Analytical Estimation of Uncertainties in Biogenic Emissions Calculated by BEIS3 due to Uncertainties in Model Inputs and Parameters

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ABSTRACT

BEIS3 was developed by the U.S. EPA to estimate emissions of biogenic substances such as isoprene, monoterpenes, oxygenated volatile organic compounds (OVOCs), and biogenic nitric oxide (BNO). These emissions are used as inputs to chemical transport models (CTMs) to calculate concentrations of ozone and other air pollutants. The current study addresses the uncertainties in biogenic emissions and the subsequent uncertainties in CTM predictions due to uncertainties in BEIS3 inputs and parameters. The primary focus of the study was on use of Monte Carlo probabilistic methods. However, because of the relative simplicity of the emissions equations, it was decided to also apply a standard analytical approach, as described in the current paper. In the analytical method, the partial derivative of the emissions equation is taken. Then both sides of the equation are squared and normalized, yielding an analytical expression for the relative uncertainty or variance in a given emission component, expressed as a function of the relative variance of the inputs and parameters. The relative uncertainties or variances in inputs and parameters had been estimated earlier by a combination of analysis of data and expert elicitation. To simplify the equations, it is assumed that there is no correlation between any of the inputs and/or parameters.

The results of the analytical equations for relative uncertainties agreed approximately with the results of the full Monte Carlo method. For example, the total relative variance in isoprene emissions varied from 0.10 to 0.40, depending on T_A. Total OVOC and monoterpene relative variances were similar, with values ranging from 0.10 to 0.26. Total BNO relative variances ranged from 0.22 to 0.71. By taking the square root of these relative variances, we obtain estimates of relative uncertainty in BEIS3 emissions in the range from about 0.3 to 0.8 (i.e., ± 30 to 80 %). It is suggested by the analytical equations that the relative uncertainties in emissions depend on the air temperature, T_A, in the sense that one model input would contribute most of the variance at T_A of 10 C and another input would contribute most at 30 C.

INTRODUCTION

This paper uses an analytical approach to estimate uncertainties of the emissions outputs of the Biogenics Emissions Inventory System, Version 3 (BEIS3) model (Pierce, 2001) due to uncertainties in BEIS3 model parameters and input variables. BEIS3 has been developed by the U.S. EPA to estimate emissions of isoprene, monoterpenes, and oxygenated volatile organic compounds (OVOCs) due to biological activity in or on plant tissues, and to estimate emissions of biogenic nitric oxide (BNO) due to biological activity in soils. The results briefly described in this paper are discussed in detail by Hanna *et al*. (2002). It should be noted that the primary focus of that report and a subsequent report (Hanna et al., 2003) was on use of the Monte Carlo (MC) probabilistic approach to estimate emissions uncertainties. The MC results are not the emphasis of the current paper, which uses a much simpler approach to show that similar results may be obstained.

Numerous reports and journal articles (e.g., Lamb et al.,1999, and Guenther et al., 1993, 1999 and 2000) have been written on the biogenic VOC and biogenic NO model formulations that are in BEIS3 (Pierce, 2001). BEIS3 (version 0.9) has improved on prior versions and has incorporated the Biogenic Emissions Landuse Database version 3 (BELD3), new emissions factors, and new light attenuation/canopy effects. BELD3 (Pierce *et al*.,1998) provides a spatial representation of the land cover for over 95% of North America. As is the case with all environmental model parameterizations, BEIS3 model parameterizations are based on limited observations over a narrow range of conditions. Uncertainties are likely to grow for geographic regions and for combinations of weather conditions and vegetation conditions outside of the central range of conditions used in model derivation. For this reason, the BEIS3 uncertainty study described by Hanna et al. (2002, 2003) is intended to cover a range of seasons and geographic locations. The study uses three episodes (24-29 May, 11-15 July and 4-9 September 1995) that have been extensively investigated using several chemical transport models. The geographic domain for all three time periods covers most of the Eastern U.S. and parts of the Midwest. The domain is divided into 36 km by 36 km grid squares. Input files for these three episodes are well established as a result of previous studies by the EPA and others, and are used to define the median inputs for this project. Figure 1 illustrates the domain size and typical distributions of temperature and PAR (Photosynthetically Active Radiation) for one day (11 July 1995) that has been studied using the MC method.

Seventeen BEIS3 model parameters and model data input variables have been assumed to vary. The model parameters refer to the various coefficients and integral scales that are not input by users but whose values are part of the BEIS3 code. The model data input variables refer to the required user inputs to BEIS3. Although the basic texts on MC analysis (e.g., Cullen and Frey, 1999) distinguish between “uncertainty” and “variability”, both components are assumed to be lumped together in the estimates of uncertainties used here. The model parameters are described in more detail below but, in general, are identified as the six “BVOC Model Parameters” and the three “BNO Model

