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Estimating Taiwan biogenic VOC emission: Leaf energy balance consideration

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ABSTRACT

The goal of the present study is to provide a comprehensive model to estimate biogenic volatile organic compounds (BVOCs) in Taiwan. In addition to metrological data, the model consists of (1) 83 land-use patterns, (2) emission factors for various vegetations, (3) energy balance equation to account for leaf temperature, and (4) correction terms for photosynthetically active radiation. The model output includes 4 categories of 33 BVOCs [isoprene, methylbutenol (MBO), 14 species of monoterpenes and 17 other BVOCs]. The results of model verification based on several approaches include: (1) predicted isoprene emission flux correlates relatively good with the observed isoprene concentration ($R^2 = 0.66$); (2) correlation between leaf temperature and observed isoprene levels is better than that between ambient temperature and isoprene concentrations ($R^2 = 0.63$ vs. 0.58); (3) model-predicted isoprene fluxes match well with observed 3-day diurnal isoprene concentration variations; and (4) subsequent model-predicted O_3 concentrations with the BVOC input obtained in the present study match well than that with previous estimated BVOC data with the observed 6-day diurnal O_3 levels in 8 air quality monitoring stations.

Based on the meteorological data in 2000, the total emission of BVOCs in Taiwan was simulated to be about 433,000 ton (33% of total VOCs) of which both isoprene and 14 species of monoterpenes account for about 34%, with 17 species of other BVOCs being 31% and <2% contribution from MBO. Total emissions of BVOCs are higher in lower and medium altitude (300–1000 m) mountain areas with an average of around 15–30 ton $km^{-2}\,y^{-1}$. The implication of the other results is also discussed.

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1. Introduction

Biogenic volatile organic compounds (BVOCs) have a great variety of species, and different species vary tremendously in photochemical reaction. BVOCs include isoprene, monoterpenes, 2-methyl-3-buten-2-ol, hexenal family compounds, alkenes, and alkanes, among others (Guenther et al., 2000). These BVOCs are more widely distributed than anthropogenic VOC emissions. Often in the selection of O_3 control strategy, if VOC is the so-called limiting precursor, then the need to accurately estimate total VOC emissions in general and BVOC emission in particular is apparent. This is especially true in some countries, in which BVOCs account for a major share of total VOC emissions, e.g., the BVOC emission contributed about 60% to the total VOC emission in Ukraine and 45% in Spain (Simpson et al., 1999) with more than 50% in the USA (Guenther, 1997).

Located at 21–25° N latitude, Taiwan borders on the subtropical and torrid zones (the Tropic of Cancer crossing the middle of Taiwan). Ocean current and the monsoon are the two most important elements responsible for the climate here leading to a warm (annual average temperature 24 °C), humid weather [relative humidity (RH) 65% with annual precipitation of 2500 mm] and dense forests. The vegetation cover ratio in Taiwan is now close to 78%. There are also many varieties of plants in urban areas. Thus, the high emission of BVOCs is expected and adequate quantification of BVOCs is of extreme importance.

Many factors should be considered in estimating BVOC emission: (1) simulated species of BVOCs, (2) leaf temperature, (3) spatial resolution, and (4) others including ambient temperature, photosynthetic available radiation (PAR), leaf age, etc. Most models only predict 3 classes of BVOC species (e.g., Pierce et al., 1998; Scott and Benjamin, 2003) although some models are able to predict more species of BVOCs (e.g., Sakulyanontvittaya et al., 2008; Song et al., 2008). A simple classification of only a few BVOCs would underestimate the total quantity of BVOCs emitted; the omission of some BVOCs, like α-pinene, β-pinene, limonene and methylbutenol (MBO), would underestimate the quantity of O_3 formation, due to their high O_3 formation potential (Guenther et al., 2000). In fact, Geron et al. (2000) have indicated that more species of monoterpenes emitted

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by plants have been identified resulting in possible errors of 30–50% in earlier BVOC emission studies. Further, Carlo et al. (2004) have reported much differences between the measured and model-predicted values for terpenes and other BVOCs, apparently due to unknown reactive BVOCs. Consequently, the latest version 3 of US Biogenic Emission Inventory System US (BEIS-3) has classified BVOCs into 33 species (Pierce et al., 2002).

One of the major setbacks of the existing models is that they use ambient temperature and not leaf temperature in estimating BVOC emission. Others use a simple canopy model to obtain leaf temperature from ambient temperature (Lamb et al., 1993; Geron et al., 1994), or with different underlying assumptions (e.g., Grote, 2007), although a new MEGAN model (Müller et al., 2008) includes the calculation of leaf temperature using a detailed canopy environment model. In fact, the US BEIS-3 assumes that leaf temperature within the canopy is equal to ambient temperature (Pressley et al., 2006). Apparently, the temperature that controls BVOC emission is leaf temperature and not the ambient temperature. Previous studies (Gates, 1968; Rinne et al., 2002) have indicated that leaf temperature may be higher than ambient temperature by about 10 °C in places exposed to direct insolation; on the contrary, leaf temperature can be lower than ambient temperature in a shady place with higher wind speed. Thus, the errors in using ambient temperatures for estimating BVOCs are expected (Haapanala et al., 2006).

