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Estimation of Biogenic VOC Emissions in East Asia with New Emission Factors and Leaf Energy Balance Considerations

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ABSTRACT

A good inventory system of biogenic VOCs emissions in East Asia is required and must function correctly alongside available meteorological data to enable adequate estimation of biogenic emissions. There is a wide body of literature concerning estimations of biogenic emissions in East Asia or larger areas; however, many use environmental temperature rather than leaf temperature; further, they only focus on three kinds of biogenic VOCs: Isoprene, Monoterpenes and other BVOCs. This may cause estimation errors, the size of which are unclear. The purpose of this study is to establish an estimation model of biogenic VOC emissions for East Asia giving due consideration to the leaf energy system, ensuring it can be used effectively with appropriate meteorological data, while estimating hourly emissions of 33 specific species of biogenic VOCs from plants in East Asia. Estimation errors found using environmental temperature instead of leaf temperature were also investigated. Finally, uncertainty of estimation results was analyzed with regard to land use and emission factor datasets.

Total annual BVOC emissions in East Asia (the domain of this study) estimated by the model established by this study can be up to 40.9 Tg yr^{-1} and are comprised of 24.6% isoprene, 45.1% of 14 species of monoterpenes, 28.9% of 17 species of other BVOCs and just 1.4% MBO. The replacement of leaf temperature with environment temperature results in overestimations of annual amounts for all BVOC species. Results indicated that total BVOC emissions were overestimated by 30.7%, with significant overestimations of isoprene, 46.7%, and a smaller but still significant overestimation of monoterpenes of around 24.2%. Not all areas exhibited overestimations as zonal and seasonal differences were influential. In summer, when leaf energy instead of ambient temperature was used, BVOC emissions in all areas of the simulation region were overestimated. In winter, overestimations appeared in areas at lower latitudes, and underestimations appeared in areas at higher latitudes. With regard to uncertainty, three different kinds of emission factors and two types of land use data were applied. Results showed that estimated emissions of BVOCs varied more than 200% when either emission factors or land use data were used. Besides, the daily maximum O_3 concentration changed significantly in some areas (-15 – 9 ppb). To reduce uncertainty in estimation results, a suitable database of land use and emission factors that gives consideration to vegetation features in different areas is required.

Keywords: Biogenic VOCs, leaf temperature, land use, East Asia.

1. INTRODUCTION

The recent rapid economic growth in East Asia has resulted in large population migrations, increases in fossil fuel consumption and even land form changes due to planting of economic crops. Some of these events may increase the quantity of air pollutants, which then go on to produce secondary pollutants in the atmosphere through physical and chemical processes. These atmospheric pollutants may influence surrounding countries such as China, Japan, Korea or Taiwan (Itahashi *et al*. 2013). These pollutant effects are well known and recorded in Taiwan, where for the past few years, the average maximum 8-hr O_3 concentration has not improved. In some places it has even deteriorated, despite the emission control measures governing O_3 precursors implemented by the Taiwanese Environmental Protection Administration (EPA). Previous studies on the causes of worsening air quality in Taiwan show the impact of long range transport pollutants from nearby countries in East Asia, and show that these must be accounted for in addition to the known local sources. Chang *et al*. (2017) analyzed observed data from 2000 to 2014, and found that surface ozone increased over East Asia, showing a sharp rise after 2011 (>10 ppb), with statistically significant trends of 0.40 and 0.37 ppb yr^{-1} estimated for summertime mean of daytime average and daily maximum 8-hour average, respectively. Tropospheric ozone in East Asia may also be influenced by the transport of ozone from foreign regions around the world. Han *et al*. (2019) used GEOS-Chem emission perturbation simulations and found that foreign ozone was transported to East Asia, mainly through the middle and upper troposphere, resulting in a 22 ppb increase of annual mean surface ozone concentrations in East Asia.

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For an understanding of the causal relationship with regard to regional transports, a three dimensional air quality model is required to simulate and analyze the interactions of pollutants among different East Asian areas. Consequently, it is becoming increasingly necessary to establish a comprehensive and standardized emissions database in East Asia.

NOx and VOCs are precursors of O_3, but VOC emissions can be anthropogenic or biogenic in nature. In some cases, biogenic sources have a greater effect on secondary pollutants than anthropogenic sources (Guenther *et al*. 1995; Olendrzyński 1997; Simpson *et al*. 1999). The importance of biogenic volatile organic compounds (BVOCs) in research concerning air quality and climatology on regional to global scales have been explored in a number of modeling and observational studies. (Tsai *et al*. 2020; Chen and Chang 2004; Kim *et al*. 2013; Wang *et al*. 2008; Bao *et al*. 2010; Ran *et al*. 2011; Geng *et al*. 2011). BVOCs are generally expected to play a major global role since total BVOCs emissions are much higher than anthropogenic volatile organic compounds (AVOCs) (Guenther *et al*. 2006; Goldstein and Galbally 2007).

Though a small portion of NO emissions comes from fertilizers for crops, it is not significant compared with emissions from anthropogenic sources. Short-term variations in emissions from anthropogenic sources are less obvious as they are less sensitive than meteorological data. As estimations of emissions from biogenic sources are strongly affected by meteorology, estimation results vary depending on the simulations type and dates used. Chang and You (2009) set up the Taiwan Biogenic Emission Inventory System, version 2 (TBEIS2) and integrated meteorological data for estimating emissions of BVOCs in Taiwan. However, BVOC emissions of other districts in East Asia were estimated using an overly simplistic approach (Chang 2000) and models using leaf energy balance were not considered. Thus, to simulate and analyze O_3 pollution and interactions among areas in East Asia more corretly, it is necessary to construct a more unified and scientific-based biogenic emission estimation model that gives considerations to emission factors and leaf energy balance.

TBEIS2 is a model that already includes leaf energy balance that can be used to estimate 2-D hourly emissions of 33 species of VOCs for Taiwan (Chang and You 2009). It adopted the photosynthesis balance model presented by Nikolov *et al*. (1995), which calculated the leaf temperature through ambient temperature. Consequently, the inaccurate assumption where ambient temperature is treated as being equal to the estimated emissions generated by leaf temperature can be eliminated. The revised formula (1) is as follows:

$$R_i = \frac{\rho c_p}{\gamma}[e_s(T_1) - e_a]\, g_{tv} + \rho c_p (T_1 - T_a) g_{bv} + 2\varepsilon\sigma\,(T_1 + 273.16)^4 + M_e \quad (1)$$

Where R_i: radiant flux absorbed by a leaf; ρ: density of dry air; c_p: specific heat of dry air; γ: psychrometric constant; $e_s(T_1)$: saturation vapor pressure at leaf temperature; e_a: water vapor pressure inside the leaf-boundary layer; g_{tv}: leaf total conductance for water vapor exchange; g_{bv}: all-sided leaf-boundary layer conductance to water vapor; T_a: ambient temperature; T_1: leaf temperature; ε: leaf thermal emissivity; σ: Stefan-Boltzmann constant; and M_e: energy stored in biochemical reactions.

