Asian Journal of Atmospheric Environment
Vol. 9-1, pp. 39-47, March 2015
doi: http://dx.doi.org/10.5572/ajae.2015.9.1.039

ISSN(Online) 2287-1160
ISSN(Print) 1976-6912

Emissions of Ozone Precursors from a Biogenic Source and Port-related Sources in the Largest Port City of Busan, Korea

Zang-Ho Shon*

Department of Environmental Engineering, Dong-Eui University, 995 Eom Gwang No, Busan Jin Gu, Busan 614-714, Korea

*Corresponding author. Tel: +82-51-890-2078, E-mail: zangho@deu.ac.kr

ABSTRACT

The emissions of ozone precursors, NOx and VOCs from a biogenic source and port-related sources (ship, shipping container truck, and cargo handling equipment) were estimated in Busan during 2013. Total biogenic isoprene emission in Busan during 2013 was estimated to be 4,434 ton yr^{-1} with the highest emission (e.g., 28 ton day^{-1}) in summer using a BEIS method. Seasonal ozone production rates by isoprene ranged from 0.15 (winter) to 2.08 (summer) ppb hr^{-1}, contributing the predominant portion to ambient ozone levels. Total emissions of NOx and VOCs from ship traversing Busan ports were estimated to be 29,537 and 814 ton yr^{-1}, respectively, showing the significant contribution to total NOx emission in Busan. The emissions of ozone precursors were significantly different depending on ship tonnage and port location. Compared to the ship emission, the emissions of NOx and VOCs from the shipping container trucks in Busan were insignificant (2.9% for NOx and 3.9% for VOCs). Total NOx and VOCs emissions from the cargo handling equipment were estimated to be 1,440 and 133 ton yr^{-1}, respectively with the predominance of yard tractors.

Key words: Biogenic emission, Ozone, Ship, Container truck, Cargo handling equipment, Busan

1. INTRODUCTION

Ozone production is mainly controlled by its precursors, nitrogen oxides (NOx) and volatile organic compounds (VOCs) (Sillman, 1999). For the improvement of air quality in urban area, their emissions are highly regulated in the developed countries. The magnitude and change of anthropogenic emissions from mobile sources have pivot role in the concentrations of NOx as well as ozone (O_3). Biogenic emissions of VOCs such as isoprene also have great influence on the ozone production in urban areas covered with vegetation and green belt (Duan *et al.*, 2008; Li *et al.*, 2007; Chang *et al.*, 2005; Biesenthal *et al.*, 1997). In general, ozone levels in urban and rural (and coastal) areas depend on the concentrations of VOCs and NOx, respectively (Song *et al.*, 2012). As a main anthropogenic mobile source, the number of vehicles during 1992-2011 in 7 metropolitan cities in Korea had increased gradually regardless of vehicle types except for 1998 (due to financial crisis called IMF) (National Institute of Environmental Research (NIER), 2013a). Clean Air Policy Support System (CAPSS) in Korea have reported annually the estimation of air pollutant (NOx, CO, SO_2, PM_{10}, and VOCs) emissions. National, annual emission of NOx during 2007-2011 ranged from 1,014,318 (2007) to 1,187,923 (2011) ton yr^{-1}, showing no distinct positive or negative trend (NIER, 2013a, http://airemiss.nier.go.kr/main.jsp). National, annual emission of VOCs during 2007-2009 gradually decreased, but increased since 2009, ranging from 851,162 (2009) to 874,699 ton yr^{-1} (2007) (NIER 2013a).

Over the past few decades, global exhaust emissions from shipping have increased dramatically, making a significant contribution to global anthropogenic emissions because of the heavy ship traffic caused by the rapid growth of international trade (Endresen *et al.*, 2007; Eyring *et al.*, 2005; Corbett and Koehler, 2003). In addition, local ship emissions in coastal areas including ports have contributed to the increase in O_3 concentrations around these areas (e.g. up to 29 ppb in the South Coast of California (Vutukuru and Dabdub, 2008) and 15 ppb in a coastal port city of Korea (Song *et al.*, 2010)). As a target city, Busan has the world's fifth busiest container port according to the cargo tonnage (known as "Cargo Gateway of Asia") and the best transshipment port in Northeast Asia. The container volume of about 17.7 million TEU handled at Busan Port in 2013 was accounted for approximately 75% of the national container volume and it was significantly larger than those at the other ports in

Korea (Busan Port Authority (BPA), 2013, http://www.busanpa.com/Service.do?id=engmain). In this study, the emissions of background biogenic emissions of isoprene and monoterpenes in the target city are estimated to assess the contribution of biogenic sources to ambient ozone levels. Port-related emissions of ozone precursors, NOx and VOCs from ship, shipping container truck, and cargo handling equipment are also estimated to assess the contribution of cargo handling emission to total emission in the target city.