Previously, based on BEIS-2 (Guenther et al., 1993, 1994; Geron et al., 1994), we have reported the Taiwan BEIS (TBEIS-1); the influence of parameters such as two meteorological factors (temperature and PAR for isoprene only), land-use type and leaf density was considered to simulate hour-by-hour emissions of BVOCs (Chang et al., 2005). Unfortunately, there are several shortcomings of this model. In addition to only 3 classes of BVOCs (isoprene, monoterpenes and other VOCs) as well as ambient temperature used, other important factors should have been considered. For example, the effect of PAR may be significant on the emission of some BVOCs including isoprene, MBO and certain monoterpenes (Kesselmeler et al., 1997; Sabillón and Cremades, 2001; Rinne et al., 2002). As monoterpenes are mainly emitted from coniferous forest which accounts for 20% of the timberland in Taiwan, the lack of subdivision of the emissions from monoterpenes and other BVOCs and not taking the influence of PAR on monoterpene emissions into consideration certainly cause estimation errors in the previous TBEIS-1. Another parameter, humidity, also plays an important role in some BVOC emission (Staudt et al., 2002). Since its effect is a controversial issue (discussed in Appendix 1 of the supplemental materials, SM), the direct effect of humidity on BVOC emission is not considered in the present study, but humidity is still accounted for leaf temperature in energy balance model (see Section 2.3).

Accordingly, this research was undertaken to correct the above mentioned setbacks of the previous TBEIS-1 to include: (1) leaf temperature, (2) expand BVOC species from 3 to 33 and more importantly classify BVOCs into 4 categories by separating MBO from monoterpene group as a new category, and (3) account for the impact of PAR on some BVOCs to develop TBEIS, version 2 (TBEIS-2) so that the results can better represent a better picture. In this study, the leaf photosynthesis balance model developed by Nikolov et al. (1995) was used to convert ambient temperature to leaf temperature. The emission factors of BVOCs for different plant species were obtained through literature review. Because of varying mountain height up to 3950 m within a narrow width (150 km) in Taiwan, the vertical profiles of averaged BVOC emission fluxes and total BVOC emission are presented. To the best of our knowledge, this is the 1st attempt to include the above mentioned important items in the overall estimation of BVOCs.

2. Establishment of TBEIS-2

The structure and content of TBEIS-2 model are illustrated in Fig. 1. Again the model considers the land-use pattern, emission factor for plants, energy balance for leaf temperature, and PAR corrections. The parameters on the left side of model, including RH, wind velocity, cloud cover and precipitation are needed in conjunction with ambient temperature and PAR for the simulation of leaf temperature. The output of the model is hourly emission of 4 BVOC categories. Each of these items will be briefly discussed below.

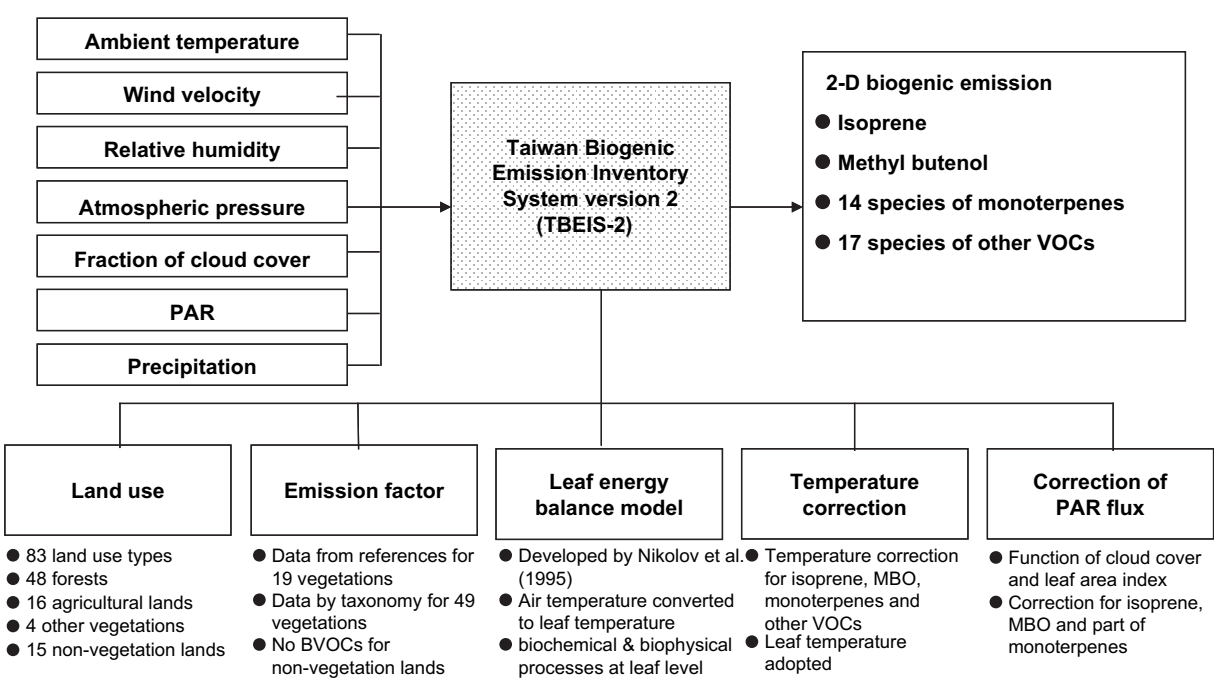

Fig. 1. Configuration of Taiwan biogenic emission inventory system version 2 (TBEIS-2).