The original three categories of BVOC species, isoprene, monoterpenes and "other" were further delineated to include 33 species in total, including isoprene, 14 species of monoterpenes (α-pinene, β-pinene, Δ3-carene, d-limoenene, camphene, myrcene, α-terpinene, β-phellandrene, sabinene, ρ-cymene, ocimene, α-thujene, terpinolene, γ-terpinene) and 18 species of other (methyl butenol (MBO), methanol, CO, ethene, hexenol, hexenal, ethane, hexenyl acetate, hexanal, acetone, formaldehyde, acealdehyde, formic acid, acetic acid, propene, ethanol, butene and butanone). Among the 18 species of other BVOCs, MBO was discovered to follow a similar emission mechanism to Isoprene where both were affected by light intensity and temperature. Hence, the formula (2) proposed by Geron *et al*. (1994) was applied to estimate Isoprene and MBO as follows:

$$I = I_s \times C_L \times C_T \quad (2)$$

Where, I: the emission rate of isoprene at temperature T with PAR as L; I_S: the emission rate of isoprene in standard conditions with temperature = 30 °C and PAR = 1000 μE m^{-2} s^{-1}; C_L: the light correction factor; and C_T: the correction factor for leaf temperature. The remaining 17 species of other BVOCs were only influenced by temperature and thus the same estimation formula (3) was used as for the 14 species of monoterpenes:

$$M = M_S \times \exp\,[\beta(T - T_S)] \quad (3)$$

Where, M: the emission rate of the species at leaf temperature T; M_S: the emission rate at the standard temperature T_S (= 303 K); and β (= 0.09): the experience coefficient (Guenther *et al*. 1993).

The Earth Resources Observation System (EROS) established and operated by the United States Geological Survey (USGS) obtains satellite remote sensing data on global land use via the Advanced Very High Resolution Radiometer (AVHRR) and divides land use into 24 categories (including Mix. dry/irrg. cropland and pasture, Herbaceous tundra and Bare ground tundra, in addition to 21 further types listed in Table 1) with a resolution of 0.00833. The remote sensing data from April 1992 to March 1993 for different continental plates, including Eurasia, North America, South America, Africa and Australia/Pacific can be downloaded and stored for use. For this study the East Asian zone was separated from Eurasia for more detailed analysis.

Estimates of BVOCs emissions in East Asia, or districts with a larger area have been made in previous studies (Guenther *et al*. 1995; Klinger *et al*. 2002; Tie *et al*. 2006); however, most of them used the assumption that leaf temperature was equivalent to ambient temperature; an approach which was also frequently adopted when simulating BVOC emissions resulting in inaccurate data conclusions. Moreover, as only three kinds of species, isoprene, monoterpenes and other BVOCs, were targeted in these studies, and the more detailed species breakdown of VOCs were not considered, this not only resulted in an underestimation of emissions, but also compounded errors when the less accurate BVOC emissions was used in air quality model.

To avoid these problems, this study used TBEIS2 data and modelling, which gives the required consideration to leaf energy balance formulae, and also contains a more detailed range of BVOC species. Land use data in East Asia from the USGS dataset and a series of emission factors are integrated by the TBEIS2 and BEIS3.12 systems to establish the East Asia Biogenic Inventory System (EABEIS). With the further addition of meteorological data simulated by the Fifth-Generation NCAR/ Penn State Mesoscale Model (MM5) (Grell *et al*. 1995) it was possible to generate an inventory, and develop an analysis of biogenic emissions in East Asia. Besides an understanding of spatial distributions and seasonal changes of biogenic emissions, further analysis of the impact of environmental temperature could also be made; as opposed to just using leaf temperature. With any new system there is some degree of uncertainty, particularly where various datasets, in this case land use data and emission factors, are combined and conclusions are then drawn; these aspects are also analyzed and discussed.

2. MATERIALS AND METHODS

2.1 Land use data adopted for EABEIS

The East Asia zone data used in this study was separated from the downloaded satellite remote sensing dataset for Eurasia, USGS, as shown in Fig. 1. Though there are 24 types of land use specified by the USGS, three types of mix. dry/irrg. cropland and pasture, herbaceous tundra, and bare ground tundra are inapplicable here, and only distributions of the remaining 21 types are observed in this study. Full lists and land types are shown in Table 1 and Fig. 1. The total simulated area in this study, water-bodies excluded, was approximately 7.2×106 square kilometers, of which irrigated cropland and pasture was the largest part 19%, followed by grassland 16%, dryland cropland and pasture, shrubland and mixed forest collectively comprised a little over 10%. The remaining types were less than 10%. Urban and built-up areas, mixed shrubland/grassland, deciduous needleleaf forest, herbaceous wetlands, wooded wetlands, wooded tundra, mixed tundra and snow or ice were less than 1%.

