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THE BEMA-PROJECT—A NORTH AMERICAN PERSPECTIVE

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Abstract—Until recently, European regulatory agencies and photochemical modelers had to use biogenic hydrocarbon emission models that were based almost entirely on the results of investigations in North America. Field studies of biogenic hydrocarbon emissions have been conducted in North America and Europe for more than two decades but it is only recently that there has been an attempt at multi-disciplinary (plant physiologists, micrometeorologists, atmospheric scientists, landscape ecologists) field studies. Whereas past studies involved a few scientists with similar backgrounds, recent studies have been much more multi-disciplinary efforts involving more scientists. In North America, investigations of biogenic hydrocarbon emissions have been important, but relatively minor, components of regional studies such as the Southern Oxidant Study in the United States and the BOREAS experiment in Canada. None of these studies approach the level of participation in biogenic emission studies that occurred in the BEMA program. The BEMA project also addressed another issue that is gaining interest in North America, seasonality. Variation in emission rates through the year need to be incorporated into models and longer field campaigns need to be incorporated into future experimental programs to better determine seasonality of hydrocarbon emissions. The BEMA study has provided valuable insight into hydrocarbon emissions in the Mediterranean ecosystem. Both the similarities and differences between this ecosystem and typical North America ecosystems help us to understand biogenic hydrocarbon emissions. © 1997 Elsevier Science Ltd.

Key word index: Biogenic hydrocarbons, BOREAS, isoprene, scaling, Southern Oxidant Study.

INTRODUCTION

Ozone pollution of the lower atmosphere is the most significant air pollution problem in large areas of the world. Substantial effort has gone into reducing human acitivities that cause ozone pollution but with somewhat disappointing results. More sophisticated measurements of the harmful effects of ozone pollution on human health and crop productivity have resulted in calls for making the ozone pollution standard even more stringent. If past efforts to control ozone have been disappointing, will it be possible to convince countries to undertake the drastic measures that may be called for in order to reduce the ozone pollution problem? This problem is especially acute in regions where pollution from one country impacts another, or in the U.S., where one state must endure more onerous restrictions than a second state to keep the air in the second state clean. A substantial flaw in early attempts to control ozone pollution was the assumption that the only chemicals entering the atmosphere that needed to be considered in models were anthropogenic chemicals. Emissions of the pleasant smelling monoterpenes from pines, etc. were obvious but considered small. Less obvious was the large amount of isoprene emitted, especially from North-American oaks. Finally, there may be substantial amounts of other, especially oxygenated, hydrocarbons emitted which cannot yet be reliably measured. These biogenic emissions of hydrocarbons probably play an important role in atmospheric chemistry but assessments of total biogenic emissions have been hampered by a lack of data, both in North America and in Europe. These reports from the BEMA project and studies in North America have provided important new information on isoprene and monoterpenes, but the amount of biogenic oxygenated hydrocarbons, possibly the most important compounds, remains difficult to quantify.

A high point in the road to realizing that biogenic hydrocarbons contribute substantially to the hydrocarbon load on the atmosphere was published by Chamedies *et al.* (1988). The idea of pollution from trees, put into words 16 years earlier by Rasmussen (1972), caught the attention of the public and government regulators. How much hydrocarbon was coming from the vegetation? Surprisingly little was known. How could biogenic emissions be estimated? Only crude models were available. Plant physiologists were generally unaware of the substantial emissions of hydrocarbons from plants and so the basic physiological and ecological understanding necessary to make high quality models of hydrocarbon emissions did not exist.

Until recently, European regulatory agencies and photochemical modelers had to use biogenic hydrocarbon emission models that were based almost entirely on the results of investigations in North America. Simpson *et al.* (1995) made an initial attempt to incorporate European measurements into a regional biogenic HC emission model but even this effort relied heavily on models developed for the United States. The BEMA program began a move towards supplying the necessary information for estimating biogenic emissions in Europe. Field studies of biogenic hydrocarbon emissions have been conducted in North America and Europe for more than two decades but it is only recently that there has been an attempt at multi-disciplinary (plant physologists, micrometeorologists, atmospheric scientists, landscape ecologists) field studies. Whereas past studies involved a few scientists with similar backgrounds, recent studies have been much more multi-disciplinary efforts involving more scientists. Biogenic hydrocarbon emission studies are now recognized as an important component of many earth system science research programs. In North America, investigations of biogenic hydrocarbon emissions have been important, but relatively minor, components of regional studies such as the Southern Oxidant Study in the United States and the BOREAS experiment in Canada. None of these studies approach the level of participation in biogenic emission studies that occurred in the BEMA program. The North American effort was more fragmented than BEMA and less basic physiology was supported. This reflected a strong desire in North America to get workable, regional, atmospheric models that could be defended in the regulatory arena as quickly as possible.

