A NATIONAL INVENTORY OF BIOGENIC HYDROCARBON EMISSIONS

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(First received 9 October 1986 and in final form 8 January 1987)

Abstract—Emission rate vs temperature algorithms for different vegetation types, including deciduous, coniferous and agricultural sources, were used with available biomass and land use data for the U.S. to develop a national emission inventory with county spatial and monthly temporal scales. The estimated total NMHC emission rate from the U.S. is 30.7 Mt annually; more than half of these emissions occur in the summer, and approximately half arise in the SE and SW U.S. Total emission rates of isoprene from deciduous forest and α-pinene from deciduous and coniferous forests are 4.9 and 6.6 Mt annually. Emissions from agricultural crops contribute less than 3% of the annual total. The average flux of biogenic NMHC in the U.S. is estimated to be 450 pg m⁻² h⁻¹ which is 20 times less than reported emissions of anthropogenic NMHC averaged over urban land areas in the U.S. Geochemical NMHC emissions from hydrocarbon rich soils in the U.S. are estimated to be negligible compared to vegetative sources. The uncertainty in the inventory is estimated to be on the order of a factor of three.

Key word index: Biogenic, hydrocarbons, isoprene, α-pinene, emission inventory, natural sources, vegetation.

1. INTRODUCTION

Estimates of natural hydrocarbon (HC) emissions from vegetation have been of interest for more than a decade. The reasons for this interest include concern for the role of natural HCs in photochemical oxidant formation, uncertainty in the global carbon cycle, and recent recognition of significant contributions of organic acids to acidic deposition in rural and urban areas. In response to these questions about the emissions of natural HCs, a number of extensive, but localized studies of biogenic HC emissions rates have been conducted. Zimmerman (1979a, b) developed a vegetation enclosure procedure and made more than 600 measurements of biogenic HC emissions in Tampa Bay, FL and Houston, TX. This data base covers 69 specific types of vegetation in 10 broad categories. Winer et al. (1983) reported a similar detailed investigation of natural emissions in the Los Angeles basin. Vegetative enclosure samples were collected from 60 species in 5 categories. Other HC emissions data have been described by Lamb et al. (1985) for trees and crops in Pennsylvania and Georgia and for Pseudotsuga menziesii (Douglas fir) in Washington state. Emission rates from Quercus garryana (Oregon white oak) have also been recently reported (Lamb et al., 1986). In these latter studies, emission measurements obtained with an enclosure technique were in reasonable agreement with results from a micro-meteorological method and with an atmospheric tracer approach. Additional estimates of HC emissions from trees have been reported by Knoerr and Mowry (1981) and Arnts et al. (1982) for various locations in the SE U.S.

Laboratory studies of biogenic HC emissions have shown that emission rates from Quercus virginiana (Live oak) and Pinus elliottii (Slash pine) increase with increasing temperature and that isoprene emissions from oak are a function of solar radiation (Tingey et al., 1981; Tingey, 1981). The effects of temperature upon isoprene and monoterpen emission rates have also been observed in many of the field studies mentioned previously.

The availability of these natural emissions data provides the basis for developing a spatially and temporally resolved national inventory. The estimates of land use surface areas needed to calculate such an inventory are available through the Geoecology Data Base (Olson, 1980) which contains a variety of environmental parameters on a county scale of resolution. In particular, the Geoecology Data Base contains estimates of land use area, agricultural areas and yields, adjusted natural vegetation surface areas and climatological data such as monthly average temperatures and growing seasons.

The goal of this work was to develop a national inventory of biogenic HC emissions. This was accomplished by combining emission rate data from the various field studies and emission algorithms developed in laboratory studies in order to establish best-estimates of emission functions for natural HCs. These data were then combined with biomass data from the literature and the appropriate data sets from the Geoecology Data Base to yield an estimate of the U.S. inventory of natural HC emissions resolved by month and county.
2. EMISSION RATE MEASUREMENTS

There are currently three field methods and one laboratory method which have been used to measure HC emission rates. In the field enclosure technique developed by Zimmerman (1979a, b) a Tedlar bag is placed around a branch (or over a crop or soil sample) and the mass accumulation of HCs is determined from the difference in concentration over a measured period of time. The advantages of this method are the simplicity, ease of operation and the ability to sample different species individually. The disadvantages which include uncertainties about enclosure effects, the need to conduct a detailed biomass survey and the requirement for extrapolation from a single branch to a forest or region have provided motivation to use other techniques.

