atmospheric dispersion model (i.e., ISCST3 and SKYDM) and the multimedia model (SKYMM).

Table 1 describes emission source category and major pollutants

emitted from non-point sources (a line source and an area source) and point sources. Point sources (stationary emission) include stacks (manufacturing facilities, refineries, chemical production facilities, other facilities that produce or utilize chemicals,) and incinerators. Such stack point sources are primarily in industrial regions but limited to the urban areas. Manufacturing processes tend to be the dominant sources of VOC. VOC emissions from point sources can be estimated by using a variety of methods such as emission factors and predictive emission monitoring systems. Given an emission factor and a known activity level, SKYEM uses simple multiplication to estimate the emission of VOCs, based on published emission factors in the U.S. EPA EIIIP and in Europe EMEP/CORINAIR (Co-operative Program for Monitoring and Evaluation of the Long Range Transmission of Air Pollutants in Europe/Coordination of Environmental Air), and the estimation formulae for point and non-point sources that were previously developed in Korea [13-16];

$$\text{Emission} = \sum \text{Activity} \times \text{emission factor}$$

More detailed formulae for each emission source are introduced in Table 2. The above references define emission factors as ratios that relate the emission of a pollutant to an activity level at a plant that can be easily measured, such as the amount of material processed, or the amount of fuel used, and published emission factors are available from numerous sources.

**Table 1. Activity level and emission coefficients for calculating the emission of VOCs in SKYEM**

Source	Category	Activity level	Emission coefficients	Major emission pollutants
Area	Coating/painting	Usage of products by facilities	Efficiency of removal	Toluene, Xylene, Styrene, 2-butanone (MEK)
	Publishing/printing	Usage of products by facilities	Efficiency of removal	Toluene, Xylene, Methyl Ethyl Ketone
	Dry cleaning/cleaner	Total quantity of dry cleaning by a cleaner per year	Efficiency of removal	Tetrachloroethylene, Trichloroethene, 1,1,1-trichloroethane, Dichloromethane
	Consumer solvents	Population in the target area	An annual product sales by businesses	Benzene, Perchloroethylene, Toluene, Trichloroethylene, Xylenes, Methyl Ethyl Ketone
	Fuel consumption	Annual amounts of fuel consumption by fuel types throughout the nation	Emission factors by fuel types	Benzene, Toluene, Xylene, Cd, Pb, Hg
	Fuel retail sale (gas service station)	Annual amounts of gas sales	Emission factors by materials	Benzene, Toluene, Xylene
	Asphalt Pave	Consumption of cutback asphalt throughout the nation	Emission coefficients of VOCs in cutback asphalt	Ethylbenzene, Toluene, Xylene
	Sewage treatment plant	Annual outlet amounts	Mean concentration of selected species in the outlet	Depending upon removal efficiency
	Source contamination of water supply	Annual outlet amounts	Mean concentration of selected species in the outlet	Depending upon pollutants of the neighboring region
	Mobiles on other roads	Registered vehicles due to the vehicle model in the target area	Mass composition ratio	Benzene, Toluene, Xylene, Styrene, Cd, Pb
Line	Mobiles on main roads	Number of registered vehicles by vehicle model	Emission coefficient due to the vehicle model	Benzene, Toluene, Xylene, Styrene, Cd, Pb
	Mobiles on railroads	Fuel consumption within the block of the railroad track	Emission coefficient by chemicals	Benzene, Toluene, Xylene, Cd
Point	Incinerators	Annual amounts of industrial wastes burned up, kg yr <sup>-1</sup>	Emission factors by chemicals per unit amount of industrial waste burned up	SO <sub>2</sub> , NO <sub>x</sub> , VOCs, CH <sub>4</sub> , CO, CO <sub>2</sub> , As, Cd, Cr, Cu, Hg, Ni, Pb, Zn, PAH, HCl, Mn, Co

The amounts of pollutants emitted from line (Traffic or Mobile) sources such as a main road can be estimated by using the actual distance (discharge coefficient of a distance) covered in a given time (mileage) when it is impossible to determine the amount of the fuel consumption based on the limited mileages over the entire target region. Based on current traffic volume investigation data, the multiplication of the average traffic volume and the road extension distance (RL) within the target block determines the annual total mileage for the vehicle model within the target area. This method can be applied to mobiles on the main road or railroad vehicles.

According to earlier studies [4,13], area (non-point) sources are smaller and more widespread sources that may be abundant but that individually release only small amounts of a given pollutant. As non-point area sources are fugitive, they generally are not required to submit individual emission estimates and their arbitrary natures cause difficulty in estimating the boundaries of activities associated with these sources. SKYEM includes only ten fugitive area emission source categories: fossil fuel consumption, consumer (domestic) solvents, architectural coating/painting, printing/publishing, asphalt paving, fuel retail sales, dry cleaning, sewage treatment plant, source

contamination of water supply, and mobiles on other roads.

