Journal of Atmospheric Chemistry **42:** 159–177, 2002.

Emission of Biogenic Volatile Organic Compounds: An Overview of Field, Laboratory and Modelling Studies Performed during the 'Tropospheric Research Program' (TFS) 1997–2000

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(Received: 1 June 2001; accepted: 11 September 2001)

Abstract. The present paper summarises results on the emission of biogenic volatile organic compounds (BVOC) achieved within the frame of the national 'German Tropospheric Research Programme' (TFS) between 1997 and 2000. Field measurements were carried out at the meteorological monitoring station 'Hartheimer Wald' located in the vicinity of Freiburg (upper Rhine valley), Germany, within a pine plantation dominated by Scots pine (*Pinus sylvestris* L.). The measured BVOC emission rates were used to determine the daily and seasonal variation of BVOC emission and its dependence on important meteorological and plant physiological parameters. In parallel, laboratory experiments using young trees of pine (*P. sylvestris*), poplar (*Populus tremula* × *P. alba*) and pedunculate oak (*Quercus robur* L.) were performed, and the influence of abiotic (e.g., light, temperature, seasonality, flooding) factors on the biosynthesis and emission of BVOC was quantified. Based on these data, emission algorithms were evaluated and a process-oriented numerical model for the simulation of the isoprene emission by plants was developed. In addition, newly calculated land use and tree species distributions were used for the calculation of an actual BVOC emission inventory of Germany.

Key words: biogenic volatile organic compounds, BVOC, models, emission inventory of Germany, isoprene, monoterpene, acetaldehyde.

1. Introduction

Volatile organic compounds (VOC) play an important role in atmospheric chemistry. VOC globally interact with atmospheric radicals which influence the oxidation capacity of the troposphere and hence the concentration and distribution of other environmentally important trace gases (Thompson, 1992). In addition, volatile compounds formed during the degradation of VOC are able to depose on existing particles or lead to the formation of secondary particles. These particles influence the chemistry of the atmosphere and the radiation balance of the earth (Brasseur *et al.*, 1999).

The estimation of annual global flux of isoprene and monoterpenes from vegetation ranges from 250 to 450 and from 128 to 450 Tg C per year, respectively (Fall, 1999) corresponding to about 2% of globally photosynthetically fixed carbon (Lal, 1999). Due to the lack of data concerning emission rates, the flux of oxygenated volatile organic hydrocarbons from the biosphere into the atmosphere cannot be calculated exactly. Guenther *et al.* (1995) roughly estimated that the emission of volatile organic compounds other than methane, isoprene and monoterpenes, (OVOC), including oxygenated species such as aldehydes, alcohols and carboxylic acids, amounts to about 24% of the total budget of hydrocarbons in forest ecosystems. The contribution of VOC from anthropogenic sources to the emission is much lower, approximately 150 Tg C per year, indicating that on the global scale biogenic emissions play a dominant role in atmospheric chemistry.

However, the mass balance between biogenic and anthropogenic VOC emissions is changed in industrialised and heavily polluted areas compared to remote environments. On a yearly basis anthropogenic emissions dominate in these areas. Nevertheless, two important aspects have to be considered when assessing the contribution of different VOC sources to regional photosmog episodes. (a) The contribution of BVOC to the overall emission is strongly influenced by temperature and light intensity as well as seasonal fluctuations, which are related to the physiological activity of plants. During summer, especially during sunny and warm high-pressure weather episodes, the estimated biogenic emission of Germany can exceed the anthropogenic VOC emission (Richter *et al.*, 1998). (b) BVOC are mostly unsaturated and partly oxygenated hydrocarbons that are more reactive and have a higher ozone formation potential compared to most of the anthropogenic VOC (Derwent *et al.*, 1998). As a consequence, BVOC emissions contribute significantly to the formation of photosmog episodes in densely populated areas.

In recent years, much progress was made regarding the production pathways of volatile organic hydrocarbons in plants; this is particularly true for the understanding of the synthesis of isoprenoids and oxygenated VOC as well as setting up BVOC emission inventories. The present overview summarises the current

progress concerning the biosynthesis and emission of isoprenoids as well as oxygenated volatile organic hydrocarbons of important European forest trees (*P. sylvestris*, *Q. robur*, and *P. tremula* × *P. alba*) obtained in the frame of the 'German Tropospheric Research Programme' (TFS) between 1997 and 2000. In addition, it discusses biochemical and physiological aspects leading to a validation of existing monoterpene emission algorithms and the formulation of a process-based isoprene emission model for oak leaves. In addition, newly calculated land use, European tree species and leaf area index (LAI) distributions were used to calculate an actual, grid-based BVOC emission inventory of Germany with high temporal and spatial resolution.

