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Characteristics of Ozone Precursor Emissions and POCP in the Biggest Port City in Korea

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ABSTRACT

Emissions of ozone precursors (NO_x and VOCs) and photochemical ozone creation potentials (POCPs) of VOC emission sources were investigated in the largest port city (i.e., Busan), Korea during the year 2011. This analysis was performed using the Clean Air Policy Support System (CAPSS) national emission inventory provided by the National Institute of Environmental Research (NIER), Korea. For NO_x, the emissions from off-road mobile sources in Busan were the most dominant (e.g., 31,202 ton yr^{-1}), accounting for about 60% of the total NO_x emissions. The emission from shipping of off-road mobile sources (e.g., 24,922 ton yr^{-1}) was a major contributor to their total emissions, amounting to 47% of the total NO_x emissions due to the port-related activities in Busan. For VOCs, the emission source category of solvent usage was predominant (e.g., 36,062 ton yr^{-1}), accounting for approximately 82% of the total VOC emissions. Out of solvent usages, the emission from painting was the most dominant (22,733 ton yr^{-1}), comprising 52% of the total emissions from solvent usages. The most dominant VOC species emitted from their sources in Busan was toluene, followed by xylene, butane, ethylbenzene, n-butanol, isopropyl alcohol, and propane. The major emission sources of toluene and xylene were found to be painting of coil coating and ship building, respectively. The value of POCP for the off-road mobile source (61) was the highest in ten major activity sectors of VOC emissions. Since the POCP value of ship transport of off-road mobile source (72) was also high enough to affect ozone concentration, the ship emission can play a significant role in ozone production of the port city like Busan.

Key words: CAPSS, Emission, Busan, POCP, Ozone

1. INTRODUCTION

Ozone precursors such as nitrogen oxides ($NO_x = NO + NO_2$) and volatile organic compounds (VOCs) can play a pivotal role in ozone production through complex sunlight-driven nonlinear photochemistry (Sillman, 1999, 1995; Kleinman *et al*., 1997). In general, air quality issues in metropolitan areas such as Los Angeles, Mexico City, Beijing, and Seoul have been associated with ozone nonattainment due to the precursor's emission from on-road mobile sources. Thus, the accurate estimation of ozone precursor emissions from emission sources is prerequisite to resolve the issues before ozone control strategies are implemented to improve the air quality in metropolitan areas. Changes in the emissions of ozone precursors from on-road mobile sources in various atmospheric environments are highly sensitive to ozone formation (Song *et al*., 2012). Ozone formation in urban areas such as New York, Los Angeles, and Seoul is typically sensitive to VOC concentration, but that in rural (and suburban) and coastal areas is sensitive to NO_x concentration (Song *et al*., 2012, 2010; Kim, 2011; Steiner *et al*., 2006; Kleinman *et al*., 2000). In contrast, ozone production was reported to be sensitive to NO_x concentration in Atlanta, Gerogia (Sillman *et al*., 1995).

Accurate estimation of air pollutant emissions in northeast Asia (especially China) is a key input parameter for simulation of a 3-dimensional chemical transport model (CTM) to study ozone related to the significance of long-range transboundary ozone and its precursors. Several studies have developed emission inventories of air pollutants for China (Wang *et al*., 2005; Streets *et al*., 2003). The emissions of NO_x and VOCs in eastern China in year 2000 were reported to be 5,999 and 4,167 kton with the largest sector contributor of power generation (35%) for NO_x (Wang *et al*., 2005). Their emissions of NO_x and VOCs are projected to be 130% and 50% higher in 2020, respective-

ly, without additional controls utilized (Business As Usual: BAU). In Korea, national emission inventory of air pollutants during 1999-2011 are provided by National Institute of Environmental Research (NIER) (http://airemiss.nier.go.kr/main.jsp). For NO_x, annual national emissions during 2007-2011 ranged from 1,014 (2009) to 1,188 kton (2007), with no distinct trend, while those for VOCs ranged from 851 (2009) to 875 kton (2007). Note that VOC emissions provided by the NIER in Korea did not consider biogenic emissions. The national biogenic emissions of isoprene and monoterpenes in 2010 were 342 and 98 kton, respectively based on an emission inventory of Model of Emissions of Gases and Aerosols from Nature (MEGAN)-Monitoring Atmospheric Composition and Climate project (MACC) (http://eccad.sedoo.fr/eccad_extract_interface/JSF/page_login.jsf).

When ozone production is sensitive to VOC concentrations under certain atmospheric conditions, it depends on speciation of VOCs due to different reactivity. Thus, the concept of photochemical ozone creation potential (POCP), which is a relative amount of photochemical ozone concentration contributed by various VOC species, was introduced by Derwent and Jenkin (1991). Some a few studies on the POCP in Asian countries have been carried out during recent decades. Lee *et al.* (2007) found that toluene and m/p-xylene were reported to be the predominant contributors to ozone production in Seoul. Aromatics (toluene and m-xylene) also played a dominant role in Shanghai ozone formation (Ran *et al.*, 2009). Furthermore, the studies in diverse atmospheric condition such as Busan, which is the world's fifth busiest seaport by cargo tonnage and surrounded by high mountains, are unique opportunities for ozone chemistry. However, the study on the contribution of VOC to ozone production in Korea is still scarce and thus more studies are needed to implement ozone control strategies. During the last decade (2001-2013), Busan has experienced the upward trend in annual mean ozone concentration and the number of ozone exceedance days (1-hr and 8-hr) with slope of 0.4 ppb yr^{-1} for annual mean ozone long-term trend (Fig. 1). In this study, the emissions of NO_x and VOCs from specific emission sources in Busan in 2011 were in detail estimated and POCP values for the emission source were also estimated to identify the significant contributor to ozone production.