2. METHODS

2.1 Estimation Method of Biogenic Emission and Its Ozone Production

The biogenic emissions of isoprene and monoterpene were estimated using BEIS (Biogenic Emission Inventory System) v3.14 developed by USEPA. Land-use/land-cover categories in the target city used for the calculation are provided by EGIS (Environmental Geography Information System, http://egis.me.go.kr/main.do) of KMOE (Korean Ministry of Environment) and FGIS (Forest Geography Information System, http://116.67.44.22/forest/) of Korea Forest Service (KFS). The emission factors of biogenic VOC compounds and leaf area index were adopted from BEIS v3.14. Biogenic emissions of isoprene and monoterpene were estimated using normalized emission at the standard temperature (303°K) and PAR (photochemically active radiation, 0.4-0.7 μm) flux (1,000 μmol m^{-2} s^{-1}). PAR values during 2013 were estimated using the ratio of PAR to SR (solar radiation), 0.43 (Bat-Oyun *et al.*, 2012). Data for solar radiation and temperature in Busan during 2013 were provided by KMA (Korea Meteorological Administration, http://web.kma.go.kr/eng/index.jsp). Daily emissions of isoprene and monoterpene during 2013 were corrected using temperature and/or radiation (Eq. 1 and Eq. 4).

$$I=Is\times C_L\times C_T \tag{1}$$

$$C_L=\frac{\alpha C_{L1}L}{(1+\alpha^2L^2)^{1/2}} \tag{2}$$

$$C_T=\frac{\exp[C_{T1}(T-T_S)/(RT_ST)]}{1+\exp[C_{T2}(T-T_M)/(RT_ST)]} \tag{3}$$

where I=isoprene emission rate. Is=isoprene emission rate at the standard temperature (303°K) and PAR flux (1,000 μmol m^{-2} s^{-1}), C_L=light correction factor, C_T=temperature correction factor, L=PAR flux, μmol m^{-2} s^{-1}, T=temperature, K, T_S=standard temperature, 303 K, T_M=314 K, α=0.0027, C_{L1}=1.066, R=8.314 JK^{-1} mol^{-1}, C_{T1}=95,000 $Jmol^{-1}$, C_{T2}=230,000 $Jmol^{-1}$.

$$M=Ms\times\exp[\beta\cdot(T-Ts)] \tag{4}$$

where M=monoterpene emission at leaf temperature T (K), Ms=standard emission rate at Ts (303°K), β=0.09.

The photochemical box model (PCBM) was employed to assess the photochemical production of ozone by isoprene emission. The PCBM included the reactions for a full spectrum of HOx/NOx/CH_4/VOCs chemistry, containing 72 HOx/NxO_Y/CH_4 gas kinetic/photochemical reactions, 227 VOC reactions, and 7 heterogeneous processes (e.g. the reactions of N_2O_5, NO_3, and HO_2 on aerosol surfaces). Detailed information regarding the PCBM have been described previously (Song *et al.*, 2012; Shon *et al.*, 2004). The net ozone production rate ($N(O_3)$) by isoprene was calculated using following equations 5-7.

$$P(O_3)=[NO]\{k_{RO2+NO}[RO_2]+k_{HO2+NO}[HO_2]+k_{CH3O2+NO}[CH_3O_2]\} \tag{5}$$

$$D(O_3)=k_{O(1D)+H2O}[O(^1D)][H_2O]+[O_3](k_{OH+O3}[OH]+k_{HO2+O3}[HO_2]+k_{VOCs+O3}[VOCs][O_3]+k_{OH+NO2}[OH][NO_2] \tag{6}$$

$$N(O_3)=P(O_3)-D(O_3) \tag{7}$$

Where $P(O_3)$ and $D(O_3)$ denotes photochemical production and destruction rates of O_3, respectively. $N(O_3)$ denotes the net rate of the photochemical production of O_3 or the O_3 tendency, i.e. a measure of the O_3 productivity of an air mass neglecting the transport and deposition processes (Salisbury *et al.*, 2002). k_{X+Y}=a reaction rate constant between X and Y, [X]=chemical species [X] concentration. $[RO_2]$=alkyl peroxy radical concentrations. Isoprene (and other 55 VOC species) concentrations were obtained from 5 PAMS (Photochemical Assessment Monitoring Station). The effect of isoprene on ozone production was simulated by ozone production difference between with isoprene and without isoprene.

2.2 Estimation Methods of Ship Emission at the Port

The emissions of ozone precursors, NOx and VOCs from ship at the Busan port were estimated by multiplying fuel consumption by emission factors (Eq. 8).

$$Es=EF_i(g\,kg^{-1}\text{ fuel})\times FC \tag{8}$$

where EFs=emission rate from ship, EF_i=emission factor for species i, FC=fuel consumption (kg fuel).

At the port, the category of emissions of air pollutants from ship can be divided by maneuvering and berth. Thus, the fuel consumption can be divided by these two categories. The fuel consumption for maneuvering and berth were calculated by Eq. 9 and 10, respectively.

$$FC_m = \sum(Ns \times CD)/FE \qquad (9)$$

$$FC_b = Na \times FCC \times DB \times R_{FC} \qquad (10)$$

where Ns=sum of the number of ship departing and arriving at port for each ship tonnage, CD=cruising distance (km), FE=fuel economy (km kL^{-1}), Na=the number of ship arriving at port, FCC=fuel consumption coefficient (ton day^{-1}), DB=the number of day at berth (day, 0.79, NIER 2013b), R_{FC}=the ratio of fuel consumption at berth to that for maximum ship engine power (0.2).