2. Isoprene Emission of Oaks

Isoprene (2-methyl-1,3-butadiene) is one of the most studied biogenic VOC. The global annual isoprene flux from vegetation is of a similar magnitude to that of methane (Guenther *et al.*, 1995). Plants mainly emit isoprene, but not all plants emit isoprene. In general, most of the isoprene emitters are woody tree species with the highest emission rates found in the genera *Quercus* (oaks) and *Populus* (poplar) (Harley *et al.*, 1998; Kesselmeier and Staudt, 1999) but also some herbaceous species as well as fern and moss species emit isoprene (Harley *et al.*, 1998). There is no clear phylogenetic basis for isoprene emission in plants. Isoprene is produced in many plant families, and in families containing isoprene-emitting species also non-isoprene emitters were found. A good example for this variability is the isoprene emission potential of oak trees. While all North American oaks are high isoprene emitters, many European oak species are non-isoprene emitters and many of them, especially the evergreen ones, emit monoterpenes in a light-dependent manner (Cisky and Seufert, 1999).

Despite its importance as a significant carbon loss for the plant, the function of isoprene for plants still remains unclear. Since isoprene formation is stimulated by high irradiance and warm temperatures, it is suggested that isoprene production improves the thermotolerance by helping photosynthesis to cope with high temperatures (Sharkey *et al.*, 2001, and references therein). The proposed mechanisms of this profound effect are an actual matter of debate (Logan *et al.*, 2000).

2.1. MECHANISMS OF ISOPRENE FORMATION

Plants synthesise isoprene via a recently identified isoprenoid pathway (named MEP-pathway according to the first specific intermediate) localised in the chloroplasts of the cells and not via the mevalonic acid pathway, as was originally proposed (for review see Lichtenthaler, 1999; Logan *et al.*, 2000, and references therein). In this new pathway pyruvate and glyceraldehyde 3-phosphate are the initial substrates for an initial reaction resulting in 1-deoxy-D-xylulose 5-phosphate (DOXP). The next step is the formation of 2-*C*-methyl-D-erythritol 4-phosphate

(MEP). In three further reaction steps MEP is converted to 2-*C*-methyl-D-erythritol 2,4-cyclodiphosphate (MECDP). To date this is the last known reaction leading to isopentenyl diphosphate (IDP) and dimethylallyl diphosphate (DMADP). Several lines of evidence confirm that all plastid-derived isoprenoid compounds of plants, including isoprene, mono- and diterpenes, carotenoids, plastochinones, as well as the prenyl side chains of chlorophyll (see Lichtenthaler, 1999) are synthesised via the MEP-pathway.

The final step in isoprene formation, the conversion of DMADP to isoprene and pyrophosphate, is catalysed by isoprene synthase. Isoprene synthases have been isolated and characterised several times from different plant species (Fall, 1999, and references therein) including pedunculate oak (*Q. robur*) (Lehning *et al.*, 1999), and recently an isoprene synthase gene from poplar was isolated and functionally expressed in bacteria (Miller *et al.*, 2001). All enzymes have similar catalytic properties including a pH optimum of approximately 8.0, a requirement for divalent metal ions (usually Mg^{2+} or Mn^{2+}), and relatively high K_m-constants in the range of 0.5–8 mM for its substrate DMADP. All isoprene synthases are strongly temperature dependent reaching an optimum at 45–50 °C. Regulation of isoprene synthase activity *in vivo* is still an actual matter of debate (Logan *et al.*, 2000). *In vitro* measurements of extracted isoprene synthase activity from oak (*Q. robur*) (Lehning *et al.*, 1999; Zimmer *et al.*, 2000; Brüggemann and Schnitzler, 2001) demonstrated that under optimal conditions in the illuminated chloroplast stroma, enzymatic isoprene formation from oak leaves can account for the observed leaf isoprene emission rates. Regulation of isoprene emission by light may be due to light-dependent activation of isoprene synthase and/or light-dependent production of DMADP from photosynthetic intermediates. A light-attributed increase in DMADP concentration could be attributed to light-induced increase in fluxes of intermediates through the plastidal MEP-pathway leading to increased stromal DMADP concentrations. Preliminary measurements of DMADP concentrations in oak leaves (Brüggemann and Schnitzler, personal communication) indicate that in illuminated chloroplasts DMADP concentrations of up to 1 mM can be reached. This supports the hypothesis that isoprene formation in oaks is regulated, at least at the level of isoprene synthase, by control mechanisms such as supply of DMADP, rather than by activation or deactivation of the mature isoprene synthase protein.