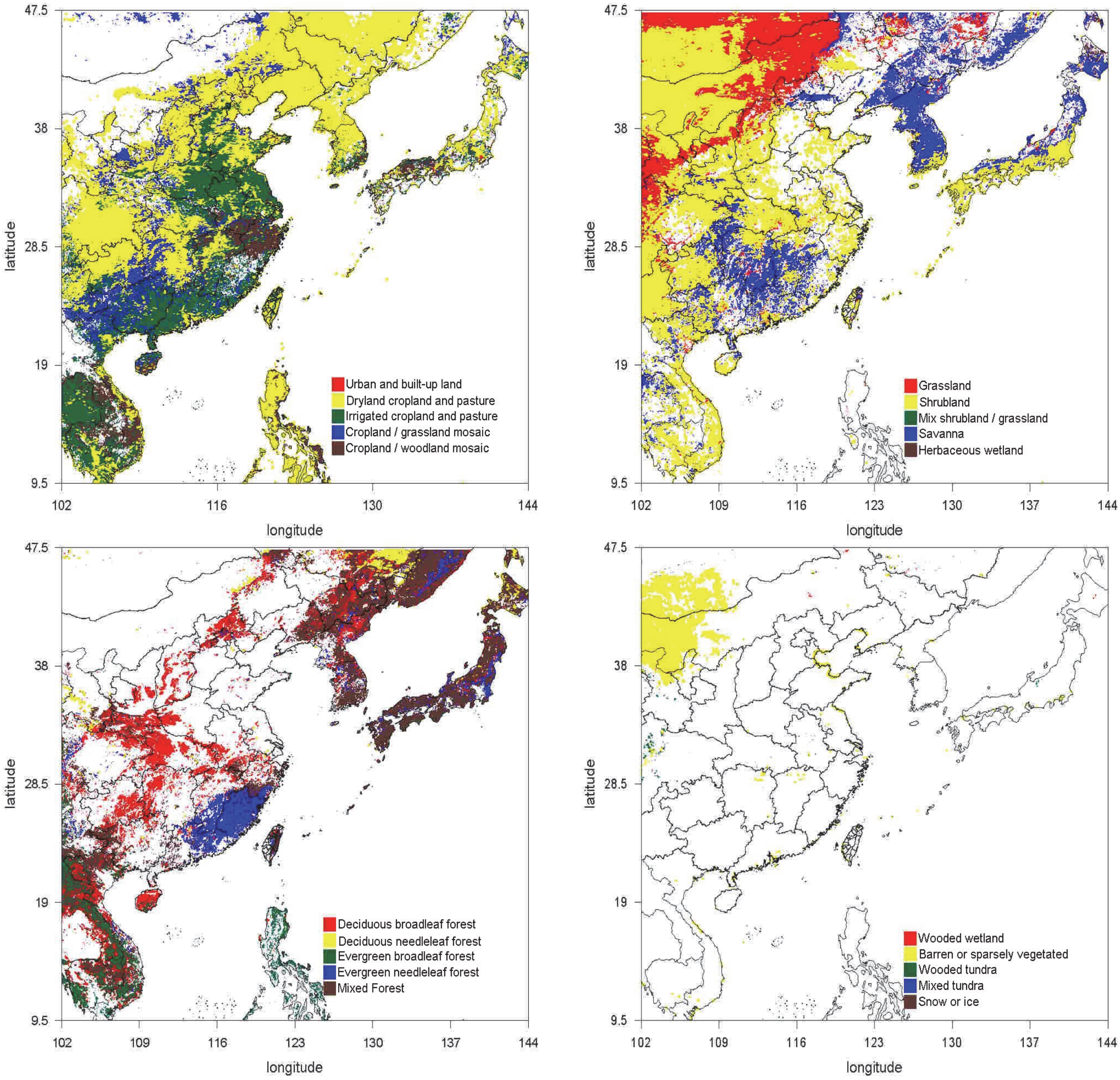

Fig. 1 Spatial distributions of various types of land use in East Asia.

Table 1 Land use types in EABEIS and their normalized emission factors (μg m^{-2} h^{-1}) for isoprene, monoterpenes, other BVOCs and MBO

	Categories	Isoprene	Monoterpenes*	MBO	Other BVOCs**
1	Urban and built-up land	10	20	75	173
2	Dryland cropland and pasture	1880	625	0	850
3	Irrigated cropland and pasture	240	649	0	712
5	Cropland/grassland mosaic	613	581	0	581
6	Cropland/woodland mosaic	1338	514	70	429
7	Grassland	390	1049	0	766
8	Shrubland	38	39	0	249
9	Mixed shrubland/grassland	214	544	0	508
10	Savanna	1765	60	0	173
11	Deciduous broadleaf forest	5374	3651	0	1594
12	Deciduous needleleaf forest	631	7086	2397	3102
13	Evergreen broadleaf forest	8598	2448	0	1439
14	Evergreen needleleaf forest	631	7086	2397	3102
15	Mixed forest	10771	4371	599	1984
16	Water bodies	0	0	0	0
17	Herbaceous wetland	5816	320	0	692
18	Wooded wetland	5816	320	0	692
19	Barren or sparsely vegetated	0	2	8	88
21	Wooded tundra	3360	200	0	246
22	Mixed tundra	1680	17	0	261
24	Snow or ice	0	0	0	0

* The sum of 14 species of monotepenes (α-pinene, β-pinene, Δ3-carene, *d*-limoenene, camphene, myrcene, α-terpinene, β-phellandrene, sabinene, ρ-cymene, ocimene, α-thujene, terpinolene, γ-terpinene)

** The sum of 17 species of other BVOCs (methanol, CO, ethene, hexenol, hexenal, ethane, hexenyl acetate, hexanal, acetone, formaldehyde, acealdehyde, formic acid, acetic acid, propene, ethanol, butene and butanone)

2.2 Emission factors for EABEIS

As TBEIS2 served as the major framework for this study to estimate biogenic emissions, the database of emission factors from TBEIS2 was used. Because the categories of land use in TBEIS2 were not the same as those used by the USGS, the emission factors could not be used directly. Instead, a proper series of emission factors were generated via integration. The first step was to classify the 60 types of land use known to TBEIS2 into eight main kinds (deciduous broadleaf forest, evergreen broadleaf forest, evergreen needleleaf forest, mixed forest, dryland cropland, irrigated cropland, shrubland, and grassland) and then get the emission factors of each main kind by calculating area weights. Second, the emission factors of the 12 types of land use known to the USGS determined based on the aforementioned eight major types. Then emission factors of the 6 types of land use in USGS could then be related to the main TBEIS2 types directly. The emission factor of dryland cropland and pastures in USGS was the average of the emission factors of grassland and dryland cropland; the emission factor of irrigated cropland and pasture was the average of the emission factors of irrigated cropland and grassland; the emission factor of mixed shrubland/grassland was the average of the emission factors of shrubland and grassland; the emission factor of cropland/grassland mosaic was the average of the emission factors of dryland cropland, irrigated cropland and grassland; the emission factor of cropland/woodland mosaic was the average of the emission factors of dryland cropland, irrigated cropland, deciduous broadleaf forest, evergreen broadleaf forest, evergreen needleleaf forest and mixed forest; deciduous needleleaf forest and evergreen needleleaf forest had the same emission factor. For the remaining 9 types of land use found in USGS, the numbers from BEIS3.12 were used directly since no emission factors for these land use types were available in TBEIS2.

According to the integrated database, the greatest emission factor of isoprene is mixed forest, which had 10771 μg m^{-2} h^{-1}, followed by the evergreen broadleaf forest with 8598 μg m^{-2} h^{-1}; whereas, the evergreen needleleaf forest and the deciduous needleleaf forest had the highest emission factor of monoterpenes, 7086 μg m^{-2} h^{-1}, followed by mixed forest with 4371 μg m^{-2} h^{-1}; MBO emission only occurred in urban and built-up areas, cropland/woodland mosaic, evergreen needleleaf forest, deciduous needleleaf forest, mixed forest and barren or sparsely vegetated land. The highest MBO emission factor appeared in evergreen needleleaf forest and deciduous needleleaf forest areas, 2397 μg m^{-2} h^{-1}; the greatest emission factor of other BVOCs was from evergreen needleleaf forest and deciduous needleleaf forest, 3102 μg m^{-2} h^{-1}, followed by mixed forest, 1984 μg m^{-2} h^{-1}.

2.3 Estimation of BVOCs emission by EABEIS

To make a fast inventory of annual biogenic emissions in East Asia and reveal the emission variations for the four seasons, one day in every month (the fifteenth) was selected for simulation processing. Hourly meteorological data for the whole day was used. The meteorological information from the selected day of each month was determined by taking averages of the daily data for each month, simulated by MM5. The simulation day data was multiplied by the number of days relevant to each month to render the total annual amount. The meteorological parameters required for estimating biogenic emissions consisted of cloud cover, wind speed, environment temperature and relative humidity.

In terms of emission factors, besides those established in paragraph 2.2 for the simulations from April to September, leaf-fall needed to be accounted for. Thus, it was presumed that zero emissions occurred in urban and built-up areas, dryland cropland and pastures, irrigated cropland and pastures, cropland/ woodland mosaic, savanna, deciduous broadleaf forest, deciduous needleleaf forest, herbaceous wetland, barren or sparsely vegetated, wooded wetland, wooded tundra and mixed tundra. Half reduced emissions were used in cropland/grassland mosaic, grassland, shrubland, mixed shrubland/grassland and mixed forest, and complete emissions occurred in evergreen broadleaf forest and evergreen needleleaf forest areas.