## 2. Design of the SKYEM Application

Seven towns, Dobong-gu (DB), Nowon-gu (NW), Jungnang-gu (JR), Seungbuk-gu (SB), Seungdong-gu (SD), Dongdaemoon-gu (DDM), and Gwangjin-gu (GJ), with 151 divisions were selected to cover a range of estimated emissions in the northeastern portion of Seoul (see Table 3 and Fig. 2). The middle of the target area contains the Jung-Rang stream, which is the longest stream (45.3 km) flowing into the Han River, and residential/commercial divisions and industrial facilities are located in close proximity to the Jung-Rang stream. The target area is densely populated (about 30% of the entire population of Seoul), less industrialized, and a very heavy traffic inner-city community. The topography and geographical proximity of this area cause serious air pollution problems and the growing population has exacerbated air pollution conditions. Seven major non-methane hydrocarbons (NMHC), benzene, toluene, xylene, styrene, PCE (perchloroethylene), phenol, and MEK (methyl ethyl ketone) were selected for the emission inventory and for measurement of ambient air concentrations. BTXS (Benzene, Toluene, Xylene, and Styrene) were known to be the dominant VOC measured

in the major cities of the world, including Seoul [17,18]. Fig. 2 shows a map of the target area showing VOC emissions from anthropogenic point and non-point (area and mobile) sources in ten monitoring locations.

### 3. Canister VOC Measurements

Samplings were done four times during the year 2002 by season: Jan., 31-Feb., 1 (M1), Apr., 10-11 (M2), Sept., 17-18 (M3), and Nov., 28-29 (M4). On the first day of each measurement time, sites 1 to 5 were monitored from 10 am to 5 pm, while concentrations from sites 6 to 10 were measured on the second day of each period. From

**Table 2. Governing formulae for calculating emissions of VOCs based on the classifying data of the emission sources in EIIP [13], in EMEP/CORINAIR, and ME of South Korea**

Area sources	
Coating/painting $E = \sum_h tVC_h$ $tVC_h = \sum_c \sum_i [IC_{ich} \times VR_{ih} \times (1 - AE_c)]$	E=emission rate of selected species into air, kg yr <sup>-1</sup> $tVC_h$ =E by classifying products, kg yr <sup>-1</sup> <i>i</i> =types of products (or solvents used or items) <i>h</i> =classification of products <i>c</i> =types of business
Publishing/printing $E = \sum_h tVC_h$ $tVC_h = \sum_c \sum_i [IC_{ich} \times VR_{ih} \times (1 - AE_c)]$	$IC_{ich}$ =usage of products by facilities, kg yr <sup>-1</sup> $VR_{ih}$ =mass content rates of selected species by products $AE_c$ =efficiency of removal from treatment facilities when released after treating emission gases (or after treating exhaust gases)
Dry cleaning/cleaner $E = \sum_c [MC_i \times EF_i \times R \times (1 - AE_c)]$	<i>c</i> =each cleaner $MC_i$ =total quantity of dry cleaning by a cleaner per year, kg yr <sup>-1</sup> $EF_i$ =amounts of solvents emitted into air per quantity of dry cleaning by solvents, kg kg <sup>-1</sup>
Domestic solvents (1) Emission into air $E = EF \times P$ $EF = \frac{TE}{TP}$ $TE = \sum_h (ER_h \times TVC_h)$ $TVC_h = \sum_c \sum_i (R_{ich} \times PC_{ich})$ (2) Effluent into Sewage treatment plant $E' = EF' \times P$ $EF' = \frac{TE'}{TP} = \frac{TVE + TNVE}{TP}$ $TVE = \sum_h [(1 - ER_h) \times TVC_h]$ $TNVE = \sum_c \sum_i (R'_{ich} \times PC_{ich})$	<i>P</i> =population in the target area, people $EF$ =an annual VOCs emission rate into air a person, kg person <sup>-1</sup> yr <sup>-1</sup> $TP$ =population by the nation, people $TE$ =an annual total emission rate of selected species into air throughout the nation, kg yr <sup>-1</sup> <i>h</i> =detailed categorizes of items $ER_h$ =an annual VOC emission rate into air by <i>h</i> , kg yr <sup>-1</sup> $TVC_h$ =a national annual total sales by <i>h</i> , kg yr <sup>-1</sup> <i>c</i> =a class of manufacturing industry $R_{ich}$ =Mass fraction of VOCs among formation components of products $PC_{ich}$ =an annual product sales by businesses, kg yr <sup>-1</sup> $E'$ =emission rate of selected species into water, kg yr <sup>-1</sup> $EF'$ =an annual VOCs emission rate into water a person, kg person <sup>-1</sup> $TE'$ =an annual total emission rate of selected species into water throughout the nation, kg yr <sup>-1</sup> $TVE$ =an annual total emission rate of VOCs into water, kg yr <sup>-1</sup> $TNVE$ =an annual total emission rate of non-VOCs into water, kg yr <sup>-1</sup> $1 - ER_h$ =an annual VOC emission rate into water by <i>h</i> , kg yr <sup>-1</sup> $R'_{ich}$ =Mass fraction of non-VOCs among formation components of products
Fuel consumption $E = EF \times P$ $EP = \frac{TE}{TP}$ $TE = a \times \sum_f (FC_f \times EF_f)$	$EP$ =emission rate of selected species per person per year, kg yr <sup>-1</sup> person <sup>-1</sup> <i>P</i> =population by cities (people) $TP$ =population by the nation (people) $TE$ =an annual total emission rate of selected species throughout the nation, kg yr <sup>-1</sup> $FC_f$ =annual amounts of fuel consumption by fuel types throughout the nation, TOE yr <sup>-1</sup> $EF_f$ =emission factors by fuel types, g GJ <sup>-1</sup> $a=0.04196; 4.196 \text{ KJ Kcal}^{-1}$
Fuel retail sale (gas service station) $E = GC \times EF$	$GC$ =annual amounts of gas sales, kl yr <sup>-1</sup> $EF$ =emission factors by materials, kg kl <sup>-1</sup>
Sewage treatment plant/Source contamination of water supply $E = C \times FV$	<i>C</i> =mean concentration of selected species in the outlet, kg T <sup>-1</sup> $FV$ =annual outlet amounts, Ton