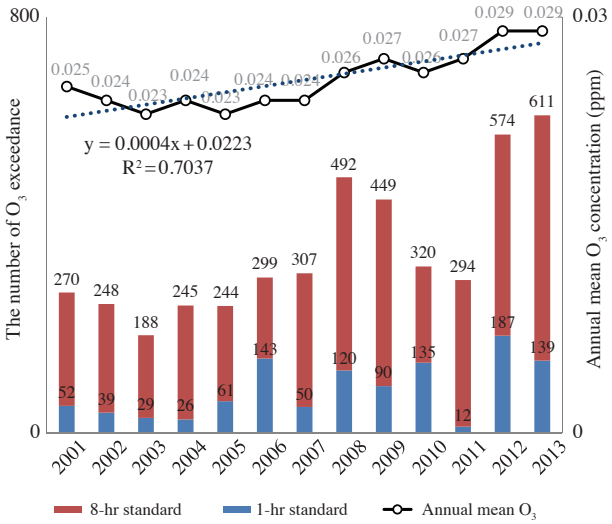

Fig. 1. The number of ozone standard exceedance (1-hr and 8-hr) and variation of annual mean ozone concentration during 2001-2013 (Source: BMCIHE, 2014, http://ihe.busan.go.kr/04data/09_01.jsp).

2. METHODS

2. 1 Estimation Method of Ozone Precursors

Korea emissions inventory in 2011, developed as an effort in the Clean Air Policy Support System (CAPSS) database, was used in this study (http://airemiss.nier.go.kr/main.jsp). The study area is Busan, is the second largest metropolis after Seoul, with a population of approximately 3.6 million and an area of 767 km^2. In CAPSS, the emission category was based on EMEP/CORINAIR framework and it was classified into 12 source classification codes (SCCs). The SCC consists of four levels. Level 1 means a major classification, and the higher level represents more detailed classification (Table 1). The number of emission sources in levels 2, 3, and 4 are 58, 334, and 579, respectively. The point source pollutant emissions by fuel combustion for the emission categories of electric generating utility (GEU) combustion, non-EGU (NEGU), and industrial combustion were calculated using stack emission management system (SEMS) as a bottom-up approach. The area source emissions are calculated using statistical data as top-down approach. Detailed descriptions on the emission calculation method are given in the NIER (NIER, 2013). In general, the emission of air pollutants were estimated by the product of emission factors of air pollutants and fuel consumption. In contrast, for the estimation of aircraft emissions in off-road mobile sources, its emission rate was calculated based on an activity (Landing/Take-Off, LTO)-based approach. In the estimation of ship and aircraft emissions, fishing boats and military aircrafts were not considered due to limited information. The emissions during cruise mode of aircraft were not considered, assuming that it may not contribute to ground-level concentration. The emission factors were adopted from

Table 1. Characteristics of ozone precursor's emissions in Busan city for 2011.

Classification		NO_x	VOCs	VOC/NO_x ratio
Level 1	Level 2			
Electricity generation utility	Public	963 (1.8%)	410 (0.9%)	0.42
	Private	387 (0.7%)	2 (<0.1%)	0.01
Non-industrial utility combustion	Agricultural and livestock facility	503 (1.0%)	7 (<0.1%)	0.01
	Commercial and public facility	3,102 (5.9%)	84 (0.2%)	0.03
	Residential	2,540 (4.8%)	109 (0.2%)	0.04
Manufacturing combustion	Process furnace	923 (1.7%)	45 (0.1%)	0.05
	Combustion facility	50 (0.1%)	1 (<0.1%)	0.03
	Others	881 (1.7%)	34 (0.1%)	0.04
Industrial process	Wood and pulp	0	0	
	Inorganic chemicals	30 (0.1%)	0	
	Food and beverage	0	850 (1.9%)	
	Ammonia	0	0	
	Organic chemicals	0	1 (<0.1%)	
	Iron and steel	375 (0.7%)	169 (0.4%)	0.45
	Others	408 (0.8%)	41 (0.1%)	0.10
Storage and transport	Gasoline supply	0	668 (1.5%)	
Solvent utilization	Painting	0	**22,733 (51.5%)**	
	Degreasing	0	1,288 (2.9%)	
	Dry Cleaning	0	1,632 (3.7%)	
	Others	0	**10,374 (23.5%)**	
On-road mobile	RV	1,207 (2.3%)	138 (0.3%)	0.11
	Bus	887 (1.7%)	368 (0.8%)	0.42
	Passenger	1,373 (2.6%)	1,089 (2.5%)	0.77
	Van	351 (0.7%)	48 (0.1%)	0.14
	Motorcycle	208 (0.4%)	1,128 (2.6%)	5.00
	Taxi	545 (1.0%)	80 (0.2%)	0.15
	Special car	285 (0.5%)	40 (0.1%)	0.14
	Truck	**6,303 (11.9%)**	621 (1.4%)	0.10
Off-road mobile	Construction	**5,102 (9.7%)**	545 (1.2%)	0.11
	Agricultural machinery	105 (0.2%)	12 (<0.1%)	0.11
	Ship	**24,922 (47.2%)**	688 (1.6%)	0.03
	Rail	390 (0.7%)	61 (0.1%)	0.16
	Aviation	684 (1.3%)	46 (0.1%)	0.07
Waste treatment	Waste incineration	230 (0.4%)	512 (1.2%)	2.50
	Others	0	232 (0.5%)	
Other area sources	Biomass burning	12 (<0.1%)	53 (0.1%)	5.00
Sum		52,765	44,106	0.83