Though monoterpenes and other BVOCs were formerly classified as the same category, here they were divided into 14 and 18 sub-species. The same estimation process remained in use for these species, except MBO as discussed previously. The following discussion is made based on the four kinds of isoprene, monoterpenes, other BVOCs and MBO, for brevity. Moreover, as the simulation area crosses several time zones, the following descriptions about time are limited the use of Taiwanese time (UMT + 8).

3. RESULTS AND DISCUSSION

3.1 BVOCs emissions in East Asia

The total BVOCs emissions estimated by EABEIS in East Asia (the domain covered by this study) for the whole year amounted to 40.9 Tg. Isoprene accounted for 24.6%, monoterpenes for 45.1%, other BVOCs for 28.9% and MBO only 1.4%. Although the annual amount of isoprene was lower than those of monoterpenes and other BVOCs, the diurnal variations (Fig. 2) indicated that isoprene emissions were significantly higher than those of monoterpenes and other BVOCs during the day, especially around noon. As monoterpenes and other BVOCs were only affected by leaf temperature, emissions also occurred at night; however, visible peaks still appear at noon. Limited to sunlight interactions, isoprene and MBO were only emitted during the day; nevertheless, their emissions began at 04:00 in low, but detectable amounts, increasing rapidly afterward to a peak at noon, thereafter decreasing until 20:00. As the emission estimation spanned several time zones, the corresponding PAR with sunlight from 04:00 to 20:00 (Fig. 6) causes the emission curves to appear inconsistent with those from a single time zone.

The monthly variation in BVOC emissions (Fig. 3) indicates that the order of magnitude of emissions from these four types of BVOCs in every month remain the same; that is, monoterpenes are the greatest, MBO is the least, and the other BVOCs are slightly higher than isoprene. The emissions of the four kinds of BVOCs reach their peaks in summer (Jun. – Aug.) with total amounts of 6 – 8 Tg/month; a total amount of 3 – 6 Tg/month in Apr., May and Sep. and totals of less than 2 Tg/month for the other months. Meteorological conditions (temperature and a lower PAR) and leaf-fall are likely the main causes of the lower emissions in those months.

The spatial distributions of various BVOCs emissions for different seasons are illustrated in Fig. 4. Every species had a greater and more extensive emission period during summer,

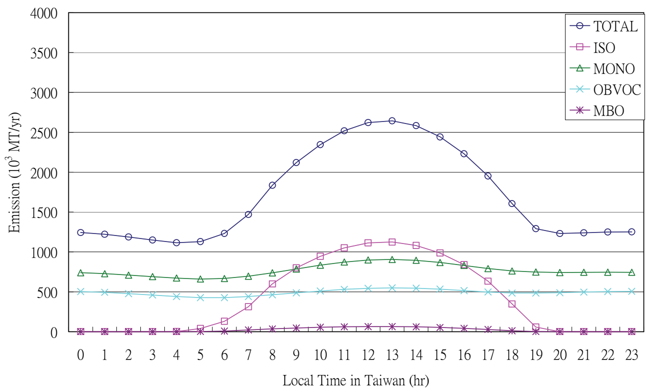

Fig. 2 Diurnal variation of annual BVOC emissions for various species in East Asia.

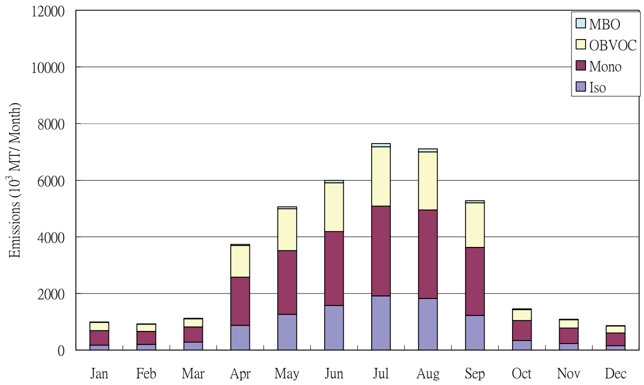

Fig. 3 Monthly variation of BVOC emissions for various species in East Asia.

followed by spring, then fall and winter. As the distributions in fall and spring were similar numerically (slightly higher in spring than autumn), only the estimation results in spring, summer and winter are shown. Fig. 4(a) shows that isoprene emission in four seasons is the most significant in Indo-China (Laos, Vietnam and Kampuchea). A high emission value (> 120 kg grid^{-1} s^{-1}) not only appeared in summer, but also in winter (> 45 kg grid^{-1} s^{-1}) for that region. A relatively lower emission value (< 15 kg grid^{-1} s^{-1}) occurred in northwest and east China and Thailand for four seasons. Moreover, high emissions (> 90 kg grid^{-1} s^{-1}) also occurred in other areas during summer, including northeastern China, Japan and Korea, but relatively lower emissions (< 15 kg grid^{-1} s^{-1}) appeared in winter. Though monoterpenes and other BVOCs had significantly different emission values, their spatial distributions were similar, as shown by Fig. 4(b) and Fig. 4(c). Both figures revealed emissions of these two types in the four seasons were most prominent in southeast China, followed by Indo-China, Japan and northeastern China. The spatial distribution of MBO emissions were somewhat similar to those of monoterpenes. As only five types of land use produce MBO under this model, its emissions appeared to be concentrated in Indo-China, Japan, Korea and southeastern and northeastern China. The most significant MBO emissions occurred in two land use types, evergreen needleleaf forest and mixed forest (Fig. 1), which were in southeastern and northeastern China, Japan and Korea, which is also consistent with the spatial distribution of MBO emissions.

3.2 Impact of leaf temperature on BVOC emissions in East Asia

The assumption that environment temperature is equal to leaf temperature was conventionally applied to estimations of biogenic emissions, which as discussed above may result in errors to an unknown degree. To reduce this range of error, environmental temperature rather than leaf temperature was adopted for this study when recalculating BVOC emissions. Hereafter, the leaf temperature method is referred to as the base case, and the environmental temperature model is referred to