2.1. Land use

The available land-use databases for Taiwan are the Taiwan Forestry Bureau gird land-use database (Chang, 1999; referred as TGLD) and the land-use database of Taiwan Emission DataBase (CTCI, 1999; TEDBLD). Both data sets have spatial resolutions of 1 km by 1 km. The area coverage of the TGLD is mostly concentrated on the governmental land around and within mountain regions. In this study, the land-use data set for emission model was based on TGLD with supplemental information from TEDBLD for areas not covered by TGLD, especially the dry agriculture land and paddy fields in the plain regions. Consequently, the land-use patterns are classified into 83 land-use types including 48 forests, 16 agricultural-lands, 4 other vegetations, and 15 non-vegetation lands (shown in the 3rd column of Table SM-1 (Supplemental Materials)). As can be seen, such detailed land-use pattern would render better BVOC emission resolution/estimation. Although the grid area in TBEIS-2 is 1 km^2, each grid covers each land-use type.

2.2. Determination of emission factors for 33 species of BVOCs

The emission factor differs tremendously from various tree species and even the species within the same genus of tree variety (Geron et al., 2000). In the present study, BVOCs were first classified into 4 major categories: isoprene, MBO, 14 species of monoterpenes and 17 other VOCs as shown in Table 1. MBO, only emitted from vegetations, has the same emission mechanisms as isoprene but with much higher emission factor for some coniferous forests (Baker et al., 1999; Schade et al., 2000); i.e., MBO emissions exceed isoprene emissions up to a factor of ten in the lodgepole and ponderosa pine forests (Schade and Goldstein, 2001; Karl et al., 2002). Thus, the separation of MBO from others is essential and the subdivision of previous used 3 or 4 major classes (Geron et al., 2000) into more detailed diverse VOC species should have a direct impact in the subsequent emission estimation.

The emission factors related to these 33 BVOCs were collected through literature as function of plant type or species; they are shown in Tables SM-2, SM-3, SM-4 for 14 species of monoterpenes, isoprene/MBO, and 17 other BVOCs, respectively. Clearly, spruce (*Picea*) has the highest emission factor of 19 $\mu g\,g^{-1}\,h^{-1}$ for isoprene (Table SM-3). The highest emission factor out of 14 species of monoterpenes is d-limonene emitted by Orange plants, or 196 $\mu g\,g^{-1}\,h^{-1}$ (item 15, Table SM-2), while methanol exhibits the highest emission factor by Rye plants (39 $\mu g\,g^{-1}\,h^{-1}$, Table SM-4) among 17 other BVOCs.

Next is to incorporate these emission factors into land-use patterns shown in Table SM-1. The botanical classification method of Benjamin et al. (1996) was adopted to establish the emission fluxes for 68 vegetation land-use types in Taiwan. Briefly, plant taxonomy approach was first used to sort out the types of plants in the database of Taiwan land-use type, or classified into genus, family, order, class and phylum. After comparison, if the tree species belong to the same genus (e.g., *Pinus*, *Chamaecyparis* spp., and *Tsuga chinensis*), the product of the corresponding emission factors (Tables SM-2, SM-3 and SM-4) and the leaf density was directly applied to obtain emission fluxes shown in Table SM-1 (14 species of monoterpenes), Table SM-5 (isoprene and MBO) and Table SM-6 (17 species of other BVOCs). For instance, the 750 $\mu g\,m^{-2}\,h^{-1}$ emission flux of α-pinene for nature and plantation of *Pinus* spp. (item 5 and 6, Table SM-1) was obtained from the emission factor for *Pinus pinea* (1.07 $\mu g\,g^{-1}\,h^{-1}$; item 9, Table SM-2), multiplying by the leaf density of *P. pinea* (700 $g\,m^{-2}$; item 9, Table SM-2). In addition, because *T. chinensis* belongs to the same genus of Eastern hemlock, the emission flux of α-pinene for *T. chinensis* (1050 $\mu g\,m^{-2}\,h^{-1}$; item 7, Table SM-1), was calculated directly from the emission factor for Eastern hemlock (1.50 $\mu g\,g^{-1}\,h^{-1}$; item 6, Table SM-2), multiplying by the leaf density 700 $g\,m^{-2}$ (item 6, Table SM-2).

However, if they were different genus but within the same family, the emission factor corresponding to the same family was used, e.g., emission factor for peach/apple/pear species was the same as that for *Prunus* since they all belong to the Family of Rosaceae. For others, the emission factors of some gross type were calculated based on the similar types that have known emission factors and their area ratios.

Accordingly, proper emission fluxes are given to all tree species in the database of Taiwan land-use type as shown in Table SM-1 (14 species of monoterpenes), Table SM-5 (isoprene and MBO) and Table SM-6 (17 species of other BVOCs). Noted that the mixed nature and plantation of broadleaved forests (grow in areas at medium elevations, 300–1000 m) take the lion's share of total area of land-use type in Taiwan (ca. 43% of 28,200 km^2). With its high emission factor for isoperene and others BVOCs, the impact of this type of trees on the overall BVOCs is apparent. Again, each grid covers each of 83 land-use types as mentioned earlier. The emission fluxes used in this present study, albeit with some uncertainty, are by far the most comprehensive one used in BVOC modeling. With the future measurement/refinement of emission factors for some plants in Taiwan, the errors for BVOC estimation can be greatly reduced.