A second method, based upon micrometeorological surface layer theory, involves measurement of HC concentration gradients above an essentially infinite, uniform plane source. Temperature and wind speed or water vapor concentration gradients must be measured, also. The meteorological data are used to determine the eddy diffusivity so that the HC flux can be calculated from the concentration gradient. This method has been used primarily as an independent check upon enclosure measurements (Lamb et al., 1985; Knoerr and Mowry, 1981). These gradient methods are difficult to set-up, and have extremely stringent sensor and site requirements.

A third method, which we have used as a test of enclosure methods, involves simulation of forest emissions with a SF₆ tracer release and measurement of the downwind concentration profiles of SF₆ and natural HCs. The flux of HCs can be calculated from the measured SF₆ flux and the HC concentrations. The results from this technique applied at an isolated Oregon white oak grove were in excellent agreement with enclosure measurements of isoprene emission rates given the mid-range of plausible biomass estimates at the site (Lamb et al., 1986).

In the past several years, these different methods have been used in a number of studies at a number of sites as indicated in Table 1. In one of the most comprehensive studies to date, Zimmerman (1979b) collected more than 600 vegetation enclosure samples in the Tampa Bay, FL region. These samples included 10 major categories with 69 different species or sample types. Winer et al. (1983) conducted a similar detailed inventory of HJC emissions in the Los Angeles basin. Approximately 190 samples were collected from 60 species using an enclosure method. Approximately 30% of these samples were from deciduous trees and 10% were from coniferous trees. Most of the remaining samples were collected from grasses, flowers and ornamental shrubbery.

As shown in Table 1, we have conducted two studies in Pennsylvania as part of the EPA NEROS program and in Atlanta as part of an urban photochemical oxidant study. In Pennsylvania and Atlanta, we used the Zimmerman enclosure system to collect 54 tree samples approximately evenly distributed among deciduous isoprene emitters, non-isoprene emitting deciduous species and coniferous trees. Samples from six different crops were also collected as part of this work.

The work in Pennsylvania also included comparison of a micrometeorological method with the enclosure data. Nine gradient profile tests were conducted at a mixed hardwood forest. The results were in reasonable agreement given the range of experimental uncertainty estimated for the two techniques.

We have also performed two other comparison studies. The first was near Seattle in a Douglas fir forest also using a gradient profile method vs the enclosure method. The second involved the tracer flux approach vs the enclosure method at a stand of Oregon white oak. The comparison in Seattle was relatively poor, primarily because the dry zero air in the enclosure system did not simulate the very wet and humid ambient conditions. On the other hand, the results for the tracer and enclosure systems were in good agreement.

Finally, Tingey and co-workers have conducted a number of studies of emissions using Live oak or Slash pine seedlings in environmental growth chambers under carefully controlled conditions (Tingey et al.,

| Investigator        | Location            | Measurement | Species |
|---------------------|---------------------|-------------|---------|
| 1. Zimmerman (1979b)| Tampa Bay, FL       | enclosure   | variety |
| 2. Winer et al. (1983)| Los Angeles, CA | enclosure   | variety |
| 3. Lamb et al. (1985)| Lancaster, PA     | enclosure   | deciduous, crops |
| 4. Lamb et al. (1985)| Atlanta, GA        | micrometeorological enclosure | deciduous |
| 5. Flyckt (1979)    | Lancaster, PA       | enclosure   | red oak  |
| 6. Lamb et al. (1986)| Pullman, WA       | tracer flux | Oregon white oak |
| 7. Lamb et al. (1986)| Goldendale, WA    | enclosure   | Oregon white oak |
| 8. Lamb et al. (1985)| Seattle, WA       | micrometeorological enclosure | Douglas fir |
| 9. Lamb et al. (1985)| Seattle, WA       | enclosure   | Douglas fir |
| 10. Knoerr and Mowry (1981)| Raleigh, NC | tracer model | loblolly pine |
| 11. Arnts et al. (1982)| Raleigh, NC | laboratory chamber | knob pine |
| 12. Tingey (1981)   | —                   | laboratory chamber | live oak, slash pine |
1981; Tingey, 1981). With this parametric approach, it was possible to determine the dependence of emission rates upon light and temperature separately. Tingey found that isoprene emissions were dependent upon light, little or no isoprene is emitted in the dark, and the emission rate is temperature dependent for constant light conditions. In contrast, terpene emissions from slash pine do not vary with light, but the emissions do increase with increasing ambient temperatures.