FCC was adopted from EEA (1999). The cruising distance of 35 km (distance affected by sea breeze) was adopted from NIER 2013b. The emission factor was obtained from NIER (2013b).

2. 3 Estimation Method of Emission from Shipping Container Truck

The emissions (hot-start) of ozone precursors from container truck at shipping container terminal located in Busan port were estimated using the calculation method of mobile source emission (Eq. 11).

$$Ect = EF_i \times VKT \qquad (11)$$

where Ect=emission rate from the container truck, EF_i=emission factors (g km^{-1}), VKT=vehicle kilometers traveled (km).

VKT was calculated by multiplying the number of container truck traveled at each terminal by distance allocating Busan territory between terminals. The number of container truck traveled at each terminal was obtained from the traffic database of KOTI (Korea Transport Institute, http://gis.ktdb.go.kr/). The emission factors of NOx and VOCs for heavy duty vehicles (diesel engines, a gross vehicle weight over 5 ton) were adopted from the NIER air pollutant emission inventory guidebook (NIER, 2013b).

2. 4 Estimation Method of Cargo Handling Equipment

The emissions of ozone precursors from port-related equipment were estimated using the calculation method of off-road mobile source emission (Eq. 12, ICF International, 2009).

$$E_{EQ} = EF_i \times N_{EQ} \times EP \times LF \times OD \qquad (12)$$

where E_{EQ}=emission rate from cargo handling equipment, N_{EQ}=the number of cargo handling equipment, EP=engine power, LF=loading factor, OD=equipment operating duration.

The cargo handling equipment used for emission calculation are rubber tire gantry crane, reach stacker, yard tractor, forklift, crane, loaders, and excavator. The N_{EQ} was obtained from Korea Port Logistics Association (KOPLA, 2013). The EF_i was obtained from NIER (2013). The LF was obtained from ICF international (2009). The EP and OD in Busan port were adopted from Han *et al.* (2011) due to the lack of data.

3. RESULTS AND DISCUSSION

3. 1 Biogenic Emission and Its Ozone Production

Since forest area (e.g., 776 km^2) in Busan occupies 40% of total area of Busan city (http://egis.me.go.kr/da/grcCoverStatistics.do), the biogenic emission of VOCs is significantly important for natural ozone production. Among biogenic VOC emission, the contribution of isoprene ($CH_2=C(CH_3)CH=CH_2$) to ozone production is known to be significant (up to 75%) under high temperature and enhanced solar radiation (summer) due to its strong emission (Duane *et al.*, 2002). Monoterpenes ($C_{10}H_6$) are also biogenic VOCs which are class of terpenes consisting of two isoprene. The emissions of monoterpenes were calculated using 14 species such as α-pinene, β-pinene, Δ-3-carene, D-limonene, camphene, myrcene, β-terpinene, β-phellandrene, sabinene, p-cymene, ocimene, α-thujene, terpinolene, and γ-terpinene.

Total biogenic isoprene emission in Busan during 2013 was estimated to be 4,434 ton yr^{-1}. The emission of isoprene (e.g., 28 ton day^{-1}) in summer was about 15 times higher than that (e.g., 2 ton day^{-1}) in winter (Table 1 and Fig. 1). Total emission of monoterpenes is estimated to be 14,081 ton yr^{-1}. Compared to iso-

Table 1. Biogenic VOC emissions, isoprene concentration, and ozone production rate by biogenic isoprene.

Season	Emission (ton day^{-1})		Isoprene conc. (ppb)	Ozone production rate (ppb hr^{-1})
	Isoprene	Monoterpenes		
Spring	7	29	0.009	0.51
Summer	28	76	0.073	2.08
Fall	12	41	0.018	0.92
Winter	2	13	0.003	0.15
Sum (ton yr^{-1})	4,434	14,081	–	–

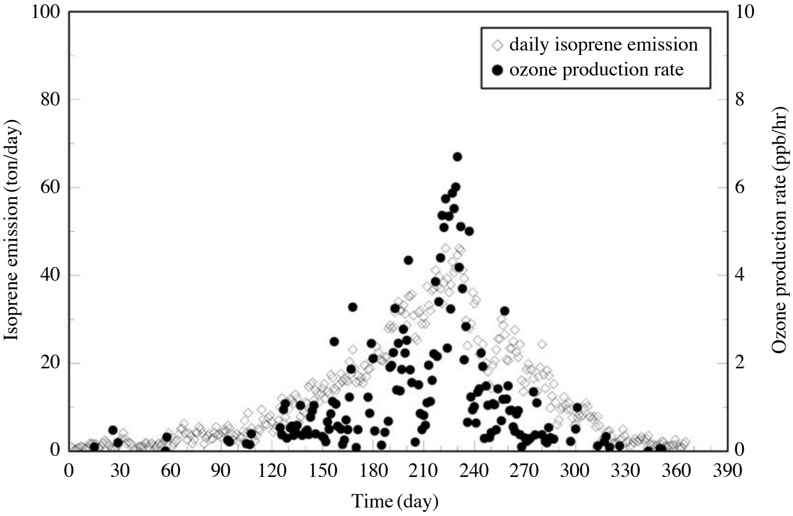


Fig. 1. Daily isoprene emissions and ozone production rate by biogenic isoprene in Busan during 2013.