Table 2. Continued

Area sources	
Asphalt pave $E = IR \times CCA \times R \times EF$ $IR = \frac{OR + PR}{tOR + tPR}$	<p>IR=a ratio of the increased area of paved roads in the target area to those in the city including the target area</p> <p>OR=expanded areas of paved roads in the target area</p> <p>PR=improved or repaired areas of paved roads in the target area</p> <p>tOR=total expanded areas of paved roads in the city including the target area</p> <p>tPR=improved or repaired total areas of paved roads in the city including the target area</p> <p>CCA=consumption of cutback asphalt throughout the nation, kg</p> <p>R=a ratio of asphalt consumption in the selected city to that in the nation=CA/tCA</p> <p>EF=emission coefficients of VOCs in cutback asphalt.</p>
Mobiles on other roads $E = 1000 \times \sum_i \left( DVN_i \times \frac{VN_i}{tVN_i} \times F_i \times d_i \times R \right)$	<p>i=the vehicle model related to the fuel type and business use</p> <p>DVN<sub>i</sub>=the registered vehicles due to the vehicle model for each division in the target area</p> <p>VN<sub>i</sub>=the registered vehicles due to the vehicle model in the target area</p> <p>tVN<sub>i</sub>=the total registered vehicles in the target area</p> <p>F<sub>i</sub>=the annual fuel consumption, kl vehicle<sup>-1</sup> yr<sup>-1</sup></p> <p>d<sub>i</sub>=the fuel density, kg L<sup>-1</sup></p> <p>R=the mass composition ratio kg kg<sup>-1</sup>.</p>
Point sources	
Incinerator $E = \sum_i (WI_i \times EF_i)$	<p>i=the incinerator</p> <p>WI<sub>i</sub>=the annual amounts of industrial wastes burned up, kg yr<sup>-1</sup></p> <p>EF<sub>i</sub>=emission factors by chemicals per unit amount of industrial waste burned up</p>
Line sources	
Road mobiles $E = \frac{1}{1000} \times \sum_i \left( TV \times \frac{VN_i}{tVN} \times RL \times EF_i \times R \right)$	<p>i=the vehicle model</p> <p>TV=the annual traffic volume (vehicles year<sup>-1</sup>)</p> <p>VN<sub>i</sub>=the number of registered vehicles by vehicle model</p> <p>tVN=the total registered vehicles</p> <p>RL=the road extension (km vehicle<sup>-1</sup>)</p> <p>EF<sub>i</sub>=the emission coefficient due to the vehicle model (g km<sup>-1</sup>). Note that EF<sub>i</sub> is estimated by the average speed within the block as a function of vehicle speed.</p> <p>R=the mass composition ratio.</p>
Railroad mobiles $E = FC \times EF$ $FC = \sum_L FC_L$ $FC_L = \sum_c \left( tFC_{cL} \times \frac{RL}{tRL} \right)$	<p>EF=the emission coefficient by chemicals</p> <p>FC=the fuel consumption within the block of the railroad track, kl yr<sup>-1</sup></p> <p>FC<sub>L</sub>=the fuel consumption by a route within the block of the railroad track, kl yr<sup>-1</sup></p> <p>c=a type of vehicles</p> <p>tFC<sub>L</sub>=the total fuel consumption by a route by a vehicle within the block of the railroad track throughout the nation, kl yr<sup>-1</sup></p> <p>RL<sub>c</sub>=the railroad extension by a route within the block of the railroad track, km</p> <p>tRL<sub>c</sub>=the railroad extension by a route within the block of the railroad track throughout the nation, km</p>

the 10 monitoring sites as shown in Fig. 2, a total of 40 samples were collected following the U.S. Federal Reference Method (TO-15) in silonite canisters for 3-hr at each site continuously. To minimize the contamination of samples, the canisters were flushed with high quality Nitrogen (99.999%) at least 5 times before sampling. The analytical equipment, HP6890GC/Agilent 5973N MSD, was used to analyze the samples quantitatively and qualitatively with 1 ppmv concentration of TO-15 standard gas (SPECTRA gases, USA). The advantages of the HP6890GC/Agilent 5973N MSD are that the loss of samples is negligible and measurements can be made repeatedly. A sample size of 500 ml was used in order to detect ex-

tremely small quantities of VOCs in the air. All samples were analyzed within 4 days after sampling. Xylenes were measured as two sets of isomers, o- and m, p-xylene. These two isomers were summed to give the total xylene for comparability with the emissions that are available for total xylene. The entire reproducibility was  $\pm 5\%$  of the initial concentrations, which can be ignored.