In Fig. 1, the geometric mean isoprene emission rate is given as a function of the mean sampling temperature for each study along with the limits within one standard deviation of these means. The vegetation enclosure data from Zimmerman and Winer et al. lie at higher temperatures, while the results from our studies in Pennsylvania and Washington, along with work by Flyckt (1979), exhibit considerable overlap at the lower temperatures. The best-fit line through these data has a correlation coefficient of 0.66 and is approximately parallel to the line for Live oak from Tingey. The regression curve accounts for about half of the observed variability. In general, emission rates vary from more than 1 \( \mu g \text{ g}^{-1} \text{ h}^{-1} \) at low temperatures to more than 35 \( \mu g \text{ g}^{-1} \text{ h}^{-1} \) above 30°C. At 25°C, the regression curve predicts an emission rate of 8.5 \( \mu g \text{ g}^{-1} \text{ h}^{-1} \).

For \( \alpha \)-pinene, shown in Fig. 2, the degree of variability is greater among data sets than for isoprene. The work from the Washington Douglas fir study represents the parallelograms at the low temperatures. At higher temperatures, the tower data from Knoerr and Mowry (1981) yield the highest mean emission rate. Zimmerman's data bridge the gap between these studies as do the results from Winer et al. in Los Angeles. The work by Arnts is in the range 1-2 \( \mu g \text{ g}^{-1} \text{ h}^{-1} \) at 37°C. The best-fit line through all of the emission rate vs temperature data has an \( r \) of 0.58 which accounts for about 34% of the variability. The line is approximately parallel to the line for Slash pine from Tingey. The overall geometric mean is 0.9 \( \mu g \text{ g}^{-1} \text{ h}^{-1} \) at 26.4°C and the predicted emission rate at 25°C is 0.7 \( \mu g \text{ g}^{-1} \text{ h}^{-1} \).

Another illustration of these data is shown in Fig. 3 in terms of total non-methane hydrocarbon (NMHC) vs temperature for isoprene-emitting deciduous trees. Here all of the data are shown (multiple points in black). In this case, the mean emission rate is 10.7 \( \mu g \text{ g}^{-1} \text{ h}^{-1} \) at 28.7°C which is essentially identical to the value for isoprene alone. In general, isoprene accounts for 80% of NMHC from isoprene-emitting deciduous trees.

For terpenes emitted from coniferous trees (Fig. 4), there is less apparent dependence upon temperature, more variability and total NMHC emissions are much higher than for \( \alpha \)-pinene emissions alone. The geometric mean of these data is 3.5 \( \mu g \text{ g}^{-1} \text{ h}^{-1} \) at 29.4°C, and the predicted emission rate at 25°C is 2.8 \( \mu g \text{ g}^{-1} \text{ h}^{-1} \). On a unit mass basis, coniferous trees thus emit about three times less than deciduous isoprene emitters.

These comparisons of emission rate data from the various field and laboratory studies show relatively good agreement in view of the fact that the data were obtained from a variety of vegetation at many sites (Table 1) during different seasons using a number of different methods. It is clear that the temperature emission rate model only accounts for a portion of the variability in emissions, and that a multi-parameter model is required to reduce the uncertainty in emission rates predicted for a national inventory. Nevertheless, the simple temperature-emission algorithm can be used to provide a first estimate of the U.S. inventory of biogenic HC emissions.
3. DEVELOPMENT OF THE EMISSION INVENTORY

As a preliminary estimate we will use results from Zimmerman (1979a) along with the temperature correction curves developed from Tingey's lab data (Tingey, 1981). Here we follow Zimmerman's approach and consider three classes of deciduous emissions, coniferous emissions, agricultural crops, water and grasslands and scrublands as shown in Table 2.