prene, seasonal emission difference was somewhat smaller. The emission of monoterpenes (e.g., 76 ton day^{-1}) in summer was a factor of 6 higher than that (e.g, 13 ton day^{-1}) in winter. Biogenic isoprene emission was about a factor of 3 lower than monoterpene emission. Isoprene emission in 2013 was a factor of 3.5 higher than that (e.g., 1,278 ton yr^{-1}) in 2000 by Cho *et al.* (2006) in part due to temperature and solar radiation difference. The mean temperature in summer of 2000 was 24.1°C, while that in 2013 was 25.3°C. Sunshine duration in 2013 was 228 hr, while that in 2000 was 168 hr. Pétron *et al.* (2001) found that the emission capacity doubled when growth temperature was increased from 25 to 30°C. In general, there is linear relationships between light intensity and isoprene emissions at intensities ranging from 500 to 2000 μmol m^{-2} s^{-1} (Lerdau and Keller, 1997). Thus, isoprene emission in 2013 is higher than that in 2000 due to higher temperature and enhanced solar radiation.

Ozone production by biogenic isoprene in Busan during 2013 was calculated based on PAMS isoprene concentration (5 stations) using the PCBM. The significant data sets of isoprene concentration in most seasons except for summer were below detection limit. Mean concentrations of isoprene in spring, summer, fall, and winter were 0.009, 0.073, 0.018, and 0.003 ppb, respectively (Table 1). Seasonal ozone production rate by isoprene ranged from 0.15 to 2.08 ppb hr^{-1} (Table 1 and Fig. 1). In a recent study of impacts of biogenic isoprene emission on ozone in the Seoul metropolitan area was reported by Lee *et al.* (2014). The contribution of biogenic isoprene emission to ozone concentration was up to 37 ppb in Seoul region. Ozone concentration in inland area and coastal area of Busan is known to be sensitive to VOCs and NOx levels, respectively (Song *et al.*, 2010). Meanwhile, the lifetime of ozone in troposphere is about 3 weeks varying with altitude and that in the boundary layer is about 1-2 days (Stevenson *et al.*, 2006). Assuming the lifetime of ozone in Busan is 2 days, ozone production during the day (12 hr) in summer might be reach up to 50 ppb by biogenic isoprene emission.

3.2 Emission from Ship

Emissions of NOx and VOCs from ship in Busan port were summarized in Table 2. Fuel consumption at berth during 2013 was estimated to be 209,721 kL, while that (e.g., 129,812 kL) at maneuvering mode was a factor of 1.6 lower than that at berth. The correlation between the volume of container cargo and fuel consumption was also used to estimate current fuel consumption. The fuel consumption using the correlation method was overestimated by 73% compared to the method (based on the number of ship at ports for ship tonnage) used in this study. The emissions of NOx and VOC for each port was estimated using total emission at Busan ports and the number of ships for each ship tonnage arriving each port. The emission at North port (Fig. 2) was the highest accounting for 61% of total emission, while the emissions of NOx and VOCs at New port (Fig. 2) were 9295 and 256 ton yr^{-1}, respectively, accounting for 31% (Table 2). The emissions of ozone precursors were significantly different depending on ship tonnage. At New port, the large ship with 60,000-75,000 tonnage showed the largest ship emission, whereas at North and Gamcheon ports, the small ship with 100-500 tonnage showed the largest ship emission. Total emissions of NOx and VOCs at Busan

Table 2. The number of ship arriving port and the emissions of NOx and VOCs at each port in Busan.

Ship tonnage	No. of ship arriving port				Emission							
	New Port	North Port	Gamcheon Port	Sum	New Port		North Port		Gamcheon Port		Sum	
					NOx	VOCs	NOx	VOCs	NOx	VOCs	NOx	VOCs
<100	680	4,875	1,088	6,643	221	6	1,582	43	353	10	2,156	59
100-500	197	11,211	1,453	12,861	73	2	4,133	114	536	15	4,742	131
500-1,000	110	3,400	487	3,997	41	1	1,274	35	183	5	1,498	41
1,000-3,000	150	4,747	738	5,635	64	2	2,037	56	317	9	2,418	67
3,000-5,000	132	2,624	863	3,619	60	2	1,198	33	394	11	1,652	46
5,000-7,000	410	1,377	323	2,110	216	6	726	20	170	5	1,112	31
7,000-10,000	556	3,562	214	4,332	312	9	2,001	55	120	3	2,433	67
10,000-15,000	250	629	84	963	179	5	451	12	60	2	690	19
15,000-20,000	230	1,705	41	1,976	181	5	1,338	37	32	1	1,551	43
20,000-25,000	215	466	54	735	183	5	398	11	46	1	627	17
25,000-30,000	298	480	18	796	275	7	443	12	17	0	735	19
30,000-50,000	924	1,009	64	1,997	1,011	28	1,104	30	70	2	2,185	60
50,000-60,000	895	193		1,088	1,523	42	328	9	0	0	1,851	51
60,000-75,000	1,024	139		1,163	1,918	53	260	7	0	0	2,178	60
75,000-100,000	839	160		999	1,802	50	344	9	0	0	2,146	59
$>100,000$	533	141		674	1,236	34	327	9	0	0	1,563	43
Sum	7,443	36,718	5,427	49,588	9,295	256	17,944	495	2,298	63	29,537	814