Part of the focus of the BEMA project was selection of one site for all investigators. This site needed to be varied enough to provide examples of important ecological communities and weather patterns. In order to study diverse communities, the North-American Southern Oxidants Study targeted one city for an intensive one to two year campaign, then moved on to another city. Members of the BEMA project were able to focus on just one site, Castelporziano. Ozone is a particular problem in the southeastern U.S. and much of the U.S. data are for conditions in that region. Ozone is often well above air quality standards in the Mediterranean area and it is not well established whether the factors that control ozone production in North America will be the same as those in the Mediterranean.

The Presidential estate of Castelporziano is a very favorable site to study the emission of biogenic compounds from Mediterranean vegetation and the fate of these chemical species in the atmosphere. This site: (a) has been preserved from agricultural and urban exploitation and represents one of the oldest natural preserved areas in Italy; (b) includes a large and relatively pristine forest with a plant community highly representative of the natural vegetation in Mediterranean environments; (c) is located within a large strip between the Mediterranean sea and the urban area of Rome. This important characteristic allows study of the interaction between compounds of marine, vegetative, and anthropogenic origins in an environment which is nowadays typical in Mediterranean countries. (d) It is exposed to a typical Mediterranean climate and the vegetation copes with frequent episodes of stress including recurrent summer drought and the exposure to sea aerosols across the year. A detailed description of the site is reported by Manes *et al.* (1997a).

One remarkable and commendable aspect of the BEMA project is the interlaboratory cooperation. The intercomparison of laboratory methods reported by Larsen *et al.* (1997) gives confidence that monoterpenes can be accurately quantified. The basic ecophysiology of some of the important plant species was reported by Manes *et al.* (1997b). They found that species differed in their response to environmental stress in ways likely to impact VOC emission. This background information will be useful in designing reasonable scenarios for the physiological condition of different plant species throughout the year.

Plant level measurements were made using branch enclosure chambers with a flowing air stream (Enders *et al.*, 1997). The air stream was sampled by pulling air through an absorbant trap in most cases. The trap and branch chamber was varied in order to optimize each system for the intended measurement. The branch chamber method has the advantage of integrating over several parts of the tree or plant but the disadvantage of some loss of physiological information because signals from different leaves will be averaged and differences in responses among leaves will get smoothed out. The branch chamber method makes an important step up in level of complexity from the biochemical reactions in each cell to the atmospheric level. The intercomparison showed that isoprene is relatively robust, and many different measurement techniques work well. However, for some less stable molecules, the collection and measurement system can strongly influence the results.

SCALING TO CANOPIES

In order to scale hydrocarbon fluxes from the leaf to canopy scale, leaf emission algorithms need to be parameterized. The generally accepted model originates with work by Guenther and colleagues. They have demonstrated that isoprene emissions are a function of absorbed sunlight and leaf temperature, while VOC emissions tend to be predicted solely as a function of leaf temperature.

Several teams attempted to fit their data to the Guenther model (e.g Steinbrecher *et al.*, 1997; Bertin *et al.*, 1997; Staudt *et al.*, 1997). Of note are the data of Steinbrecher *et al.* They attempted to parameterize the Guenther model for several Mediterranean oak species. They found the algorithm to work well for predicting maximum rates, but it did not mimic the diurnal pattern well. It is well known from plant physiology studies of carbon and water exchange that diurnal patterns of fluxes are asymmetric when vegetation is water stressed (Körner, 1994). Vegetation stress is a common occurrence for Mediterranean vegetation. As part of this study, Manes *et al.* made relevant gas exchange measurements and reported that limited soil moisture and large vapor pressure deficits limit carbon assimilation through stomatal closure. On the basis of key physiological data, Steinbrecher *et al.* speculate that changes in carbon partitioning affected the carbon flow into isoprene synthesis. A conclusion drawn from Steinbrecher's study is that diurnal effects may need to be incorporated into the Guenther algorithms for application to dry Mediterranean systems. This may be accomplished at a process level by evaluating how carbon is partitioned and how much is available for isoprene synthesis.