2.2. ENVIRONMENTAL CONTROLS OF ISOPRENE EMISSION

A substantial volume of information has accumulated over the last decade about the response of isoprene emission rates to a number of environmental factors (for review see Fall, 1999; Logan *et al.*, 2000, and references therein). Most of the responses can be interpreted in terms of the response of isoprene synthase activity to prevailing light and temperature conditions. Daily short-term variations of isoprene emission rates can be explained by the temperature dependence of isoprene synthase activity and other related enzymes of the isoprenoid pathway, e.g. IDP

isomerase (Zimmer *et al.*, 2000) and reflects the response of leaf isoprene emission to temperature (Monson *et al.*, 1992). The correlation with photosynthetic active radiation (PAR) is consistent with the light saturation response of photosynthetic processes in the leaves (Harley *et al.*, 1997). Other factors such as soil moisture fluctuations, CO_2 mixing ratio and stomatal conductance seem to a have minor influence on the short-term variations of leaf isoprene emission rates (Guenther *et al.*, 1991). Although regulatory mechanisms controlling isoprene emission are not fully elucidated, experiments with pedunculate oak (*Q. robur*) gave good evidence that long-term and seasonal variations in basal isoprene emission capacity (Monson *et al.*, 1994) can be explained by long-term variations in the amount of active isoprene synthase (Lehning *et al.*, 2001). This basal emission capacity depends on physiological adaptations, e.g., leaf expansion and development, or the position of the leaf in the tree canopy, which seem to be triggered by growth temperatures in spring, availability of nutrients, UV-B radiation, or genetic disposition (for overview see Fall, 1999).

2.3. EMISSION MODELLING: FROM BIOCHEMICAL MECHANISMS TO A PROCESS-BASED EMISSION MODEL

The rapid increase of molecular and biochemical knowledge about isoprenoid biosynthesis in chloroplasts (see sections above) have been used to develop a process-based **B**iochemical **I**soprene emission **M**odel (BIM) which considers the enzymatic reactions in pedunculate oak (*Q. robur*) leaf chloroplasts leading to the formation of isoprene under varying environmental conditions. Isoprene biosynthesis is strongly correlated with the formation of the first stable product of photosynthetic CO_2 fixation, 3-phosphoglyceric acid (see Logan *et al.*, 2000). Thus BIM is based on the photosynthetic supply of carbon. Therefore, important prerequisites for the model development had been the determination of relevant enzyme activities and metabolic pools which are potentially indicative of metabolic switches. This includes the characterisation of key enzymes (IDP-isomerase, isoprene synthase) involved in plastidic isoprene biosynthesis, the quantification of isoprenoid precursors (DMADP), of regulators of carbon partitioning, of ratios of ATP/ADP and NADPH/NADP, of storage (starch) (Bauknecht, 2001) and transport forms of photoassimilates, sugars and amino acids (Heizmann *et al.*, 2001), as well as measurements of photosynthetic gas exchange and isoprene emission rates. Based on these experimental data, especially by considering the temperature dependencies of enzyme activities, BIM was developed (Zimmer *et al.*, 2000). In the model a light fleck photosynthesis model (Kirschbaum *et al.*, 1998) provided the concentrations of the photosynthetic precursors of isoprene formation, 3-phosphoglyceric acid and glyceraldehyde 3-phosphate.

The comparison of isoprene emission rates calculated by BIM and by the algorithm of Guenther (1997) revealed that the empirical algorithm (Guenther, 1997) reacted too sensitive to changes in temperature and light intensity. The real plant

leaf and also the 'oak leaf' modelled by the BIM responded much less dramatically to these changes, because production of isoprene includes a series of metabolite pools so that the sum of turnover times leads to a smoothing of light and temperature dependency. As a result the average deviation between measured and modelled isoprene emission obtained with BIM were 50% lower than the results obtained by the calculation with the Guenther (1997) algorithm (Zimmer *et al.*, 2000).

BIM is able to calculate short-term variations of isoprene emission rates. To predict isoprene emission for longer time scales annual fluctuations of oak isoprene synthase activity and photosynthetic pigment contents were surveyed from 1995 to 1997 (Lehning *et al.*, 2001), the latter as a parameter for the development of the photosynthetic apparatus of oak leaves. Based on these measurements and phenological data collected from *Q. robur* of 89 ecological regions covering all of Germany a **S**easonal **I**soprene synthase **M**odel (SIM) was developed to calculate the seasonal variation of oak isoprene synthase activity in relation to annual fluctuations of temperature and PAR (Lehning *et al.*, 2001). SIM describes the annual trends of isoprene synthase activity in oak leaves fairly well and in a realistic manner. The coupling of the seasonal model to the biochemical isoprene emission model (BIM) improved the calculation of the diurnal fluctuations of isoprene emission rates in sun as well as shade leaves of forest canopies, since annual data of temperature and light are the only driving variables of the model. In contrast to models (Pier and McDuffie, 1997; Guenther, 1997) where the standard emission factors followed fixed functions, SIM considers the historical variations in temperature and light during the vegetation period. In particular, this dynamic adaptation of the model enables the calculation of isoprene synthase activity for sun and shaded leaves without any further corrections.

The application of BIM and SIM to other deciduous isoprene-emitting trees of temperate regions, however, awaits further species-specific details of the biochemical properties of crucial enzymes as well as of temperature and light-activation of isoprene synthase in these tree species. In particular, the factors describing synthesis and decline of daily isoprene synthase activity (see Lehning *et al.*, 2001), have to be calculated for the model development once from experimental data, and species specific phenological data have to be implemented in the model. In respect of a changing global climate the coupled version of BIM and SIM might be also of considerable predictive value when used for sensitivity studies that simulate isoprene emission rates under elevated temperatures during different annual seasons and atmospheric CO_2 levels. Ongoing development on SIM and the input parameter database will lead to the development of a process-based emission module to be coupled to chemistry transport models for setting up more realistic BVOC emission inventories.

