A GIS-based national emission inventory of major VOCs and risk assessment modeling: Part I - methodology and spatial pattern of emissions

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Abstract−This paper presents a method for assessing and managing the South Korean atmospheric emission inventory of volatile organic compounds (VOCs) based on a geographic information system (GIS). The use of this GIS-based assessment technique makes it possible to obtain the geographical characteristics of anthropogenic emission sources, observe spatial patterns within the emission inventory, and develop a new bottom-up method for improving the spatial accuracy of emission inventories. As a case study, we estimated the emission rates of five major VOCs (benzene, ethylbenzene, styrene, toluene, and xylene) throughout South Korea for the year 2004. The spatial pattern of emissions and relative contributions of various sources showed considerable spatial variability. A comparison of estimated emissions data and observed environmental concentration revealed a reasonable degree of accuracy for the estimated values. The proposed methodologies and information provided in this study can assist in the development of environmental policy, and can be adopted internationally to obtain a more precise emission inventory.

Key words: Emission Inventory, GIS, Point Source, Non-point Source, Management

INTRODUCTION

Atmospheric emission inventories of pollutants, especially of volatile organic compounds (VOCs), play an important role not only in developing policies regarding emission regulations but also in analysis of air quality. Policy makers have to efficiently assess the quantity of the spatial density of emission sources at the finest resolution possible in order to plan abatement strategies in controlling emissions. Such databases are fundamental and necessary tools for environmental researchers who wish to assess the human and environmental risks posed by anthropogenic pollutant sources.

Most estimates of anthropogenic source emissions are based on statistical data and methods. Statistical databases are compiled by governments in many countries; accordingly, most research regarding the compilation of emission inventories is performed at the national scale or at the scale of administrative units [1-3]. In recent decades, many studies have sought to estimate the emissions of VOCs from national-scale statistical databases of various sources and sites [4]; the calculation of such estimates, and their validation, remains a challenging issue in many parts of the world [5-9]. There exists a lack of knowledge and databases for the South Korean emission inventory, even though South Korea is a major source of hazardous emissions in East Asia. Emissions of toxic chemicals from South Korea have a direct effect on surrounding nations such as China, Japan, North Korea, and Taiwan.

The Ministry of Environment (MOE) in South Korea investigates an annual Toxic Release Inventory (TRI) (388 pollutants assessed in 2004) compiled for various facilities [10]. These TRI data provide important information regarding point-source emissions; however, they do not contain geographical characteristics, meaning that researchers in the field of transport modeling encounter difficulties in assessing the environmental fate of pollutants.

Recently, several resources have been established to provide information on non-point-source emissions in South Korea. The Clean Air Policy Support System (CAPSS) is available in support of air-quality modeling, and has proven useful as input data for air-quality modeling that sought to investigate the formation of tropospheric ozone [11]; however, the system focuses on the emission of total VOCs or groups of VOCs, even though different chemical compounds show contrasting toxicological effects. We previously investigated methods of assessing emissions from point [12] and non-point-source [13,14] emission inventories for various chemicals in northeastern Seoul for the year 2002. This method has yet to be applied in a study conducted at the national scale.

Emission inventory maps are conventionally compiled by either bottom-up or top-down approaches [15]. The top-down method usually assesses emission rate based on aggregated-statistical methodologies [16], whereas the bottom-up method is generally employed to compile a site-specific emission inventory based on the detailed characteristics of each geographical segment [4]. Compared with the top-down method, the bottom-up approach requires greater amounts of site-specific information and much greater computing resources; consequently, it is difficult to realize the implementation and man-

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agement of an emission inventory generated using the bottom-up approach. Most previous research performed to assess emission inventories has adopted the top-down approach, although the bottom-up method can yield information with greater spatial accuracy.

Recently, the integration of emission inventories with geographical information systems (GIS) has been of great interest to environmental researchers and environmental policy-makers [17]. Effective GIS techniques can help in managing large amounts of emission information (such as that available in the bottom-up approach), analyzing spatial patterns within emission inventories, and enhancing the accuracy and resolution of emissions maps.

This paper represents an advance on previous related studies [12-14], and has the aim of developing a national-scale emission inventory for various chemical compounds based on a GIS database. The estimation methodologies employed in establishing the emission inventory and related information are described considering various sources such as industrial installations, road transport, railways, households, agriculture, and small-sized companies. Spatial information regarding point sources and their attributes was built into a GIS. A database of traffic density, vehicle speeds, vehicle types, and geographical characteristics for each road segment was linked with a GIS-based road map, enabling road-transport emissions to be as-

sessed via the bottom-up method. A comparison study was carried out between the bottom-up method and the top-down method in terms of road-transport emissions.

This work also provides a detailed discussion of estimates of South Korean VOC emissions for the year 2004. Based on previous studies [18,19], benzene, ethylbenzene, styrene, toluene, and xylene were selected from 388 listed chemicals as the major VOCs for analyzing emission trends and validating the accuracy of estimated emission rates. The work undertaken to date is part of a national-scale integrated environmental management project supported by the Korean Ministry of Environment and ECO-Technopia-21 over the period 2005-2008.