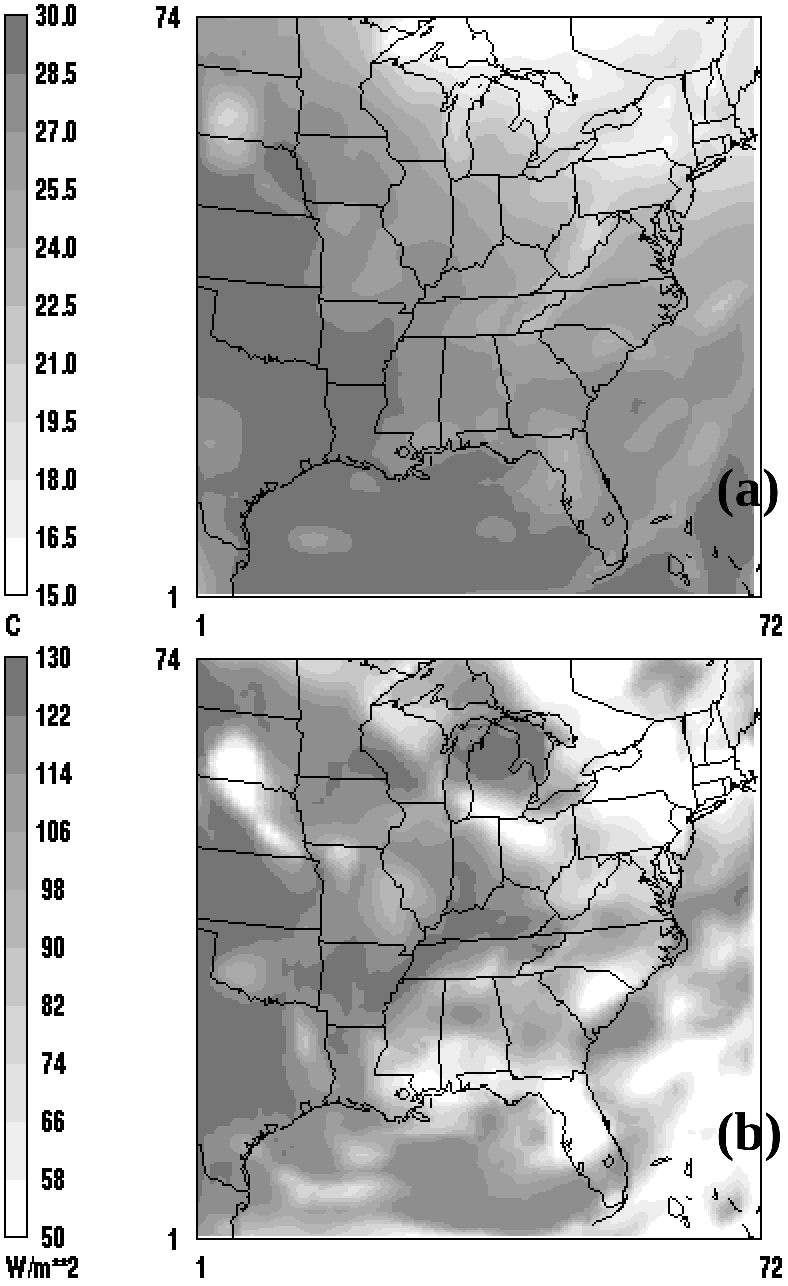

Figure 1. Observed mean daily temperatures (Figure 1a, in C) and mean daily PAR values (Figure 1b, in W/m2) for 11 July 1995 over geographic domain studied by Hanna et al. (2002, 2003). Values represent averages over a 36 km by 36 km grid.

Parameters." The model data input variables are identified as the four "Biogenic Emissions Factors" (one each for isoprene, monoterpenes, OVOCs, and BNO), the two "Leaf Area Index," (one for summer and one for spring/fall/winter), the one "Ambient Temperature," and the one "Total Incoming Solar Radiation."

ANALYTICAL APPROACH

The analytical approach is used to estimate the uncertainties associated with the emissions of BNO, monoterpenes and OVOC, and isoprene based on the emissions formulas. The general methodology is given and then the results are given for the three categories of emissions. The conclusions concerning the total uncertainties and the input parameters whose variability have the greatest effect on the uncertainties of the emissions are listed and the analytical results are compared with the results of the Monte Carlo study that were summarized by Hanna et al. (2002).

For simplified modeling systems that can be expressed as a few algebraic equations, it is possible to estimate the uncertainty in the model prediction analytically. For example, consider the equation:

$$Y = AB \qquad (1)$$

Assume that variations in A are not correlated with variations in B. Then for relative perturbations less than about one, the relative mean-square uncertainty in the model prediction of Y can be expressed as:

$$\frac{(\Delta Y)^2}{Y^2} = \frac{(\Delta A)^2}{A^2} + \frac{(\Delta B)^2}{B^2} \qquad (2)$$

Assuming that $(\Delta Y)^2 = s_Y^2$, Equation (2) can be written in the form:

$$\left(\frac{s_Y}{Y}\right)^2 = \left(\frac{s_A}{A}\right)^2 + \left(\frac{s_B}{B}\right)^2 \qquad (3)$$

Suppose the relative uncertainty in A, or $\frac{s_A}{A}$, is 0.3 and the relative uncertainty in B, or $\frac{s_B}{B}$, is 0.4, then Equation (3) tells us that the relative uncertainty in Y, or $\frac{s_Y}{Y}$, is 0.5.

RESULTS

Results of application of analytical approach to BNO emissions

The analytical approach is first applied to the equation for emissions, *E*, of Biogenic Nitric Oxide (BNO):

$$\frac{E}{A} = E_A = E_S \exp\left[T_3\left(T_1\left(T - 273.15\,\mathrm{K}\right) + T_2 - 30\,\mathrm{C}\right)\right] \tag{4}$$

We begin with the applications of the analytical approach to BNO and to monoterpenes and OVOCs because those equations are much simpler (i.e., a single equation such as Equation 4) than the set of equations for isoprene.

Table 1. Summary of parameters used to determine analytical uncertainty in the BNO emissions estimates.