3. Monoterpenes Emission of Scots Pine

Monoterpenes also belong to the most abundant biogenic VOC emitted from vegetation (Guenther *et al.*, 1995). It is known that plants, especially those of the conifer, mint, citrus, and composite families, accumulate these substances in ducts, glands and cavities, and that the synthesis itself occurs in the cells lining these specialised structures (Steinbrecher and Ziegler, 1997). These isoprenoids are believed to serve as defence purposes against insect, fungi, herbivores, other plants, and, when volatilised, can be signals for pollinators, can mediate tritrophic interactions, and act as signals for conspecific herbivores (for review see Harborne, 1991). Their synthesis is mainly constitutive, but it may also be induced by herbivores or pathogen attacks (Litvak and Monson, 1998) as shown for several conifer species. It has also been shown that monoterpene emission in Norway spruce (*Picea abies* (L.) Karst.) includes both a light- and temperature-dependent emission accompanied by a temperature-dependent emission from reservoirs (Schürmann *et al.*, 1993).

3.1. MECHANISMS OF FORMATION

The biosynthesis of several monoterpenes has been worked out in detail (McGarvey and Croteau, 1995; Bohlmann *et al.*, 1998, and references therein). Similar to the biosynthesis of isoprene, monoterpenes are formed in plastids via the novel MEP-pathway (see above), while sesquiterpenes are synthesised in the cytoplasm from IDP, which is derived from mevalonate (McGarvey and Croteau, 1995). Most monoterpenes have cyclic structures and are synthesised by so called monoterpene synthases or cyclases. In each case geranyl diphosphate (GDP) serves as the precursor. GDP itself is derived from the condensation of IDP and DMADP. Apparently, a relatively small number of monoterpene synthases, with very similar chemical properties and protein structures, can catalyse the synthesis of many different monoterpenes (Bohlmann *et al.*, 1998). This finding has received confirmation by molecular cloning of monoterpene synthase genes from a number of species (for review see Bohlmann *et al.*, 1998), including Grand fir (*Abies grandis* L.) as conifer species.

3.2. ENVIRONMENTAL CONTROLS OF MONOTERPENE EMISSION FROM PINES

The terpene emission of Scots pine (*P. sylvestris*) was investigated under outdoor and controlled laboratory conditions. The studies focussed on diurnal and seasonal cycles of terpene emissions, branch-to-branch and plant-to-plant variability of emission rates, and on the transferability of results from laboratory to outdoor measurements. Holzke (2001) and Komenda (2001) described the studies in detail.

For the outdoor experiments, dynamic flow-through enclosure systems and automated sampling systems were developed. Air samples were collected on cartridges containing solid adsorbents. The analysis was performed in the laboratory

by GC-MS and GC-FID. For the calibration of air samples a diffusion source that produced standard gas mixtures of biogenic VOC was used. The sampling, analysis, and calibration procedure are described in detail by Komenda *et al*. (2001). The laboratory studies were conducted in the continuously stirred tank reactors described in detail by Wildt *et al*. (1997).

The outdoor enclosure systems were used to measure monoterpene emission rates from 8 individual 3–4 year old Scots pine seedlings and from branches of three 40-year-old pine trees. The studies with these trees were carried out in 1998 and 1999 at the 'Hartheimer Wald' site. The site is equipped with an 18 m (z/H = 1.3, H: stand height) and a 30 m (z/H = 2.1) tower for micrometeorological measurements (Mayer *et al*., 2000). The lower tower was used for the emission measurements with the enclosure systems inside the canopy (12 m). In addition to these outdoor experiments, laboratory studies have been conducted with young Scots pine trees originating from the 'Hartheimer Wald' to investigate the dependence of VOC emissions on parameters such as temperature and PAR (Shao *et al.*, 2001).

Generally, no significant differences between the results obtained under laboratory and ambient environmental conditions were found (Komenda, 2001). Thus, the continuously stirred tank reactors used as enclosure chambers in the laboratory were capable of providing ambient-like conditions and therefore have proven to be a useful tool for emission rate studies and the derivation of emission algorithms. The VOC emitted from Scots pine were monoterpenes (Δ^3-carene, α-pinene, β-pinene, myrcene, limonene, sabinene, camphene, and tricyclene), sesquiterpenes, acetone, oxygenated VOC, and small amounts of isoprene. Surprisingly, it was found that Scots pine also emit toluene (Heiden *et al.*, 1999).

Under both laboratory and field conditions, monoterpene emission rates were found to increase with needle temperature (typically 10% per Kelvin). Only in the laboratory under controlled environmental conditions, also a dependence of the emission on PAR was detected. The dependence of emission rates on temperature and PAR was described using the algorithm by Schuh *et al.* (1997).