The emission rates from the algorithms are in terms of $\mu g \text{HC}_s g^{-1}$ of dry leaf biomass. Leaf biomass density is an appropriate indicator of vegetative biomass because it tends to be uniform throughout a vegetation association and is relatively insensitive to site-specific variables (Satoo, 1967). Leaf biomass density factors are available in the literature for converting specific surface areas to biomass (Lieth and Whittaker, 1975; NAS, 1975). Natural vegetation surface areas used in this analysis include five broad classes: oak forest, other deciduous forests, coniferous forests, scrublands and grasslands. Total contiguous U.S. surface areas for each class, shown in Table 3, were used. The biomass density factors are similar to those determined by Zimmerman (1979a) and are listed in Table 4. They are derived from literature values for biome types (Lieth and Whittaker, 1975; NAS, 1975) and approximate biome compositions (Rasmussen, 1972; Dasmann, 1976).
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### Table 2. Emission rate estimates (30°C) (µg g⁻¹ h⁻¹)

| Type                  | Examples | Isoprene | α-pinene | Other NMHC |
|-----------------------|----------|----------|----------|------------|
| High isoprene         | oak      | 22.9     | 0        | 1.8        |
| Low isoprene          | sycamore | 8.4      | 0        | 2.3        |
| Deciduous, no isoprene| maple    | 0        | 1.4      | 4.3        |
| Coniferous            | loblolly pine | 0    | 2.8      | 8.9        |
| Agriculture           | alfalfa, wheat | —    | —        | 0.015      |
|                       | tobacco  | —        | —        | 0.35       |
|                       | corn     | —        | —        | 2.0        |
|                       | other    | —        | —        | 0.015      |
| Water                 | —        | —        | —        | 145 µg m⁻³ h⁻¹ |

### Table 3. Contiguous U.S. surface areas

| Classification       | Area (10⁴ km²) | Percent coverage |
|----------------------|----------------|------------------|
| Oak forest           | 0.713          | 9%               |
| Other deciduous forest| 0.814         | 10%              |
| Coniferous forest    | 0.964          | 12%              |
| Scrubland            | 1.365          | 20%              |
| Grassland            | 0.957          | 12%              |
| Total natural vegetation | 5.01      | 64%              |
| Total harvested croplands | 1.59    | 20%              |
| Urban                | 0.24           | 3%               |
| Pasture              | 0.11           | 4%               |
| Unharvested croplands| 0.24           | 3%               |
| Miscellaneous lands  | 0.30           | 4%               |
| Total area not included in inventory | 1.08  | 14%              |
| Water                | 0.15           | 2%               |
| Total U.S. surface area | 7.83        |                  |

### Table 4. Vegetation biomass estimates (kg ha⁻¹)

| Emission category   | Deciduous | Coniferous |
|---------------------|-----------|------------|
| Natural vegetation  | High isoprene | Low isoprene | No isoprene |
| Oak forest          | 1850      | 600        | 600         | 700        |
| Other deciduous forest | 600      | 1850       | 900         | 1350       |
| Coniferous forest   | 390       | 260        | 260         | 5590       |
| Scrubland           | 300       | 450        | 2100        | 150        |
| Grassland           | 250       | 375        | 375         | 500        |