Parameter	Units	Uncertainty Range	Note
E_A	µg·hectare^{-1}·hr^{-1}	Computed	The emissions rate of BNO per unit area per unit time. The uncertainty is calculated as a result of our study. However, it is the average daily value of E_A that is used as the fundamental output variable.
A	hectare	No uncertainty assumed.	Area over which BNO emissions are calculated.
E_S	µg·hectare^{-1}·hr^{-1}	s is assumed to be 26 % of nominal value	BNO emissions factor. Nominal value varies by plant species.
T_3	C^{-1}	Median = 0.071 C^{-1} and s is assumed to be 0.007 C^{-1}	Inverse temperature scale for exponential term.
T_1	Dimensionless	Median = 0.72 C^{-1} and s is assumed to be 0.36 C^{-1}	Scaling parameter.
T	K	s is assumed to be 1.9 C	Ambient temperature.
T_2	C	Median = 5.8 C and s is assumed to be 2.9 C	Temperature parameter.

As with the Monte Carlo analysis described by Hanna et al. (2002), the fundamental output variable of interest is the average daily emissions of BNO. BEIS3 considers only BNO emissions from soils. It is important to understand the definitions and units of the variables and parameters and constants in Equation (4), as listed in Table 1. The assumed median values are given for T_3, T_1, T, and T_2. Table 1 also includes the standard deviation (σ) of the uncertainty range assumed for the variable or parameter for our BEIS3 Monte Carlo uncertainty study. Note that in Table 1 the uncertainty for the BNO emissions factor is reported as $\pm$50 % at the 95 % confidence interval. This is approximately 26 % at one standard deviation as reported in Table 1.

Note the mixture of usage of degrees Celsius (C) and Kelvin (K) in Table 1. This is not corrected here because Equation (4) has a long history of usage with the mixture of units. However, we do have to remember to use the correct unit (C or K) in the appropriate places.

The exponential term (dimensionless) in Equation (4) is known as the temperature correction factor, C_T, for BNO. The first few terms inside the parenthesis in the exponential are the soil temperature, T_{soil}, which is estimated by the following empirical formula:

$$T_{soil} = T_1 \left(T - 273.15\,\mathrm{K}\right) + T_2 \qquad (5)$$

Note that (T – 273.15 K) is simply the ambient temperature expressed in C rather than K. Therefore, using the median values of T_1 = 0.72 and T_2 = 5.8 C, Equation (5) shows that the soil temperature equals the ambient temperature at about 20.7 C, and that the soil temperature is about 3 C warmer than the ambient temperature at an ambient temperature of about 10 C, and about 3 C cooler than the ambient temperature at an ambient temperature of about 30 C. These magnitudes of temperature differences are consistent with the observations from which the equation was derived. These relatively small differences between soil and ambient temperature implied by Equation (5) are important to recognize when the analytical uncertainty results are given below.

When the analytical differential method is applied to Equation (4) for BEIS3 BNO emissions, and it is assumed that $\frac{E}{A} = E_A$ (μg·hectare^{-1}·hr^{-1}) and that the ambient temperature in units C is given by T_A = (T – 273.15 K) the following result is obtained:

$$\begin{aligned}\frac{\Delta E_A}{E_A} = \frac{\Delta E_S}{E_S} + \frac{\Delta T_3}{T_3}\left(T_1 T_3 T_A + T_2 T_3 - (30\,\mathrm{C})T_3\right) + \\ \frac{\Delta T_2}{T_2}\left(T_2 T_3\right) + \frac{\Delta T_1}{T_1}\left(T_1 T_3 T_A\right) + \Delta T_A \left(T_1 T_3\right)\end{aligned} \qquad (6)$$

If both sides of the equation are squared and it is assumed that there are no correlations between variations in T_A, T_3, T_2, and T_1, then an analytical expression for the mean square uncertainty in BNO emissions is obtained.

$$\left(\frac{\Delta E_A}{E_A}\right)^2 = \left(\frac{\Delta E_S}{E_S}\right)^2 + \left(\frac{\Delta T_3}{T_3}\right)^2 \left(T_1 T_3 T_A + T_2 T_3 - (30\mathrm{C})T_3\right)^2 + \left(\frac{\Delta T_2}{T_2}\right)^2 \left(T_2 T_3\right)^2 + \left(\frac{\Delta T_1}{T_1}\right)^2 \left(T_1 T_3 T_A\right)^2 + \left(\Delta T_A\right)^2 \left(T_1 T_3\right)^2 \tag{7}$$

For each of the input variables, such as T_1, $(\Delta T_1)^2 = s^2_{T1}$, where s is the assumed uncertainty defined in Table 1. After substituting s and the median values of the variables and parameters, Equation (7) becomes:

$$\left(\frac{s_{EA}}{E_A}\right)^2 = \left(\frac{s_{ES}}{E_S}\right)^2 + \left(\frac{s_{T3}}{T_3}\right)^2 \left(\left(0.051\mathrm{C}^{-1}\right)T_A + 0.41 - 2.73\right)^2 + \left(\frac{s_{T2}}{T_2}\right)^2 (0.41)^2 + \left(\frac{s_{T1}}{T_1}\right)^2 \left(\left(0.051\mathrm{C}^{-1}\right)T_A\right)^2 + \left(s_{TA}\right)^2 \left(0.051\mathrm{C}^{-1}\right)^2 \tag{8}$$