METHODOLOGY EMPLOYED IN ESTIMATING THE EMISSION RATE

The present study requires three kinds of geographical representations (points, lines, and areas; see Fig. 1) along with their attributes (emission activity and emission rate). Recently, various geographical map formats (DXF, DWG, IGES, and SHP) have been widely adopted. Among these formats, we selected the SHP (shape file) format, which is a vector format GIS file developed by the Envi-
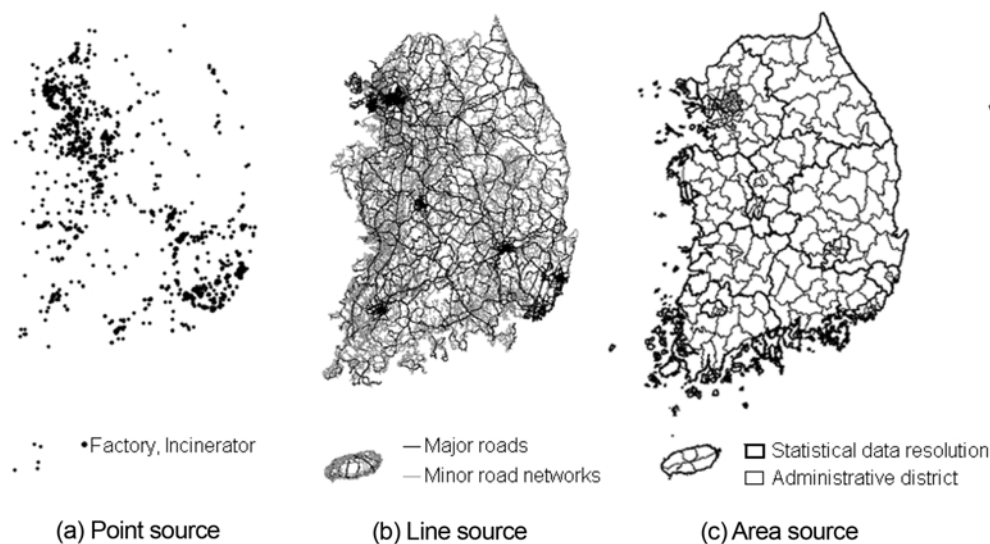

• Factory, Incinerator   — Major roads   □ Statistical data resolution
                              — Minor road networks □ Administrative district

(a) Point source   (b) Line source   (c) Area source

Fig. 1. Maps showing the geographic distribution of various source types.

Table 1. Categories of emission sources

Geographical type	Source	Sub-categories
Point	Industrial installations	Facilities, Incinerators, Factories
Line	Road transport	Major roads, Minor road networks
Area	Railways	Trains
	Households	Domestic fossil fuel consumption
		Domestic solvent use
	Small-sized enterprises and establishments	Coating/painting in the construction industry and other industries
		Dry cleaning/cleaner
		Retail fuel sales (gas stations)
		Publishing/printing
	Agriculture	Agricultural chemicals

ronmental System Research Institute (ESRI) [20]. This file format meets our requirements regarding the need to support point, line, and area shapes, and considers the relationship between geometry and attributes.

The different geographical emission sources for the major VOCs can be divided into six main categories, as listed in Table 1 (see the column headed 'Source'). These main categories are further subdivided into 10 sub-categories. The "small-sized enterprise" and "railway" categories were originally point and line sources, respectively; however, they were ultimately treated as area sources because of the limited availability of statistical data. To estimate the emission rate for each emission source, we used both the bottom-up approach (for industrial installations and road networks) and the top-down approach (for area sources, using regional activity data). The detailed methodologies employed for the various emission sources are described below.

1. Industrial Installations

Since 1998, industrial companies have submitted an annual TRI report to the MOE. The 2004 TRI report contains an inventory of 388 potentially harmful pollutants released into the atmosphere, water, and soil. The industrial installations included in the 2004 TRI report were those owned by 2893 companies (with 36 different industrial classifications) with more than 30 employees. The release rates of pollutants included in the report were generally determined by direct calculations or estimation techniques, as recommended previously by our research group [12]. The 2004 report did not contain the exact geographic coordinates of the monitored installations, even though such information is important as input data for environmental transport modeling. We therefore compiled a database of the geographic coordinates of the target companies based on the addresses included in an address database [21], combined with direct measurements via a global positioning system. Fig. 1(a) shows the locations of the 2893 installations. Most of the geographical positions were located exactly from the address database, although 5.9% of the positions contained a slight error because the address data were incomplete; in such cases, we set the position as the center of the town in which the installation was located.

2. Road Transport

Estimates of road emissions in South Korea are generally based on the zonal method (a top-down approach), which uses regional-scale activity data (e.g., number of registered vehicles (tVN), annual average mileage of vehicles (VKT, km year^{-1}), average speed) [13]:

$$E_{zone}^{car} = \sum_a (tVN \cdot VKT \cdot EF_{VOC,a} \cdot RV_a) \tag{1}$$

where E_{zone}^{car} is the emission rate from vehicle traffic in the target zone (kg year^{-1}), a is vehicle type, $EF_{VOC,a}$ is the emission factor for VOCs emitted from vehicle type a (kg km^{-1}), and RV_a is the mass fraction of the target pollutant among VOCs by vehicle type. This top-down method has been widely used in previous studies, and has proven useful in assessing the trends of regional-scale emission rates [16]. However, significant discrepancies are possible between regional data and data for individual roads, depending on the social and geographical characteristics of each road. We therefore compiled an emission activity database for each road in GIS format, and applied this database to a bottom-up method.

Fig. 1(b) shows a geographical representation of the main roads

in South Korea, based on data obtained from the National Geographic Information Institute [22] and the Korea Transport Database [23]. These data contain not only the geographical shape of each road but also several attributes (number of lanes, speed limit, road name). In South Korea, seven types of roads are generally recognized: highway, megalopolis highway, urban highway, national road, national rural road, rural road, and town road. We regrouped these roads into just two categories: major roads (highway, megalopolis highway, urban highway, national road, national rural road, and rural road) and minor road networks (town road) because traffic flow data are unavailable for minor roads. Data regarding traffic density and average vehicle speed were obtained from various national agencies [24-27] and linked with the geographical data. We did not estimate the amount of emissions from motorcycles and mopeds because of insufficient data regarding traffic density and the total number of mopeds in South Korea.