ports were estimated to be 29,537 and 814 ton yr^{-1}, respectively. The emission ratio of NOx to VOCs was estimated to be 36.3.

In general, two methods were used to estimate the emissions of air pollutants from ship. One is the method using fuel consumption (Tier 1) and the other is activity (Tier II/III) method. Based on the fuel consumption method, the emissions of NOx and VOCs in Busan ports during 2009 were estimated to be 8,710 and 350 ton yr^{-1}, respectively, whereas those based on the activity method were a factor of 2.7 and 1.8 lower than the fuel consumption method (Park *et al.*, 2011). The emissions of air pollutants from ship were also significantly different depending on ship types (Song and Shon, 2014). NOx emission from the container ship during three years (2006, 2008, and 2009) in Busan ports was 47% of total ship emission. Ship emissions for NOx and VOCs estimated using the activity method in Busan ports during three years were about 1 and 0.04% of their national emissions, respectively, while those were 13-17% and 0.7% of total emissions in Busan city, respectively.

3. 3 Emissions from Shipping Container Truck

The emissions of NOx and VOCs from shipping container truck in Busan city limit were summarized in Table 3. Traffic volumes (2.2 millions) at Hutchison and KBCT base terminals were dominant accounting for 30% of total traffic volumes (7.6 millions) of shipping container truck (Fig. 3). Total NOx and VOCs emissions from the truck allocating to the Busan city were 867 and 32 ton yr^{-1}, respectively. NOx emissions

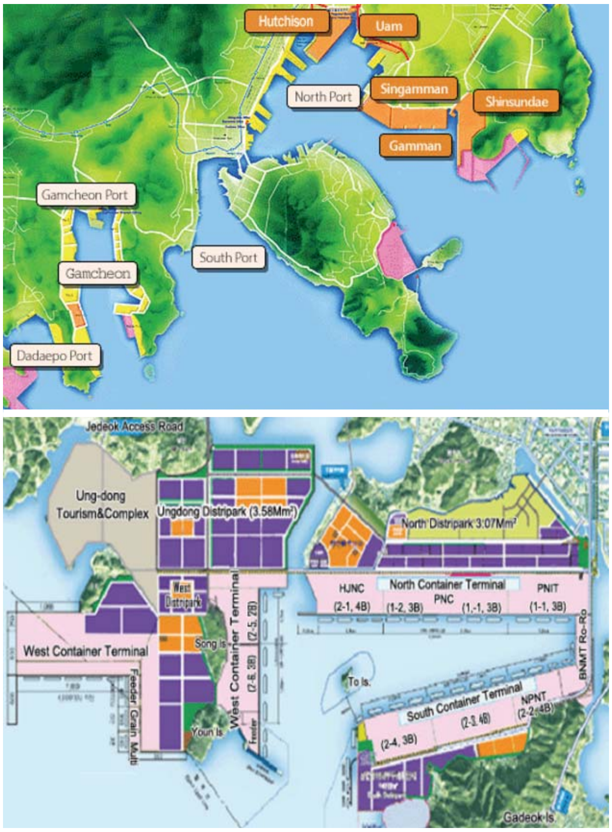
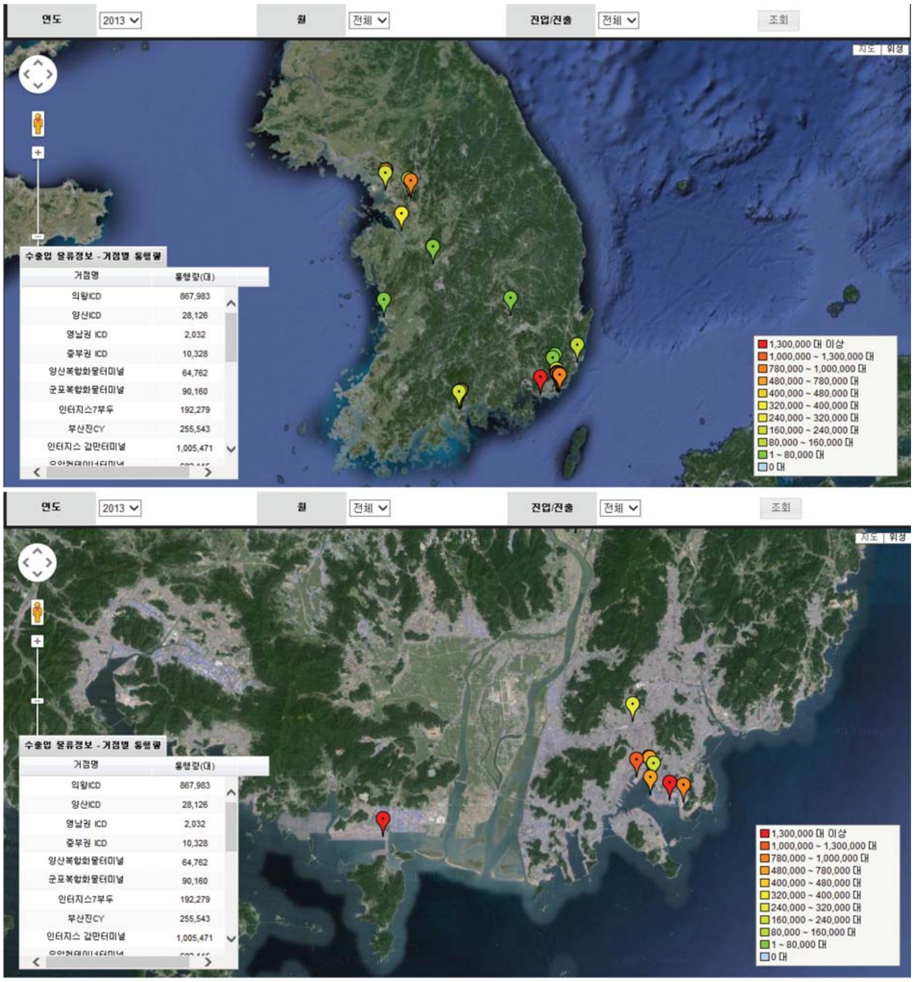