2.3. Leaf temperature energy balance model

The leaf energy balance model developed by Nikolov et al. (1995) was incorporated into the model to account for the conversion of ambient temperature (T_a) to leaf temperature (T_l) via biochemical and biophysical processes at leaf level as:

Table 1
4 Categories and 33 species of biogenic VOCs simulated in TBEIS-2.

Category	Class	Species			
1	Isoprene	Isoprene			
2	Methylbutenol	Methylbutenol (MBO)			
3	14 Monoterpenes	α-Pinene	Camphene	Sabinene	α-Thujene
		β-Pinene	Myrcene	Pcymene	Terpinolene
		Δ^3-Carene	α-Terpinene	Ocimene	r-Terpinene
		d-Limoenene	b-Phellandrene		
4	Other 17 BVOCs	Methanol	3-hexenal	Formaldehyde	Propene
		Carbon oxide	Hexenyl acetate	Acetaldehyde	Ethanol
		Butane	Acetate	Formic acid	Butane
		Hexenol	Hexanol	Acetic acid	Butanone
		2-Hexenal	Acetone		

$$R_i = \frac{\rho c_p}{\gamma}[e_s(T_l) - e_a]g_{tv} + \rho c_p(T_l - T_a)g_{bv} + 2\varepsilon\sigma(T_l + 273.16)^4 + M_e \quad (1)$$

where R_i is bi-directional absorbed short and long-wave radiation ($W\,m^{-2}$), ρ is density of dry air ($kg\,m^{-3}$), c_p is specific heat of dry air ($1010\,J\,kg^{-1}\,K^{-1}$), γ is psychrometric constant ($Pa\,K^{-1}$), e_s (T_l) is saturation vapor pressure at leaf temperature (Pa), e_a is water vapor pressure inside the leaf-boundary layer (Pa), g_{tv} is leaf total conductance for water vapor exchange ($m\,s^{-1}$), g_{bv} is all-sided leaf-boundary layer conductance to water vapor ($m\,s^{-1}$), ε is leaf thermal emissivity (0.975), σ is Stefan–Boltzmann constant ($5.67 \times 10^{-8}\,W\,m^{-2}\,K^{-4}$), and M_e is the energy stored in biochemical reactions ($W\,m^{-2}$). Some of these parameters including c_p, ε, and σ were constants and some were calculated from theoretical or empirical considerations using meteorological parameters (Nikolov et al., 1995). For example, R_i is function of the ambient air temperature, PAR, RH and wind velocity (Campbell and Norman, 1998) and is a critical element in simulating leaf temperature. The γ value is function of atmospheric pressure, latent heat of water vaporization, specific heat of air at constant pressure, and the ratio of water vapor/dry air (Alexandris and Kerkides, 2003). In general, ambient temperature, PAR, RH, wind velocity and atmospheric pressure are the major input parameters in Eq. (1). The algorithm solving the leaf energy balance model adopts the computer code of the LEAFC3 model (Nikolov et al., 1995) with some modifications for coupling with other parts of TBEIS-2.

The model explicitly couples all major processes and feedbacks including biochemical reactions, stomatal function, and leaf-boundary layer heat- and mass-transport mechanisms. It has been shown that the model can successfully predict measured photosynthesis and stomatal–conductance data as well as simulate a variety of observed leaf responses (Nikolov et al., 1995; Zeller and Nikolov, 2000). Sensitivity analysis of the model is shown in Appendix 2 of the SM. According to the results of sensitivity analysis, the more sensitive parameters of leaf temperature are ambient temperature, R_i and wind speed. The leaf temperature can be varied from 19 to 31 °C for the ambient temperature of 25 °C, while R_i from −50 to 50% based on the referred condition of $1500\,W\,m^{-2}$. The inverse effect of wind speed on leaf temperature is significant. High wind speed renders a lower leaf temperature.

2.4. Environmental factors for monoterpenes and other VOCs

The effect of PAR on isoprene and certain monoterpenes (e.g. α-pinene and β-pinene) is profound (Kesselmeler et al., 1997; Rinne et al., 2002; Ciccioli et al., 2002). E.g., Owen et al. (2002) have pointed out that the error could be greater than ±100% if the influence of PAR was not considered. Consequently, the impact of PAR on emissions of MBO, α-pinene and ocimene are taken into account for all coniferous

