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Authors

Kesselmeier, Juergen
Guenther, Alex
Hoffmann, Thorsten
et al.

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Natural Volatile Organic Compound Emissions From Plants and Their Roles in Oxidant Balance and Particle Formation

Jürgen Kesselmeier,[1] Alex Guenther,[2] Thorsten Hoffmann,[3]
Maria Teresa Piedade,[4] and Jörg Warnke[3]

Numerous biogenic volatile organic compounds (VOC) species are released into the atmosphere from tropical forests. Measuring all those which are relevant for atmospheric chemistry or for the carbon budget is challenging. Large-Scale Biosphere-Atmosphere (LBA) Experiment field campaigns substantially increased the number of field studies of isoprene and monoterpene emissions, as well as of the exchange of several other VOC species. This chapter reports about the progress made within LBA from primary emission measurements at the plant species level up to discussions of the oxidative capacity of the atmosphere and formation of secondary organic aerosol particles and cloud condensation nuclei from biogenic hydrocarbons. VOC emission from Amazonian ecotypes has strong effects on atmospheric chemistry, which are obviously not fully understood in the case of the tropical atmosphere. Atmospheric flux studies within numerous field experiments resulted in new knowledge about local to regional scale biogenic VOC exchange and improved modeling. New data obtained from field as well as from laboratory studies helped to characterize VOC emissions from the Amazonian forest underlying seasonality within dry and wet seasons. Furthermore, first insight was obtained into the potential of floodplain areas affected by long-lasting flooding periods which can cause special emission adaptation.

[1]Max Planck Institute for Chemistry, Mainz, Germany.

[2]National Center for Atmospheric Research, Boulder, Colorado, USA.

[3]Institute of Inorganic and Analytical Chemistry, Johannes Gutenberg University of Mainz, Mainz, Germany.

[4]Instituto Nacional de Pesquisas da Amazônia, Manaus, Brasil.

1. PROCESSES CONTROLLING TRACE GAS EXCHANGE BETWEEN VEGETATION AND THE ATMOSPHERE

1.1. Ecological Biodiversity in Amazonia and Volatile Organic Compounds Exchange

Among the many challenges in studying the exchange of trace gases between forests and the atmosphere, how to extrapolate emission rates and fluxes is of highest importance. The emission of reactive volatile organic compounds (VOC) is highly plant species dependent [*Kesselmeier and Staudt*, 1999]. Furthermore, because we need to go to the level of a branch or leaf in a given plant species to identify the release of trace gases, results from measurements made above the forest will be biased by chemical reactions occurring

during the time of transport. A reasonable approach for modeling VOC release for European forests is to take into account the main forest tree species and their emission rate estimates which have been identified at a branch or leaf level. However, this approach is impossible to apply to a tropical rainforest with its huge biodiversity of species and phytogeographic regions, for which knowledge on the biotic and abiotic components and relations is still scarce [*Junk et al.*, 2000]. Brazilian Amazonia comprises an area of 5 million km^2, 80% of which is classified as so-called terra firme [*Pires and Prance*, 1985; *Pires*, 1973]. The remaining 20% can be divided into six phytogeographic formations according to their floristic and structural characteristics, namely, the mixed and transitional forests, the savannas, secondary forests, agricultural areas, and floodplains [*Braga*, 1979; *Junk*, 1993].

In floodplains, the seasonality imposed by the regular flooding of the big rivers is the most conspicuous feature inducing environmental constraints on the biota [*Junk et al.*, 1989; *Ayres*, 1986, 1993; *Junk*, 1997]. Water level fluctuation exhibits amplitudes of 7 to 13 m between the high and low water conditions with flooding periods of 1 to 8 months per year [*Junk*, 1989; *Kubitzki*, 1989]. Different plant communities become established depending on the length of inundation. Thus, changes in the big river's water levels and duration of inundation will drive species composition, diversity, and physiognomy of the floodplain forests [*Junk*, 1989; *Worbes*, 1997; *Ayres*, 1993; *Wittmann et al.*, 2006; *Piedade et al.*, 2001]. Plants exhibit different capacities for tolerating periods of hypoxia or anoxia as a consequence of the inundation, which can last from hours, to days, weeks, or months [*Parolin et al.*, 2004]. One of these adaptations might be energy production by fermentation and detoxification of compounds such as ethanol by transport into the canopy leaves with a subsequent re-metabolization and/or release into the atmosphere (see section 1.4) [*Rottenberger et al.*, 2008]. Such a strategy, by the plants, could increase the significance of floodplain areas for atmospheric chemistry. However, the impact of fermentation processes on VOC release under long-term flooding is not known.

These examples highlight the importance of studying VOC emissions, adaptation, and physiology of key species in each one of these six environments, as well as the importance of comparing a key species which grows in all the environments. Different key species as well as different adaptation strategies may have a significant influence on the release of volatile organic compounds that we should know about and understand.

1.2. Volatile Organic Compounds in the Atmosphere

Numerous biogenic VOC species are released into the atmosphere, and measuring all those which are relevant to atmospheric chemistry or the carbon budget is challenging. Measurement techniques used are always limited to special groups of compounds and can only give a view into parts of the story. Proton transfer reaction mass spectrometry (PTR-MS) [*Lindinger et al.*, 1998], which is now broadly used [see *Karl and Guenther*, 2004] can simultaneously detect a large number of VOC species. *Crutzen et al.* [2000] report on a large number of organic species measured using this instrument over the rain forest in Suriname during an aircraft campaign and also discuss a weakness of the PTR-MS measurements, which is detecting ion masses without clear identification. Nevertheless, the PTR-MS has become a valuable tool to look for emissions of trace gases into the atmosphere.