The parameter describing the temperature dependence of emissions from pools, c_{TP} R^{-1} (for a detailed explanation see Schuh *et al.*, 1997), ranged between $4.0 \cdot 10^3$ K and $13.9 \cdot 10^3$ K and was independent of the type of monoterpene (Komenda, 2001). Variations of c_{TP} R^{-1} were randomly distributed without a clear seasonal trend and without significant differences from plant-to-plant. A light saturation of the emissions in parallel to VOC biosynthesis was found at very low PAR levels of about 200 μmol photons m^{-2} s^{-1}, corresponding to 15% of full sunlight. The increase in the emission rates at a constant temperature due to a light-dependent process was only about 20–30% (Shao *et al.*, 2001).

The algorithm of Schuh *et al*. (1997) is based on the model of two emission pathways as already suggested by Schürmann *et al*. (1993). A temperature-dependent emission due to evaporation out of reservoirs and a light- and temperature-dependent emission which is related to the photosynthetic activity of the

needles. The amount of monoterpenes emitted in parallel to biosynthesis was determined by exposing young pine trees with fully developed needles to $^{13}CO_2$. The exposure led to a labelling of the emitted monoterpenes showing that these terpenes were synthesised from CO_2 taken up recently. The rate of labelling was in the range of 20 to 30%; the fraction of monoterpene emissions caused by emissions in parallel to monoterpene biosynthesis was in the range of 20 to 30%. This amount was similar to the modulation of the emission rates caused by PAR at constant leaf temperature.

The existing emission algorithm was capable of describing the temperature and PAR dependence of the monoterpene emissions, but was found to be insufficient to fully describe all experimental results. The temperature normalised, so-called 'standard emission rate', was found to be highly variable (by one order of magnitude). Measurements carried out to investigate a seasonal trend in monoterpene emissions from Scots pine showed highest standard emission rates in spring. In summer and fall standard emission rates were lower by approximately one order of magnitude (Holzke, 2001). The sum of standard emission rates of all monoterpenes ranged between 0.06 and 0.65 μg g (dw)$^{-1}$ h^{-1} for young pines and between 0.24 and 3.7 μg g (dw)$^{-1}$ h^{-1} for the adult pine trees (Komenda, 2001). The observed maximum in spring could be due to the accumulation of terpenes in the resin ducts of the developing young pine needles (Riba and Torres, 1997) This assumption is supported by radioactive labelling studies with *Pinus pinaster* (Soland.) (Bernard-Dagan *et al.*, 1982) showing that the epithelial cell surrounding the resin ducts in the needles incorporate ^{14}C into mono- and diterpenes only within a very short time period in early spring. In similar experiments performed in November no ^{14}C was incorporated into terpenes.

The variation in the standard emission rates from the same plant measured at different times of the year was in the same order as the plant-to-plant variability (i.e., about one order of magnitude). This indicates that these variations were not due to differences between plants, but were induced by environmental factors. Seasonality in the standard emission rates due to the physiological development of the plants may be a possible explanation for these variations, but also stress effects may induce the observed variations. Seasonal variations in the monoterpene emission spectrum from the same plant were very low and the monoterpene spectrum remained nearly unchanged (Holzke, 2001; Komenda, 2001). On the other hand, different individual Scots pines emitted a completely different spectrum of monoterpenes (Holzke, 2001; Komenda, 2001). The monoterpene emission spectra from two branches of the same tree agree very well. Stress (e.g., high temperatures) was found to influence the spectrum of monoterpene emissions, but we observed that stress-induced changes in the emissions were smaller than the plant-to-plant variability of emissions.

Besides the monoterpene emission spectrum, also the sesquiterpene emission was investigated. Here, a seasonal change in the emission spectrum was observed (Holzke, 2001). A wide variety of sesquiterpenes and oxygenated compounds

was emitted (1,8-cineol, camphor, β-caryophyllene, α-terpineol, β-cedrene, γ-cadinene, and δ-cadinene), the sum of which contribute up to 6% of the sum of all terpenoids emitted. The emissions of the complete spectrum of sesquiterpenes and oxygenated compounds occurred in springtime whereas in summer and fall only a reduced spectrum was emitted, namely 1,8-cineol and camphor.

With regard to future emission rate studies, the following recommendations are made: It seems to be sufficient to measure the emission rates of just one branch of a tree to get a measure of the emissions of that specific tree, but it is absolutely necessary to investigate the emissions of more than one individual tree to estimate the plant-to-plant variability of emissions. The existing emission algorithms describing monoterpene emissions as a function of environmental parameters (such as temperature and PAR) need to be improved. Especially stress effects (e.g., high temperatures, pathogen attack, and insect attack) and a possible seasonality in terpenoid emissions has to be investigated thoroughly in future laboratory studies.