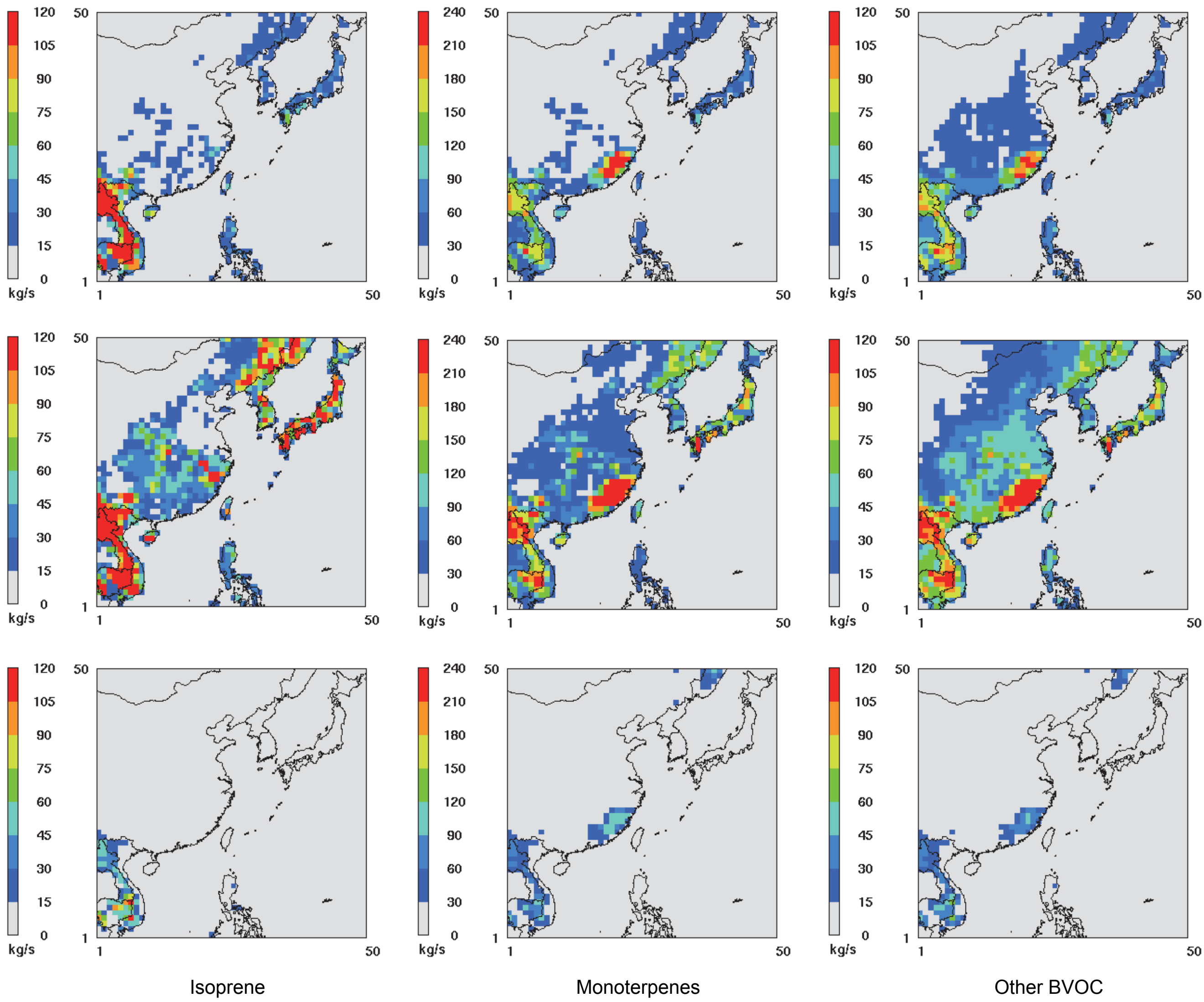

Fig. 4 Spatial distributions of seasonal BVOCs emissions for spring (upper), summer (middle) and winter (lower). The figures are arranged in the order (a) isoprene (first column), (b) monoterpenes (second column) and (c) other BVOC (third column)

as control case 1. The total annual emission amount for the base case was 53.5 Tg, which was comprised of 27.6% isoprene, 42.9% monoterpenes, 28.1% of other BVOCs and only 1.4% for MBO, while control case 1 showed 69.9 Tg, and 31.0% isoprene, 40.8% monoterpenes, 26.6% other BVOCs and 1.6% MBO. Compared with the base case, the annual total amounts of all species in control case 1 were overestimated to be 16.4 Tg totally with 6.9 Tg of isoprene, 5.6 Tg of monoterpenes, 3.6 Tg of other BVOCs and 0.3 Tg for MBO. By this calculation, total BVOC emissions were overestimated by 30.7%, with the most significant overestimation being isoprene (46.7%) and the least being monoterpenes (24.2%). Thus, the replacement of environment temperature with leaf-temperature would render an obvious overestimation of BVOC emissions in East Asia, as far as the annual total amount was concerned. The seasonal, regional, diurnal and nocturnal differences resulting from the environment temperature for BVOC emissions is further analyzed and investigated below.

The diurnal variations in total BVOC emissions shown by control case 1 are presented in Fig. 5. Comparison with the base case (Fig. 2) clearly shows the total annual amount in each given time interval for control case 1 is greater than that in the base case; with a left-skewed emission curve, which is significantly different from the bell curve found in the base case. The emission curve differences also exhibit differences in the various emission peaks; for example, when the base case is replaced with the control case, the emission peak is postponed from noon (12:00 ~ 13:00) to mid-afternoon (14:00 ~ 15:00). Nevertheless, the greatest difference in emissions from each species do not show up at peak times, but around the period 15:00 ~ 17:00 (16:00 for isoprene and other BVOCs, 17:00 for monotepenes, 15:00 for MBO). The greatest variation of total annual BVOC emission (1.36 Tg yr^{-1}) occurs at 16:00. Differences in the models become smaller at night, and the time when the annual BVOC emissions are most similar (0.12 Tg yr^{-1}) is at 2 AM. These findings can be explained by Fig. 6, which illustrates the annual average diurnal variations of environment and leaf temperature data for all grids. The differences between the highest environmental and leaf temperatures also resulted in peak variations in both cases. Leaves are somewhat able to adjust themselves to maintain a steady temperature, protecting themselves from damage in extremely high or low temperatures depending on their environment. This caused less diurnal and nocturnal variations in leaf temperature, which would bring it closer to the data from the environment temperature model. It also provides the reason for greater differences being observed during the day and not at night, in both cases. It is worthwhile to note that the environment temperature is significantly higher than the leaf temperature (reaching a maximum of over 3 °C) during the day, whereas the leaf temperature model is only slightly higher than the ambient temperature (less than 1 °C) at night; however, the emissions in control case 1 are still higher than those for the base case. This is because the simulation domain covers areas including high, medium and low latitudes. Though the leaf temperature was higher than the environment temperature in areas with a higher latitude in the early morning, leaf temperature become lower than the environment temperature in areas at medium and lower latitudes in the early morning. As a result, the average leaf temperature in the early morning turned out to be only a little higher than the average environment temperature, as shown in Fig. 6.

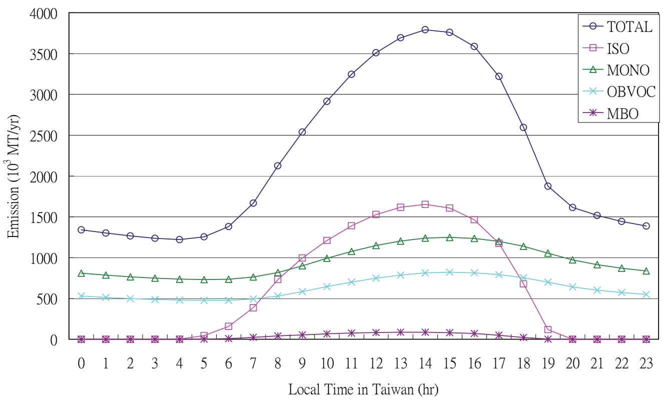

Fig. 5 Diurnal variation of BVOC emissions for various species in East Asia with leaf temperature replaced by environment temperature.