From Table 1, the following values can be derived:

$$\left(\frac{s_{ES}}{E_S}\right)^2 = 0.26^2 = 0.0676\,;$$

$$\left(\frac{s_{T3}}{T_3}\right)^2 = \left(\frac{0.007\,\mathrm{C}^{-1}}{0.071\mathrm{C}^{-1}}\right)^2 = 0.00972 \approx 0.01;$$

$$\left(\frac{s_{T2}}{T_2}\right)^2 = \left(\frac{2.9\mathrm{C}}{5.8\mathrm{C}}\right)^2 = 0.25\,;$$

$$\left(\frac{s_{T1}}{T_1}\right)^2 = \left(\frac{0.36\mathrm{C}^{-1}}{0.72\,\mathrm{C}^{-1}}\right)^2 = 0.25\,;\ \text{and}$$

$$\left(\frac{s_{TA}}{T_A}\right)^2 = (1.9\mathrm{C})^2 = 3.61\mathrm{C}^2$$

Equation (8) has been solved for three alternate values of ambient temperature, T_A, equal to 30 C, 20 C, and 10 C. The individual uncertainty terms in Equation (8) are given in Table 2, along with the total uncertainty $\left(\frac{s_{EA}}{E_A}\right)^2$ on the right.

Table 2. Summary of analytical uncertainty estimate in BNO emissions.

T_A (C)	E_S Term	T_3 Term	T_2 Term	T_1 Term	T_A Term	$\left(\frac{s_{EA}}{E_A}\right)^2$
30	0.068	0.006	0.042	0.585	0.009	0.71
20	0.068	0.017	0.042	0.260	0.009	0.40
10	0.068	0.033	0.042	0.065	0.009	0.22

It is seen that the T_1 uncertainty term dominates the total uncertainty in BNO emissions at higher temperatures. This same result was found in the Monte Carlo (MC) uncertainty runs in Hanna et al. (2002). At lower temperatures, the E_S uncertainty term becomes more important, and this result was also found from the MC runs, since the correlation between E_A and E_S for BNO was found to be near zero in the southern U.S. but as high as 0.5 to 0.9 in colder parts of the geographic domain. The contribution of the ambient temperature, T_A, uncertainty is very small according to the analytical calculations and also is not significantly different from 0.0 from the MC runs. It is concluded that the analytical results are similar to the MC results, as would be expected for this relatively simple emissions equation.

The results given above point out a difficulty in carrying out MC uncertainty runs without accounting for correlations among perturbations to inputs or without setting limits to certain variables so they remain within reasonable bounds. For example, for the given uncertainties in T_1, T_A, and T_2, it is possible to select combinations of random numbers such that the effective soil temperature would be 10 or 20 C different from the ambient temperature. This difference is much larger than the maximum 3 or 4 C difference implied by Equation (5) for typical T_A. Consequently if a very high soil temperature occurs in a MC run as a result of the random number selections, a very high estimated BNO emission would result from that MC run. This is exactly what was found with the MC runs – there were several large numbers on the upper tail of the BNO emissions distribution.

It is recommended that, because of the possibility of high estimates of effective soil temperature and hence BNO emissions, that the upper end of the MC BNO emissions distribution not be considered. For BNO emissions, the focus should be on the more robust relative variance, or $\left(\frac{s_{EA}}{E_A}\right)^2$.

Results of application of analytical approach to Monoterpene and OVOC emissions

In this section, the analytical uncertainty approach is applied to the equations for emissions, E, of monoterpenes or OVOCs, which are modeled by the same equation in BEIS3:

$$\frac{E}{A} = E_A = E_S \exp\left(b\left[T - T_S\right]\right) \tag{9}$$

Equation (9) is a simpler equation than Equation (4) for estimating the emissions of BNO. As for BNO, it is important to understand the definitions and units of the variables and parameters and constants in Equation (9), as listed in Table 3. The assumed median values are given for *ß*. Table 3 also includes the standard deviation (s) of the uncertainty range assumed for E_S, b and T for our BEIS3 Monte Carlo uncertainty study. The uncertainty for the OVOC and monoterpene emissions factor is reported as ±50% at the 95% confidence interval. This is approximately 26% at one standard deviation as reported in Table 3.

Table 3. Summary of parameters used to determine analytical uncertainty in the monoterpene and OVOC emissions estimates.

Parameter	**Units**	**Uncertainty Range**	**Note**
E_A	µg·hectare^{-1}·hr^{-1}	Computed	The emissions rate of OVOCs and monoterpenes per unit area per unit time. The uncertainty is calculated as a result of our study. However, it is the average daily value of E_A that is used as the fundamental output variable.
A	hectare	No uncertainty assumed.	Area over which OVOC and monoterpene emissions are calculated.
E_S	µg·hectare^{-1}·hr^{-1}	σ is assumed to be 26 % of nominal value	OVOC and monoterpene emissions factor. Nominal value varies by plant species.
?	K^{-1}	Median = 0.09 K^{-1} and σ is assumed to be 0.02 K^{-1}	Inverse temperature scale for exponential term.
T	K	σ is assumed to be 1.9 C	Ambient temperature.
T_S	K	No uncertainty assumed. Nominal value is 303 K.	Temperature parameter.

The exponential term (dimensionless) in Equation (9) is known as the temperature correction factor, C_T, for monoterpenes or OVOCs emissions estimates. Using the assumed median value for b and recognizing that $b = 0.09\,\mathrm{K}^{-1} \approx \frac{1}{11\mathrm{K}}$, C_T can be expressed in the following form:

$$C_T = \exp\left(\frac{T - 303\,\mathrm{K}}{11\mathrm{K}}\right) \tag{10}$$

Thus for each 11 K increase in temperature, C_T (and hence the emissions, E_A) increase by a factor of e = 2.71 according to Equation (10). This strong dependence on temperature is important to recognize when the analytical uncertainty results are given below.

