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Project Summary

Natural Hydrocarbon Emission Rate Measurements from Selected Forest Sites

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Studies of biogenic hydrocarbon emissions were conducted in a hardwood forest in Pennsylvania during 1979 and in a coniferous forest in Washington during 1980. The principal objective of the studies was to compare a branch enclosure method with a micrometeorological gradient technique for measuring biogenic hydrocarbon fluxes for forested areas. A second important objective for the Pennsylvania work was to develop a regional natural hydrocarbon emission inventory for use in the Northeast Regional Oxidant Study.

Isoprene emission fluxes determined by the gradient profile procedure in the deciduous forest agreed reasonably well with those measured using the enclosure technique. The isoprene flux from the gradient profile data was 10% higher than the enclosure flux at 30°C, but was approximately three times greater than the enclosure flux at 20°C. The differences at the low temperatures possibly were caused by the lack of profile data at the lower temperatures. The combined enclosure and gradient profile data were correlated with ambient temperature to the same degree as the correlation of each data set alone. In the Washington study, the alpha-pinene flux as measured by the gradient profile method ranged from 76 to 1,320 $\mu g/m^2$-hr whereas, the range determined using the enclosure method was 9 to 700 $\mu g/m^2$-hr. The mean fluxes from the two methods were within the estimated limits of uncertainty. Alpha-pinene fluxes determined with the gradient profile method increased exponentially with increasing relative humidity. Emission fluxes calculated from the branch enclosure samples were not correlated with ambient relative humidity, but were strongly correlated with temperature when wet and dry branches were considered separately.

Total biogenic hydrocarbon emissions from the state of Pennsylvania were calculated to be 3400 tons/day during August. Approximately 75% of these emissions were from forested lands, and the remainder were from agricultural crops, primarily corn. The forest emissions were approximately evenly divided among isoprene-emitting and non-isoprene-emitting hardwoods and softwood trees.

This Project Summary was developed by EPA's Environmental Sciences Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The significance of naturally emitted hydrocarbons in rural atmospheric chemistry remains uncertain. This uncertainty arises in part from a lack of information concerning the magnitude of sources and the distribution of hydrocarbon species in the atmosphere. Current estimates of natural hydrocarbon emission rates have been obtained using a vegetation enclosure technique, a micrometeorological gradient profile method, and an energy balance/Bowen ratio approach. Confidence in these methods has been limited by uncertainties about the effects of enclosing vegetation and in measurements of small vertical gradients of

temperature, wind speed, and hydrocarbon concentrations above a forest. These experimental problems have prevented widespread agreement upon actual hydrocarbon emission rates.

In this report, field measurements of biogenic hydrocarbon emission rates are reported for the predominant species of trees and some agricultural crops in the northeastern U.S. and for a coniferous forest in the Pacific Northwest. These data were obtained using a vegetation enclosure method and, for the forests, a micrometeorological gradient profile technique. The major objectives of the investigation were (1) to obtain natural hydrocarbon emission rates from vegetation in the northeastern U.S. as a basis for modeling natural hydrocarbon fluxes in the Northeast Regional Oxidant Study (NEROS), (2) to compare emission fluxes determined by a vegetation enclosure technique and a micrometeorological gradient profile method, and (3) to compare the chemical composition of essential plant oils with the composition of gas emissions from selected vegetation.

Procedure

In the forest studies, the flux of a particular hydrocarbon was calculated from surface layer theory, based upon measurements of vertical wind speed, temperature, and hydrocarbon concentration profiles collected along a tower rising above the forest canopy. For the hardwood forest, 30-min average air samples were collected at six levels on the tower using Teflon sampling pumps and 6-L Tedlar bags. For the coniferous forest, 30-min average air samples were collected at five levels on a tower in stainless steel tubes packed with Tenax-GC adsorbent. Vegetation enclosure samples in each of the study areas were obtained using a branch enclosure method. This involved enclosing a branch in a 100-L Tedlar bag, collecting a background sample from the bag, filling the bag with hydrocarbon-free air, and, after a measured length of time, collecting a second sample of the bag air.. When used to develop an area emission inventory, the individual branch emission rates (μg/g-hr) were multiplied by an appropriate biomass factor (g/m^2) to give the area emission flux (μg/m^2-hr). All hydrocarbon samples were analyzed with Perkin-Elmer and Hewlett-Packard gas chromatographs equipped with subambient temperature programming capabilities.