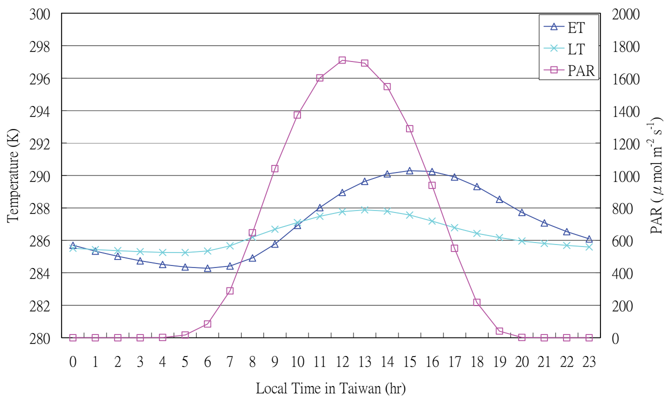

Fig. 6 Diurnal variation of average environmental temperature (ET), leaf temperature (LT) and photosynthetically active radiation intensity (PAR) in East Asia.

As far as seasonal (or monthly) variations with overestimated emissions are concerned, the trends of seasonal changes in control case 1 (Fig. 7) are similar to those in the base case, Fig. 3; *i.e.*, less emissions in winter and more obvious emissions in summer, Fig. 7. However, a comparison of Fig. 3 and Fig. 7 revealed the total BVOC emissions in every month were greater in control case 1 than in the base case, except for Jan. and Dec. Overestimations from Apr. thru Sep. were even more significant, by over 1 Tg/month, with a ratio of more than 25%, this effect was most notable in Jul., which was greater by about 2.9 Tg/month at a rate of 40.4%. A notable underestimation appeared in Jan., showing about 0.2 Tg/month, at a ratio of 21.7%. The least outstanding overestimations and underestimations show up in Feb. and Dec. by 0.04 and 0.06 Tg/month, respectively. As for emission differences from each individual species, isoprene emissions in control case 1 were higher than those in the base case for the whole year, and overestimations in summer, from Jun. – Aug., were over 50%. Likewise, MBO emissions in the control case were overestimated for the whole year, and reached 40% in summer. Monoterpenes and other BVOC emissions were overestimated by up to 30 ~ 40% in summer, but underestimated in the winter months Jan., Feb. and Dec. These results implied striking overestimations of BVOC emissions in the summer generally. Overestimations in spring and fall, combined with underestimations in winter may even be possi ble when replacing environment temperature with the leaf

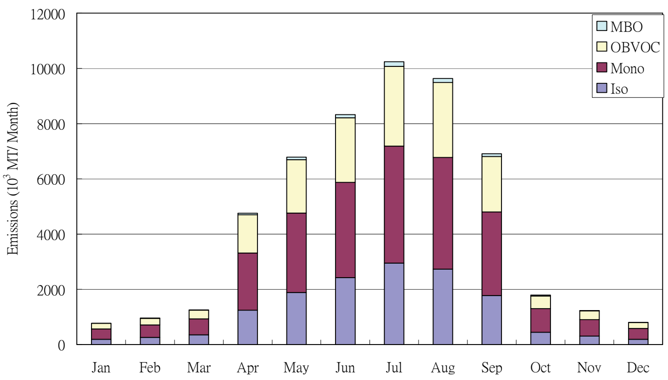

Fig. 7 Monthly variation of BVOC emissions for various species in East Asia with leaf temperature replaced by environmental temperature.

temperature. Each species seems to contribute significantly to these remarkable BVOC emission estimations, particularly in summer. Underestimations in Jan. and Dec. were due to underestimations of monoterpenes and other BVOC emissions. The reason for seasonal variations is due to plants self-adjusting themselves to maintain a lower leaf temperature during summer when environment temperatures are higher. Contrarily, they would maintain a higher leaf temperature in the winter to survive the cold environment.

The effect of using leaf temperature rather than ambient temperature in different seasons can be further explored by examination of the differences in emissions of spatial distributions for both cases. This approach would verify the differences by geographical location. The spatial distribution differences in emissions during summer for both cases (Fig. 8) show that emissions in control case 1 are higher than those in the base case for most of the simulation domain. Further, the increase becomes greater in places of high emissions for the base case. Thus, it goes without saying that replacement of the leaf temperature with environment temperature in summer months resulted in significant overestimations of BVOC emissions in almost all the simulated areas. Though the total monthly (quarterly) isoprene emissions in control case 1 during winter were overestimated, and those of monoterpenes were underestimated, the spatial distributions (Fig. 8) indicate that not all simulated areas were overestimated or underestimated in the same manner. Instead, more notable underestimations were seen in control case 1, appearing in areas at higher latitudes, and the opposite was found in areas at lower latitudes. Spatial variations during winter likely occurred due to the ambient weather environment still being warmer in low latitude regions, therefore the plants only needed to maintain a lower leaf temperature; however, as the weather become colder in higher latitude areas, plants had to keep a higher leaf temperature.

3.3 Uncertainty analysis of BVOC emission estimations

Two further aspects of uncertainty over BVOC estimation methods should be emphasized: one is the incompleteness of the estimation mechanism; the other is the accuracy of data derived from the EABEIS dataset, including land use data, corresponding emission factors, and meteorological data. Several studies in the past have focused on the uncertainty or incompleteness of the estimation mechanism adopted in this paper (Guenther *et al*. 1993; Lerdau and Keller 1997; Staudt *et al*. 1997; Tambunan *et al*. 2006). As for data accuracy, the larger part comes from databases of emission factors and land use that