The BEMA project also addressed another issue that is gaining interest in North America. Plants exhibit pronounced seasonality of carbon and water flux rates so it is reasonable to expect VOC emission to vary seasonally too. Staudt *et al.* (1997) provide good evidence that the emission factors for monoterpenes vary over the growing season between May and October. Such variations need to be incorporated into models and longer field campaigns need to be incorporated into future experimental programs to better determine seasonality of hydrocarbon emissions.

Complex interactions between vegetation and the atmosphere can cause leaf and air temperature to be decoupled and the amount of sunlight incident upon the canopy to vary with depth within a plant crown and on sunlit and shaded leaves. Experimental measurements by Manes *et al.* showed that within canopy gradients of temperature, humidity and light were great enough to cause substantial variations of emission rates throughout the canopy. Hence, proper scaling fluxes from the leaf to canopy level requires coupling leaf-level fluxes to a canopy micrometeorological model. While the BEMA project did an excellent job parameterizing leaf-level fluxes and collecting canopy-scale fluxes, relatively little effort was made developing and testing big-leaf (BEIS) and multi-layer (CANOAK)-type models. This is an activity we would recommend in the future.

TYPES OF PLANTS AND EXISSIONS

The prevalent tree species in the forest of Castelporziano are of the *Quercus* family. North-American oaks are among the most important emitters of isoprene, the most abundant biogenic emission in that continent, but do not emit other hydrocarbons in any appreciable amount. In contrast, the Mediterranean evergreen *Quercus ilex* emits a wide range of biogenic compounds including at least 14 monoterpenes and many other derivatives (Loreto *et al.*, 1996) but do not emit isoprene. Because of the wide range of oak species present in the forest, Castelporziano is an ideal site to carry out field studies on the emission of these plant species. The reported results show that Mediterranean oaks include both strong isoprene (*Q. pubescens*) and monoterpene (*Q. ilex*) emitters, a circumstance that makes emission from vegetation different with respect to North America (Steinbrecher *et al.*, 1997). A question therefore arises: despite the observed differences in the emitted compounds, is it possible to model the biogenic emission from Mediterranean vegetation by using the algorithms proposed for North-America vegetation? Recent laboratory studies have shown interesting similarities between the biosynthetic pathway, of monoterpenes in *Q. ilex* and of isoprene in North-American *Quercus spp.* (Loreto *et al.*, 1996). Consequently, the response to environmental factors is similar, irrespective of the emission type. This result, if confirmed by field studies and extended to other oak species, may make it possible to use the Guenther algorithms used for isoprene emission, even if minor modification may be required depending on regional differences of vegetation and emission types. The study conducted in Castelporziano forest is a first step in this direction and the results collected and released by the participating groups are of extreme interest both for a better understanding of the emission from vegetation around the globe and for refining the models presently available to predict biogenic emission and their reactivity in the atmosphere (Bertin *et al.*, 1997; Ciccioli *et al.*, 1997; Hansen *et al.*, 1997; Staudt *et al.*, 1997).

While the plants of the oak family are favorite specimens for laboratory research and process-studies, information about the emission from other plants composing the natural Mediterranean vegetation are scarce. The Castelporziano field campaigns also offered a nice opportunity to examine qualitatively and quantitatively the emission of biogenic compounds from a vegetation typical of the Mediterranean (Ciccioli *et al.*, 1997; Hansen *et al.*, 1997; Owen *et al.*, 1997). This ranges from grass-dominated dunal vegetation, to semi-desertic plant communities (pseudo-steppe), to areas reforested with pines and Eucalyptus, to groves composed by Mediterranean shrubs both of natural origin (mainly plants of the genera *Pistacia, Olea, Quercus, Myrtus*), and of anthropogenic origin (mainly cork oaks).

In Castelporziano, the presence of the same plant species in areas characterized by different soil and by different exposure to the environment, allowed interesting observations on the response of the emission to environmental factors. For instance *Q. ilex* is present in the dunes where it is exposed to salt stress and to coastal winds. The same species constitutes groves and forests in more secluded areas where growth is improved by water availability and wind protection. These communities of *Q. ilex* show different canopy architectures, and physiological characteristics (Manes *et al.*, 1997b). Such differences may well account for different emission of biogenic compounds in plants grown under different microclimate, a possibility which deserved to be assessed both with respect to total canopy flux and effect of stressful condition on emission models (Owen *et al.*, 1997).