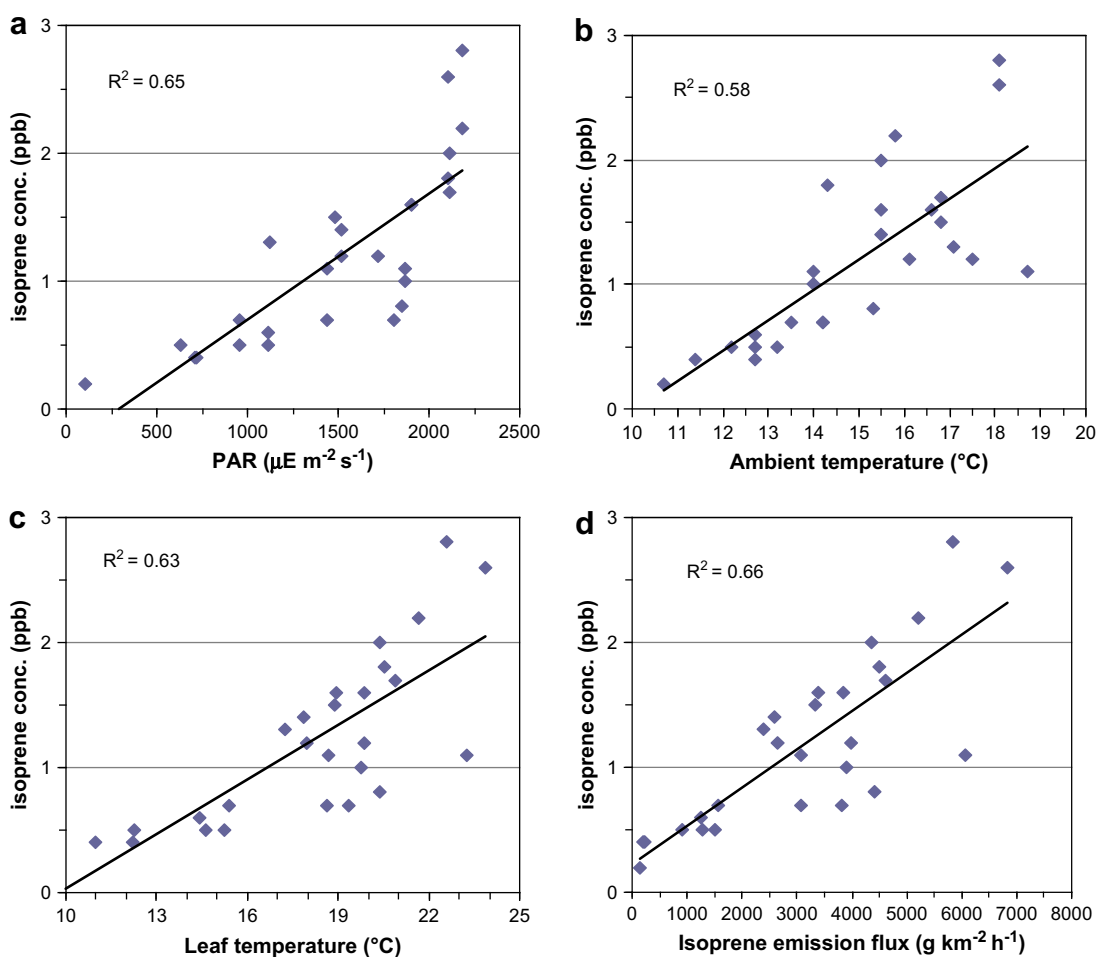

Fig. 2. Relationship between observed isoprene concentration and related parameters. (a) Observed PAR, (b) observed ambient temperature, (c) simulated leaf temperature, and (d) simulated isoprene emission flux. (Duration of observation: 2006/11/29–2006/12/1; Place of observation: Mt. North Tungyen.)

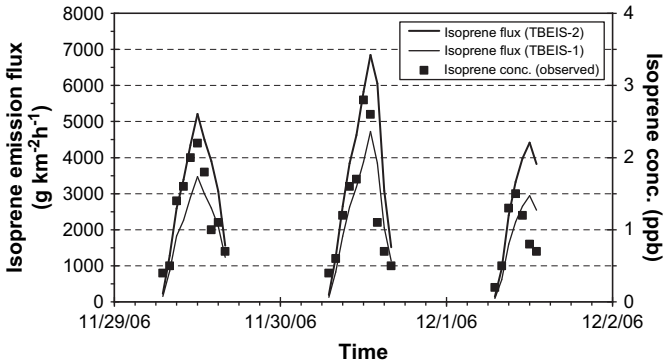

Fig. 3. Comparison of diurnal variation of simulated emission flux and observed concentration for isoprene in Mt. North Tungyen.

forests in the present study. In addition, since oak is affected by PAR (Rinne et al., 2002; Ciccioli et al., 2002) and the genus of oaks is the major species in different forests in Taiwan (mixed natural broadleaved, mixed natural coniferous-broadleaved and mixed natural bamboo broadleaved forests), the influence of PAR on emissions of 14 species of monoterpenes shall be accounted for these land-use types. Since the emission mechanism of MBO and monoterpenes is the same as that of the isoprene (Baker et al., 1999; Fisher et al., 2000), the emission flux of these BVOCs is estimated as the following isoprene expression (Guenther et al., 1993):

$$E = E_s C_L C_T \tag{2}$$

where E refers to the emission flux of monoterpene and E_s refers to the emission flux at the standard temperature (30 °C) and PAR (1000 μE m^{-2} s^{-1}). C_L stands for the light correction factor and C_T refers to leaf temperature correction factor; they are related to PAR and leaf temperature.

For some monoterpenes and 17 other BVOCs that are not related to PAR, but is affected by leaf temperature, the emission flux can be estimated as (Guenther et al., 1993)

$$M = M_s \exp[\beta(T_l - T_s)] \tag{3}$$

where M refers to the emission flux at T_l (leaf temperature), M_s stands for the emission flux at T_s (303 K), β refers to the empirical proportionality coefficient and value of 0.09 was adopted in this study (Guenther et al., 1993).

2.5. Meteorology

The meteorological data required for the model include ambient temperature, wind velocity, atmospheric pressure, RH, precipitation, PAR and fractional area of cloud coverage every hour. These data primarily from the weather stations (185 total) around the island were processed before use in TBEIS-2. Pre-processing the meteorological data means to interpolate hourly meteorological data from 185 weather stations into the hourly meteorological data in each grid. Also, topographic influence during interpolation needs to be considered for ambient temperature; wind directions have to be taken into account for wind velocity. It is noted that data on the fraction of cloud coverage were obtained from 25 ground weather stations established throughout the island.