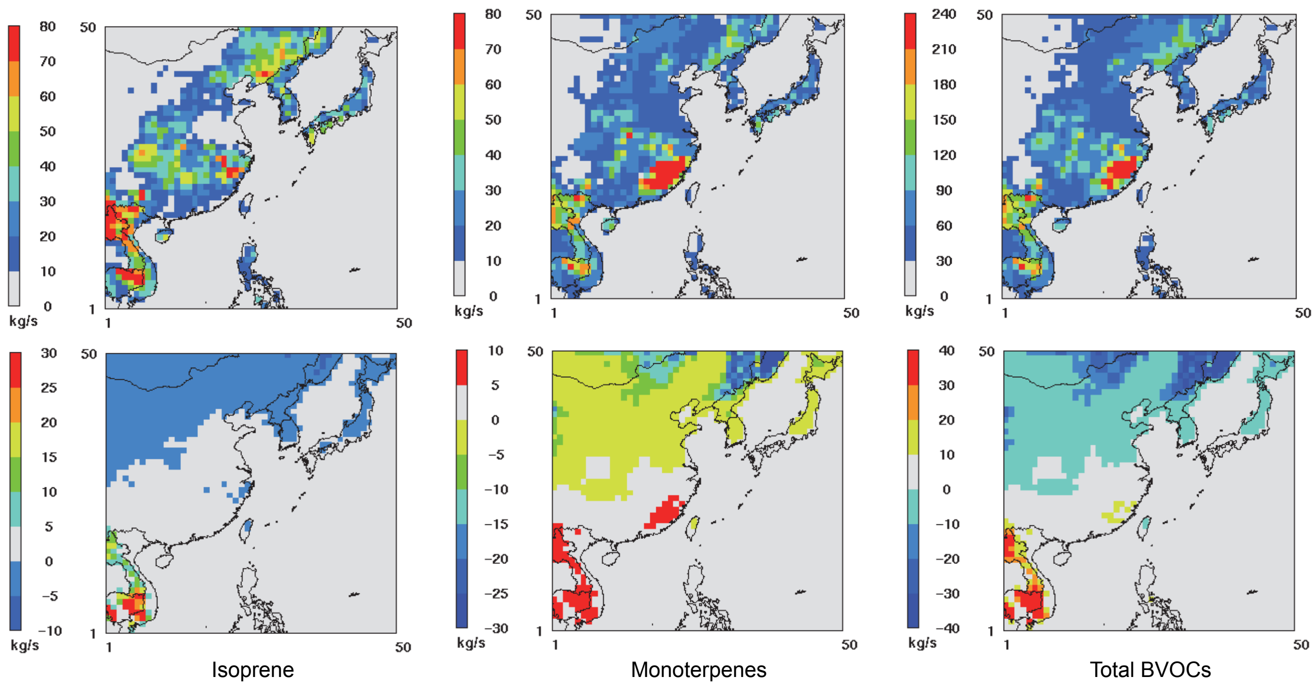

Fig. 8 Spatial distributions of seasonal biogenic VOC emissions. Differences between base case and control case 1 (control case 1 minus base case) in East Asia for summer (upper) and winter (lower). Control case 1 is the simulation result by EABEIS with leaf temperature replaced by environmental temperature.

maintain these databases, due to the tremendous amount of human, financial and material resources, in addition to time of tree constraints. Consequently, many studies have no choice but to use the data of emission factors from a highly limited number are fundamental elements of computation for biogenic emission estimation models. It is a considerable effort to establish and-species, with which they must generate the data needed to model hypotheses. As the estimation results in this study also contain such uncertainty factors, a discussion and analysis are thus offered here.

To assess the uncertainty of emission factors, the emission factors in BEIS3.12 and Table 1 of Tie *et al*. (2006) are adopted (hereinafter called control case 2 and control case 3) to create an inventory of BVOC emissions in East Asia. The former (control case 2) had an annual amount of about 10.1 Tg of isoprene, slightly higher (0.06 Tg) than that of the base case, and an annual amount of about 1.8 Tg of monoterpenes, just 10% of the base case number. Control case 3 had an annual amount of about 5.9 Tg of isoprene, 41% less than the base case, and an annual amount of about 3.2 Tg of monoterpenes, just 17% of the base case. As a whole, these three emission factors rendered significant estimation differences given otherwise identical inputs. Though the estimated isoprene emissions in the base case were close to those of control case 2, and the estimated monoterpene emissions were similar for both control cases 2 and 3, the same variations applied to the estimations at different latitudes, as well for these three factors. The category-type emission factor referred to a certain weight (*e.g*. area weight) average of the emission factors of all experimental tree species with the same category within a simulated area. The representative strength of this emission factor depends on the acquisition of the emission factor of the representative tree species in the simulated area (e.g. tree species with a larger area or a greater emission factor). Whether the aforesaid three kinds of category-type emission factors could stand for the representative tree species in the simulated area is also a topic requiring further discussion. When estimating large-scale BVOC emissions, distributive features of tree species differed, even if all representative tree species in the simulated region were obtained. Thus, errors of a certain degree are possible even when using category-type emission factors established by representative tree species, As a result, it is necessary to use different emission factors with various characteristics for different zones to reduce the estimation uncertainty. In addition, a detailed comparison of estimated monoterpenes and isoprene emission variations by these three factors indicates that isoprene changed from 5.9 to 10.1 Tg/yr, monoterpenes from 1.8 to 18.4 Tg/yr. The monoterpene variation being notably larger than that of isoprene. This may be because isoprene is only a single species and monoterpenes is a collective species, but this only causes further experimental difficulty and greater uncertainty (Geron *et al*. 2000).

With regard to land use uncertainty evaluation, use of the database of TBEIS2 for Taiwan was adopted for this study specifically to replace the original land use data for central Taiwan, hereafter referred to as control case 4. The results for Taiwan showed that the annual total amount of BVOC emissions estimated using TBEIS2 (525 thousand MT) was higher than that of the base case (282 thousand MT) by 86%. Isoprene was higher by 137%, monotepenes and MBO by 80% and other BVOCs by 57%. Naturally, these differences emerge as a result of variations in land use data, as meteorological conditions and emission factors remain constant across the datasets. In the TBEIS2 dataset, there are 4,000 km^2 of mixed forests, with high isoprene and monoterpene emission factors, 13,400 km^2 of broad-leaved forests, 3,200 km^2 of needle-leaved forests with only a high monoterpenes emission factor, and 6,300 km^2 of cropland with relatively lower emission factors. USGS land use data gives the lion's share of land use to cropland and pasture (up to16,800 km^2), which only makes a limited contribution due to its low emission factors. Though the area of mixed forests (6,200 km^2) is greater than that in TBEIS2, the areas of broad- leaved forests (1,900 km^2) and needle-leaved forests (1,000 km^2) account for just 14% and 31% in TBEIS2, respectively. Hence, both parties produce strikingly different estimation results. Moreover, estimated emission results also differ in their spatial distributions since vegetation distributions vary spatially.

3.4 Uncertainty analysis of ozone simulation results

The impact of different emission factors and land use data on estimation results was evaluated previously. Simulated ozone variations can now be explored via leaf temperature calculations using the Taiwan Air Quality Model (TAQM) (Chang 2008; Chen and Chang 2006; Chang *et al*. 2000) and adoption of various emission factors and the land use data. A serious ozone pollution event in Taiwan (May 8 ~ 13, 2003) was selected for examination in this study. This event can be used for a comparison of the influences of different emission estimations on simulated ozone with other identical simulation conditions.

The average of daily maximum O3 concentration differences between the base case and control case 1 (using the presumption that leaf temperature is equal to environment temperature) during the 6-day ozone pollution event (May 8 ~ 13, 2003) is shown in Fig. 9(a). This figure shows that the difference in most of the simulated areas is within 1 ppb; the greatest difference of 5-6 ppb occurs around the Bohai Sea, followed by the southwestern side of Taiwan that exhibits a difference of 1-2 ppb. Fig 9(b) is the average daily maximum O_3 concentration differences between the base case and control case 2, while Fig. 9(c) shows the differences between the base case and control case 3. Fig. 9(b) and Fig. 9(c) have similar spatial distributions because of the higher negative differences appearing in areas around the Bohai Sea and southwest Taiwan (with a max. of about -15 ppb) and higher positive variations (up to 9 ppb) in southeast China. This obviously indicates that such a distribution is similar to that shown in Fig 9(a), however the measured positive and negative values are reversed. Fig 9(d) refers to the average daily maximum O_3 concentration differences between the base case and control case 4. This shows the emission differences are only limited to Taiwan itself. More apparent differences were also observed in Taiwan and the surrounding sea areas, and most of these were negative values (a max. of about -12 ppb).