The hardwood forest was located in gently sloping terrain approximately 10 km northeast of York, Pennsylvania. A vegetation inventory of the forest indicated that the woodland was a second growth oak and chestnut forest. The biomass factor for isoprene-emitting species was determined to equal 379 g/m^2 from the vegetation inventory and an empirical relationship between the diameter of the tree at breast height (DBH) and the biomass. The biomass factor for non-isoprene emitting species was 206 g/m^2. The average canopy height was 20 m.

The coniferous forest was located 36 km southeast of Seattle, Washington, in the A. E. Thompson Research Forest (University of Washington). The forest consisted almost entirely of Douglas fir, with red alder, western hemlock, and western red cedar present in small amounts. The age of the stand was 52 years and the average canopy height was 31 m. The biomass factor was estimated to equal 830 g/m^2 from a relationship between biomass and the age of the stand developed specifically for the Thompson forest.

Results

Northeastern Biogenic Hydrocarbon Emissions

Results from the Pennsylvania study indicated that volatile hydrocarbon emissions can be divided into four categories based on similarities in composition and emission source. The first two categories are represented by hardwood trees that (1) emit isoprene and (2) do not emit isoprene. The two remaining groups are (3) monoterpene emitting softwood trees and (4) agricultural crops.

Included in the group of isoprene emitting hardwood trees measured were oak, black locust, and sycamore. Isoprene, which is only emitted during daylight hours, accounted for 78% of the total volatile hydrocarbon emissions from this group. As shown in Figure 1, the emission rates were directly related to temperature in an exponential manner, with 90% of the variation in emission rates associated with temperature variations. The regression relationship between temperature and emission rate predicts a total hydrocarbon emission rate of 6.1 μg/g-hr at 25°C.

The non-isoprene-emitting hardwood trees measured included black gum, sassafras, tulip tree, red maple, dogwood, red hickory, black cherry, beech, silver maple, and birch. The hydrocarbon emissions from these species were also related to temperature in a exponential manner, with 91% of the variation in emission rates associated with temperature fluctuations. The regression relationship between temperature and emission rates shown in Figure 1 predicts an emission rate of 3.4 μg/g-hr at 25°C. Major identified components of the volatile emissions were the monoterpenes α-pinene, sabinene, β-pinene, myrcene, camphene, β-phellandrene, Δ^3-carene, and linalool.

The monoterpene-emitting softwood species measured included eastern white pine, Virginia pine, eastern hemlock, and pitch pine. The volatile emissions from this group consisted of α-pinene, sabinene, camphene, β-pinene, myrcene, β-phellandrene, limonene, and Δ^3-carene. These compounds comprised 50-95% of the volatile emissions. Correlation between emission rate and temperature was not observed for this group; thus, the release of the monoterpenes must be controlled by some temperature-independent process.

The agricultural crop category measured included tobacco, corn, clover, alfalfa, and pasture. This group is poorly defined at present and may require further divisions. The members emitted compounds eluting near the monoterpenes and very small amounts of isoprene. There appeared to be no relationship between emisison rate and temperature.

The emission rates established in this study can be combined with vegetation surveys and biomass relationships to provide estimates of the magnitude of biogenic emissions. Total biogenic hydrocarbon emissions from the state of Pennsylvania were calculated to be 3400 tons/day during August. Approximately 74% of these emissions were from forested lands. The balance was estimated to result primarily from corn (25%) and other agricultural crops and pasture. The forest emissions were approximately equally divided among isoprene-emitting hardwoods (890 tons/day), non-isoprene-emitting hardwoods (710 tons/day), and conifer species (910 tons/day).

In order to gain insight into the processes that control hydrocarbon emissions from vegetation, extracts of essential oils from leaf and branch samples were obtained at the Pennsylvania study site. For the monoterpene-emitting softwoods, the composition of the oils in the needles and branches match the range of compounds identified in the emission samples quite closely. This agreement suggests that volatilization of oils is the major source of emissions from these species. For isoprene-emitting hard-