Fig. 2. Locations of North Port (top panel) and New Port (bottom panel) in Busan.

at terminals basing Busan ranged from 12 (Intergis 7 pier) to 200 (New-port) ton yr^{-1}. NOx (and VOCs) emi-

Table 3. The number of traffic volume at base container terminals in Busan travelling other terminals in Korea and their NOx and VOCs emissions.

Terminal	Traffic volume	NOx emission (ton yr^{-1})			VOCs emission (ton yr^{-1})			NOx/VOCs ratio
		Inside Busan	Outside Busan	Sum	Inside Busan	Outside Busan	Sum	
Busanjin CY	308,457	21	46	67	0.7	1.8	2.5	26.8
Hutchison Term.	1,100,986	105	25	130	3.9	1.0	4.9	26.5
Uam Term.	846,441	41	9	49	1.5	0.3	1.9	25.8
Saebang Term.	858,511	53	12	65	1.4	0.2	1.6	40.6
Intergis 7 pier	640,441	11	2	12	0.4	0.1	0.5	24.0
KBCT Term.	1,130,723	123	21	145	4.7	0.8	5.5	26.4
Dongbu Busan Term.	960,309	90	13	102	3.3	0.5	3.8	26.8
New-Port Term.	765,793	158	42	200	5.8	1.6	7.5	26.7
Intergis Gamman Term.	976,137	79	16	95	3.0	0.6	3.6	26.4
Sum	7,587,798	680	186	867	24.8	6.9	31.8	27.3


연도 2013
월 전체
진입/진출 전체

수출입 물류정보 - 거점별 통행량

거점명	통행량(대)
의왕ICD	867,983
양산ICD	28,126
영남권 ICD	2,032
중부권 ICD	10,328
양산복합화물터미널	64,762
군포복합화물터미널	90,160
인터지스7부두	192,279
부산진CY	255,543
인터지스 감만터미널	1,005,471

Fig. 3. Location and the number of traffic volume for each ship container base terminals in Korea (top panel) and those inside Busan city (bottom panel).

ssions between terminals basing Busan city ranged from 11 (0.4) to 158 (5.8) ton yr^{-1}, while those emissions between terminals basing Busan and terminals outside Busan ranged from 2 (0.1) to 46 (1.8) ton yr^{-1}.

Table 4. Characteristics of cargo handling equipment used in port and their NOx and VOCs emissions during 2013.

	Crane	Forklift	Excavator	Loader	RTGC	Reach stacker	Yard Tractor	Sum
No. of equipment	28	365	19	4	72	13	720	1,221
Engine Power (hp)[a]	385	186	214	290	472	292	173	–
Operating Hour (hr)[a]	2,269	1,512	2,400	1,872	3,971	3,112	3,000	–
LF[b]	0.43	0.30	0.57	0.51	0.43	0.30	0.65	–
NOx EF (g kW h^{-1})	4.78*	6.02*	5.10*	5.02*	6.41[a]	5.38[a]	5.23[a]	–
VOCs EF (g kW h^{-1})	0.29	0.78	0.48	0.38	0.52	0.42	0.48	–
NOx emission	37	138	21	4	277	14	947	1,440
VOCs emission	2	18	2	0.3	23	1	87	133

*NIER (2013)
[a]Han *et al.* (2011), [b]ICF counsulting, 2009

Emissions between terminals basing Busan were a factor of 3.6 higher than those between terminals basing Busan and terminals outside Busan. Emissions of NOx and VOCs from the shipping container trucks in Busan during 2013 were 41% and 30% of total emission from (diesel engine) heavy-duty vehicles in Busan during 2011. The mean emission ratio of NOx to VOCs from the truck was estimated to be 28. Compared to ship emission, the emissions of NOx and VOCs from the shipping container trucks in Busan were insignificant (2.9% for NOx and 3.9% for VOCs). Compare to mobile source emissions in Busan, the emissions of NOx and VOCs from the shipping container trucks in Busan were also insignificant (7.8% for NOx and 0.9% for VOCs).