| Agricultural crops  | Yield (1000 Mt) | Area harvested (1000 ha) | Dry biomass/ economic yield | Biomass density (Mt ha⁻¹) |
|---------------------|-----------------|--------------------------|-----------------------------|--------------------------|
| 1 Corn              | 266,822         | 31,460                   | 1.9                         | 16.1                     |
| 2 Hay               | 118,642         | 24,388                   | 1.1                         | 5.4                      |
| 3 Alfalfa           | 67,858          | 10,471                   | 1.3                         | 32.5                     |
| 4 Soybeans          | 46,885          | 24,851                   | 3.9                         | 7.4                      |
| 5 Wheat             | 43,669          | 21,892                   | 3.7                         | 7.4                      |
| 6 Sorghum           | 21,433          | 3377                     | —                           | 31.8                     |
| 7 Potatoes          | 13,639          | 475                      | 0.6                         | 17.2                     |
| 8 Barley            | 9137            | 3536                     | 5.0                         | 12.9                     |
| 9 Oats              | 7258            | 3989                     | 4.1                         | 7.5                      |
| 10 Rice             | 6003            | 1200                     | —                           | 10.5                     |
| 11 Cotton           | 2329            | 5131                     | 3.5                         | 1.6                      |
| 12 Peanuts          | 1608            | 567                      | 2.6                         | 7.4                      |
| 13 Tobacco          | 857             | 383                      | 2.2                         | 4.9                      |
| 14 Rye              | 189             | 107                      | —                           | 24.3                     |
| Miscellaneous crops | 25,772          |                          |                             |                          |
Crop biomass data are taken from the Geoecology Data Base, which is under development as part of the National Acid Precipitation Assessment Program (NAPAP). It includes environmental parameters such as temperature, soil order distributions, land use data, as indicated in Table 3, and crop yields as shown in Table 4 for the 14 major crops in the U.S. These crop yield and coverage data can be combined with the ratio of total plant weight to economic yield to provide biomass factors for various crops in the U.S. also shown in Table 4.

We arbitrarily consider the U.S. in five regions: NE, SE, central, NW and SW as shown in Fig. 5. Each region accounts for about 20% of the U.S.

Given the vegetation and crop data from the Geoecology Data Base and using the emission estimates from Zimmerman and the temperature relationship from Tingey, national emissions inventories for the two example compounds, isoprene and a-pinene, and total NMHC can be calculated. In this inventory, a-pinene emissions are assumed to occur 24 h daily and temperature effects are incorporated via county mean monthly temperatures.

For isoprene, daylight hours are changed from 15 h in summer to 9 h in December—no emissions are allowed at night. Emissions are also stopped for deciduous species between the date of the first frost in the fall and the last springtime frost. Crop biomass was allowed to increase linearly during the growing season.

4. PRESENTATION AND DISCUSSION OF RESULTS

The results of the inventory procedure are summarized in terms of seasonal averages on a regional basis for isoprene, a-pinene and other NMHC emissions from all source types in Fig. 6. Isoprene emissions are greatest in the summer; emissions in the spring and fall are approximately equal and wintertime emissions are minimal. By region, the SE accounts for almost half (48%) of the isoprene emitted while the NW contributes only 3%. The total value for the U.S. is 4.9 Mt y⁻¹.

Monthly mean temperatures were used for isoprene in this case. In a kind of sensitivity analysis, we also used the maximum daily average temperature by county to yield isoprene emissions of 8.3 Mt y⁻¹ and the average of the daily mean and daily maximum to yield isoprene emissions of 6.5 Mt y⁻¹. The latter case best represents the temperature conditions associated with daytime isoprene emissions. The range of these changes varies approximately ±30%.

Results for a-pinene are somewhat different than for isoprene even though the total emission of 6.6 Mt y⁻¹ is essentially the same. As indicated in Fig. 6, summertime emissions remain the most significant. There is a small wintertime contribution of a-pinene as well, that was not seen with isoprene. On a regional basis, emissions from the SE are approximately equal to those from the SW and NW at 25% of the total. The central and NE regions have the lowest proportion of the emissions at approximately 13%.