The traffic flow data in the main roads database is incomplete, and traffic data are unavailable for minor road networks; accordingly, we replaced the missing data with estimated data, based on the assumptions that vehicle speed is proportional to the speed limit and that traffic density is proportional to the number of lanes. A regression analysis of speed limit versus annual averaged observed traffic speed yielded a coefficient of determination of 0.61, and a regression analysis of the number of lanes versus traffic volume yielded a coefficient of determination of 0.33 (Fig. 2). The slopes of the regression lines for traffic speed and traffic volume were about
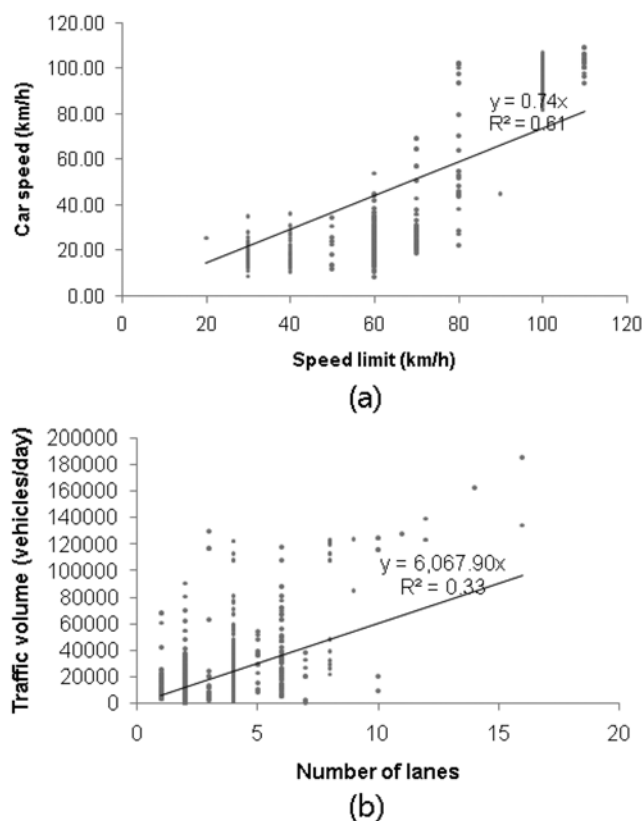

Fig. 2. Relations between monitored vehicle speed and speed limit (a), and between traffic volume and the number of lanes (b).

0.74 and 6,000, respectively. In the case of missing data for minor road networks, we therefore assumed a speed equal to 74% of the speed limit, and traffic volume of 6,000 vehicles per day per lane. For major roads, the same method was applied to each road group. Missing data regarding traffic volume upon major roads were replaced by the total traffic flow per total number of lanes by road type for each road segment. Finally, the annual amount of emissions from each road was estimated as follows:

$$E^{car} = \sum_a (TF_a \cdot RL \cdot EF_{VOC,a} \cdot RV_a) \tag{2}$$

where E^{car} is the annual emissions of the pollutant of concern from each road segment (kg year^{-1}), TF_a is the traffic flow by vehicle type for each road segment (year^{-1}), and RL is the length of road (km). The values of the emission factors are taken from previous studies [13,14].

3. Trains

Emissions from railway transport were calculated by the following zonal method:

$$E^{train} = \sum_b (TFC_b \cdot EF_b) \tag{3}$$

where E^{train} is the total emission rate of the target chemical from the target site (kg year^{-1}), b is the type of train, TFC_b is the total fuel consumption of train type b at the target site (L year^{-1}), and EF_b is the emission factor of the target chemical from train type b (kg L^{-1}). Fuel consumption data were obtained from Korea Railroad [28], and emission coefficients were taken from the Australian National Pollutant Inventory (ANPI) [29].

4. Domestic Fossil Fuel Consumption

Domestic consumption of fossil fuel in South Korea generally involves boiler-based heating using various fuel types (briquettes, coal, oil, diesel gas). This type of fuel consumption represents an anthropogenic source of VOCs. We estimated emissions using regional fuel-consumption data and a relevant emission factor:

$$E^{boiler} = \sum_c (FC_c \cdot EF_c) \tag{4}$$

where E^{boiler} is the emission rate of the target compound (kg year^{-1}), FC_c is the consumption of fossil-fuel type c in a specific administrative district (L year^{-1}), and EF_c is the emission factor (kg L^{-1}) taken from ANPI. Data regarding the amount of fuel consumed in each local area were obtained from Report on Energy Census [30].

5. Domestic Solvent Use

Fugitive emissions arising from the use of domestic products (haircare products, toiletries, propellants, laundry products, waxes, and car-care products) are the main source of VOCs [14]. The emission rate from such sources is calculated according to following equation:

$$E^{solvent} = \frac{\sum_d \left(ER_d \cdot \sum_e \sum_f RV_{def} \cdot PC_{def} \right)}{TP} \cdot PO \tag{5}$$

where $E^{solvent}$ is the emission rate arising from domestic solvent use (kg year^{-1}), d is the category of product, e is the class of manufacturing industry, f is the product type, ER_d is the ratio of emissions of volatile chemical into the atmosphere to the amount of VOC content by d, RV_{def} is the mass fraction of VOCs among the ingredients of each product, PC_{def} is the annual amount of product sold by each business (kg year^{-1}), TP is the national population, and PO is the population of the target area. Data on the annual product sales by business and class of manufacturing industry were sourced from the Chemical Substances Distribution Amount Investigation (CSDAI) [31]. Data regarding the ratio of volatile chemical emissions to the total product ingredients were sourced from Emission Inventory Improvement Program (EIIP) [32].

6. Coating/Painting in the Construction Industry and other Industries

Emissions arising from coating/painting in the construction industry and other industries (hereafter 'coating/painting') can be estimated from the amount of product use (as activity data) in a target area. In estimating emissions, it is assumed that all VOCs in the used product volatilize into the atmosphere. The governing formula in this regard is

$$E^{product} = \sum_g PC_g \cdot RV_g \tag{6}$$

where $E^{product}$ is fugitive emissions of volatile substances arising from the coating/painting process (kg year^{-1}), g is the product type, PC_g is product use in the target domain (kg year^{-1}), and RV_g is the mass fraction of the volatile substance in the specified product. Data regarding product use were obtained from CSDAI. Administrative districts in South Korea do not maintain product-use databases for coating/painting; therefore, spatial allocations were made using a database of workplace size, which is freely accessible from the Korea National Statistical Office [33]. The mass fraction of each volatile substance was sourced from CSDAI.