2.6. Isoprene monitoring

In order to verify the model simulation results, the ambient isoprene concentrations were measured from Nov 29 to Dec 2, 2006 at the flux tower of Mt. North Tungyen. This tower is one of FLUXNET (http://daac.ornl.gov/FLUXNET) stations in Taiwan (2050 m above sea level). It is surrounded by forest with natural broadleaved plants being the most abundant.

A personal sampler (SKC model 222-4) was used for purging air into a glass tube (11 cm long) containing the absorbent, Tenax-TA (Supelco, 60/80 mesh). The GC/MS (Agilent Technologies, 6890N/5973N) with a capillary column (J&W Scientific, DB-502, 60 m length) was used for isoprene analysis of desorbed gas. The method detection level for isoprene (standard obtained from Chem Service, Inc.) is 0.1 ppb.

3. Results and discussion

3.1. Model verification

The verification of the developed model results was performed in three ways: (1) correlation analysis of model results with observed data, (2) diurnal pattern comparison of model results with observed data, and (3) comparison of air quality O_3 modeling results using estimated BVOC emission from this study with the observed O_3 data.

The observed isoprene concentrations were used to (1) correlate with the observed PAR and ambient temperature, and (2) to compare the model results of isoprene emission flux with the leaf temperature. The relatively good correlation between the observed isoprene concentration and PAR ($R^2 = 0.65$, Fig. 2a) refers to the impact of PAR; the results are similar with experimental results of Guenther et al. (1994). A better correlation between isoprene concentrations and leaf temperature ($R^2 = 0.63$, Fig. 2c) as compared to that between isoprene levels and ambient temperature ($R^2 = 0.58$, Fig. 2b) illustrates less errors in using the leaf temperatures for modeling BVOCs. As a result, the simulation results of TBEIS-2 for isoprene emission flux indicate a relatively good correlation ($R^2 = 0.66$) with observed isoprene concentrations at the same period and the same place (Fig. 2d).

Table 2
Emissions (10^4 ton) of 4 categories of BVOCs in Taiwan for year 2000.

	Isoprene	14 Species of monoterpene	17 Species of other BVOCs	MBO	Total	Ratio of total emission (%)
1st quarter (Jan–Mar) emission	1.6	2.2	2.1	0.1	5.9	14
Ratio of annual total emission (%)	11	15	16	12		
2nd quarter (April–June) emission	4.7	4.3	3.7	0.2	12.9	30
Ratio of annual total emission (%)	32	29	28	30		
3rd quarter (Jul–Sept) emission	5.8	5.0	4.4	0.3	15.5	36
Ratio of annual total emission (%)	39	34	34	39		
4th quarter (Oct–Dec) emission	2.7	3.2	3.0	0.1	9.0	20
Ratio of annual total emission (%)	18	22	23	19		
Annual total emission	14.8	14.7	13.2	0.7	43.3	100
Ratio of annual total emission (%)	34	34	31	1	100	