## RESULTS AND DISCUSSION

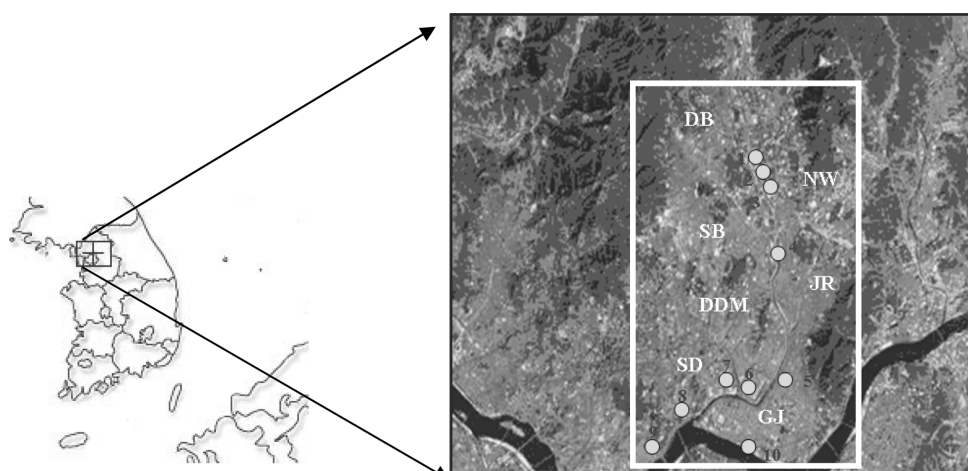
### 1. Characteristics of the Emission Area

The northeastern portion of Seoul has the characteristics of a local

**Table 3. Information on northeastern Seoul**

Name of town	Number of divisions	Area (Km <sup>2</sup> )	Population	Registration of vehicles	Monitoring sites
GJ	16	17.05	388,478	70,984	5, 10
NW	24	35.44	643,585	123,070	1-3
DB	15	20.84	373,086	46,486	
DDM	26	16.20	384,356	63,759	
SD	20	16.84	343,018	64,321	6-8
SB	30	24.57	446,968	75,746	
JR	20	18.50	443,246	73,514	4
NE of Seoul	151	149.44	3,022,737	517,880	

\*Monitoring site 9 is located in Yongsan-Gu (outside of the target area).



**Fig. 2. Satellite picture of northeastern Seoul topography; the white box indicates the target area, which includes 151 small specific communities in 7 towns.**

environment causing air pollution by non-point emission sources (line and area sources) as well as by point sources such as incinerators, and water pollution by domestic/industrial wastewater. The population, industry, and traffic conditions in this area are representative of metropolitan Seoul. Emission source categories are based on universal point and non-point emission inventories found in national and/or international database, and are also considered to be local characteristics. Emission sources, in principle, are classified as heavy emission sources without separating point or non-point sources, and are completed by adding water pollution sources. Soil pollution is omitted from the emission source list because there is no public emission source (e.g., landfills) causing soil pollution in the target area.

SKYEM provides an annual VOC emission inventory for non-point area sources in the target area during 2002. The seven selected major airborne VOCs arise from mobile sources and various area sources including organic solvent use (coating/painting, dry cleaning/cleaner, publishing/printing, and consumer solvents), material handling/storage (fuel consumption including apartment/institutional incinerators, fuel retail sales such as gasoline service stations), waste treatment and disposal (sewage treatment, source contamination of water supply), and miscellaneous (asphalt paving, etc.).

The traffic or mobile emissions are calculated for three reference road types: railroads, main roads, and other roads excluding the main road. Traffic emissions from the main road and the rail-

roads are treated as line sources and those from other roads are considered to be non-point area sources. In the case of a railroad vehicle, hazardous compounds are emitted from fuel combustion during operation. However, the amount of railroad emissions is comparatively much lower than that from road mobiles. The eastern main road is a representative road in the area along the Jung-Rang stream, while other roads are located in 151 divisions and are treated as area sources.

The target area indicated no emissions of the seven major VOCs from a point source (incineration plants) and from non-point sources such as dry cleaning, sewage treatment, and source contamination of the water supply. However, mobiles on other roads, publishing/printing, asphalt paving, coating/painting, fuel consumption, fuel retail sales, and consumer (domestic) solvents were significant sources of emission of the major VOCs (BTXS (Benzene, Toluene, Xylene, and Styrene), PCE, MEK, and Phenol).

## 2. VOCs Emission Distribution

The figures and tables show the results for the annual emission inventory of major VOCs from these significant sources during 2002. The total emissions from seven towns in the northeastern portion of Seoul are approximately 2,507 T yr<sup>-1</sup>, as shown in Fig. 3. When comparing the total emissions by town, the highest emission (about 555.7 T yr<sup>-1</sup>) was estimated from the NW and the lowest value (about 259.4 T yr<sup>-1</sup>) was obtained from DB. Fig. 3(a) shows the emissions from each of the divisions in the towns, including 16 divisions in