7. Dry Cleaning

Dry cleaning is any cleaning process for clothing and textiles that employs a chlorinated organic solvent rather than water. The process can be divided into four steps: cleaning in a solvent bath, drying with hot air and recovery of solvent, deodorization, and regeneration of the used solvent. Emissions are largely produced during the deodorization process. The governing equation for calculating emissions produced by the dry cleaning process is

$$E^{dry} = \sum_h \frac{MC_h \cdot RV_h \cdot DP}{TP} \tag{7}$$

where E^{dry} is the emission rate from the dry cleaning process (kg year^{-1}), h is the number of companies that produce the chlorinated organic solvent used in dry cleaning, MC_h is the annual amount of solvent produced (kg year^{-1}), RV_h is the mass fraction of VOCs in the solvent employed in dry cleaning, and DP and TP are the population densities in the specified administrative district and in South Korea, respectively. All data were sourced from CSDAI.

8. Retail Fuel Sales

Emissions arising from retail fuel sales are mainly derived from oil supplied at gas stations. Emissions also occur during transport, storage, and distribution of the fuel; however, the emission rate in such cases is insignificant compared with that for oil supplied at gas stations. The emission rate is estimated by

$$E^{gas} = GC \cdot EF \tag{8}$$

where E^{gas} is the total emissions of a specific pollutant in the target domain (kg year^{-1}), GC is the amount of oil supplied in the target domain (kL year^{-1}), and EF is the emission factor for the target pol-

Table 2. Methods of spatial allocation employed for the main area sources

Source categories	Allocation index to the municipal scale	Landuse categories to allocate to grid cell network from the municipal scale
Train	Amount of fuel consumption	Human living area
Domestic fossil fuel consumption	Amount of fuel consumption, Population density	Human living area
Domestic solvent use	Amount of product sales, Population density	Human living area
Coating/painting in the construction industry and other industries	Workplace size, Amount of product consumption Population density	Human living area
Dry cleaning/cleaner	Population density	Human living area
Retail fuel sale (gas stations)	Amount of fuel consumption, Population density	Human living area
Publishing/printing	Amount of product consumption by company	Human living area
Agricultural chemicals	Agricultural area of object crop	Agricultural area

lutant (kg kL^{-1}). Data on the quantity of supplied oil were sourced from the Korea Oil Station Association [34], and emission factors were taken from the EIIP.

9. Publishing and Printing

Emissions arising from the publishing and printing industry were estimated according to the number of products used and the mass fraction of VOCs. The effectiveness of the removal of exhaust gas was considered in cases where the company operated a removal system for VOCs:

$$E^{print} = \sum_h \sum_c \sum_i (IC_{ich} \cdot RV_{ih} \cdot (1-AE_c)) \qquad (9)$$

where E^{print} is the emission rate of selected species to the atmosphere (kg year^{-1}), i is the type of product, h is the product classification, c is the type of business, RV_{ih} is the mass content of the selected species by product, and AE_c is the efficiency of removal from the treatment facility when released after treating exhaust gases. The activity data used to estimate emissions from publishing and printing were obtained from CSDAI.

10. Agriculture

Agricultural VOC emissions occur during the application of agricultural chemicals (e.g., insecticide, fungicide, acaricide, nematocide, herbicide, rodenticide, plant growth regulator, mollucicide, and bacteriocide). Emissions to the air compartment are calculated as the sum of the emission rates of active ingredients (the main components of agricultural chemicals, which act to protect the crop) and inert ingredients (solvents, additive chemicals, and surfactants):

$$E^{agri.} = E^{active} + E^{inert} \qquad (10)$$

for which

$$E^{active} = EF \cdot \sum_p tTPAC_p \cdot \frac{PA_p}{TPA_p} \cdot \frac{CA_p}{tCA_p} \qquad (11)$$

and

$$E^{inert} = \sum_p tTPAC_p \cdot \frac{PI_p}{TPA_p} \cdot \frac{CA_p}{tCA_p} \qquad (12)$$

where $E^{agri.}$, E^{active}, and E^{inert} are the agricultural emissions of the total, active, and inert ingredients, respectively (kg year^{-1}); p is the product type of agricultural chemicals; $tTPAC_p$ is the amount of active ingredients sold nationally (kg year^{-1}); PA_p and PI_p are the mass frac-

tions of the target active and inert ingredients, respectively; TPA_p is the mass fraction of total active ingredients in product p; and CA_p and tCA_p are the areas under cultivation in the object crop in the target domain and nationally, respectively. Data on the product list of agricultural chemicals, amount of active ingredients sold nationally, and the mass fraction of active ingredients in each product were obtained from the Agrochemical Year Book [35]. The mass fraction of inert ingredients was sourced from the Rural Development Administration [36], and emission factors were taken from the EIIP.
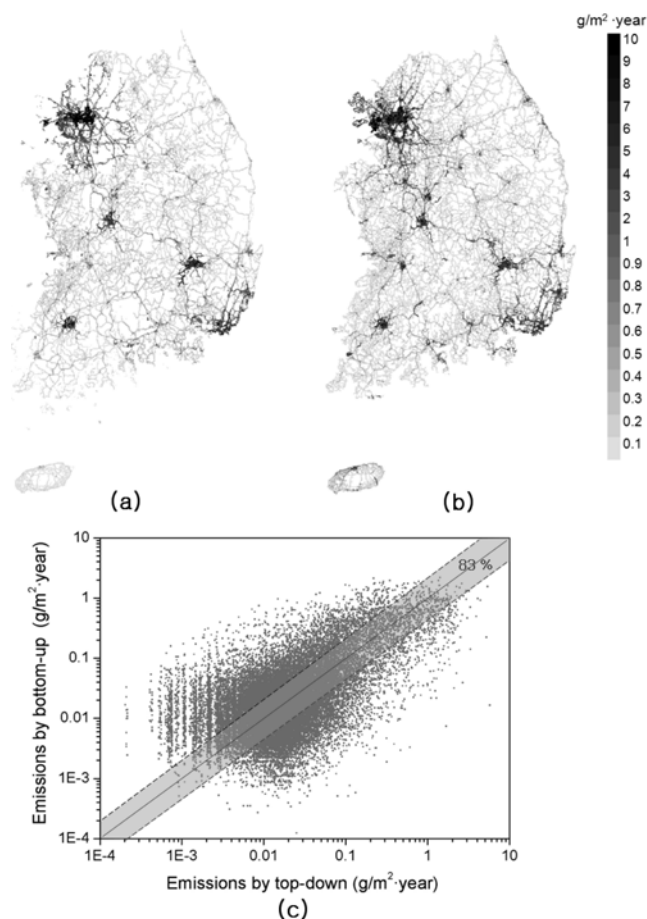
11. Spatial Allocation