Note that the temperature scale, T_S = 303 K, is being held constant in this study. It is assumed that T_S is relatively well known and has minimal uncertainty.

When the analytical differential method is applied to Equation (9) for BEIS3 monoterpene or OVOC emissions, the following result is obtained:

$$\frac{\Delta E_A}{E_A} = \frac{\Delta E_S}{E_S} + \frac{\Delta b}{b}\left(b\left[T - 303K\right]\right) + b\left(\Delta T\right) \tag{11}$$

If both sides of the equation are squared and it is assumed that there are no correlations between variations in E_S, b, and T, then an analytical expression for the mean square uncertainty in monoterpene or OVOC emissions is obtained.

$$\left(\frac{\Delta E_A}{E_A}\right)^2 = \left(\frac{\Delta E_S}{E_S}\right)^2 + \left(\frac{\Delta b}{b}\right)^2\left(b^2\left[T - 303K\right]^2\right) + b^2\left(\Delta T\right)^2 \tag{12}$$

For each of the input variables, such as b, $(\Delta b)^2 = s_b^2$, where s is the assumed uncertainty defined in Table 3. After substituting s and the median values of the variables and parameters, Equation (12) becomes:

$$\left(\frac{s_{EA}}{E_A}\right)^2 = \left(\frac{s_{ES}}{E_S}\right)^2 + \left(\frac{s_b}{b}\right)^2\left(\frac{T - 303\,\mathrm{K}}{11\mathrm{K}}\right)^2 + \left(\frac{s_T}{11\mathrm{K}}\right)^2 \tag{13}$$

From Table 3, the following values can be derived:

$$\left(\frac{s_{ES}}{E_S}\right)^2 = 0.26^2 = 0.0676\,;$$

$$\left(\frac{s_b}{T_b}\right)^2 = \left(\frac{0.02\,\mathrm{K}^{-1}}{0.09\,\mathrm{K}^{-1}}\right)^2 = 0.0494\,;\text{ and}$$

$$(s_T)^2 = (1.9\,\mathrm{K})^2 = 3.61\mathrm{K}^2$$

Equation (13) has been solved for three alternate values of ambient temperature, *T*, equal to approximately 30 C, 20 C, and 10 C. The individual uncertainty terms in Equation (13) are given in Table 4, along with the total uncertainty $\left(\frac{s_{EA}}{E_A}\right)^2$ on the right.

Table 4. Summary of analytical uncertainty estimate in the OVOC and monoterpene emissions.

***T* (K)**	***E_S* Term**	**ß Term**	***T* Term**	$\left(\frac{s_{EA}}{E_A}\right)^2$
303	0.068	0.0	0.030	0.10
293	0.068	0.040	0.030	0.14
283	0.068	0.160	0.030	0.26

For average temperatures of 293 K, which are typical of those found across the geographic domain, $\frac{s_{EA}}{E_A}$ is estimated by the analytical method to be about 0.37, which is close to what was found from the Monte Carlo exercise.

The MC results (in Hanna et al., 2002) for correlations between variations in input parameters and variations in estimated emissions also agree approximately with the expectations from the above analytical analysis. For example, it is seen that the E_S uncertainty term dominates at higher temperatures, while the b term dominates at low temperatures. The contribution of the T term is relatively small for all temperatures. For the MC runs, the correlation between variations in E_A and variations in E_S for monoterpenes or OVOCs was found to be close to 1.0 in the south and the Midwest, where temperatures were high, and was found to be relatively low, about 0.3, in the northeast where temperatures were low. In contrast, the correlation between variations in E_A and variations in b for monoterpenes or OVOCs was found to be only about 0.2 in the southern and midwestern U.S. but as high as 0.9 in colder parts of the geographic domain. It is concluded that the analytical results are similar to the MC results, as would be expected for this relatively simple emissions equation.

Results of application of analytical approach to isoprene emissions

The two previous sections dealt with an analytical approach to estimating BNO, monoterpene, and OVOC emissions using equations in BEIS3. The current isoprene example is slightly more difficult because of the larger number of equations. The following equation is used in BEIS3 to estimate emissions, E, of isoprene:

$$\frac{E}{A} = E_A = E_S C_L^A C_T \tag{14}$$

where C_L^A is the correction factor that accounts for the attenuation of PAR (i.e. L), by the leaves and C_T is the temperature correction factor, with the seasonal adjustment factor set equal to 1.0 for summer. The C_L^A factor was not contained in the previous emissions equations for BNO and monoterpene and OVOC. The temperature correction factor, C_T, was contained in those equations, but in a slightly different form. The equation for C_T for isoprene is:

$$C_T = \frac{\exp\left(\frac{c_{T1} \cdot (T - T_S)}{R \cdot T_S \cdot T}\right)}{1 + \exp\left(\frac{c_{T2} \cdot (T - T_M)}{R \cdot T_S \cdot T}\right)} \tag{15}$$

where R is the ideal gas constant (8.314 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$) and T_S = 303 K and T_M = 314 K are scaling constants adopted by the isoprene emissions researchers. Our current uncertainty study assumes that T_S does not vary but that T_M has an uncertainty with standard deviation of 3 K. The exponential term in the numerator of Equation (15) dominates at ambient temperatures, T, less than about T_M = 314 K, which covers most of the naturally-occurring temperature range.