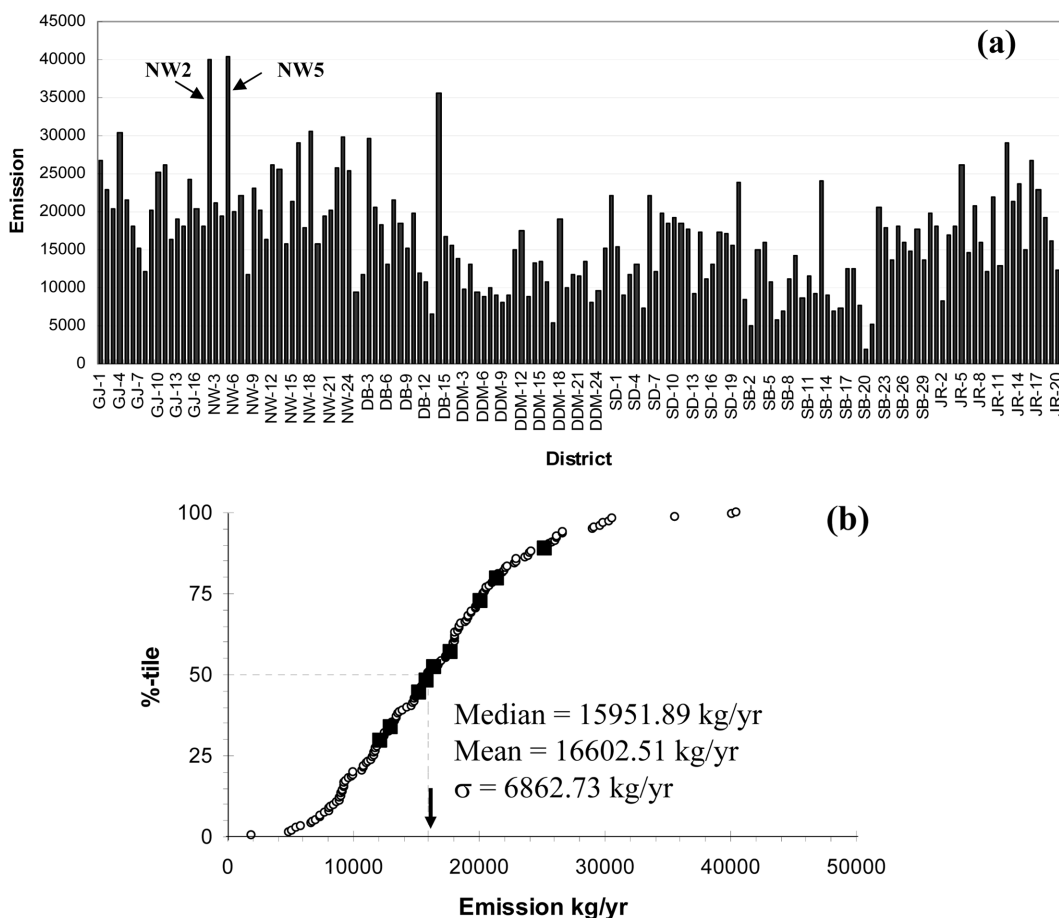


Fig. 3. Emission rates of major VOCs in the northeastern portion of Seoul during the 2002; (a) emission rates [ $\text{kg yr}^{-1}$ ] by 151 small specific communities (districts) in 7 towns, (b) Statistical distribution of BTXS emission with Mean, Median, Standard Deviation ( $\sigma$ ). Squares mark the percentile of emission at the measurement sites. Unit of BTXS (Benzene, Toluene, Xylene, and Styrene) emission is [ $\text{Kg yr}^{-1}$ ].

GJ, 24 divisions in NW, 15 in DB, 26 in SD, 30 in SB, and 20 divisions in JR. Among all 151 small specific divisions, two divisions (NW-5 and NW-2 in NW), with values of over  $40 \text{ T yr}^{-1}$ , are ranked in the first and second place, respectively, and the third place is DB-14 in DB with an emission of around  $35.57 \text{ T yr}^{-1}$ . The lowest emission ( $1.9 \text{ T yr}^{-1}$ ) is estimated from SB-20 in SB.

Fig. 3(b) shows a statistical analysis of the distribution of emission distribution. Over 95 percentiles of emissions (over  $29 \text{ T yr}^{-1}$ ) resulted from GJ and NW and some divisions in SB were within about 5 percentiles (less than  $6.9 \text{ T yr}^{-1}$ ). The emission rate,  $15.952 \text{ T yr}^{-1}$ , takes the median value (50%-tile) which is quite close to the mean value ( $16.603 \text{ T yr}^{-1}$ ). The normal distribution within the mean  $\pm$  the standard deviation ( $\sigma = 6.863 \text{ T yr}^{-1}$ ) accounts for 68.9% of the total emissions. The emissions estimated from the ten measurement sites are distributed between the 29 and 89 percentiles (see the square marks in Fig. 3(b)).

Toluene is the major component for all sources, accounting for about 73.34% of all calculated VOCs, followed by Xylene (16.33%), Benzene (6.27%), Styrene (2.77%), and MEK (1.29%). Road mobile sources (both line and area) indicate BTXS only with Toluene (40%), Xylene (35%), Benzene (22%), and Styrene (3%). For fuel consumption, Benzene is present as the major component (about 60%)

followed by Toluene (about 36.5%). Consumer solvents show that Toluene is the dominant component, at about 95% and Xylene at 4% is next. Coating/painting sources emit Toluene (43.61%), Xylene (35.18%), Styrene (11.03%), and MEK (10.18%). Finally, the fraction of VOCs from the fuel retail sales sources is comprised of Toluene (50%), Benzene (31.82%), and Xylene (18%). Fig. 4 shows the main sources of emission for each component. In Fig. 4(a), all 7 VOCs are mostly accounted for as consumer solvents (60%), road mobiles (26.44%), and coating/painting (12%). The major source of Benzene is road mobiles (92.68%) including the main road, other roads, and railroads, and fuel retail operations (7.11%). The total Toluene in Fig. 4(c) is made up of consumer solvents (77.58%), road vehicles (14.23%), coating/painting (7.20%), and etc. (1.0%). Xylene is contributed by road mobiles (56.61%), coating/painting (26.21%), consumer solvents (16.10%), etc. (1.61%) as shown in Fig. 4(d). The emission of styrene from coating/painting is 48.48% and 27.86% from road mobiles (see Fig. 4(e)). Fig. 4(h) presents the emission sources for MEK, 96.07% from coating/painting and 3.89% from consumer solvents. In Fig. 4(f) and 4(g), the major source of PCE is consumer solvents (99.718%) and Phenol is emitted from coating/painting processes (85.48%). The United States of America concludes that PCE emitted from dry cleaning is the major VOC.