The point and line emissions were directly allocated to 1×1 km grid cells. For area-type emission sources, we used various surrogate indices for the spatial allocation of emissions (top-down method). In most cases, a multi-step allocation method was applied: first from national or regional emissions to municipal emissions [Fig. 1(c)], and then to a 1×1 km grid cell network. The indices employed for allocation from the national or regional level to the municipal level were population density, sales and consumption data for each chemical product, and workplace size (see Table 2). The index used to allocate data to the grid cell network from the municipal scale was a landuse map. Among the different landuse categories, manufactured anthropogenic VOCs (i.e., not naturally generated VOCs) are only released in relevant categories employed in the landuse map. We assumed that most of the manufactured VOCs were emitted from human living areas such as houses, industrial areas, business districts, recreational areas, and public areas. Agricultural chemicals were only emitted from agricultural areas.

RESULTS AND DISCUSSION

1. Comparison of Top-down and Bottom-up Methods for Estimates of On-road Vehicle Emissions

In comparing the top-down and bottom-up methods, we estimated national toluene emissions. The total emissions of toluene by on-road vehicles, as calculated using the top-down and bottom-up methods, were 2,084 and 2,326 tons year^{-1}, respectively, yielding similar rates. The estimate based on the bottom-up method is 11.6% larger than the estimate based on the top-down method, although local or site-specific emission rates show considerably variation (Fig. 3).

Fig. 3(a) and (b) show the spatially allocated (to 1×1 km grid

Fig. 3. Graphical representation of spatially allocated emission rates (1×1 km grid) calculated using the top-down method (a) and bottom-up method (b), and comparison of emission rates estimated using the two methods (c).

cells) on-road emission data calculated by the top-down and bottom-up methods, respectively. The spatial pattern of the emissions calculated by the top-down method shows a more isolated higher emission rate in urban areas than the pattern calculated by the bottom-up method. The emission pattern calculated with the bottom-up method shows a greater spatial spread in emissions, and corridors of emissions between urban sites. Fig. 3(c) shows a site-matched point-to-point comparison of emissions estimated by using the top-down and bottom-up methods. Eighty-three percent of the emission rates estimated by the bottom-up method fall within a 2-fold difference of the values calculated by the top-down method; the remaining 17% fall within a 2-fold to 100-fold difference of the values calculated with the top-down method. This significant difference between the two estimation methods can lead to errors in interpreting the present state of local air pollution.

2. Spatial Distribution of VOC Emissions

Fig. 4 shows the estimated annual emissions of target VOCs in South Korea during 2004. The annual emissions of the major VOCs add up to 50,409 tons, representing benzene (3,109 tons), ethylbenzene (1,296 tons), styrene (2,815 tons), toluene (33,329 tons), and xylene (31,656 tons). The different materials show different spatial patterns of emissions: the emission patterns of benzene and ethyl-

benzene reflect the road pattern [Fig. 4(b) and (c)], the area sources of toluene and styrene are more conspicuous than point and line sources [Fig. 4(d) and (e)], and xylene emissions are widespread throughout South Korea [Fig. 4(f)].

To clearly discern the spatial pattern of emissions, the study area was divided into 170 numbered sub-sections (Fig. 5). Sections 23, 24, 34, 65, 88, and 103 are considered representative of urban areas; sections 100, 115, and 125 are industrial areas; sections 33, 44, 54, 55, 108, and 109 are mixed urban-industrial areas; and the remaining sections are mostly rural areas.

Fig. 6 shows histograms of the emissions of various compounds from each of the 170 sub-sections, along with pie graphs that show the percentage contributions of different sources at the national scale. There exist considerable differences in the dominant source types between national-scale data and that for individual sub-sections.

Nationally, benzene is principally generated by road traffic (72%), industrial installations (18.5%), and retail fuel sales (5.7%); however, in sub-sections 42, 90, 100, and 115, the majority of benzene emissions are generated by industrial installations (96%, 65%, 86%, and 87%, respectively) [Fig. 6(a)]. In urban areas (sub-sections 33 and 34), only a minor proportion of benzene emissions are generated by retail fuel sales (6.4% and 8.8%, respectively).

Nationally, half (50.3%) of all ethylbenzene emissions are generated by road transport, 34.8% by industrial installations, and 12.7% by coating/painting activities [Fig. 3(b)]. In contrast to this national-scale trend, industrial installations are locally the main emission source in sub-sections 42 (97.5%), 53 (91.6%), 100 (88.1%), 108 (71.9%), 109 (35.3%), 112 (93.5%), 115 (76.2%), and 118 (85.9%), which represent typical industrial areas and several industrial installations located within rural areas. In addition, a significant amount of ethylbenzene was generated by coating/painting activities in sub-sections 23 (21.8%), 24 (17.2%), 33 (22.8%), 34 (19%), 44 (22.2%), 65 (18.3%), 88 (16.4%), 103 (32.8%), 106 (32.5%), 107 (32.8%), 108 (10.6%), and 109 (16.9%). These sub-sections are mostly urban and mixed urban-industrial areas.

As shown in Fig. 6(c), styrene is mainly emitted by coating/painting in the construction industry and other industries (70%), with lesser emissions observed from industrial installations (16.8%) and domestic solvent use (10.3%). Industrial installations are the major emission source in sub-sections 42 (98%), 100 (74.2%), and 115 (88.3%). Subsections 100 and 115 are representative industrial areas, and sub-section 42 contains a factory that contributes most of the recorded styrene emissions in this sub-section. Domestic solvents make a considerable contribution to styrene emissions in urban areas such as sub-sections 23 (10%), 24 (13.3%), 33 (9.3%), 34 (12%), 88 (13%), and 109 (10.9%).