For NMHC emissions other than isoprene and a-pinene, the spring and autumn contribute significant proportions, and there are some wintertime emissions. The S regions are the areas of largest emissions; together the SW and SE contribute 50%. The NE and NW regions are the next largest source areas at

Fig. 5. Regions of the U.S. used for analysis of the emission inventory. Each region constitutes about 20% of the U.S.
approximately 18% each; and the central region is the lowest at 14%. These other NMHC emissions sum to a much larger total than either of the specific compounds. Total NMHC—excluding isoprene and α-pinene—equals 19 Mt yr⁻¹ which is approximately three times larger than for isoprene or α-pinene alone. On an annual basis, the total NMHC including isoprene and α-pinene equals 30.7 Mt. It should be noted in this regard that the available emission rate measurements emphasized isoprene and α-pinene more than other non-methane HCs. Zimmerman reported emission rates for a number of specific compounds, but also included a number of unidentified compounds in the reported total NMHC emission rates. In several of the method intercomparison studies only isoprene or α-pinene emissions were reported. As a result, the data base for total NMHC emission rates is less complete and more sparsely documented than for either isoprene or α-pinene.

The distribution of emissions among source types is shown in Fig. 7. The total NMHC emissions are evenly distributed between coniferous and deciduous forests, while agriculture crops contribute approximately 3% of the total. Isoprene and α-pinene emissions each constitute approximately 15% of the total emissions from all vegetation with the other terpenes contributing the remainder. However, isoprene emissions contribute more than 50% of the total deciduous emissions, while α-pinene emissions amount to approximately 25% of the total NMHC from coniferous vegetation.

On an areal basis, the predominance of the SE, SW and Pacific NW coastal regions is evident in the U.S. map of total NMHC emissions shown in Fig. 8. The lack of forests in the central area of the U.S. accounts for the low fluxes estimated there. Maximum county average fluxes range from 112 kg ha⁻¹ (1280 µg m⁻² h⁻¹) in the NW region to 224 kg ha⁻¹ (2560 µg m⁻² h⁻¹) in the SE on an annual basis. During the summer, the maximum county average flux in the SE is 79 kg ha⁻¹ (3610 µg m⁻² h⁻¹). Throughout the U.S. during the summer, approximately 37% of the counties have fluxes less than 15 kg ha⁻¹ (690 µg m⁻² h⁻¹), and only 3% of the counties have summertime fluxes exceeding 50 kg ha⁻¹ (2280 µg m⁻² h⁻¹).

On an annual average basis, the NMHC flux is 450 µg m⁻² h⁻¹ as indicated in Table 5. Estimates by other workers range from 780 µg m⁻² h⁻¹ by Winer et al. (1983) in L.A. to 8890 µg m⁻² h⁻¹ by Salop et al. (1983) for Virginia forests. Zimmerman's estimate for the U.S. in 1978 at 830 µg m⁻² h⁻¹ is a factor of two higher than our estimate. While the emission algor-
Fig. 7. Nonmethane hydrocarbon emissions in Mt by season and source type for the entire U.S. □ Isoprene; □ α-pinene; □ other NMHC.

Algorithm errors are very similar and the biomass estimates are essentially the same, the differences between the calculations include: (1) calculation by county, not by latitudinal region; (2) use of variable biomass in some categories; (3) no incorporation of soil/litter emissions throughout the U.S. (160 μg m⁻² h⁻¹ was included by Zimmerman); and (4) incorporation of land-use adjusted vegetation areas.

Fig. 8. U.S. map of county averaged NMHC flux (kg ha⁻¹) during the summer.
### Table 5. Biogenic emission fluxes

| Location | µg m\(^{-2}\) h\(^{-1}\) | Remarks | Tg y\(^{-1}\) |
|----------|-----------------|---------|-------------|
| SCAB, CA (Winer et al., 1983) | 780 | L. A. basin | |
| Lake Tahoe, CA (JSA, 1978) | 1950 | Entire basin | |
| Lake Tahoe, CA (JSA, 1978) | 2438 | Forested area of basin | |
| San Francisco Bay (Sauders et al., 1978) | 1389 | | |
| San Francisco Bay (Hunsaker, 1981) | 2265 | Daytime | |
| San Francisco Bay (Hunsaker, 1981) | 777 | Night-time | |
| Tampa/St Petersburg, FL (Zimmerman, 1979b) | 7540 | | |
| Southeastern VA (Salop et al., 1983) | 8890 | Forested area only | |
| Houston, TX (Zimmerman, 1980) | 1170 | | |
| U.S.A. (Marchesani et al., 1970) | 1712 | | |
| U.S.A. (Zimmerman, 1977) | 1099 | | |
| U.S.A. (Zimmerman, 1979a) | 884 | 65 | |
| U.S.A. (this work) | 447 | | |