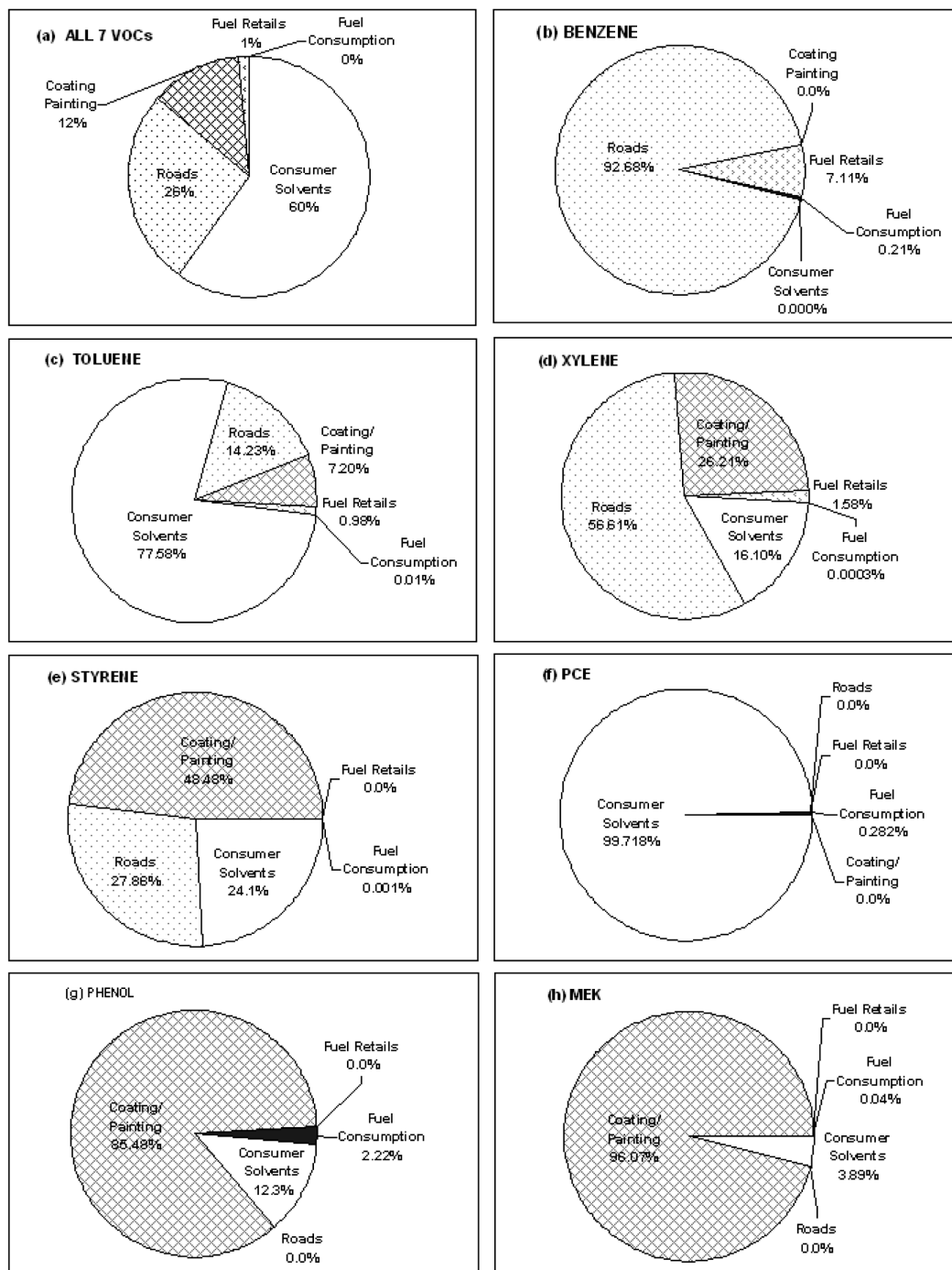


Fig. 4. Emission distribution from non-point sources in northeastern Seoul during the 2002.

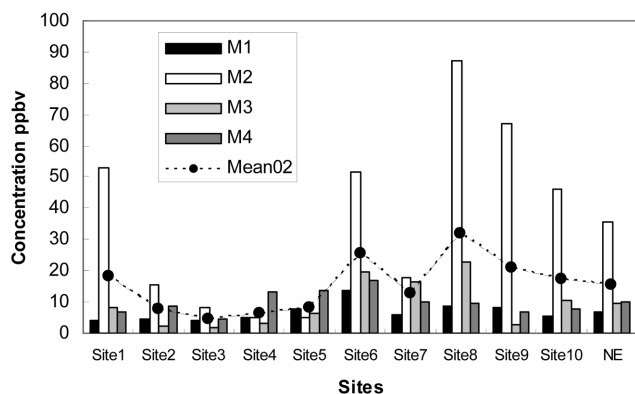
Unlike the U.S.A, currently in Korea, there is no accurate information of detergent types and amounts in estimating the emission inventory for dry cleaning. Several previous studies provided data of toluene, styrene, and xylene; however, they were greatly different according to an analytical method and a sampling method. Thus, it is difficult to decide criteria for the analytical method and to collect data for the emission inventory from the dry cleaning because various laundry detergents are used in dry cleaning. Hence, we estimated the emission for dry cleaning based on distribution data given by the Ministry of Environment in Korea during 2002. The current study

presented the major VOCs from dry cleaning in the target area during 2002 as Formaldehyde, 2-propanol, Acetic acid, Trichloroacetic acid, and Dimethyl sulfate and the seven major VOCs considered in this study were not included in the emission inventory for dry cleaning.