3. 4 Emission from Cargo Handling Equipment

Emissions of NOx and VOCs from the cargo handling equipment (diesel engine) were summarized in Table 4. Rubber tire gantry crane (RTGC) and yard tractor (YT) are main equipment for ship cargo handling. Loader, forklift, and crane are auxiliary equipment. Dump truck and trailer used for transporting the ship container to outside the terminals were excluded in calculating the emission due to the emission category of mobile source. The characteristics of the cargo handling equipment is given in Table 4. Total NOx and VOCs emission from the cargo handling equipment were estimated to be 1,440 and 133 ton yr^{-1}, respectively. The emissions of NOx and VOCs equipment (e.g., 947 ton yr^{-1} for NOx and 87 ton yr^{-1} for VOCs) from YT were predominant among the cargo handling equipment. The emissions from the cargo handling equipment were higher than those from shipping container trucks by a factor of 1.7 for NOx and 4.2 for VOCs. The emissions from the cargo handling equipment in Busan port were significantly higher than those in the ports of other cities (Incheon, Yeosu/Gwangyang etc.) by more than a factor of 4 (Han *et al.*, 2011).

4. CONCLUSIONS

The target city of Busan, Korea has unique urban atmospheric environment due the presence of internationally recognized hub port, highly industrialized area, and significant forest area. Thus, the air quality of ozone in Busan is affected by the combination of biogenic emission of its precursors and anthropogenic emissions especially port-related sources such as direct ship emission, shipping container trucks, and cargo-handling equipment. Thus, we investigated the characteristics of these emission and contribution to city total emissions. The emissions of ozone precursors at coastal areas from port related sources are highly important in ozone production due to the sensitivity of ozone production to NOx. Since these port-related emission sources are highly localized in coastal area, ozone production can be enhanced in this area with the high emission ratios of NOx to VOCs (e.g., 11-36).

Biogenic isoprene emission in Busan during 2013 was estimated to be 4,434 ton yr^{-1} with the highest emission in summer, contributing a predominant portion to ambient ozone levels. Total emissions of NOx and VOCs from ship traversing Busan ports were estimated to be 29,537 and 814 ton yr^{-1}, respectively, showing the significant contribution to total NOx emission in Busan. According to the previous study by Song *et al.* (2010), the ozone production rate by ship emission was estimated to be 1.5 ppb hr^{-1}, implying the significant of ship emission in ozone levels in coastal area. The emissions of ozone precursors were significantly different depending on ship tonnage and port. Emissions between terminals basing Busan were a factor of 3.6 higher than those between terminals basing Busan and terminals outside Busan. Emissions of NOx and VOCs from the shipping container trucks in Busan during 2013 were 41% and 30% of total emission from heavy-duty vehicles in Busan during 2011. The emissions from the cargo handling equipment (1,440 for NOx and 133 ton yr^{-1} for VOCs) were higher than those from shipping container trucks by a factor of 1.7 for NOx and 4.2 for VOCs. The yard tractor as the significant source in emission from the cargo handling equipment is the emission source to be regulated for the improvement of air quality in coastal area.

ACKNOWLEDGEMENT

This work was funded by the Busan Green Environment Center Grant 14-2-40-41. This work was also supported by Dong-Eui University Grant (2014AA017).

REFERENCES

Bat-Oyun, T., Shinoda, M., Tsubo, M. (2012) Effects of cloud, atmospheric water vapor, and dust on photosynthetically active radiation and total solar radiation in a Mongolian grassland. Journal of Arid Environments 4, 349-356.

Biesenthal, T.A., Wu, Q., Shepson, P.B., Wiebe, H.A., Anlauf, K.G., Mackay, G.I. (1997) A study of relationships between isoprene, its oxidation products, and ozone in the Lower Fraser Valley, BC. Atmospheric Environment 31, 2049-2058.

Chang, C.-C., Chen, T.-Y., Lin, C.-Y., Yuan, C.-S., Liu, S.-C. (2005) Effects of reactive hydrocarbons on ozone formation in southern Taiwan. Atmospheric Environment 39, 2867-2878.

Cho, K.-T., Kim, J.-C., Hong, J.-H. (2006) A study on the comparison of biogenic VOC (BVOC) emissions estimates by BEIS and CORINAIR methodologies. Journal of Korean Society for Atmospheric Environment 22, 167-177.

Corbett, J.J., Koehler, H.W. (2003) Updated emissions from ocean shipping. Journal of Geophysical Research 108 (D20), 4650.