4. Emission of Oxygenated VOC

Oxygenated VOC (OVOC) are ubiquitous chemical constituents in the atmosphere which are partially emitted from plants. Numerous publications indicate the quantitative and qualitative importance of short-chained compounds such as formaldehyde and acetaldehyde for tropospheric chemistry (Carter, 1994, and references therein). They are present in the atmosphere in concentrations of 0.3 to 5.0 ppbv at rural and forested sites, and up to 170 ppbv in urban areas. Other OVOC believed to be emitted by plants are the saturated C_6–C_{10} aldehydes heptanal, octanal, nonanal, and decanal (Ciccioli *et al.*, 1993). These compounds have been observed in the troposphere in concentrations up to more than 1 ppbv (Yokouchi *et al.*, 1990; Ciccioli *et al.*, 1993; Wedel *et al.*, 1998). However, the origin of these compounds remained speculative. Due to the short atmospheric lifetime in the range of some hours, the ambient mixing ratios of oxygenated VOC must depend directly on the rates of production and destruction and only to a minor extent on long-range transport. The following section summarises the actual knowledge on the generation and emission of these OVOC by plants and discusses the factors controlling these processes.

4.1. FORMATION AND EMISSION OF ACETALDEHYDE AND ETHANOL OF POPLAR

Studies during the present program with poplar (*Populus tremula* $\times$ *P. alba*) trees (Kreuzwieser *et al.*, 1999, 2000, 2001) clearly indicated that acetaldehyde and ethanol generation in the leaves of plants are tightly connected through alcoholic fermentation. This pathway is important if the oxygen supply is limited, for example, due to root submergence or at sites with compact soils where the diffusion of oxygen to the roots is reduced. Under such conditions alcoholic fermentation is induced and pyruvate is converted into ethanol via acetaldehyde by the sequen-

tial action of pyruvate decarboxylase (PDC) and alcohol dehydrogenase (ADH). Beside roots, alcoholic fermentation is known to take also place in the cambium of trees (MacDonald and Kimmerer, 1991), in fruits especially during ripening (see Zuckerman *et al.*, 1997), or in pollen (Tadege and Kuhlemeier, 1997). Surprisingly ADH is constitutively expressed in the leaves of numerous tree species. Since leaves are in an aerobic environment and even produce oxygen during photosynthesis, the constitutive expression of ADH activity does not appear to be necessary. However, the actual results (Kreuzwieser *et al.*, 1999, 2000, 2001) suggest that ADH may be of significance if ethanol, produced in hypoxic parts of plants, is transported to the leaves in the xylem as driven by the transpiration stream (MacDonald and Kimmerer, 1991; Kreuzwieser *et al.*, 1999, 2000). Ethanol is often found in the xylem sap of trees (MacDonald and Kimmerer, 1991); considerably increased amounts can be detected if the roots are flooded (MacDonald and Kimmerer, 1991; Kreuzwieser *et al.*, 1999, 2000). The major portion of ethanol transported to poplar leaves by the transpiration stream is oxidised in leaf cells thereby releasing acetaldehyde from which minor portions are emitted into the atmosphere (Kreuzwieser *et al.*, 1999. Using enzyme inhibitors, Kreuzwieser *et al.* (2001) showed that this reaction is catalysed by ADH. As a consequence flooded poplar trees have been identified to emit large amounts of acetaldehyde (Kreuzwieser *et al.*, 1999, 2000; Holzinger *et al.*, 2000). The acetaldehyde not emitted by the leaves is further converted into acetate by the action of aldehyde dehydrogenase (Kreuzwieser *et al.*, 2001).

The origin of acetaldehyde emitted by non-flooded trees still remains to be clarified. The relatively low emission rates frequently observed may be caused by oxidation of ethanol generally present in the xylem sap of trees. However, other production pathways cannot be excluded. Kimmerer and Kozlowski (1982) observed that wounding and oxidative stress led to ethanol and acetaldehyde emission by the leaves of birch and pine. They assumed that the stress caused oxygen shortage even in an oxygen-rich environment, which led to an activation of PDC at the expense of pyruvate dehydrogenase resulting in the synthesis of ethanol and acetaldehyde. The release of acetaldehyde and ethanol due to oxidative stress can also be explained by the oxidation of membrane lipids by radicals as proposed by Halliwell and Gutteridge (1989). Another factor leading to the synthesis of acetaldehyde in plants is postanoxic stress which occurs when plants are re-supplied with oxygen after anaerobic periods (e.g., after flooding) (Zuckerman *et al.*, 1997). However, a quantification of the emissions has so far not been determined under such conditions.

4.2. EMISSIONS OF SATURATED C_6–C_{10} ALDEHYDES

Although it has been suggested that saturated C_6–C_{10} aldehydes are emitted from vegetation very little is known with respect to emission rates, emission mechanisms or biosynthetic pathways in plants that produce these OVOC. In this chapter we

give an overview of results obtained for emissions of these compounds from plants investigated in laboratory experiments. The experimental design allowed studying the VOC emissions from plants under well-defined conditions. The air entering the continuously stirred tank reactors (CSTR) was free of trace gases such as NO, NO_2, or ozone. For exposure experiments these compounds could be added in well-defined amounts. A detailed description of the GC-MS system used for VOC analysis is given by Heiden *et al.* (1999).