Nationally, 56.5%, 27.2%, 7%, and 5.6% of toluene emissions are generated by coating/painting, industrial installations, road transport, and publishing/printing, respectively. Toluene is widely used as a solvent in paint, ink, and adhesives, and as a precursor material in producing aromatic compounds in various chemical industries. Fig. 6(d) shows that toluene is emitted from various industrial installations and in the coating/painting and publishing/printing industries, which are concentrated in specific sub-sections. Traffic flow in urban areas also leads to considerable emissions of toluene.

Nationally, most xylene is emitted by publishing/printing (57%), industrial installations (28.8%), and domestic solvent use (7.4%).
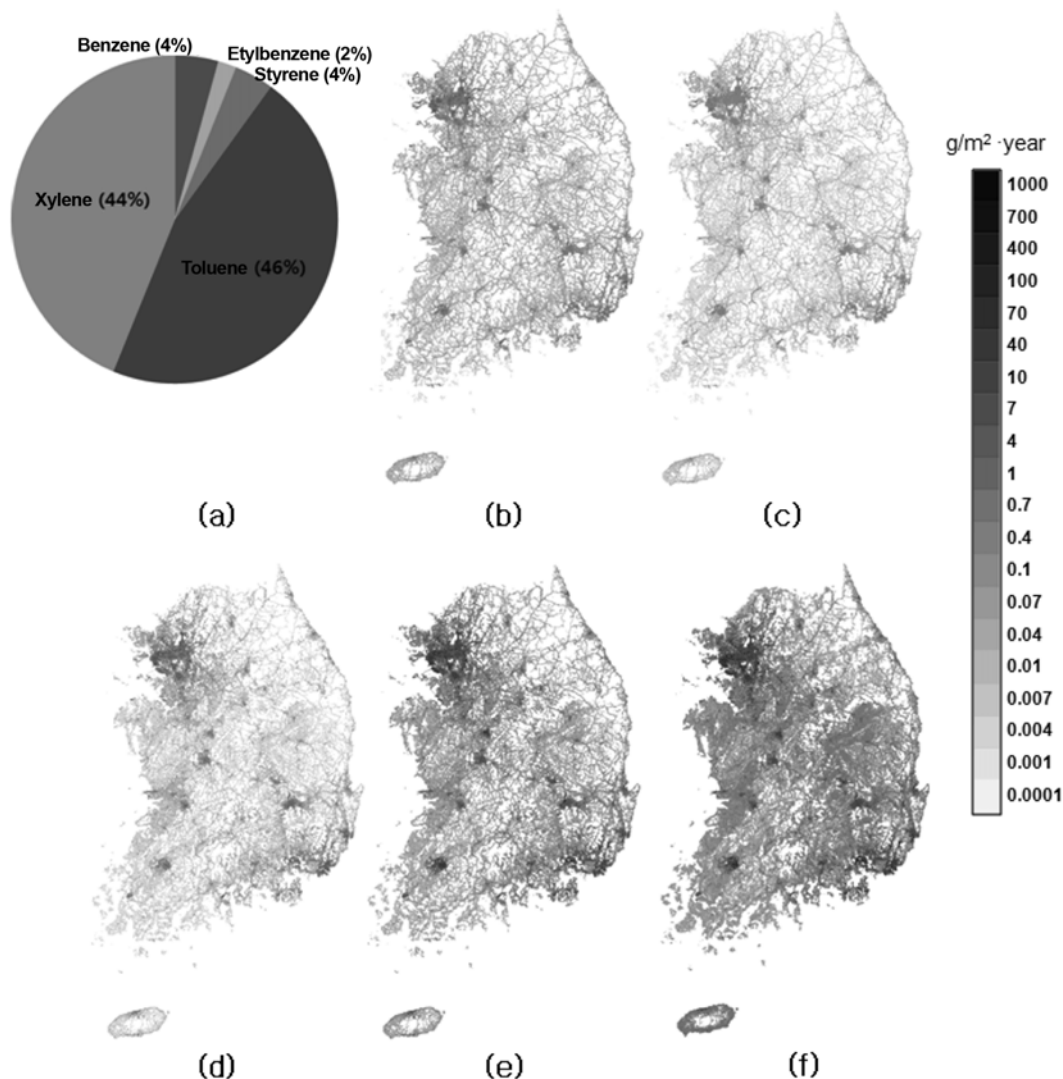
Fig. 4. National emission rates of major VOCs in South Korea during 2004 (a), and the spatial distribution of total annual emissions of benzene (b), ethylbenzene (c), styrene (d), toluene (e), and xylene (f) for 2004.

Xylene emissions from the 170 sub-sections are shown in Fig. 6(e). Coating/painting is the major emission source in urban areas [sub-sections 23 (85.2%), 24 (86.5%), 34 (87.7%), 44 (80.6%), and 103 (91.3%)], while industrial installations are the main source of toluene in industrial areas and at specific factories [sub-sections 100 (88.8%), 112 (93.5%), and 118 (90.4%)]. The publishing/printing industry and industrial installations are important sources of styrene emissions in mixed urban-industrial areas [sub-sections 33 (75.2% and 17.6%, respectively), 43 (43.4% and 49.1%), 108 (58.7% and 36.4%), and 109 (63.2% and 29.6%)]. As expected, agricultural emissions of xylene are observed in rural areas.

The estimated VOC emissions in South Korea can be compared with estimates for other nations, yielding information on the accuracy of emission trends estimated in the present study and enhancing our understanding of differences in emission trends between South Korea and other countries. In Spain, the highest values of VOC emissions are found in the largest cities, reflecting evaporative emissions from road traffic and the use of solvents in the domestic and commercial sectors [4]. These observations are consistent with

the findings of the present study. In Japan, the contribution of vehicle emissions to benzene concentrations in ambient air is estimated to have been 85% in 2003 [37]. Similarly, in the present case, 75% of benzene is generated by road transport. Wei et al. studied VOC emissions in China during 2005 [38], finding that the order of contributions by source type and species was (1) biofuel combustion>transportation>energy combustion>solvent use for benzene; (2) industrial÷process energy combustion>biofuel combustion for styrene; (3) solvent use>transportation>biofuel combustion>industrial process for toluene; and (4) solvent use>transportation>industrial process for xylene. The order of contributions in China is remarkably different from that in South Korea, probably reflecting life-style differences [e.g., biofuel (vegetation residue) is rarely used in South Korea].