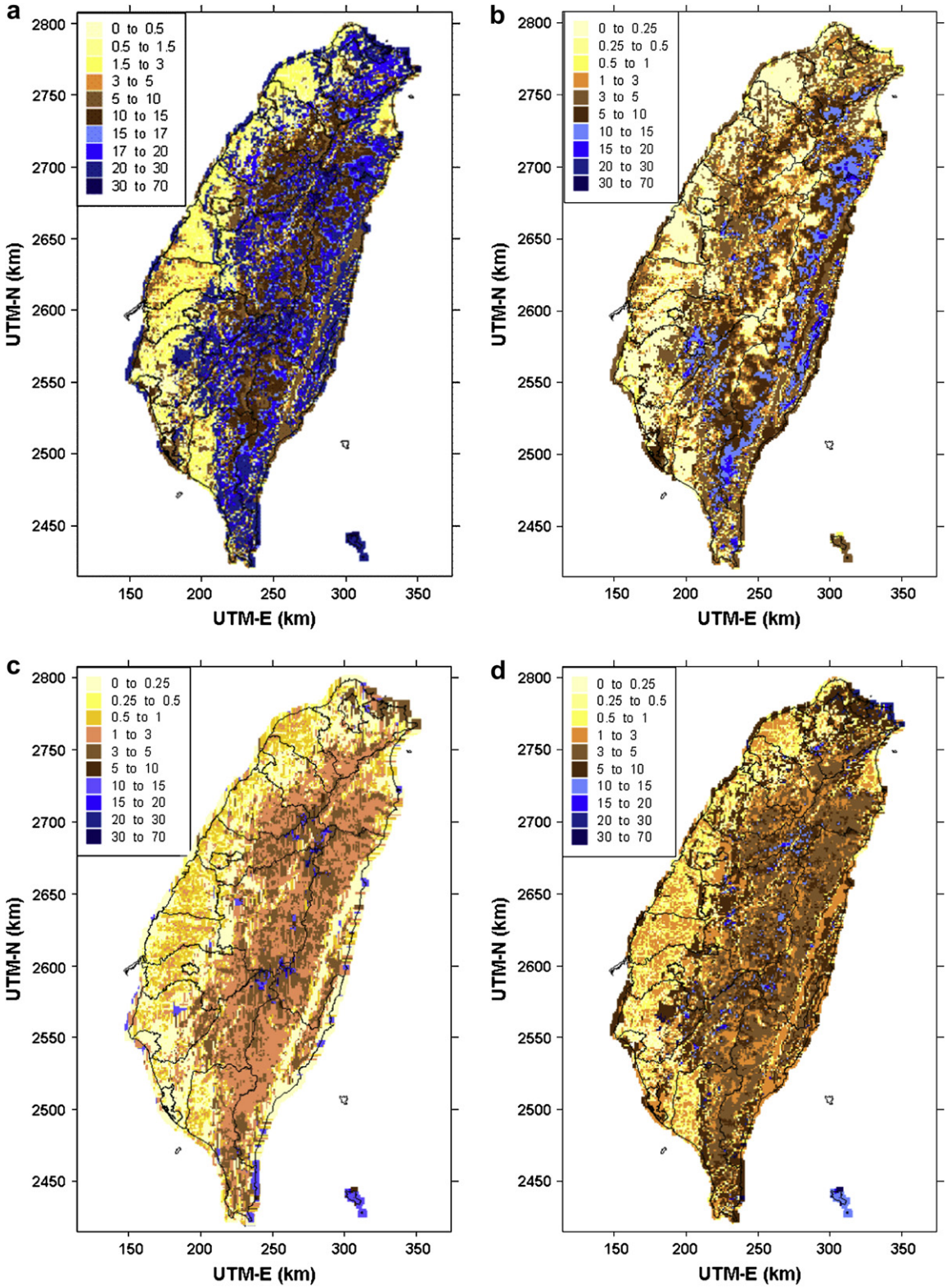

Fig. 4. The spatial distribution of emission fluxes (ton km^{-2} yr^{-1}) in year 2000 for (a) total biogenic VOCs, (b) isoprene, (c) total of 14 monoterpenes, and (d) total of 17 other VOCs.

Verification of model-predicted diurnal BVOC flux variations with the observed concentrations is another approach to test the validity of the model (Nunes and Pio, 2001). The results of isoprene emission flux simulated by TBEIS-2 are closely correlated with the observed 3-day isoprene concentrations (Fig. 3). The results of the previous TBEIS-1 are also included for comparison. Although both TBEIS-2 and TBEIS-1 simulation results agree well with the observed isoprene concentrations (correlation coefficients are close to 0.82), the TBEIS-2 can better match the peak O_3 levels. The underestimation of the BVOC fluxes from the previous model without considering important factors mentioned above (e.g., leaf temperature and PAR) is apparent.

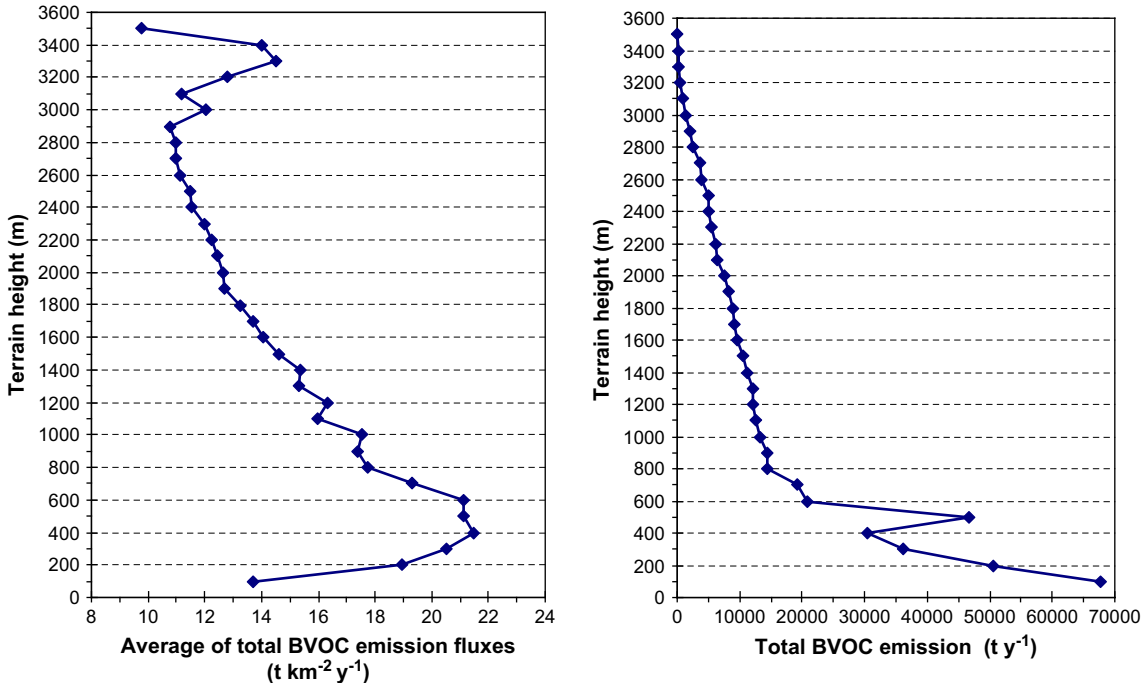

Fig. 5. Vertical profiles of total BVOC emission flux (left) and total emission (right) in Taiwan.