Experiments were conducted with different plant species with a focus on the emission from Scots pine (*P. sylvestris*). Emissions of these aldehydes were not observed from plants growing under stress free conditions. However, in all cases an ozone exposure (5 to 170 ppbv) led to emissions of saturated C_6–C_{10} aldehydes with emission rates between 0.2 and $6 \cdot 10^{-16}$ $mol \cdot cm^{-2} \cdot s^{-1}$. For individual experiments the emission rates of aldehydes were correlated to each other indicating a common emission mechanism for all of these compounds. Comparing the emission pattern observed for different plant species (pine, canola, tobacco, sunflower, corn) it was found that these patterns were similar implying also a similar emission mechanism for different plant species. The emissions started directly with the beginning of ozone exposure lasted as long as the exposure was continued and stopped after finishing the exposure. The emissions were observed already at ozone concentrations of 5 ppbv, a concentration below those often observed in the troposphere.

Several experiments were conducted to study the effects of ozone concentrations, PAR, and temperature on these emissions. It was found that aldehyde emission rates were regulated by the ozone flux into the plants and not by ozone concentrations alone. For example, exposing plants to high ozone concentrations in darkness led to lower aldehyde emissions than exposing the plants to lower ozone concentrations during illumination. Hence, stomatal conductivity influenced these emissions directly or indirectly. Aldehyde emissions increased with temperature by about 12 to 13% per degree. For pine plants exposed to ozone the PAR dependence was not significant. However, a PAR dependence of these emissions may be superimposed by the PAR dependence of the ozone flux. From the results of measurements obtained with ozone exposed Scots pine an algorithm was developed. This algorithm considered only ozone flux and temperature as important variables determining the aldehyde emission rates. A possible PAR dependence was not considered. Nevertheless, the diurnal variation of aldehyde emissions from ozone exposed Scots pine could be described well (Wildt, personal communication).

We estimated the global emissions of C_6–C_{10} aldehydes by assuming these emissions to be general for plants exposed to ozone. Furthermore, a global annual ozone uptake of 500 to 1500 Tg C per year (e.g., Chameides, 1989) was used for this estimation and the relation between ozone uptake and aldehyde emissions as determined from the experiments. The result was a global emission in the range of 7–22 Tg C per year (Wildt, personal communication). Since emissions from

plants under biotic stress or possible synergistic effects of stress were neglected, the global emissions of C_6–C_{10} aldehydes may be higher.

The global emission estimated for the aldehydes is by far lower than the global emission rates estimated for monoterpenes (e.g., Guenther *et al.*, 1995). However, with regard to atmospheric chemistry it is also the fate of the OVOC that may be important. The C_6–C_{10} aldehydes absorb light in the near UV and thus, may be photolysed by sunlight, which can lead to additional radical formation.

5. BVOC Emission Inventory of Germany

Highly resolved spatial and temporal emission inventories are important input parameters for applying numerical chemistry and transport models for calculating tropospheric ozone distributions. VOC emissions of biogenic sources contribute significantly to the formation of summer photosmog episodes. Therefore, reliable information on BVOC surface emission rates is essential for establishing an effective air quality management. Currently available global and regional emission inventories employ the empirical approach based on algorithms developed by Guenther *et al.* (1993, 1994) and Simpson *et al.* (1999). However, field and laboratory studies on the monoterpene emission of selected resin duct-containing plants, i.e., Scots pine (see Section 3.2), showed that emission from resin vaporisation in addition to an emission of actually formed monoterpenes in leaves is likely (Schürmann *et al.*, 1993; Schuh *et al.*, 1997; Steinbrecher *et al.*, 1999). This additional emission process has been considered in an empirical emission model (Richter *et al.*, 1998) by adding a term to the monoterpene emission module considering the *de novo* synthesis for several plant species (Steinbrecher *et al.*, 1999; Mannschreck *et al.*, 2002, this issue).

For the determination of a BVOC emission inventory meteorology data input, data on the area of the emitting land use in each grid cell of the modelling area, leaf biomass or leaf area index (LAI) and appropriate emission factors are needed. Land use data are generally given in categories, such as agriculture, deciduous, coniferous or mixed forest. This classification is available at high resolution, i.e., CORINE database (EU, 1991) but this coarse land cover classification causes high systematic errors in the emission inventories, especially in Germany where deciduous forest consists of non-emitting beech (*Fagus sylvatica* L.) and high-emitting oak species (*Q. robur, Q. petraea*). Plant species-specific land cover data are therefore necessary to improve the quality of the inventories.

Plant species-specific data are usually only available from statistical surveys and refer to regions, such as forest districts (i.e., BML, 1990) or other administrative units. For use in a grid-based emission inventory these data have to be either disaggregated (forest statistic data) or aggregated (CORINE database).