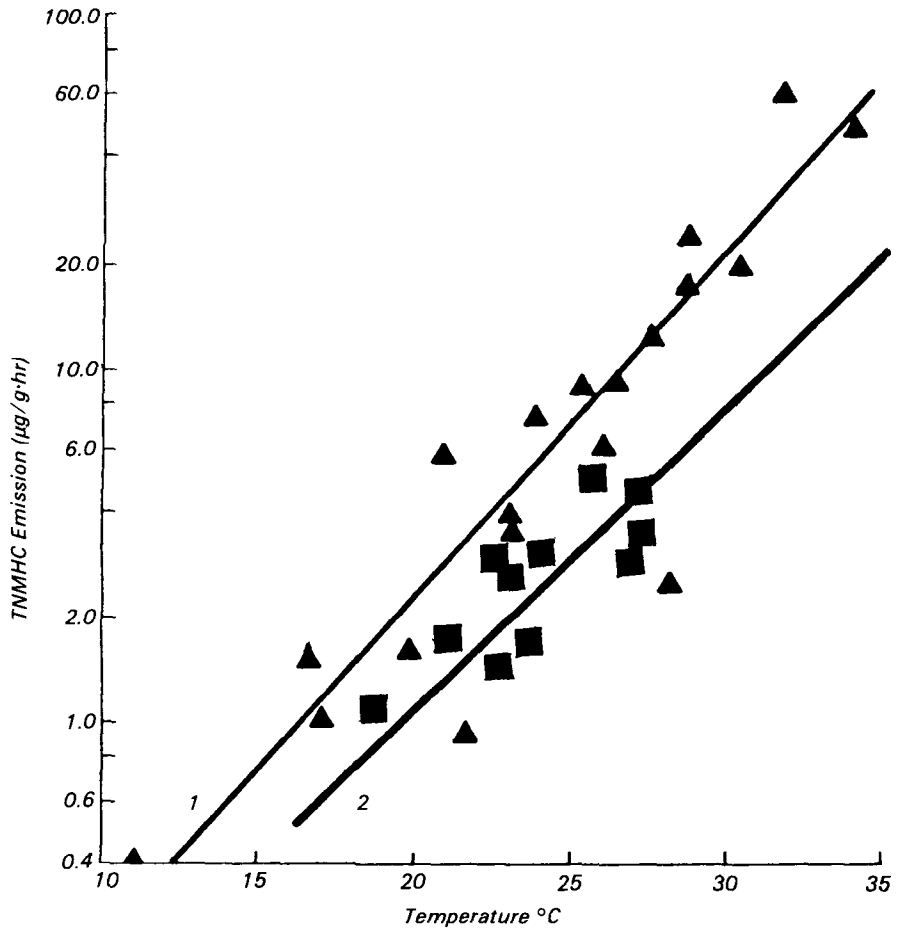

Figure 1. Total nonmethane hydrocarbon emission rate as a function of temperature for isoprene-emitting hardwoods (PA ▲ 1---) and non-isoprene-emitting hardwoods (PA ■ 2---).

woods, the extraction results showed little similarity to the emission samples and no isoprene was measured in the extraction samples.

Comparison of Vegetation Enclosure and Micrometeorological Gradient Techniques

In Pennsylvania, isoprene fluxes measured by both techniques were observed to vary exponentially with temperature. The isoprene flux estimated from the enclosure data at 20°C ambient was 890 μ-g/m^2-hr and the flux calculated from the gradient profile data was 2510 μ-g/m^2-hr. At 30°C ambient, the difference between estimates obtained using the two methods was approximately 10% (7300 μ-g/m^2-hr from the enclosure data and 8000 μ-g/m^2-hr from the gradient profile method). The differences at 30°C were within the estimated experimental uncertainty of the two methods of measurement, but the results at the lower temperature were not within the error limits. However, very few gradient profile experiments were conducted at low temperatures. Furthermore, as shown in Figure 2, the combined data from the enclosure and gradient profile measurements were correlated with ambient temperature to the same degree as either data set alone. Thus, the data obtained in Pennsylvania indicate that the two independent methods for measuring isoprene flux yield results that are in reasonable agreement.

In Washington, alpha-pinene flux measured via the gradient profile technique increased exponentially with increasing relative humidity at relative humidities greater than approximately 60%. The calculated flux was also positively correlated with the ratio of relative humidity to wind speed as shown in Figure 3. Alpha-pinene fluxes were only weakly correlated with ambient temperature. The mean flux of alpha-pinene measured in seven gradient profile experiments was 440 μg/m^2-hr (median = 230 μg/m^2-hr), with a range of 76 to 1320 μg/m^2-hr.