### 3. Distribution of Ambient Concentration

A total of 40 samples were collected from 10 sites along the Jung-Rang stream, which is a branch of the Han River in the northeastern portion of Seoul, during the year 2002. Ambient concentrations of BTXS at 10 sites were measured four times during 2002 and these





**Fig. 5.** 3-Hr mean concentration of BTXS measured at the 10 sites located in northeastern Seoul during the 2002. Various sampling time: Site 1 and 6 (starting at 10:00 am for 3 hours), Site 2 and 7 (starting at 11:00 am), Site 3 and 8 (starting at 12:00 noon), Site 4 and 9 (starting at 14:00 pm), and Site 5 and 10 (starting at 15:00 pm).

seasonal concentrations were averaged to determine the annual mean value for 2002 (see Fig. 5). Some concentrations are indicated as 'no detection (ND)' due to equipment limitations. The 3-hr mean concentration of BTXS was analyzed and the unit of concentration is a mixing ratio, parts per billion in volume (ppbv). The results obtained during the second period, M2, and the fourth period, M4, control the spatial variation patterns for the annual mean concentration of BTXS. At all sites except sites 4, 5, and 7, the annual BTXS are dependent on the concentrations measured during M2, while those at sites 4, 5, and 7 are influenced by the concentrations obtained during M4.

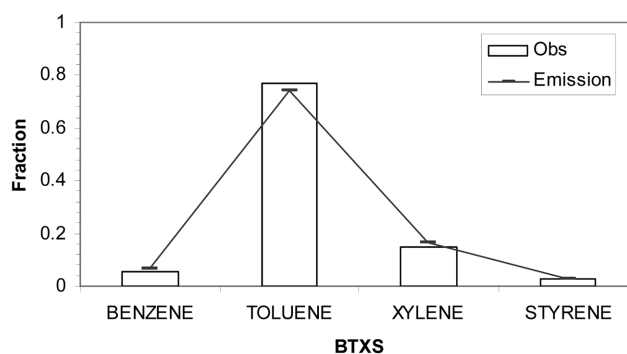
All measurements are influenced by dilution due to the increase in mixing height during daytime to avoid traffic effects during the morning and evening rush hours. Samplings at the sites 1 to 5 were taken on the first day, and on the second day samplings were done at sites 6 to 10. During the first day, measuring sites 1 to 4 were located in a valley, which indicated strong local emission effects with weak ventilation. Concentrations at sites 1 to 5 decreased with an increase in mixing height during the sampling periods, M2 and M3, while those concentrations during M1 and M4 changed irregularly for all sites. Otherwise, the results from site 6 to site 10 during the second day showed different temporal variation patterns compared to those during the first day. Sampling sites from 6 to 10 were located on relatively flat terrain along the Han River and were affected by strong ventilation. Concentrations from site 8 to site 10 decreased with time during all sampling periods. With less dilution effect by an increase in mixing height with time dependence and less photochemical destruction, however, the concentrations at sites 6 and 7 were lower than those at sites 8, 9, and 10. Sites 6 and 7 were located along the branch of the Han River, the Jung-Rang Stream, and sites 8, 9, and 10 were located along the main Han River. There are many bridges across the Han River with high volumes of traffic. Thus, the sites 8, 9, and 10 could be affected more by this traffic and by other emission sources from the other areas with stronger ventilation caused by higher wind speeds even though they had more dilution effects by the increase in mixing height and more photochemical destruction occurred.

We examined spatial variations but not seasonal variations using the 3-hr mean concentration of BTXS. It was difficult to examine the seasonal variation because of insufficient measured data. Each site showed different temporal distribution. Sites 1, 6, 8, and 10 showed similar temporal distributions of high concentrations, but other sites showed different temporal distributions. As in the previous report [15], the temporal (seasonal) differences at the measurement sites were not big except the second period M2. During the M2, most of the wind speeds were relatively strong, about 4 to 7 m s<sup>-1</sup>. The wind flow field in the complex terrain would be complicated too. Sampling sites from 6 to 10 were located on relatively flat terrain along the Han River and were affected by strong ventilation. Sites 1 to 5 were located under mountains or the hills and site 1 was close to the valley between two big mountains. It was possible to inflow from the outside of Seoul and sites from 1 to 3 and sites from 6 to 10 could be affected by the concentration transported from the outside of Seoul. Site 7 was close to site 6; however, the concentration at site 7 was much lower than that at site 6 because site 7 is surrounded by high buildings. Sites 4 and 5 may be located in the isolated region which was not affected in the wind field. Also, the high concentrations during the M2 may have been caused by an accident event such as chemical exposure.