Duan, J., Tan, J., Yang, L., Wu, S., Hao, J. (2008) Concentration, sources and ozone formation potential of volatile organic compounds (VOCs) during ozone episode in Beijing. Atmospheric Research 88, 25-35.

Duane, M., Poma, B., Rembges, D., Astorga, C., Larsen, B.R. (2002) Isoprene and its degradation products as strong ozone precursors in Insubria, Northern Italy. Atmospheric Environment 36, 3867-3879.

EEA 1999: European Environment Agency, EMEP/CORINARI Emission Inventory Guidebook-1999.

Endresen, Ø., Sørgård, E., Sundet, J.K., Dalsoren, S.B., Isaksen, I.S.A., Berglen, T.F., Gravir, G. (2003) Emission from international sea transportation and environmental impact. Journal of Geophysical Research 108 (D17), 4560, doi: 10.1029/2002JD002898.07.

Eyring, V., Kohler, H.W., Lauer, A., Lemper, B. (2005) Emissions from international shipping: 2. Impact of future technologies on scenarios until 2050. Journal of Geophysical Research 110 (D17), D17306.

Han, S., Youn, J.-S., Kim, W-J., Seo, Y.-H., Jung, Y.-W. (2011) Estimation of air pollutant emission from port-related sources in the port of Incheon. Journal of Korean Society for Atmospheric Environment 27, 460-471.

ICF international 2009. Current methodologies in preparing mobile source port-related emission inventories, final report.

Korea Port Logistics Association (KOPLA), 2013. Port cargo handling survey 2013.

Lee, K.-Y., Kwak, K.-H., Ryu, Y.-H., Lee, S.-H., Baik, J.-J. (2014) Impacts of biogenic isoprene emission on ozone air quality in the Seoul metropolitan area. Atmospheric Environment 96, 209-219.

Lerdau, M, Keller, M. (1997) Controls on isoprene emission from trees in a subtropical dry forest. Plant Cell and Environment 20, 569-578.

Li, G., Zhang, R., Fan, J., Tie, X. (2007) Impacts of biogenic emissions on photochemical ozone production in Houston, Texas. Journal of Geophysical Research 112, D10309.

National Institute of Environmental Research (NIER), 2013a. Annual report of ambient air quality in Korea, 2012.

National Institute of Environmental Research (NIER), 2013b. National air pollutant emission calculation method manual III.

Park, D.-Y., Hwang, C.-W., Jeong, C.-H., Shon, Z.-H. (2011) Estimate of ship emission in Busan port during 2009 based on activity. Journal of Environmental Sciences 20, 1-10.

Pétron, G., Harley, P., Greenberg, J., Guenther, A. (2001) Season temperature variations influence isoprene emission. Geophysical Research Letters 28, 1707-1710.

Shon, Z.-H., Kim, K.-H., Bower, K.N., Lee, G., Kim, J. (2004) Assessment of the photochemistry of OH and NO_3 on Jeju Island during the Asian-dust-storm period in the spring of 2001. Chemosphere 55, 1127-1142.

Sillman, S. (1999) The relation between ozone, NOx, and hydrocarbons in urban and polluted rural environment. Atmospheric Environment 33, 1821-1845.

Song, S.-K., Shon, Z.-H., Kim, Y.-K., Kang, Y.-H., Oh, I.-B., Jung, C.-H. (2010) Influence of ship emissions on ozone concentrations around coastal areas during summer season. Atmospheric Environment 44, 713-723.

Song, S.-K., Kim, Y.-K., Shon, Z.-H., Ryu, J.-Y. (2012) Photochemical analyses of ozone and related compounds under various environmental conditions. Atmospheric Environment 47, 446-458.

Song, S.-K., Shon, Z.-H. (2014) Current and future emission estimates of exhaust gases and particles from shipping at the largest port in Korea. Environmental Science and Pollution Research 21, 6612-6622.

Stevenson, D.S., Dentener, F.J., Schultz, M.G., Ellingsen, K., van Noije, T.P., Wild, O., Zeng, G., Amann, M., Atherton, C.S., Bell, N., Bergmann, D.J., Bey, I., Butler, T., Cofala, J., Collins, W.J., Derwent, R., Doherty, R.M., Drevet, J., Eskes, H.J., Fiore, A.M., Gauss, M., Hauglustaine, D.A., Horowitz, L.W., Isaksen, I.S., Krol, M.C., Lamarque, J.-F., Lawrence, M.G., Montanaro, V., Mueller, J.-F., Pitari, G., Prather, M.J., Pyle, J.A., Rast, S., Rodriguez, J.M., Sanderson, M.G., Savage, N.H., Shindell, D.T., Strahan, S.E., Sudo, K., Szopa, S. (2006) Multimodel ensemble simulations of present-day and near-future tropospheric ozone. Journal of Geophysical Research 111, D08301, doi:10.1029/2005JD 006 338.

Vutukuru, S., Dabdub, D. (2008) Modeling the effects of ship emissions on coastal air quality: a case study of Southern California. Atmospheric Environment 42, 3751-3764.

(Received 29 August 2014, revised 5 February 2015, accepted 5 February 2015)