To further validate the model, ambient O_3 concentrations were simulated using the BVOC quantity from the current TBEIS-2 and previous TBEIS-1, and the results then compared with the observed O_3 concentrations. A 3D multi-scale photochemical model, called Taiwan Air Quality Model (TAQM, Chen and Chang, 2006; Chang, 2008), was used for O_3 simulation in eight air quality monitoring stations. Clearly, the simulated results with TBEIS-2 emission match well with the observed data than that with TBEIS-1 emission in all stations, particularly daily peak O_3 concentrations (Fig. SM-1). The average daily O_3 maximum concentration for the simulated 5-day data is 77 and 68 ppb for the results with TBEIS-2 and TBEIS-1, as compared to the observed 80 ppb.

The total anthropogenic VOCs estimated by Taiwan EPA is about 8.9×10^5 ton in Taiwan for the year 2000 (CTCI, 2003), while the total BVOCs estimated in the present study (shown in Section 3.2) is 4.3×10^5 ton. The average ratio of BVOC to total VOC is 33% in the modeling, but it varies greatly with different areas due to the complicated terrain in Taiwan. Wherever the higher ratios of BVOC to total VOC sites were used (e.g., 0.7–0.8) [e.g. Nantou (Site 5 in Fig. SM-1) and Touliu (Site 6)], or the lower ratio sites (e.g., 0.1–0.2) [e.g. Chungmin (Site 3) and Fongyuan (Site 1)], the variations of ozone concentrations pretty agreed with observed data. It is implied that the estimation of BVOC emission in the present study is reasonable for different areas in Taiwan.

3.2. Model inventory results

The meteorological data of the year 2000 were used to simulate the emissions of BVOCs of the same year in TBEIS-2. 33 species of BVOCs can be divided into isoprene, MBO, 14 species of monoterpenes and 17 species of other BVOCs for an exploration of time and spatial characteristics for emissions.

The results were separated into four seasons so that seasonal effect on BVOC emission can be better comprehended. The inventory results shown in Table 2 indicate total amount of about 4.3×10^5 ton, including approximately 1.5×10^5 ton isoprene (34% of total BVOCs) with the same amount for 14 species of monoterpenes, in which α-pinene contributes the most with an emission amount of about 0.5×10^4 ton (13%). Total emissions of 17 species of other VOCs amount to 31%, in which methanol has the highest emission (about 10%) followed by hexenyl acetate (7%) and ethane (6%). Biogenic emissions reach the highest in the third quarter (36% of the annual total amount), due to higher temperatures/PAR effect.

Spatial distribution of total biogenic emission in Taiwan for the year 2000 is illustrated in Fig. 4a. Total annual emissions of BVOCs are higher in lower and medium altitude areas with an average of around 15–30 ton km^{-2}; the highest emission can be up to 70 ton km^{-2}, whereas they are below 5 ton km^{-2} y^{-1} on ground levels. Notice that relatively high BVOC emission along the sea shore of the western Taiwan is due to windbreak forest.

Isoprene mostly emits in lower and medium altitude mountains (300–1000 m) where broadleaved forests with much higher emission fluxes are the major forest stand. The average isoprene emission flux ranges from 10 to 20 ton km^{-2} y^{-1} (Fig. 4b). On the contrary, the emission fluxes of 14 species of monoterpenes (with α-pinene being the major one) are higher (average 15–20 ton km^{-2} y^{-1}) in high altitude mountain areas, because of distribution of coniferous forests there (Fig. 4c). The highest emission flux of 17 other species of BVOCs can be up to 20 ton km^{-2} y^{-1} and the majority of them concentrate in grids of medium and higher altitude areas with an average emission flux of 10–15 ton km^{-2} y^{-1} (Fig. 4d).

Because of varying mountain height up to 3950 m within a narrow width (150 km) in Taiwan, it is of interest to reveal the BVOC vertical variations. The profiles of averaged BVOC emission fluxes and total BVOC emission for an interval of 100 m are shown in Fig. 5. The highest of averaged BVOC emission flux (21 ton km^{-2} y^{-1}) occurs between 300 and 600 m, and then the emission fluxes diminish progressively with increasing altitude until 3000 m. However, the total BVOC emission (70,000 ton y^{-1}) is highest below 100 m due to larger forest areas in lower altitude and they reduce quickly in the lower altitude and further reduce gradually in the higher altitude.

The 24-h distribution of the emissions of four types of BVOCs around the year is illustrated in Fig. SM-2. Isoprene emits most during the day followed by 14 species of monoterpenes with the MBO the least emission amount. The emission quantity of isoprene at noon time is almost 2 times of the 14 monoterpenes and 3 times of the 17 other VOCs, while isoprene emission at night time is zero with insignificant amounts for monoterpenes and other VOCs. The emission variations between day and night are less obvious for 17 species of other BVOCs because of their emission dependence on temperature only and not on PAR. On the contrary, the effect of PAR on isoprene and MBO is significant with nil emission during night (0–4 am and 6–11 pm).

Compare to the averaged isoprene flux of the other countries (Olendrzynski, 1997; Simpson et al., 1999), Taiwan exhibits the second place with the emission flux of 4.1 ton $km^{-2}\,y^{-1}$ that is larger than the emission fluxes emitted by all European countries and only less than the one emitted by Central Africa (7.8 ton $km^{-2}\,y^{-1}$) as shown in Fig. SM-3. The results imply that BVOCs emission flux in general and isoprene in particular is strongly dominated by latitude and coverage ratio of vegetation.

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Appendix. Supplementary information

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.atmosenv.2009.06.038.

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