The mean alpha-pinene flux estimated from 13 enclosure samples was 150 mg/m^2-hr (median = 46 μg/m^2-hr) with a range of 9 to 700 μg/m^2-hr. No relation between ambient relative humidity and alpha-pinene flux was observed in the enclosure data. However, when the samples were grouped according to wet and dry branches, a distinct exponential relationship with increasing ambient temperature was evident, as shown in Figure 4.

No single environmental parameter was correlated with the fluxes determined by both methods. As a result, it was not possible to compare directly fluxes predicted for a common reference point, as was done for isoprene as a function of temperature. The mean flux of alpha-pinene for the gradient profile experiments and the mean flux predicted by the enclosure samples were within experimental uncertainties estimated for the two methods. The wide range of fluxes observed was not a result of random experimental errors. Rather, changes in environmental conditions such as temperature and humidity were observed to affect the emission rates dramatically. In view of the strong dependence of flux upon humidity, the low fluxes determined with the enclosure method suggested that humidity inside the bag was generally lower than ambient.

The error limits estimated for the two techniques were based on standard error analysis procedures. Data from typical experiments were combined with estimated or measured uncertainties in the independent variables to calculate the overall error and degree of reproducibility in each flux method. In Pennsylvania, the error in the gradient profile method was estimated to equal ± 35%; in Washington, the error was approximately ± 55%. The major sources of error were uncertainties in the zero plane displacement height and the hydrocarbon concentration gradient. The gradient profile method is estimated to be reproducible to within less than ± 17% for test conducted at a specific site. The overall error estimated for a typical enclosure sample was ± 40%, and the technique was estimated to be reproducible to within ± 20% for samples collected in a particular forest.

Summary and Conclusions

For a typical northeastern deciduous forest, isoprene emissions accounted for approximately 78% of the total non-