**Anthropogenic VOC emissions (U.S. EPA, 1983)**

| Source | Tg y\(^{-1}\) | Percent |
|--------|--------------|---------|
| Transportation | 6.1 | 33.5 |
| S.S. fuel combustion | 2.0 | 11.0 |
| Industrial processes | 7.1 | 39.0 |
| Waste disposal | 0.6 | 3.3 |
| Miscellaneous | 2.4 | 13.2 |
| **Total** | **18.2** | **100** |

Estimates of anthropogenic emissions from 1983 are also listed in Table 5. The total is 18 Mt or about half the biogenic total. However, it is important to keep in mind that these are urban and industrial emissions from about 3% of the land area. On an areal flux basis, these emissions correspond to 8600 µg m\(^{-2}\) h\(^{-1}\) or almost 20 times the flux of biogenic emissions. In view of the nonlinear chemical mechanisms which act upon these gases, it is therefore very important to be wary of simple comparisons of the total emissions.

In an attempt to identify other NMHC sources, a literature search was undertaken to examine geochemical sources of HCs. The migration of HCs upwards through the soils is a generally accepted phenomena which the oil industry uses as a prospecting tool (Horvitz, 1985; Jones and Drozd, 1983). Results from the literature survey were used in an attempt to describe emission of geochemical HCs from soils.

Fick's Law for molecular diffusion of HCs through soil was assumed as the basis for estimating HC emissions from soils. It was modified by several soil factors, including: (1) the porous structure of the soil, (2) presence of water in the soil, (3) solubility of the HCs into the soil air and soil water, (4) adsorption of the HCs onto soil particles, and (5) atmospheric pressure affecting soil gas fluxes (Campbell, 1985, Personal Communication; Goring and Hamacker, 1972; Koorevaar et al., 1983). The flux of HCs is thus described as:

\[
F = b(\phi_x)\chi D_{af} \left(\frac{\Delta C}{\Delta Z}\right)
\]

where \(\phi_x\) is the decimal % of air space within the soil, not occupied by water, \(b\) and \(m\) are tortuosity factors describing the actual diffusion path length, \(D_{af}\) is the molecular diffusion coefficient, and \(\Delta C/\Delta Z\) is the change in concentration over the diffusion length. We applied this simple model using derived diffusion coefficients for several light HCs (Bird et al., 1960), assuming soil HC concentrations ranging from 0.1 to 1.0 ppm, and using 123,000 km\(^2\) as the surface area of underground HC reserves in the U.S. (Cram, 1968). Local flux estimates range from 0.06 µg NMHC m\(^{-2}\) h\(^{-1}\) to 2.6 µg NMHC m\(^{-2}\) h\(^{-1}\). Using a mid-estimate of HC flux, the annual U.S. geogenic contribution of NMHC is 0.0007 Tg y\(^{-1}\) (700 Mt). This preliminary estimate is several orders of magnitude less than the estimated HC emissions from vegetation. These rough estimates indicate that geochemical HCs are negligible on a national scale, but could be important on a local basis (Colbeck and Harrison, 1985; Mayrsohn and Crabtree, 1976).

The implications of the inventory results with respect to the impact of biogenic HCs on regional atmospheric chemistry can best be determined from transport and chemistry modeling studies. However, several features of the inventory deserve some comment. Obviously, the impact of natural HCs will be greatest in the summer when vegetation coverage is large and temperatures are highest. The contribution of biogenic emissions during winter will be negligible in all regions of the country. The mix of biogenic HCs favors isoprene as a dominant species in the SE U.S. during summer, while monoterpenes are the dominant species in the NW U.S. in summer. It should be noted, again, that the emissions data tended to emphasize emissions of isoprene and/or α-pinene. Reports of
other specific compounds have been limited in most of the field measurements. The role of oxygenated HC emissions has not been documented at all.