The equation for C_L^A is:

$$C_L^A = L_S^f \cdot C_L\left(L = PAR_S\right) + L_D^f \cdot C_L\left(L = PAR_D\right) \tag{16}$$

where L_S^f is the fraction of sunlit leaves, L_D^f is the fraction of shaded leaves, $L=PAR_S$ is the PAR on the sunlit leaves, $L=PAR_D$ is the PAR on the shaded leaves, and C_L is the light correction factor defined by:

$$C_L = \frac{a \cdot c_{L1} \cdot L}{\sqrt{1 + a^2 \cdot L^2}} \tag{17}$$

Equation (17) is linear in L at small values of L, and approaches a constant, c_{L1}, at large values of L. The linear range ends at about a PAR value of 400 $\mu\mathrm{mol/m^2s}$. It is important to note that L and PAR are used interchangeably in these equations.

The L_S^f and L_D^f factors are estimated from:

$$L_S^f = \frac{1.0 - \exp(-k \cdot LAI)}{k \cdot LAI} \tag{18}$$

$$L_D^f = 1.0 - L_S^f$$

where k is the extinction coefficient and LAI is the leaf area index. Hanna et al. (2002) present several more equations for estimating PAR_S and PAR_D, where the effects of direct-beam and diffuse solar energy are considered separately. However, the fundamental input to the light equations is I, the observed or modeled solar radiation flux in W·m^{-2}. In the current analytical study, the asymptotic limits of these equations will be studied and rationale given for approximations.

Table 5. Summary of parameters used to determine analytical uncertainty in the isoprene emissions estimates.

Parameter	**Units**	**Uncertainty Range**	**Note**
E_A	µg·hectare^{-1}·hr^{-1}	Computed	The emissions rate of isoprene per unit area and time. The uncertainty is calculated as a result of our study. However, it is the average daily value of E_A that is used as the basic output variable.
A	hectare	No uncertainty assumed.	Area over which isoprene emissions are calculated.
E_S	µg·hectare^{-1}·hr^{-1}	s is assumed to be 26 % of nominal value	Isoprene emissions factor. Nominal value varies by plant species.
?	m^2·s·µmol^{-1}	Median = 0.0027 m^2·s·µmol^{-1} and s is assumed to be 0.0015 m^2·s·µmol^{-1}	Scaling parameter in C_L equation.
c_{L1}	Dimensionless	Median = 1.06 and s is assumed to be 0.2	Scaling parameter in C_L equation.
R	J·K^{-1}·mol^{-1}	No uncertainty assumed. Value is 8.314 J·K^{-1}·mol^{-1}	Ideal gas constant.
c_{T1}	J·mol^{-1}	Median = 95,000 J·mol^{-1} and s is assumed to be 20,000 J·mol^{-1}	Scaling parameter in C_T equation.
c_{T2}	J·mol^{-1}	Median = 230,000 J·mol^{-1} and s is assumed to be 150,000 J·mol^{-1}	Scaling parameter in C_T equation.
T	K	s is assumed to be 1.9 C	Ambient temperature.
T_S	K	No uncertainty assumed. Nominal value is 303 K.	Temperature parameter.
T_M	K	Median = 314 K and s is assumed to be 3 K.	Scaling parameter.
LAI	Dimensionless	s is assumed to be 13 % of nominal value	Leaf area index.
I	W·m^{-2}	s is assumed to be 13 % of nominal value	Solar radiation flux.

The units of the variables and parameters and constants in Equations (14) through (18) are listed in Table 5. The assumed median values are given for the constants and parameters. The list also includes the standard deviation (s) of the uncertainty range assumed for E_S, a, c_{L1}, c_{T1}, c_{T2}, T_M, T, LAI, and I for our BEIS3 Monte Carlo uncertainty study. The uncertainty for the isoprene emissions factor is reported by Hanna et al. (2002) as ±50% at the 95% confidence interval. This is approximately 26% at one standard deviation as reported in Table 5. Also, Hanna et al. (2002) indicate an uncertainty range for both LAI and I as ±25% at the 95% confidence interval. This is approximately 13% at one standard deviation as reported in Table 5.

The temperature correction term, C_T, for isoprene was given in Equation (15). The terms $\frac{c_{T1}}{R \cdot T_S \cdot T}$ and $\frac{c_{T2}}{R \cdot T_S \cdot T}$ can be thought of as inverse temperature scales, similar to those in the C_T equations for BNO emissions and for monoterpene and OVOC emissions. For those emissions, the temperature scales were about 10 K. For isoprene emissions, the $\left(\frac{c_{T1}}{R \cdot T_S \cdot T}\right)^{-1}$ temperature scale is about 7 K and the $\left(\frac{c_{T2}}{R \cdot T_S \cdot T}\right)^{-1}$ temperature scale is about 3 K. It is concluded that the four temperature scales are within about a factor of three, implying a similar rate of increase in emissions as temperature increases. For example, at an ambient temperature less than about 310 K, for each 7 K increase in temperature, C_T (and hence the isoprene emissions, E_A) increase by a factor of e = 2.71. Note that the temperature scale, T_S = 303 K, is being held constant in this study. It is assumed that T_S is relatively well known and has minimal uncertainty.