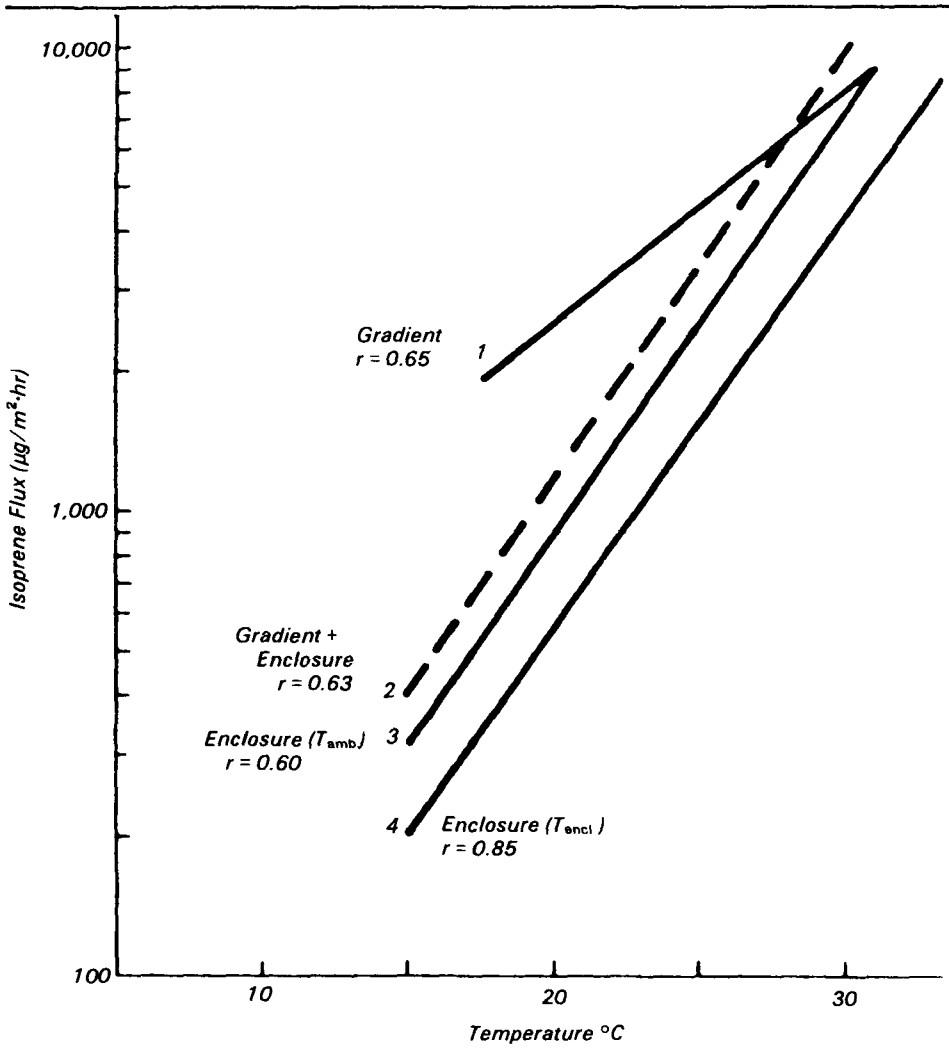

Figure 2. *Isoprene flux as a function of ambient temperature measured at 6m above the canopy by the gradient profile method (line 1), the gradient profile and enclosure method (line 2), and only the enclosure method (line 3) for Pennsylvania. Line 4 is from the Pennsylvania enclosure data as a function of enclosure temperature.*

methane hydrocarbon emission rate. Isoprene concentrations and isoprene emission fluxes increased exponentially with ambient temperature. At 30°C, the emission flux of isoprene was approximately 8000 $\mu g/m^2$-hr. Results from the vegetation enclosure method and the micrometeorological technique generally agreed well.

The emission rates of alpha-pinene measured by the gradient profile method in a northwestern Douglas fir forest were closely correlated with relative humidity. Emission rates measured by the enclosure method were not correlated with ambient relative humidity. However, emission rates from wet branches were an order of magnitude higher than those for dry branches. Alpha-pinene emission rates from both wet and dry branches increased exponentially with increasing ambient temperature. During the autumn sampling period, the emission flux of alpha-pinene was less than 1800 $\mu g/m^2$-hr and ambient concentrations above the canopy were less than 1 $\mu g/m^3$. In this case, the range of fluxes observed via the enclosure and gradient methods overlapped, but the median values did not agree within the estimated uncertainty of the methods.

The comparisons between the two measurement techniques in Pennsylvania and in Washington have better defined the reliability of emission flux estimates. Although the usefulness of data collected with the enclosure method has been disparaged previously, the results reported here show that the enclosure method yields emission fluxes quite similar to those obtained with a totally independent technique.

The enclosure system is portable, easily operated by one person and not limited to idealized sites. However, care is required to use the enclosure method. Enclosure conditions must be closely monitored in order to relate the data to ambient conditions. Biomass factors must be developed from site-specific inventories and representative biomass relationships. In comparison the gradient profile method involves considerable effort and instrumentation, the site requirements are restrictive to the point of being impractical, and the uncertainties in specifying the zero plane displacement height and property gradients reduce the applicability of the technique to the kind of comparative studies described in this report.