To validate the qualitative emission trends obtained for the subsections, we compared the emission rates estimated for 11 sub-sections with observed concentrations. Observation data for 2004 is freely accessible from the MOE Web site [39]. The locations of the 11 observation sites are indicated by black crosses in Fig. 5 upon
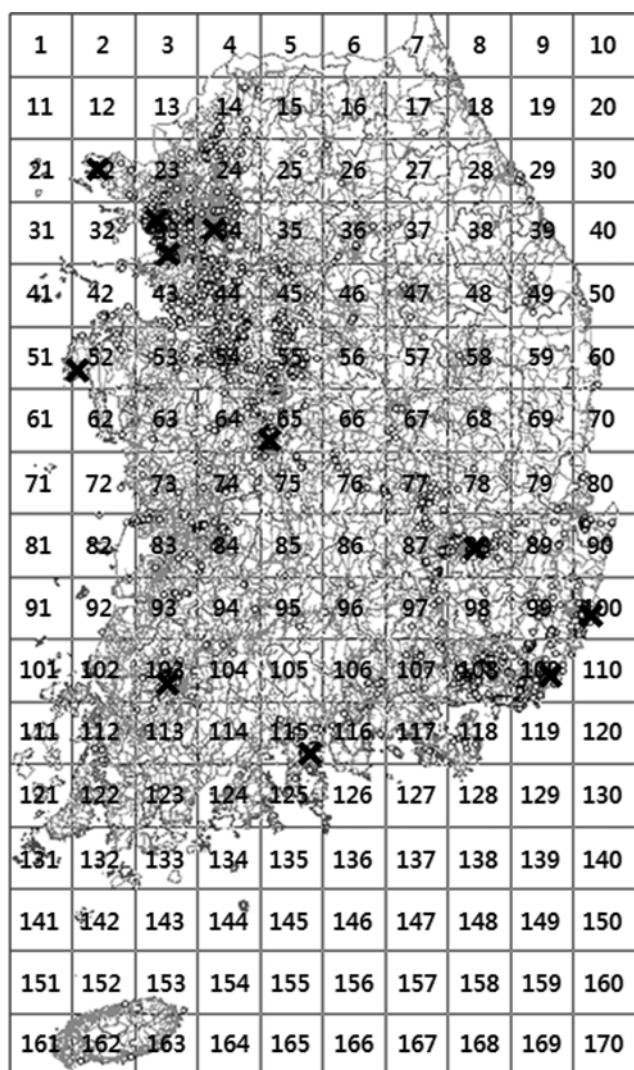
Fig. 5. Sub-sections created for the analysis of emission trends. Black crosses represent the locations of measurement sites.

sub-sections 22, 33 (two sites), 34, 52, 65, 88, 103, 109, and 115. The two sites in sub-section 33 were averaged, yielding observation data for ten sites. Fig. 7 shows a site-matched point-to-point comparison of the observed concentrations and estimated emission rates. Interestingly, a regression analysis revealed that emission rates $(g\ m^{-2}\ yr^{-1})$ are related to observed concentrations by a slope factor of 0.1. The coefficient of determination is 0.45, and most of the emission rates are within 10-fold differences (shaded area in Fig. 7) of the corresponding measured values. Even though the data do not take into account meteorological and terrestrial effects, the spatial emission trends show a strong relationship with observed concentrations. The emission rates of benzene and ethlybenzene are lower than those of toluene and xylene, and data for styrene show a high degree of scatter. The result of the comparison solely reflects the qualitative relation between the estimated emission rate and observed concentrations. Therefore, it is possible to under- or overestimate emission rates by using the proposed method. To demonstrate the accuracy of estimated emission rates would require a quantitative analysis based on environmental modeling, especially modeling of

air dispersion. Such a quantitative analysis is undertaken in Part II of this work.

3. Uncertainties in the Proposed Approach

An emission inventory is largely based on available knowledge regarding emission factors, activity data and statistics, and estimation methods; consequently, uncertainties are possible in the estimation of emission quantities because of a lack of appropriate data. The following factors have a considerable effect upon emission estimates.

In the present study, the locations of industrial installations were determined by an address searching method. Several of the locations were not clearly stated in the database (5.9% of database); this error can be an important component of inaccuracies in spatially resolved emission trends if the incorrectly located industrial installation contributes a large amount of emissions. To improve the accuracy of emission estimates, it is important to determine the location of industrial installations by on-site GPS measurement.

As stated above, motorcycle and moped emissions were not included in our estimates of transport-related emission sources because of a lack of reliable data. It has been reported that motorcycles and mopeds generate 45% of VOC emissions in Shanghai, China [9]. Although differences in transport trends exist between China and South Korea, it is possible that motorcycles and mopeds are also an important source of VOC emissions in South Korea. This possibility merits further research.

Knowledge of the species of VOCs emitted during vaporization (including in the coating/painting and printing/publishing industries, and various domestic solvent uses) is based on information regarding the composition of solvents in the product. It must be carefully considered that there exists a variety of VOC compositions in different solvent-bearing products. Fortunately, the large uncertainty that exists regarding the proportion of individual species is reduced when species are aggregated into classes [40].

Additional possible sources of VOC emissions are small businesses (e.g., dyeing, bleaching, fat removal, and cleaning businesses), waste disposal, and illegal incineration. It is possible that these types of sources make a considerable contribution in terms of overall VOC emissions.