Source: http://airemiss.nier.go.kr/main.jsp

EMEP/CORINAIR, US EPA, and field studies. In on-road mobile sources, the emissions were categorized into three parts, hot-start, cold-start, and evaporation. In this study, the emissions of NO_x and VOCs in Busan in 2011 were obtained from the CAPSS using 4 levels.

2. 2 Estimation of POCP for Emission Activity Sectors

Ozone and other photochemical oxidants are produced by numerous VOCs through complex sunlight-driven nonlinear photochemistry. Since ozone formation potential of VOCs is highly different depending on speciation, an index to rank the contribution of individual VOCs to ozone formation was introduced.

The approaches for determination of the rank of VOCs in terms of ozone creation potential were different between Europe and United States of America. In USA, ranking individual VOCs by their ozone formation potential was determined by model simulation in highly polluted atmospheric conditions, whereas that in Europe was determined by ozone formation and cumulative contribution to ozone concentration. POCP has been widely used in Europe (Derwent *et al*., 1998; Simpson, 1995; Andersson-Sköld *et al*., 1992; Derwent and Jenkin, 1991; Hough and Derwent, 1987), whereas incremental reactivity (IR), which is defined as ozone change caused by adding an arbitrarily small amount of the test VOC to the emissions in the episode, divided by the amount of test VOC added, have been widely used in USA (Carter *et al*., 1995; Carter and Atkinson, 1987).

In order to simulate ozone production by VOC emission, two cases are considered: 1) with and 2) without VOC emission. Ozone production by additional VOC amount was calculated based on the ozone difference between the two cases divided by amount of added VOC. The POCP values are defined relative to a reference value of 100, which is assigned to ethane. The POCP value for a given VOC species '*s*' is defined by Eq. (1) (Derwent and Jenkin, 1991).

$$POCP_s = \frac{\Delta[O_3]_s}{\Delta[O_3]_{ethene}} \times 100 \quad (1)$$

In order to quantify the significance of emission source in ozone production, the POCP value for an individual emission source and POCP-weighted emissions for source categories in Busan during 2011 were calculated by Eqs. (2) and (3), respectively.

$$POCP_{E,j} = E_j \times f_{j,s} \times POCP_s \quad (2)$$

$$E_{POCP} = \frac{\sum_j (E_j \times f_{j,s} \times POCP_s)}{\sum_j E_j} \quad (3)$$

where

$POCP_{E,j}$ = POCP for emission source j using the weight fraction of a species s from an emission source j

E_{POCP} = POCP-weighted mass emission of each emission source j

$f_{j,s}$ = the weight fraction of a species s from an emission source j

$POCP_s$ = the POCP value of species s.

The POCP values of VOC speciation were adopted from Derwent *et al*. (2007). The weight fraction of VOC for an individual emission source, which was available in domestic studies, was adopted from NIER (2009) and (2012). The weight fractions, which were not available in domestic studies, were adopted from Passant (2012).

3. RESULTS AND DISCUSSION

3. 1 Characteristics of Ozone Precursor Emissions in Busan

3. 1. 1 NO_x Emission

Emissions of ozone precursors NO_x and VOC for emission source classification (Levels 1 and 2) in Busan during year 2011 were presented in Table 1. For NO_x, the total emission from off-road mobile sources was estimated to be 31,202 ton yr^{-1} contributing 59% of total city emission, which was the highest in level 1 categories. The emission from on-road mobile sources was estimated to be 11,159 ton yr^{-1} contributing 21%. These two major mobile sources contributed 80% of the total city emissions. The most dominant emission source for NO_x in metropolitan areas is typically the on-road mobile source. In other words, the magnitude of NO_x emission from the on-road mobile sources was higher than that from the off-road mobile sources. For instance, the NO_x emissions from the on-road mobile sources in four metropolises (Seoul, Daegu, Daejeon, and Gwangju) of Korea in 2011 were higher than those from the off-road mobile sources by a factor of 1.5 (Daejeon)-2.3 (Seoul) (Fig. 2). However, the off-road emissions in other three metropolises (Busan, Incheon, and Ulsan) were higher than the on-road emissions by a factor of 1.1 (Incheon)-2.8 (Busan). Interestingly, these three metropolises are located in coastal area of Korean peninsula. Thus, the emissions related to port-related activities caused more NO_x emissions, especially in Busan. Detailed discussion on this is given

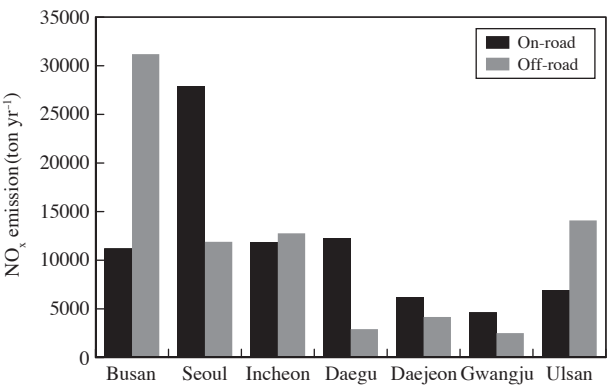

Fig. 2. NO_x emissions from on-road and off-road mobile sources in seven metropolises of Korea during 2011.

below.