THE CANOPY TO ATMOSPHERE

Micrometeorological flux measurement techniques have been used to investigate canopy-scale VOC fluxes in the U.S. for about two decades. Although the results of the earliest studies were accompanied by large uncertainties, they provided convincing evidence that the emission estimates based on enclosure techniques were reasonable. Enclosure measurements, especially for compounds such as monoterpenes, are often associated with increased emissions due to disturbance and this led many to conclude that regional flux estimates based on enclosure measurements were grossly overestimated. Arnts *et al.* (1978) used an above canopy gradient technique to investigate α-pinene emissions from a pine forest and demonstrated that the estimated fluxes were in reasonable agreement with enclosure measurements. The recent application of micrometeorological methods to measure above canopy VOC fluxes during the BEMA project is an important advancement in efforts to investigate and evaluate biogenic emissions in Europe.

The eddy covariance, flux-gradient, and relaxed eddy-accumulation method are three possible methods for measuring VOC fluxes. The eddy-covariance method measures the covariance between vertical velocity and scalar concentration fluctuations. Isoprene fluxes can be measured using the eddy-covariance technique (Guenther and Hills, 1997) but the fast response chemical sensors (time constant on the order of 0.2 s and shorter) required for this technique are not available for other VOCs. The flux-gradient method determines fluxes as the product of a turbulent diffusivity and a vertical gradient. The flux-gradient method needs to resolve very small vertical gradients. This task is difficult and analytically demanding when turbulent mixing is great or fluxes are small. The relaxed eddy-accumulation method has much promise as a tool for measuring emission rates of volatile organic compounds. Air associated with updrafts and downdrafts can be sampled in respective reservoirs and analyzed later for concentration differences ($C_{up} - C_{dn}$). Fluxes are then evaluated as

$$F = B\sigma_w(C_{up} - C_{dn})$$

where B is the Businger coefficient, which is on the order of 0.6 and σ_w is the standard deviation of vertical velocity.

The Castelporziano phase of the BEMA project included the application of two micrometeorological techniques (flux-gradient and REA) to measure VOC fluxes. Ciccioli *et al.* (1997) used the flux-gradient technique to measure fluxes of a variety of VOC from a Mediterranean pseudosteppe ecosystem. This ecosystem is a good example of a landscape where enclosure methods are not easily applied since emissions are apparently associated with a wide variety of shrubs and herbs rather than a few dominant species. Both REA and flux-gradient methods were used to measure VOC fluxes above the pine-oak forest at Castelporziano. Valentini *et al.* (1997) validated the REA method by comparing it with CO_2 fluxes measured by the eddy covariance method; they found fluxes to agree within 15%. They then applied the REA method towards the measurement of a whole spectrum of volatile organic compounds. A key finding of their work was support of chamber studies that Mediterranean oaks do not emit isoprene but emit a broad spectrum of monoterpenes and other organic compounds, e.g. α-pinene, β-pinene, limonene and *trans-β* ocimene. For cases involving VOCs with small fluxes and background concentration, the REA method had a distinct advantage over the gradient method. Valentini *et al.* were able to resolve fluxes of linalool-oxide, α-terpinene and α-thujene with the REA, but fluxes of these compounds were below the detection limit of the gradient system. Schween *et al.* (1997) found that flux-gradient method has errors on the order of 50% for monoterpene flux measurements.

While many advances have been made with regard to the REA in recent years, analytical sampling methods are still a subject of development. At present the method is very labor intensive. There needs to be developments that enable automated sampling and detection to facilitate longer term studies. There is also a major issue with regards to real-time coordinate rotation of the wind velocity axes. From first principles, small bias errors in vertical velocity will cause fluxes to be biased. Over tall forests and undulating terrain, it is impossible to mount sonic anemometers from towers that are perfectly oriented. Software and hardware development are needed and tests need to be conducted to examine errors associated with the omission or inclusion of real-time coordinate rotation and the binning of air streams into up and down draft samples.

The BEMA project has improved our understanding of biogenic emissions in the Mediterranean area. This will enable more accurate estimates of the photochemical precursors required for numerical simulations of oxidant production in this region. Additional studies are needed to encompass the entire Mediterranean area and other parts of Europe. These studies should continue to place a priority on multidisciplinary studies that include leaf and canopy-scale measurements. Future studies would benefit by integrating biogenic VOC emissions studies with regional-scale photochemistry and meteorology investigations. Since biogenic VOC emissions are also important for global-scale models, European researchers should also be working towards stronger collaborations and intercomparisons with investigators from outside of Europe in order to provide the information needed for earth system models which are beginning to be used to study potential changes to the global environment.

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