CONCLUSION

We compiled VOC species profiles for ten emission-source categories with the aim of determining the true state of pollutant emissions in South Korea. Spatial emission trends were assessed and analyzed by integrating GIS and emission assessment methods. The use of a GIS-based emission inventory makes it possible to implement a bottom-up method to manage and calculate the emission inventory, although this approach requires the handling of a large amount of data. Based on a case study of spatial trends in five major VOCs (benzene, ethlybenzene, styrene, toluene, and xylene), we found that the major source of emissions varies markedly with VOC species and location. These results suggest that policy-makers must take into account the spatial trends of individual species, and that different reduction strategies must be applied according to spatial trends. A comparison of estimated and observed emission data revealed that the estimated emissions provide a good description of qualitative emission trends. The emission data estimated in this study
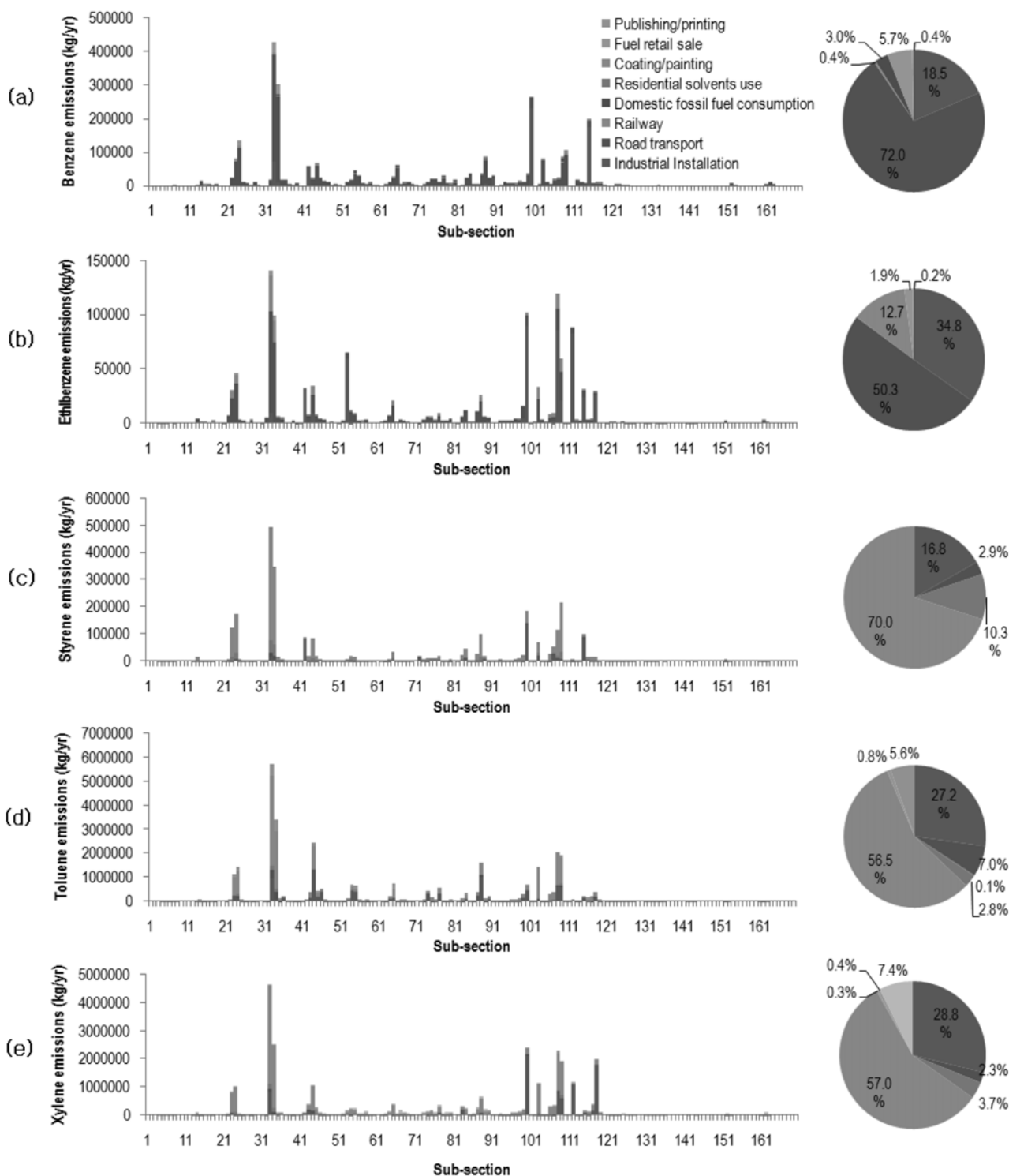
Fig. 6. Proportion of VOC emissions from various sources at the national scale (pie charts) and for each sub-section shown in Fig. 5 (histograms): (a) benzene, (b) ethylbenzene, (c) styrene, (d) toluene, and (e) xylene.

can be used as input data in atmospheric modeling studies, as basic data for developing environmental policy, and in demonstrating the reliability of estimated emission trends between different base years using long-term trends in ambient air quality.

The emission source profiles reveal several factors that might give rise to uncertainties in estimates of VOC emissions. We described

these uncertainties and recommended steps to improve the accuracy of emission estimates. Additional detailed studies are required to achieve improved quantitative results and higher spatial resolution.

This study was designed to assess the steady-state annual emissions. The steady-state assumption for the spatial emission trend is feasible for understanding of the chronic effects of hazardous ma-
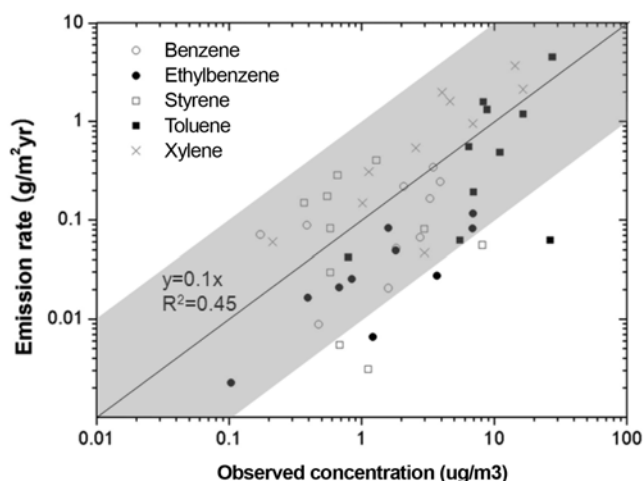
Fig. 7. Comparison of emission rates and observed concentrations.

terials; at the same time, hourly, weekly, monthly and annual variations of emissions are also an important factor for better understanding of the formation of ozone and other secondary oxidants and for better practices in management of acute adverse health effect. The consideration of temporal variation of emissions will be addressed in the future study.

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