NO_x emissions from ship operation in Busan ports contributed a significant portion (16-42%) to the total city emission (Song and Shon, 2014; Park *et al*., 2011). However, the estimates of air pollutant emissions in Busan ports were significantly different depending on estimation methods. For instance, the estimates of ship NO_x emissions between ship fuel consumption-based and ship activity (cruising hour)-based approaches were different by a factor of 2.7 (fuel consumption method: 23,209 ton yr^{-1} vs activity method: 8,710 ton yr^{-1}). Detailed discussion on the characteristics of ship emissions in Busan ports and the difference between the two estimation methods is given in Park *et al*. (2011). In brief, the emissions from container vessels contributed the largest portion (50%) to the total ship emission, while that from the North port was about 60% of total emissions. Recent transition of container cargo volume to a New port caused rapid increase of ship emissions in the New port. Based on vessel movements of containerships world widely, as collected by Lloyd's Maritime Intelligence Unit (LMIU) for May 2011, the top 5 highest container ship emissions were from Singapore, followed by Hong Kong, Shanghai, Xinggna, and Busan (Merk, 2012). Thus, ship activity is a significant contributor to NO_x emissions in Busan.

As for off-road emissions in Busan during year 2011, the NO_x emission from ships (Level 2) was largest with an annual emission of 24,922 ton y^{-1} (accounting for 47.2% of the total emissions), according to CAPSS emission inventory, which was calculated using the fuel-consumption method (Fig. 3). Compared to ship emission in 2009, the emission in 2011 increased about 10% (http://airemiss.nier.go.kr/main.jsp). The second largest emission source was truck (light-, medium-, and heavy-duty trucks) with the emission of 6,303 ton yr^{-1} (11.9% of the total NO_x emissions), followed by construction equipment (9.7%, 5,102 ton yr^{-1}) (Table 1). This might result from the container trucks in Busan ports. According to a recent study by Shon (2014), NO_x emission from the container truck associated with the ports allocating to the Busan city in 2013 was 867 ton yr^{-1} (15% of total truck emissions in Busan). NO_x emissions at container cargo terminals basing Busan ranged from 12 (Intergis 7 pier) to 200 (New-port) ton yr^{-1} (Shon, 2014). Emissions from these three categories such as ships, construction equipment, and trucks were about 70% of the total emissions. Out of truck types, the emissions form medium-duty trucks (level 3) in Busan was the highest (2,688 ton yr^{-1}).

Emissions form commercial and public facilities (Level 2) in the source category of NEGU combustion were 3,102 ton yr^{-1} (5.9%). Emissions from other level 2 sources were less than 5%. Since Gimhae international airport is located in Busan, the emissions from aircraft operating (taxi-in and out, climb-out, approaching, landing, and take-off) at this airport were 684 ton yr^{-1} (1.3%), which can be a major NO_x source near the airport. However, Song and Shon (2012) reported that NO_x emission from aircrafts in the boundary layer (1 km) of Busan during years of 2009-2010 based on an activity-based approach were about 335 ton yr^{-1}, which is a factor of 2 lower than the CAPSS inventory. Compared to two large international airports in Korea (Incheon and Gimpo), the emissions in Gimhae airport were a factor of 1.17 (801 ton yr^{-1}) and 4.25 (2,910 ton yr^{-1}) lower.

When the emission sources are categorized based fuel types, the largest amounts of NO_x were emitted by burning bunker-C (24,922 ton yr^{-1}) in off-road mobile sources (ship), followed by diesel (8,352 ton yr^{-1}) in on-road mobile sources (trucks), and by diesel (5,597 ton yr^{-1}) in off-road mobile sources (construction equipment) (not shown).

3. 1. 2 VOC Emission

For VOC emissions, solvent utilization (Level 1) was the largest emission source (36,067 ton yr^{-1}), which contributed 82% of the total VOC emissions in Busan (Table 1). This might result from the shipyard paintings in Busan, where there are a few large shipyards such as Hanjin Heavy Industries & Construction Co., STX Co, and Daesun Shipbuilding & Engineering Co. The second largest emission source in terms of Level 1 is on-road mobile sources with 3,512 ton yr^{-1} (8%). These two emission sources contributed 90% of the total VOC emissions in Busan. As for Level 2 emission source categories, the largest emission source was painting in solvent utilization with 22,733 ton yr^{-1} (51.5% of the total emissions). Emissions from other solvent utilization such as printing, asphalt pavement, household and commercial solvent usage were 10,374 ton yr^{-1} (23.5%). These two emission sources are the major VOC emission sources (75%) in Busan. Other Level 2 emission sources contributed less than 4% of total emission. As for Level 3 emission categories, the order of VOC emission strength is as follows: household and commercial solvent utilization (9,375 ton yr^{-1}) > shipbuilding (8,652 ton yr^{-1}) > coil coating (5,477 ton yr^{-1}) > architecture and building painting (5,278 ton yr^{-1}) (Fig. 3). VOC emissions from painting of shipbuilding and ship repair in Busan were a significant contributor, compared to other metropolises in Korea, except for Ulsan, in which the VOC emissions from ship-related emissions in 2011 were 14,812 ton yr^{-1} (18% of the total VOC emissions in Ulsan). Aside from solvent usage, when the emission sources are categorized based fuel types, the largest amounts of VOCs