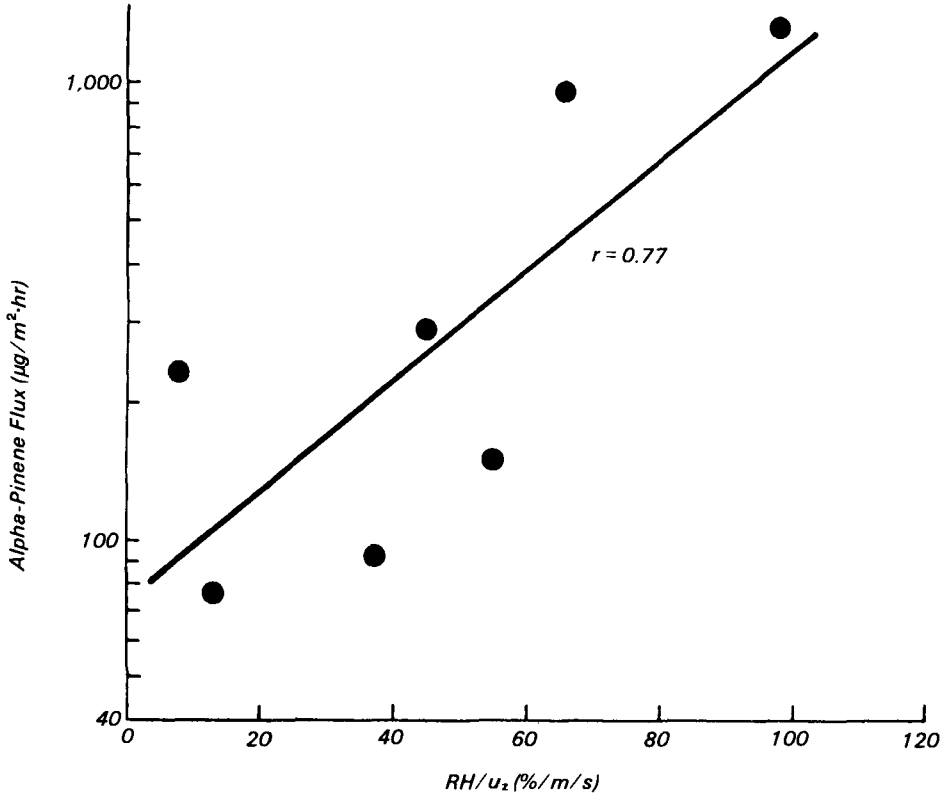

Figure 3. *Alpha-pinene flux as a function of relative humidity/wind speed measured by the gradient profile method.*

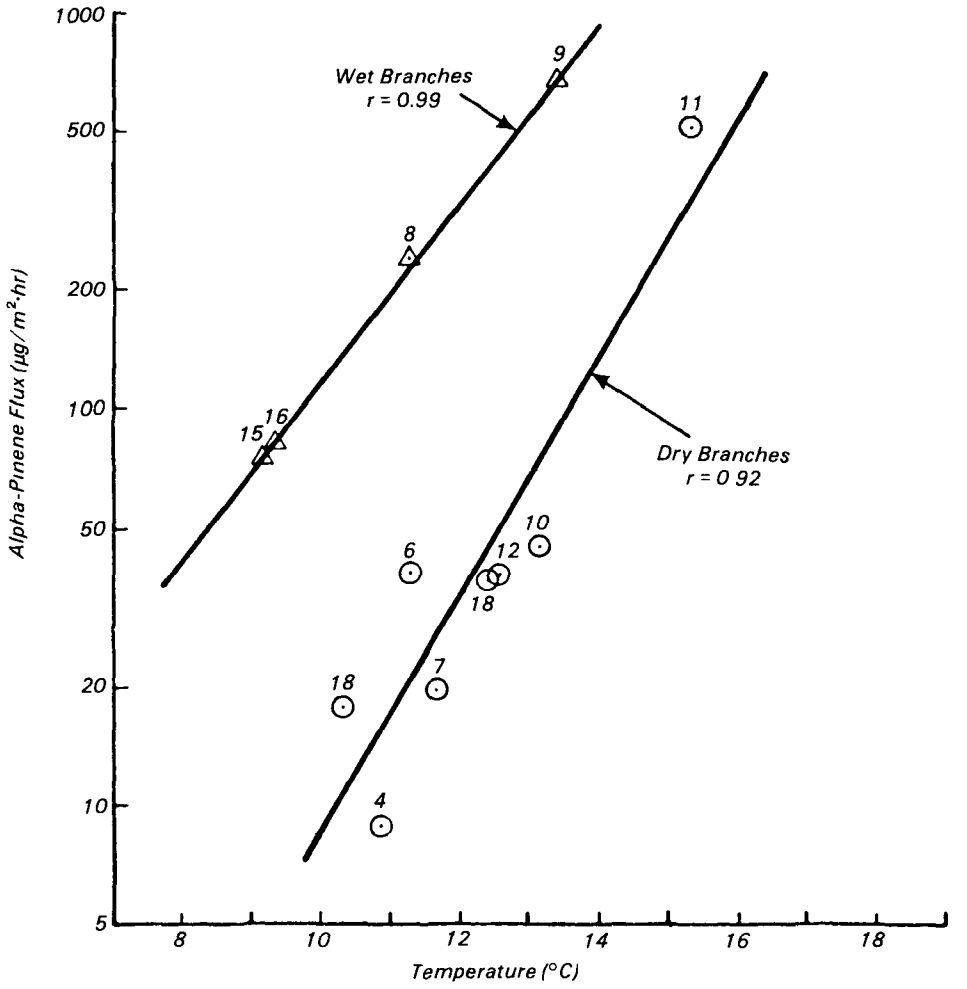

Figure 4. *Alpha-pinene flux as a function of ambient temperature measured by the enclosure method.*