For constructing BVOC emission inventories at different spatial and temporal scales a geographical information system (GIS) and a relational data base management system (RDBMS) (Smiatek and Stockwell, 1999) was set up, managing

collected land cover data and plant species-specific data (VOC emission factors, biomass and LAI values). GIS administrates all geo-data, such as land use, administrative boundaries and other data in raster or vector form. The RDBMS stores all data on the species area, biomass as well as descriptive information. In total more than 44 different land use data sets with 14 different categories, 30 data sets with vegetation index (VI) and leaf area index (LAI) data covering Germany and large areas of Europe were processed (Smiatek, 2000a, b). More than 130 European plant species, 33 chemical compounds as well as 668 emission factors for BVOC from various sources (Simpson *et al.*, 1999; Kesselmeier and Staudt, 1999; Steinbrecher *et al.*, 1999; Mannschreck et al., 2002, this issue), 3600 records of information on forest area with 6 different categories and more than 400 regions had been integrated.

The BVOC modelling system was applied to establish a BVOC inventory for Germany. Monthly emissions for the year 1998 as well as hourly emissions for a 3 days episode in August 1998 were calculated (Steinbrecher *et al.*, 2000). Required meteorological parameters, such as surface temperature and photosynthetic active radiation, were derived as hourly values by runs of the multiscale-chemistry-climate-model (MCCM) (Grell *et al.*, 2000). Alternative calculations with general land use data (CORINE), as well as with plant species distributions based on the German Frost Inventory (BML, 1990) and leaf area index (LAI) distributions (Preußer *et al.*, 1999) derived from normalised difference vegetation index (NDVI) satellite images have been performed.

Most of the biogenic emissions occur in the middle and southern part of Germany with values of more than 400 kg C km^2 $month^{-1}$. Compared to BVOC emission inventories which only consider general forest types (e.g., deciduous, coniferous, and mixed forest), the use of tree species distribution for the major six forest forming trees in Germany (beech, *F. sylvatica*; oaks, *Q. robur*, and *Q. petraea*; Norway spruce, *P. abies*; Scots pine, *P. sylvestris*; fir, *Abies alba* L.; Douglas fir, *Pseudotsuga menziesii* L.) significantly reduced systematic errors associated with the assignment of emission factors to source categories. Isoprene emissions using plant species data are in general 30% lower compared to emission estimates considering only forest types. Furthermore, the plant specific emission inventory of Germany show significantly different geographic distribution patterns shifting the focus from areas with high forest proportions to areas with large oak stands. The monthly BVOC amount estimated with LAI distribution actualised every ten days indicated significant lower amounts in springtime compared to calculations with literature-based biomass densities not considering seasonal effects.

For 1998 an annual total emission of 547 kt C BVOC has been estimated for Germany. Compared to the anthropogenic VOC emissions (Friedrich *et al.*, 2001, this issue) the biogenic VOC emission contributed about 20% to the total VOC emission. However, under high temperature and high solar irradiation during August 1998 the BVOC contribution rose up to 60% of the total VOC emission. Considering that the gas phase reactivity of BVOC is approximately a factor of

1.5 higher (Carter, 1994) than that of anthropogenic VOC, it becomes evident that the biogenic VOC emission is a major compound in the formation of photosmog, even in Germany. The total BVOC emission of 547 kt C for Germany consisted of 113 kt C isoprene, 201 kt C monoterpenes and 233 kt C oxygen containing compounds (OVOC). These emission rates are comparable to a recent biogenic trace gas emission inventory of Simpson *et al.* (1999) which estimated emission rates of 112 kt C isoprene, 152 kt C monoterpenes and 114 kt C OVOC. The difference in the calculated OVOC emission between both inventories is probably due to an underestimation of this compound class of emission (Kesselmeier and Staudt, 1999, this paper) in previous inventories.

6. Conclusion

The present project has contributed to a significant improvement of our current understanding of the processes controlling biogenic VOC emissions. Empirical algorithms for the modelling of isoprene and monoterpene emissions have been developed and validated. For isoprene also a process-oriented numerical isoprene emission model was developed which is based on a more detailed understanding of the biochemical formation pathways.

The results of field and laboratory studies show that as a first approximation emission models are a valuable tool to describe the emission rates in dependence of temperature and light intensity. But the results also indicate an influence of other factors on the BVOC emissions. The biotic and abiotic environment of plants has to be considered in more detail to understand the complex behaviour of these emissions. The uncertainties associated with oxygenated VOC emitted are still very high. Compared to isoprenoids, the processes controlling the emission of these compounds are less clear, and hence more efforts are needed to develop realistic emission models for this class of compounds.

For realistic estimates of the impact of BVOC on local and regional tropospheric photochemistry it is necessary to upscale the emissions from single plants or forest stands to larger areas. With respect to these requirements the uncertainties in highly spatial and temporal resolved BVOC emissions for Germany have been considerably reduced by using a plant-species-specific vegetation distribution, whenever possible, up-dated emission factors and emission models as well as satellite-derived LAI distributions actualised every ten days.

Acknowledgements

The German Federal Ministry of Education and Research (BMBF) financially supported the work under the national joint research project 'Troposphärenforschungsprogramm'.

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