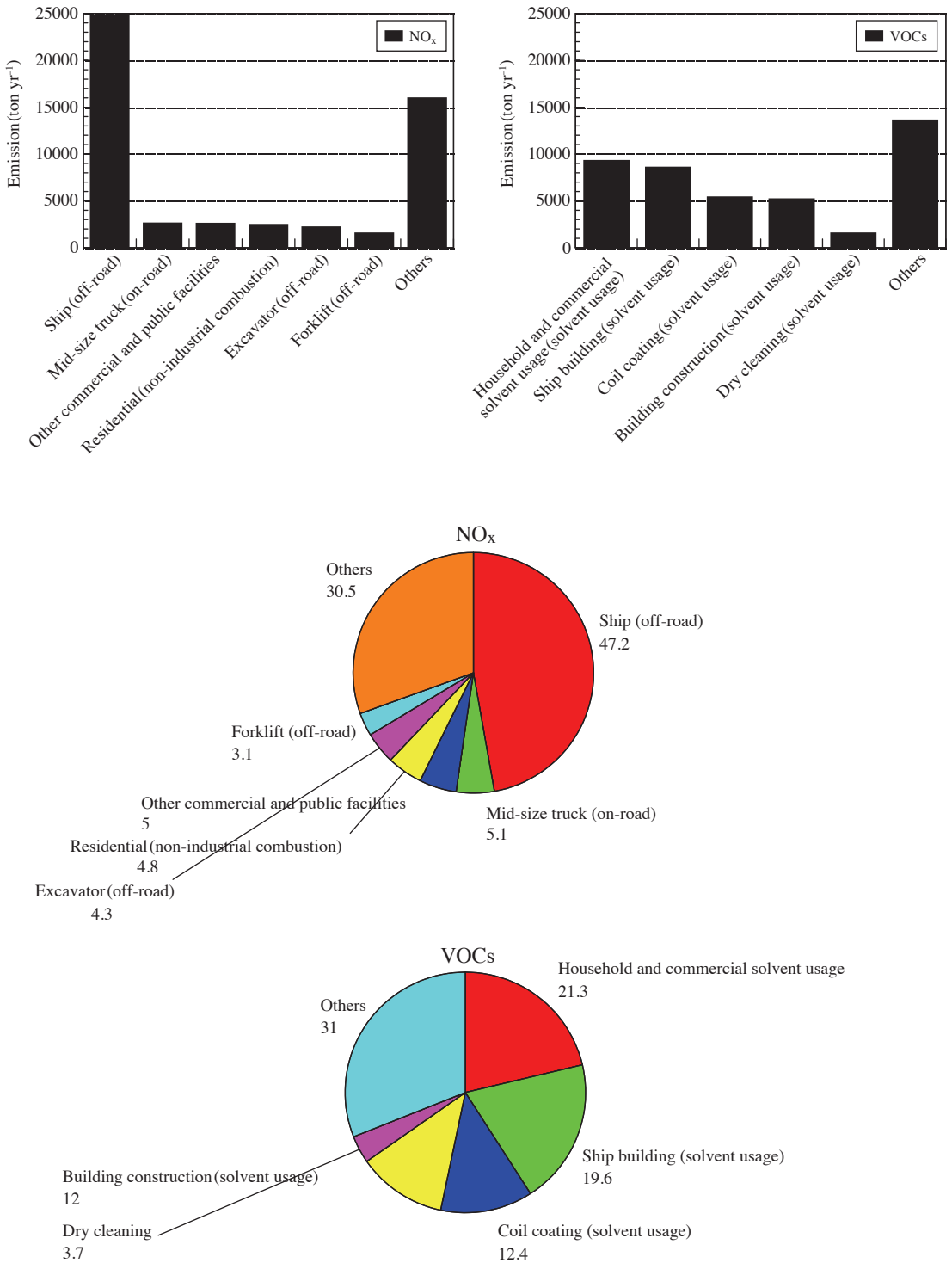

Fig. 3. Emissions of NO_x and VOCs for their emission source categories (Level 3) in Busan during the year of 2011.

were emitted by burning gasoline in on-road mobile sources (2,199 ton yr^{-1}) (not shown).

Toluene (7,109 ton yr^{-1}) comprises the largest portion of VOC emissions in Busan, followed by xylene (5,769), butane (4,208), ethylbenzene (2,151), n-butanol (1,670), isopropyl alcohol (1,359), propane, n-hep-

Table 2. Emission of VOC species in Busan during the year of 2011.