When the analytical differential method is applied to the C_T term in Equation (15) for BEIS3 isoprene emissions, the following result is obtained:

$$\begin{aligned}
\left(\frac{s_{CT}}{C_T}\right)^2 = {} & \left(\frac{c_{T1}}{RT_ST}\right)^2 \left[\left(\frac{s_{c_{T1}}}{c_{T1}}\right)^2 (T-T_S)^2 + s_T^2 \left(\frac{T_S}{T}\right)^2\right] + \\
& \left(\frac{c_{T2}}{RT_ST}\right)^2 \left[\left(\frac{s_{c_{T2}}}{c_{T2}}\right)^2 (T-T_M)^2 + s_T^2 \left(\frac{T_M}{T}\right)^2 + s_{T_M}^2\right] \cdot \\
& \left(\frac{\exp\left(\frac{c_{T2} \cdot (T-T_M)}{R \cdot T_S \cdot T}\right)}{1+\exp\left(\frac{c_{T2} \cdot (T-T_M)}{R \cdot T_S \cdot T}\right)}\right)^2
\end{aligned} \tag{19}$$

From Table 5, the following values can be derived:

$$\left(\frac{s_{C_{T1}}}{c_{T1}}\right)^2 = \left(\frac{20000\, J \cdot mol^{-1}}{95000\, J \cdot mol^{-1}}\right)^2 = 0.044\,;$$

$$\left(\frac{s_{C_{T2}}}{c_{T2}}\right)^2=\left(\frac{150000\,J\cdot mol^{-1}}{230000\,J\cdot mol^{-1}}\right)^2=0.425\,;$$

$$(s_T)^2=(1.9\,\mathrm{K})^2=3.61\,\mathrm{K}^2\ ;$$

$$(s_{TM})^2=(3.0\,\mathrm{K})^2=9.0\,\mathrm{K}^2\,;$$

$$\left(\frac{c_{T1}}{RT_ST}\right)^2=\left(\frac{95000\,J\cdot mol^{-1}}{\left(8.314\,J\cdot K^{-1}\cdot mol^{-1}\right)(303\,K)T}\right)^2=\left(\frac{37.7113}{T}\right)^2\text{; and}$$

$$\left(\frac{c_{T2}}{RT_ST}\right)^2=\left(\frac{230000\,J\cdot mol^{-1}}{\left(8.314\,J\cdot K^{-1}\cdot mol^{-1}\right)(303\,K)T}\right)^2=\left(\frac{91.3009}{T}\right)^2$$

After substituting the median values of the variables and parameters, Equation (19) becomes:

$$\begin{aligned}\left(\frac{s_{CT}}{C_T}\right)^2=&\left(\frac{37.7113}{T}\right)^2\left[0.044(T-303\,\mathrm{K})^2+3.61\,\mathrm{K}^2\left(\frac{303\,\mathrm{K}}{T}\right)^2\right]+\\&\left(\frac{91.3009}{T}\right)^2\left[0.425(T-314\,\mathrm{K})^2+3.61\,\mathrm{K}^2\left(\frac{314\,\mathrm{K}}{T}\right)^2+9.0\,\mathrm{K}^2\right]\cdot\\&\left(\frac{\exp\left(\frac{37.7113(T-314\,\mathrm{K})}{T}\right)}{1+\exp\left(\frac{37.7113(T-314\,\mathrm{K})}{T}\right)}\right)^2\end{aligned}\tag{20}$$

On expansion of Equation (20), the following terms are defined:

c_{T1} term (line 1): $\left(\frac{37.7113}{T}\right)^2\left(0.044[T-303\,\mathrm{K}]^2\right)$

T term (line 1): $\left(\frac{37.7113}{T}\right)^2\left(3.61\,\mathrm{K}^2\left[\frac{303\,\mathrm{K}}{T}\right]^2\right)$

c_{T2} term (line 2 and 3): $\left(\frac{91.3009}{T}\right)^2\left(0.425[T-314\,\mathrm{K}]^2\right)\left(\frac{\exp\left(\frac{37.7113(T-314\,\mathrm{K})}{T}\right)}{1+\exp\left(\frac{37.7113(T-314\,\mathrm{K})}{T}\right)}\right)^2$

T term (line 2 and 3): $\left(\frac{91.3009}{T}\right)^2\left(3.61\,\mathrm{K}^2\left[\frac{314\,\mathrm{K}}{T}\right]^2\right)\left(\frac{\exp\left(\frac{37.7113(T-314\,\mathrm{K})}{T}\right)}{1+\exp\left(\frac{37.7113(T-314\,\mathrm{K})}{T}\right)}\right)^2$

T_M term (line 2 and 3): $\left(\frac{91.3009}{T}\right)^2 \left(9.0\,\mathrm{K}^2\right)\left(\frac{\exp\left(\frac{37.7113(T-314\,\mathrm{K})}{T}\right)}{1+\exp\left(\frac{37.7113(T-314\,\mathrm{K})}{T}\right)}\right)^2$

Equation (20) is solved for four alternate ambient temperatures, T, equal to 314 K, 303 K, 293 K, and 283 K. The individual uncertainty terms in Equation (20) are given in Table 6, along with the total uncertainty $\left(\frac{s_{CT}}{C_T}\right)^2$ on the right:

Table 6. Summary of analytical uncertainty estimate in the isoprene emissions due to temperature terms.