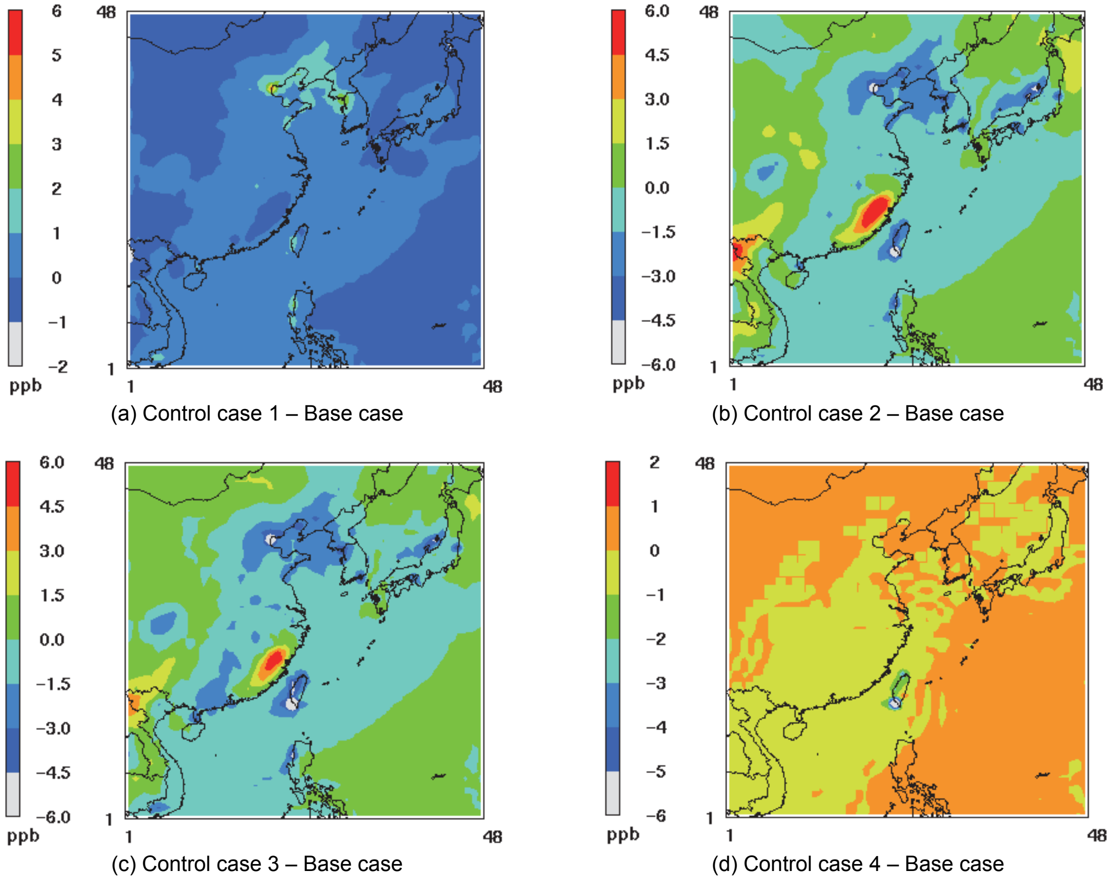

Fig. 9 Spatial distributions of averaged daily maximum O_3 concentration, differences between the base case and control cases in East Asia during the ozone pollution event (2003/05/08 ~ 13). Control case 1: leaf temperature replaced by environmental temperature. Control case 2: emission factors is replaced by those in BEIS 3.12. Control case 3: emission factors replaced by those in Table 1 in Tie *et al*. (2006). Control case 4: land use data in Taiwan are replaced with TBEIS2 data.

4. CONCLUSION

A BVOC emission inventory system with leaf energy balance considerations was established for East Asia in this study. The combination of this system and appropriate meteorological data (cloud cover, wind speed, environment temperature and relative humidity) is capable of estimating 33 species of BVOC using hourly emissions from plants in East Asia, and provides a photochemical air quality model for further application in atmospheric ozone and aerosol modeling. The total annual amount of BVOC emissions in East Asia (the domain covered in this study) estimated by EABEIS can be as high as 40.9 Tg, and is comprised of 24.6% isoprene, 45.1% of 14 species of monoterpenes, 28.9% of 17 species of other BVOCs and only 1.4% of MBO.

The replacement of leaf temperature with environment temperature for inventory in the past would result in overestimations of the annual amounts for all BVOC species. The most significant overestimation is isoprene, by 46.7%, monoterpenes are the least at 24.2%, and total BVOC emissions are overestimated by 30.7%. Such revised estimation methods also change the diurnal variation curve for annual BVOC emissions. Greater overestimations occur during the day and the peak is postponed from noon (12:00 ~ 13:00) to mid-afternoon (14:00 ~ 15:00). Relatively speaking, overestimations at night are less; however, not all areas in the simulation domain were overestimated as there are latitudinal and seasonal factors to consider. In summer, BVOC emissions in almost all areas of the domain were overestimated when leaf temperature replaced ambient temperature. In winter, overestimations also occurred in areas at lower latitudes, and the opposite was true in areas at higher latitudes. Apparently, replacement of leaf temperature with environment temperature imposes different effects on BVOC emission estimations for different seasons and areas, which further reveals the importance of leaf energy balance considerations in estimation and modelling.

For uncertainty analysis, either emission factors or land use data can cause BVOC emission changes of over 200%. Ceteris paribus, when BVOC emissions in East Asia are estimated with three different emission factors, estimated monoterpene emission variations (1.8 ~ 18.4 Tg yr^{-1}) are significantly greater than estimated isoprene emission variations (5.9 ~ 10.1 Tg yr^{-1}). When BVOC emissions in East Asia are estimated with two pieces of land use data in Taiwan (again ceteris paribus), estimated isoprene emission variations (64 ~ 151 thousand MT yr^{-1}) are slightly greater than estimated monoterpene emission variations (131 ~ 237 thousand MT yr^{-1}). Though the uncertainty of the result estimated using alternate land use data is lower than when using alternate emission factors, it is important to remember that different land use data can result in widely varying spatial distributions of BVOC emissions.

After a comparison of simulations for a 6-day ozone pollution event, it was found that the average daily maximum O_3 concentration in some areas increased by 6 ppb when leaf temperature replaced environment temperature directly. Emission factors from BEIS3.12 and Table 1 of Tie *et al*. (2006) exhibit very different effects on different areas (a reduction of 15 ppb or an increase of 9 ppb). Adoption of the land use dataset TBEIS2 results in a decreased concentration in areas surrounding Taiwan by up to -12 ppb. As a whole, the results are firm evidence that application of different emission factors and land use data, and replacement of leaf temperature with environment temperature can cause significant changes in daily maximum O_3 concentration for some areas.

To reduce uncertainty over BVOC emission estimations, it is necessary to utilize appropriate land use data and emission factors, depending on the vegetation characteristics for the relevant region. However, data acquisition and recognition is still a considerable challenge, especially land use data. Although remote sensing technology is increasingly being applied, and as technology improves costs come down, but there then also needs to be a way to confirm the accuracy and relevance of land use data. Furthermore, accurate seasonal information is an important part of reducing uncertainty in future BVOC inventory systems.

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