Rank	VOC species	Emission (ton/yr)	Percentage (%)	POCP*
1	Toluene	7,109	16.2	44
2	Xylene(o,m,p-xylene)	5,769	13.1	79
3	Butane	4,208	9.6	31
4	Ethylbenzene	2,151	4.9	46
5	n-Butanol	1,670	3.8	52
6	Isopropyl Alcohol	1,359	3.1	–
7	Propane	1,052	2.4	14
8	n-Heptane	930	2.1	35
9	1,2,4-trimethylbenzene	798	1.8	110
10	n-butylacetate	676	1.5	26
11	Others	658	1.5	–
12	Ethyl Alcohol	540	1.2	34
13	2-Butoxyethanol	504	1.1	45
14	Methyl Alcohol	499	1.1	13
15	Acetone	488	1.1	6
16	2,4-dimethylhexane	477	1.1	–
17	Ethylene	431	1.0	100
18	Nonane	424	1.0	34
19	Benzene	390	0.9	10
20	Ethyltoluene(o,m,p-ethyltoluene)	369	0.8	71
21	Methane	355	0.8	–
22	1,1,1-trichloroethane	282	0.6	1[a]
23	Dimethylcyclohexane	278	0.6	48[a]
24	2-methyl-3-hexanone	248	0.6	52[a]
25	Methyl Ethyl Ketone	219	0.5	32
26	Propylene	215	0.5	117
27	Formaldehyde	194	0.4	46
28	1,3,5-trimethylbenzene	179	0.4	107
29	Decane	177	0.4	36
30	1-Butene	172	0.4	104
Sum		32,821	74.8	

*Derwent *et al*. (2007); [a]Passant (2002)

tane, 1,2,4-trimethyl benzene, and n-butyl acetate (Table 2). Top 6 VOC species contributed about 50% of total emissions. The dominant emission sources of toluene were coil coating (2,578 ton yr^{-1}), architecture and building (1,999), and printing (872) (Fig. 4). For xylene, the dominant emission sources were painting from shipbuilding (3,530 ton yr^{-1}), coil coating (2,138), and architecture and building (431). For butane, the dominant emission sources were household and commercial solvent utilization (2,165 ton yr^{-1}) and on-road mobile sources (454). For ethylbenzene, the dominant emission sources were painting from shipbuilding (1,322 ton yr^{-1}) and coil coating (629).

3. 2 POCP for Emission Source and POCP-Weighted Emission

POCP has been used to rank VOC in VOC limited areas in Northern Europe (e.g. Derwent *et al*., 1996; Derwent and Jenkin, 1991) and can be regarded as a useful tool in ranking groups of VOC but for individual VOC the ranking differed depending on emission conditions. Thus, a representative POCP value for each emission source was determined using a VOC speciation profile of the emission source examined in domestic studies (Table 3). Level 1. emission category of off-road mobile source has the highest POCP value (72). The POCP values for EGU, NEGU, and industrial process ranged from 40 to 48, indicating intermediate level of ozone creation potential. The POCP value of on-road mobile source in Korea were calculated to be 56 (NIER, 2012), while that in the urban atmospheric environment of Europe was reported to be somewhat higher (69) (Derwent *et al*., 2007b) in part due to different emission conditions. The POCP values for the emission categories of storage and transport and waste treatment were very similar (52-54), while those for industrial combustion (process) and other areas sources (biomass burning) were 43 and 60, respectively.

As for POCP values of Level 3 emission source categories, the POCP value of ship emission source, which is key business in Busan, was relatively high (72) (Table

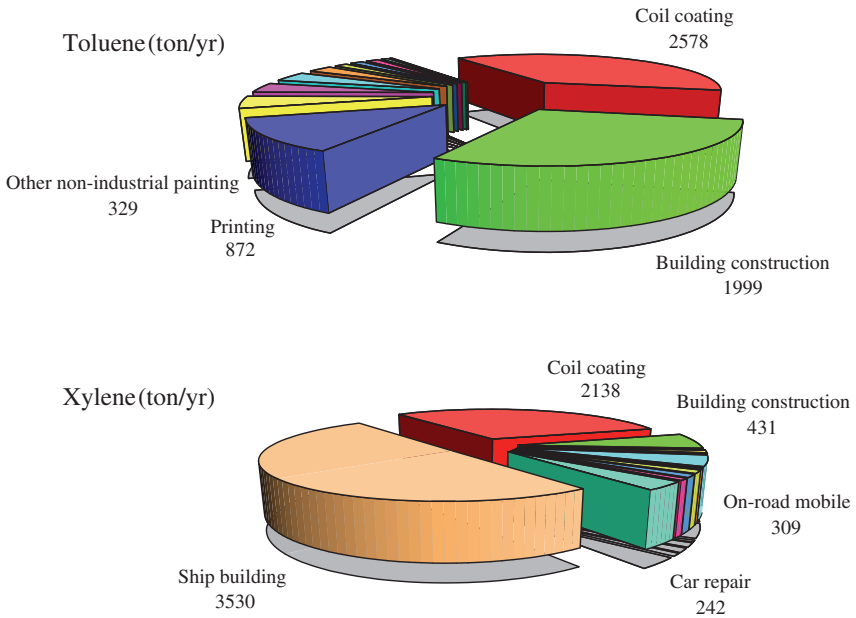

Fig. 4. Emissions of toluene and xylene for their emission source categories (Level 3) in Busan during the year of 2011.