#### 4. Comparison of Emission and Ambient Concentration

It is obvious that non-point area emissions are the major source of VOC in urban areas that are located away from industrial emission sources. When comparing BTXS emissions and ambient concentrations during the project period, a similarity between emissions and the ambient concentrations of BTXS was found and those data are shown in Fig. 6. In Fig. 6, the fraction of toluene emitted is 74% of the total BTXS emitted from non-point sources, while the fraction of ambient toluene concentration is about 77% of the total ambient BTXS concentrations. This result is consistent with a previous study by Na et al. [19], which indicated that toluene is the most important species in ozone formation as well as in the Seoul atmosphere and a species with higher concentration can be important if it is extremely reactive.

Na et al. also noted that the high ranked species obtained with the OH-reactivity-based method are toluene, m-/p-xylene, and o-xylene, which are closely associated with evaporative as the result of solvent use in the atmosphere of Seoul. According to previous studies and this study, BTXS are emitted from vehicle exhaust and



**Fig. 6.** Comparison of BTXS between emission and ambient concentrations measured from the 10 sites indicated in Fig. 2 during 2002.

the evaporation of gasoline and TXS are major compounds emitted from the use of solvents such as customer solvents, coating/painting, etc., but Benzene is not included in most of these solvents. Based on this information, we followed the method suggested by Na et al. [19] and examined two ratios: Toluene to Benzene (T/B) and Xylene to Benzene (X/B). They believed that those two ratios are a reliable indicator of solvent evaporation and photochemical removal because T and X have a higher reactivity with OH radicals compared to B. Toluene and Xylene illustrate solvent evaporation and photochemical destruction, while Benzene explains vehicle-related emissions. In this study using data for 2002, the annual mean ambient concentration and annual non-point emission are compared for the ratios of Toluene to Benzene and of Xylene to Benzene. For the entire Northeastern Seoul, these ratios for ambient concentrations are slightly higher than those for the local non-point emissions.

We conclude that ambient concentrations may be affected by long range transport as well as local emission released from northeastern Seoul. The average ratio of T/B in this study is higher than that reported in previous studies [19] but the ratio of X/B is lower. When we compared these ratios at each sampling site, the ratios by annual mean emission were not found to vary spatially but those by concentrations had different values at each site. From site 2 to site 5, lower ratios than averaged values were found for all sites, while higher values were determined at sites 6 to 10, and for site 1. These higher ratios indicate that the atmosphere of northeastern Seoul is affected by solvent emission released local sources and also emissions transported from outside sources from northeastern Seoul.

If the measured concentration is assumed to be accurate, the measured concentration of BTXS may be significantly affected by other sources or by removal and/or production processes in the atmosphere. It is noteworthy that the accuracy of ambient concentrations shows errors in concentration measurement that are within  $\pm 5\%$  and that the standard deviations are 0.003-0.005 when the total measured data is used. Thus, to assess the inaccuracy or the accuracy of the emission inventory estimated in this study, the emission inventory should be used as an input into the model for calculating the concentration of pollutants.

## SUMMARY

The present study focused on developing a new approach (SKYEM) for generating VOC emission inventories from anthropogenic sources in urban areas as a function of activity levels (e.g., populations, societal concerns, geological significance, vehicle registration data, distribution systems, and so on), emission factors, physico-chemical properties, and so on. In the urban areas, more serious pollution problems occur from non-point sources, rather than point sources. Thus, SKYEM considers emission sources within a geographic area at the small specific areas (i.e., a city, a town, or a census division) rather than those at the county level mentioned in the previous studies. In SKYEM, an emission source category includes non-point sources (a line source and an area source) and point sources. Stack point sources are primarily in industrial regions but are limited to the urban areas. Line sources are applied to mobiles on the main road or railroad vehicles by using the actual distance (discharge coefficient of a distance) covered in a given time (mileage) or using the limited mileages over the entire target region. Also,

various area sources include organic solvent use (coating/painting, dry cleaning/cleaner, publishing/printing, and consumer solvents), material handling/storage (fuel consumption including apartment/institutional incinerators, fuel retail sales such as gasoline service stations), waste treatment and disposal (sewage treatment, source contamination of water supply), and miscellaneous (asphalt paving, etc.).

During 2002, SKYEM was applied to a northeastern portion of Seoul, which includes 151 small specific divisions in seven towns (Dobong-gu (DB), Nowon-gu (NW), Jungnang-gu (JR), Seungbuk-gu (SB), Seungdong-gu (SD), Dongdaemoon-gu (DDM), and Gwangjin-gu (GJ)). The target area indicated no emissions of the seven major VOCs (BTXS (Benzene, Toluene, Xylene, and Styrene), PCE, MEK, and Phenol) from a point source (incineration plants) and from non-point sources such as dry cleaning, sewage treatment, and source contamination of the water supply. However, mobiles on other roads, publishing/printing, asphalt paving, coating/painting, fuel consumption, fuel retail sales, and consumer (domestic) solvents were significant sources of emission of the seven major VOCs.

When BTXS emissions were compared with ambient BTXS concentrations, it was obvious that non-point area emissions were the major sources of VOC in urban areas located away from industrial emission sources and that ambient concentrations may be affected by long range transport as well as local emission released from northeastern Seoul. If the measured concentration is assumed to be accurate, the measured concentration of BTXS may be significantly affected by other sources or by removal and/or production processes in the atmosphere. For further study, a comparison between the model and ambient concentrations should be performed as an indicator of the accuracy of the emission inventory.

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