***T* (K)**	**c_{T1} Term (line 1)**	***T* Term (line 1)**	**c_{T2} Term (line 2 and 3)**	***T* Term (line 2 and 3)**	**T_M Term (line 2 and 3)**	$\left(\frac{s_{CT}}{C_T}\right)^2$
314	0.077	0.048	0.0	0.076	0.190	0.39
303	0.0	0.056	0.006	0.0	0.001	0.06
293	0.073	0.064	0.0	0.0	0.0	0.14
283	0.315	0.073	0.0	0.0	0.0	0.39

The $\left(\frac{s_{CT}}{C_T}\right)^2$ contribution is seen to be a maximum of 0.39 at relatively low temperatures (for summer) of 283 K. The c_{T1} term has the major contribution. The c_{T2} term has a near-zero contribution at most ambient temperatures, which are nearly always much less than 314 K.

The uncertainties of the C_L^A term can also be studied analytically. To simplify the analysis, assume that all leaves are sunlit. Therefore $C_L^A = C_L = \frac{a \cdot c_{L1} \cdot L}{\sqrt{1+a^2 \cdot L^2}}$. Applying the same differential analysis to this equation, the following result is obtained:

$$\left(\frac{s_{C_L}}{C_L}\right)^2 = \left(\frac{s_{c_{L1}}}{c_{L1}}\right)^2 + \frac{\left(\frac{s_a}{a}\right)^2 + \left(\frac{s_L}{L}\right)^2}{\left(1+a^2L^2\right)^2} \qquad (21)$$

From Table 5, the following values can be derived:

$$\left(\frac{s_{c_{L1}}}{c_{L1}}\right)^2 = \left(\frac{0.2}{1.06}\right)^2 = 0.036\,;$$

$$\left(\frac{s_a}{a}\right)^2 = \left(\frac{0.0015\,\mathrm{m}^2\cdot\mathrm{s}\cdot m\mathrm{mol}^{-1}}{0.0027\,\mathrm{m}^2\cdot\mathrm{s}\cdot m\mathrm{mol}^{-1}}\right)^2 = 0.3086\text{; and}$$

$$\left(\frac{s_L}{L}\right)^2 = (0.13)^2 = 0.0169$$

After substituting the median values of the variables and parameters, Equation (21) becomes:

$$\left(\frac{s_{C_L}}{C_L}\right)^2 = 0.036 + \frac{0.3086 + 0.0169}{\left(1 + a^2 L^2\right)^2} \tag{22}$$

Equation (22) is solved for three values of L: 100, 300, and 600 µmol·m^{-2}·s^{-1}. The individual uncertainty terms in Equation (22) are given in Table 7, along with the total uncertainty $\left(\frac{s_{C_L}}{C_L}\right)^2$ on the right.

Table 7. Summary of analytical uncertainty estimate in the isoprene emissions due to solar radiation terms.

L **(µmol·m^{-2}·s^{-1})**	c_{L1} **Term**	***a*** **Term**	***L*** **Term**	$\left(\frac{s_{CL}}{C_L}\right)^2$
100	0.036	0.268	0.015	0.32
300	0.036	0.113	0.006	0.16
600	0.036	0.024	0.001	0.06

The $\left(\frac{s_{CL}}{C_L}\right)^2$ contribution is seen to be a maximum of about 0.32 at relatively low light intensities (L = 100 µmole/m^{2}s), which would be typical of early morning. The *a* term has the major contribution. The uncertainty decreases as light intensity, L, increases, primarily because C_L approaches a constant, c_{L1} , at high values of L, typical of mid-day conditions in the summer.

Since $\frac{E}{A} = E_A = E_S \cdot C_L^A \cdot C_T$ (Eq. 14), for this simplified analytical analysis it is possible to express the total uncertainty as:

$$\left(\frac{s_{E_A}}{E_A}\right)^2 = \left(\frac{s_{E_S}}{E_S}\right)^2 + \left(\frac{s_{C_L}}{C_L}\right)^2 + \left(\frac{s_{C_T}}{C_T}\right)^2 \tag{23}$$

or, for the maximum values of the components:

$$\left(\frac{s_{E_A}}{E_A}\right)^2 = 0.068 + 0.32 + 0.39 = 0.78 \qquad (24)$$

The value of 0.78 is approximately what was found for the maximum for the BNO emissions analysis, and is about three times larger than what was found for the monoterpene and OVOC analysis. This same relative ranking was found in the MC uncertainty study of these emissions components reported by Hanna et al. (2002).

The MC results (reported in Hanna et al., 2002) for correlations between variations in input parameters and variations in estimated emissions showed that the uncertainties in the terms a and c_{L1} in the C_L expression were the dominant contributors to the total uncertainty in isoprene emissions. Their correlations were in the range from 0.7 to 1.0 across the geographic domain. All other terms (including E_S, L, LAI, and all terms in the C_T expression) had relatively minor correlations, with magnitudes less than 0.5.

CONCLUSIONS

It is concluded that the analytical results for isoprene are similar to the MC results reported by Hanna et al. (2002), but there are a few unexpected results, probably because the isoprene emissions equation is more complicated and because some asymptotic assumptions were made above in order to derive the analytical solutions.

It is found that the total relative variance in isoprene emissions varied from 0.10 to 0.40, depending on T_A. Total OVOC and monoterpene relative variances were similar, with values ranging from 0.10 to 0.26. Total BNO relative variances ranged from 0.22 to 0.71. By taking the square root of these relative variances, we obtain estimates of relative uncertainty in BEIS3 emissions in the range from about 0.3 to 0.8 (i.e., ± 30 to 80 %). It is suggested by the analytical equations that the relative uncertainties in emissions depend on the air temperature, T_A, in the sense that one model input would contribute most of the variance at T_A of 10 C and another input would contribute most at 30 C.

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KEYWORDS

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