3). Compared to the value in Europe (51), this value is about 41% high (Derwent *et al.*, 2007b). The POCP values for Level 3 emission sources of painting (Level 2) as the major emission source category of VOCs showed significant variations, ranging from 42 to 74. The POCP values of painting of shipbuilding, automobile repair, and manufacturing were relatively high, ranging from 61 to 74; whereas those of degreasing, dry cleaning, and other solvent utilization ranged from 24 to 45.

Ozone production depends not only on the magnitude of emissions of ozone precursors but also POCP value of VOC speciation, especially VOC-limited area. In this study, POCP-weighted emissions were calculated (Table 4). The largest POCP-weighted emission source was solvent utilization (Level 1) with 15,851 ton yr^{-1}, which showed 56% decrease compared non-weighted emission (36,026 ton yr^{-1}, as shown in Table 1). In general, the rank of POCP-weighted VOC emissions did not change compared to non-weighted emissions. The second and third largest POCP-weighted emission sources were on-road mobile source with 1,967 ton yr^{-1} (90% of the total VOC emissions), and off-road mobile source with 825 ton yr^{-1} (4%), respectively. As for POCP values of Level 3 source categories, the largest POCP-weighted emission source was shipbuilding painting with 5,278 ton yr^{-1}, followed by household and commercial solvent utilization > architecture and building paintings > coil coating > dry cleaning > degreasing > food and beverage > wood and pulp > other non-industrial painting > automobile manufacturing (Table 4).

3. 3 NO_x/VOC Emission Ratio and Ozone

Ozone formation is driven by two major components of directly emitted precursors: NO_x and VOCs. The relation between O_3, NO_x, and VOC is driven by complex nonlinear photochemistry. Model simulation of peak ozone has been widely carried as a function of NO_x and VOC mixing ratio or emission rates (Seinfeld and Pandis, 2006). In general, the VOC/NO_x mixing ratio of 5.5 has been used as a key index for ozone formation based on reaction kinetics. In other words, if the VOC to NO_x ratio is greater than 5.5, VOCs are more predominant than NO_x for the reaction with OH radicals, accelerating further production of O_3 (Seinfeld and Pandis, 2006).

The emission ratios of VOC/NO_x in Busan showed wide ranges from 0.01 (EGU) to 5.00 (motorcycle of off-road mobile sources). Mean VOC/NO_x emission ratio in Busan during 2011 was estimated to be 0.83 (Table 1). Emission ratios of VOC/NO_x for administrative districts in Busan during 2011 were presented in Table 5. The highest VOC/NO_x emission ratio of 5.00 occurred in coastal district (Youngdo island), whereas the lowest emission ratio of 0.13 occurred in Dongku (the southeastern part of Busan). Thus, ozone formation in inland areas of Busan was likely to be sensitive to VOCs due to high NO_x emissions. It was found that ozone formation in coastal region of Busan was

Table 3. POCP values for emission source category based on VOC speciation profile.

Classification			POCP	References
Level 1	Level 2	Level 3		
EGU			48	1
NEGU			48	1
Industrial process			40	1
On-road mobile			56 (69)	†, (1)
Off-road mobile		Construction	(46)	(1)
		Agricultural machinery	(46)	(1)
		Rail	(72)	(1)
		Aviation	(56)	(2)
		Ship	72 (51)	ǂ, (2)
Energy transport and storage		Transport and storage	52	†
		Gas station	54	†
Waste treatment		Waste incineration	53 (57)	†, (1)
		Others	52 (45)	†, (1)
Solvent usage	Painting	Building construction	(56)	(1)
		Other non-industrial painting	(42)	(1)
		Ship building	61 (74)	3, (1)
		Other industrial painting	45 (47)	*, †
		Wood, furniture	45	*
		Car repair	65 (48)	*, †
		Car manufacturing	65 (44)	*, †
		Coil coating	57 (36)	*, †
	Degreasing	Metal degreasing Electronic components Others	43 (24)	*, †
	Cleaning	Dry cleaning	24 (45)	*, †
	Other solvent usage	Printing	45 (21)	*, †
		Asphalt road pavement	34	*
		Household and commercial solvent usage	33	*
Manufacturing combustion		Food and beverage	54	*
		Textile	62	*
		Pulp, paper products	48	*
		Chemicals	60	*
		Fabricated metals	58	*
		Electronic, picture, sound, communication devices	47	*
		Other electronics and electrical converters	47	*
		Other transportation devices	59	*
Other area sources			43	4

†NIER (2012), 1: Derwent *et al*. (2007), 2: N.R. Passant (2002) 3: Park (2010), 4: IPCC (2001), *NIER (2009), ǂDabdub and Vutukuru (2008)

sensitive to NO_x, whereas that in downtown area was sensitive to VOCs (Song and Shon, 2010). In order to assess the effects of annual emission rates of ozone precursors NO_x and VOCs and emission ratio of VOCs to NO_x, multiparametric relationship (multiple regression analysis) were carried out.

$$[O_3] = a + b\{E(NO_x)\} + c\{E(VOCs)\} + d\{E(VOC)/E(NO_x)\} \quad (4)$$

where,

$E(NO_x)$: emission rate of NO_x, E(VOCs): emission rate of VOCs, and $E(VOCs)/E(NO_x)$: emission ratio of VOCs to NO_x.