Development of the inventory inherently includes a propagation of uncertainties resulting from errors in (1) emission rate measurements, (2) biomass densities, (3) land use distributions and (4) the single parameter emission model. Previous analyses have suggested the following uncertainties:

1. Enclosure data ± 40% (Lamb et al., 1985)
   Tower data ± 55% (Ibid)
   Tracer flux data ± 30% (Lamb et al., 1986)

2. Biomass densities ± 25% (range of biomass factors, see Lamb et al., 1985)

3. Land use distributions
   ± 15% (internal consistency of Geocology data sets).

The uncertainty associated with the temperature-emission rate model includes the errors from the measurement data. Given the scatter in the data apparent in Figs 1-4, the variability associated with the model dominates the overall uncertainty in the inventory. At any given temperature, the scatter about a particular regression curve is on the order of a factor of three. If the uncertainty in the inventory is estimated as the square root of the sum of squares of the individual uncertainties, the overall uncertainty is approximately ± 210% or a factor of three. This simple uncertainty analysis provides some guidance as to the limits which could be applied when the inventory is used as input to regional acid deposition or photochemical models.

5. CONCLUSIONS

The analysis of available HC emissions data indicates a modest level of consistency among data sets given the diversity in methods, locations, species and time. It appears that the simple temperature-emission model accounts for about half of the variability exhibited among the different data sets. Isoprene emissions are estimated to contribute as much as 80% of the emissions from deciduous vegetation, while α-pinene represents approximately 25% of the total emissions from coniferous vegetation. The emissions data suggest that additional monoterpenes account for the bulk of the remaining NMHC emissions and that other classes of organics are relatively minor contributors.

The availability of the simple emission algorithm, biomass density data from the literature, and land use and temperature data from the Geocology Data Base provide the basis for developing a national inventory of biogenic HCs with a county spatial and monthly temporal scale. Because of the temperature and biomass density dependence, the emissions predicted in the inventory are greatest in the summer and in the S regions of the U.S. The total summertime HC emission rate is 15.9 Mt and the total annual emission rate is 30.7 Mt. On a regional basis, the SE and SW areas each emit approximately 4 Mt in the summer, while the NE and NW regions emit approximately 2.8 Mt during the summer. During the spring and fall, total U.S. emissions are 6.0 and 7.3 Mt, and during the winter the total emission rate is 1.5 Mt.

The emissions are distributed between deciduous and coniferous vegetation. Agricultural crops emit less than 3% of the total emissions. Because of the land area and high biomass density associated with coniferous forests, total emissions from coniferous trees equal 21.7 Mt annually, while emissions from deciduous forests equal 8.0 Mt annually. Isoprene emissions from deciduous trees equal 4.6 Mt annually which is 15% of total emissions. In comparison, α-pinene emissions from coniferous trees are 5.0 Mt annually or 16% of total emissions. Estimates of HC emissions from geochemical soils indicate that geogenic emissions are negligible on a national scale. These estimates were obtained with a simple soil diffusion model using reported soil concentrations and surface area estimates of HC reserves in the U.S.

The total U.S. average flux of biogenic HCs is approximately 430 μg m⁻² h⁻¹ which is approximately 20 times less than the average U.S. flux of anthropogenic HCs from urban land areas. The biogenic emissions estimated in this work are approximately half previous U.S. estimates primarily because of differences in prescribing the land area and land use distributions.

Uncertainties in the inventory results stem from measurement errors in the emissions data, variability in biomass densities, errors in the distribution of land use and vegetation type and the use of a single parameter temperature-emission algorithm. The scatter of data about the temperature-emission curve greatly exceeds the uncertainties from other sources so that the overall uncertainty estimated for the inventory is on the order of a factor of three. This simple analysis of errors does not account for the lack of detailed emissions data for biogenic HCs beyond isoprene and α-pinene.

Acknowledgments — This work was supported by the National Oceanic and Atmospheric Administration (Contract No. NASSRAC05105) as part of the National Acid Precipitation Assessment Program.

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