The results of multiple regression are presented in Table 6. The correlations between annual mean ozone concentrations, emission rates of VOCs to NO_x, and their emission strength were not observed, indicating the presence of other factors (metrological effects and the non-linearity, etc.).

Table 4. POCP-weighted emission (ton yr^{-1}) for classified emission source category during the year of 2011.

Classification			VOCs	POCP	POCP-weighted emission
Level 1	Level 2	Level 3			
Solvent utilization	Others	Household and commercial solvent utilization	9,375	33	3,094 (2)
Solvent utilization	Painting	Ship building	8,652	61	5,278 (1)
Solvent utilization	Painting	Coil coating	5,477	36	1,972 (4)
Solvent utilization	Painting	Building construction	5,278	56	2,956 (3)
On-road mobile			3,512	56	1,967 (5)
Solvent utilization	Dry Cleaning	Dry cleaning	1,632	45	734 (6)
Solvent utilization	Others	Printing	987	21	207 (15)
Solvent utilization	Painting	Other non-industrial painting	868	42	365 (9)
Industrial process	Food and beverage		850	54	459 (7)
Solvent utilization	Painting	Furniture	820	45	369 (8)
Solvent utilization	Painting	Car manufacturing	666	44	293 (10)
Solvent utilization	Degreasing	Metal degreasing	572	24	137 (19)
Off-road mobile	Construction		545	46	251 (12)
Solvent utilization	Degreasing	Others	520	24	125 (20)
Waste treatment	Waste incineration		512	53	271 (11)
Solvent utilization	Painting	Car repair	494	48	237 (13)
Solvent utilization	Painting	Other industrial painting	478	47	225 (14)
EGU			412	48	198 (16)
Storage and transport	Gasoline supply	Storage and transport	373	52	194 (17)
Storage and transport	Gasoline supply	Gas station	295	54	159 (18)
Waste treatment	Others		232	52	121
NEGU			199	48	96
Solvent utilization	Degreasing	Electronic devices	196	24	47
Industrial process	Iron and steel		169	40	68
Manufacturing combustion			80	48	38
Off-road mobile	Rail		61	72	44
Off-road mobile	Ship		61	72	44
Other area sources			53	43	23
Off-road mobile	Aviation		46	56	26
Industrial process	Others		41	40	16
Off-road mobile	Agricultural machinery		12	46	6
Solvent utilization	Others	Asphalt pavement	12	34	4
Industrial process	Organic chemicals		1	40	0.4
Industrial process	Wood and pulp		0.01	40	<0.1
Industrial process	Inorganic chemicals		0	40	0

4. CONCLUSIONS

To identify the major sources of ozone precursors NO_x and VOCs in Busan during 2011, a CAPSS emission inventory was used for Level 1-3 emission source categories. Compared to other major metropolises, NO_x emission from off-road mobile sources such as ship was significantly higher than that from on-road mobile sources, due to port-related activities such as direct ship emissions (cruise, berth, and maneuvering) and emissions from container cargo handling equipment at cargo terminals. For VOC emissions, out of Level 3 emission source categories, the largest emission contributor was household and commercial solvent utilization, followed by painting of shipbuilding. Toluene and xylene were the dominant VOC speciation emitted from solvent utilization sources in Busan due in part to painting of shipbuilding. As for its VOC emission control, there is still no regulation on a large-scale painting booth ($>50{,}000\ m^3$). In addition, a few large shipyards in Busan are located in coastal area, where ozone formation is sensitive to VOC concentration or emission rate. Thus, VOC emission regulation should be implemented in the future. In addition, since the emission estimate had the significant difference between activity-based (ship operating duration) and fuel-consumption approaches, the emission estimate gap should be revolved in future study to resolve the ozone issues in the study area.

Table 5. Emissions of NO_x and VOCs, the NO_x/VOC emission ratios, and annual mean concentrations for administrative districts in Busan during 2011.

District	NO_x emission (ton)	VOCs emission (ton)	VOC/NO_x ratio	O_3 conc. (ppb)
Youngdo	1,932	9,662	5.00	30
Sasang	1,662	4,044	2.44	25
Namku	1,555	2,107	1.35	27
Dongrae	1,197	1,617	1.35	27
Busanjin	2,100	2,778	1.32	25
Geejang	2,477	3,220	1.30	28
Yeonje	1,186	1,501	1.27	24
Haewoondae	2,025	2,550	1.27	29
Suyong	1,196	1,480	1.23	32
Keumjung	1,491	1,728	1.16	24
Buk	1,546	1,774	1.15	26
Jungku	694	553	0.80	24
Saha	8,449	4,416	0.52	25
Gangseo	11,240	4,892	0.43	26
Dongku	6,337	803	0.13	26
Seoku	7,679	980	0.13	
Busan	18,367	32,461	0.83	

Table 6. Statistical summary of multiple regression results.

Multiple correlation coefficient (R)	Mutliple R-squared	Adjusted R-squared	Residual standard error
0.410647	0.168631	−0.05811	2.416034
Variables	Coefficient	Standard error	p-value
Intercept	25.31066	2.44372	5.2E-07
X1 (E(NO_x))	2.01E-06	0.000716	0.997806
X2 (E(VOCs))	−3.8E-05	0.001395	0.978924
X3 (E(NO_x)/ E (VOCs))	0.911283	2.93042	0.761634

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