Measurements made with more conservative tools have nevertheless provided interesting data sets for non-methane VOC species in the atmosphere over Amazonia. During the Cooperative Large-Scale Biosphere-Atmosphere (LBA) Airborne Regional Experiment 1998 (LBA-CLAIRE-98) campaign, *Kesselmeier et al.* [2000] measured the atmospheric mixing ratios of different species of VOC at a ground station in an open forest site at Balbina, 100 km north of Manaus. The most prominent VOC species present in air during this wet season campaign (March–April) were formaldehyde and isoprene, each up to several ppb. Concentrations of methyl vinyl ketone as well as methacrolein, both oxidation products of isoprene, were significantly below 1 ppb, indicating a very low oxidation capacity in the lower atmospheric boundary layer, which is in agreement with a daily ozone maximum of <20 ppb. Total monoterpene concentration was below 1 ppb.

These data can be compared with a more comprehensive investigation during the LBA-EUSTACH campaigns (LBA-EUSTACH-1, April/May 1999, and LBA-EUSTACH-2, September/October 1999) in the Rebio Jaru, an ecological reserve 100 km north of Ji-Paraná in the state of Rondônia, in southwest Amazonia, during the "wet-to-dry season transition" and "dry-to-wet season transition" periods [*Kesselmeier et al.*, 2002b]. Here, samples were obtained at the canopy top close to the potential sources/sinks for these compounds, as well as above the forest. The most prominent VOCs identified in the air during April/May were isoprene, formaldehyde, and formic acid, with mixing ratios of each ranging up to several parts per billion (ppb), very similar to the Balbina site. Oxidation products of isoprene such as methyl vinyl ketone as well as methacrolein ranged around 1 ppb. Total monoterpene concentration was below 1 ppb. This changed at the transition phase from dry to wet in September/October. C_1-C_2 organic acids and C_1-C_2 aldehydes exhibited a significant increase up to 17 and 25 ppb, respectively, which is thought to result from vegetation fires, as are

the high methanol concentrations. Of high interest, however, were substantial increases in the atmospheric mixing ratios of biogenic compounds. Isoprene increased up to 30 ppb near the crown region and was well above 10 ppb at 10–20 m above the forest. Interestingly, monoterpene species decreased. Such atmospheric measurements give an impression about the variability and concentration of VOCs during the different seasons which are due to the seasonality of the vegetation emissions, climatologic factors, and anthropogenic influences such as fires.

Such results are in close accordance with *Guenther et al.* [1999] who predicted that dry season isoprene emissions, mainly because of higher leaf temperatures, might be higher than those in the wet season. Reports from other rain forest regions also support this scenario, i.e., isoprene flux data from central Africa [*Serça et al.*, 2001]. Furthermore, emission measurements on the branch level demonstrated a doubling of isoprene emission rates from *Hymenaea courbaril* and monoterpene emissions from *Apeiba tibourbou* also increased nearly twofold [*Kuhn et al.*, 2002a, 2004a].

1.3. Primary Emission Quality and Quantity in Amazonia at the Plant-Species Level

Despite our increasing knowledge during the last decade, we still face significant open questions concerning the composition of VOC mixtures, quantity, or seasonality, which can only be answered by using enclosures to monitor trace gas exchange as it relates to primary plant physiology. Such measurements are typically performed with enclosures at the leaf or branch level. In the course of the LBA decade, primary emissions from tropical rainforest vegetation were investigated under natural field conditions as well as within plant chambers under controlled conditions. The results obtained during these investigations were interesting.

Outside the Amazonian region, *Geron et al.* [2002] screened 20 plant species at a lowland tropical wet forest site in Costa Rica and reported that 50% of them emitted isoprene. As these species cover some 35–50% of the total basal area, these results clearly indicate that a high proportion of the canopy leaf area can be regarded as a source of isoprene, a result which was also supported by flux measurements above the canopy. Methanol and especially acetone fluxes were also found to be significant, in contrast to monoterpene emissions which were nondetectable or very low. The most recent and widest overview of biogenic VOCs in China, including some tropical regions, is by *Klinger et al.* [2002], who screened for more than 500 species with short-term measurements. *Geron et al.* [2006] continued the studies of Klinger et al. in the southern subtropical Yunnan Province, Peoples' Republic of China. In agreement with *Geron et al.*

[2002], they reported 44 out of 95 examined plant species to release significant amounts of isoprene of more than 20 µg g^{-1} h^{-1} (given as carbon on a dry weight basis). However, it should be noted that the species studied were not randomly selected or selected based solely on their local dominance. For example, a large number of *Ficus* species (all isoprene emitters) were measured in order to investigate emission variations within the *Ficus* genera. Three of the 21 *Ficus* species probed during both the wet and dry season periods showed higher isoprene emission rates in the dry season by factors of 2–10 compared to the wet season values reported by *Klinger et al.* [2002]. None of the 21 species showed significantly greater emission in the wet season. Monoterpene emissions on a carbon and leaf dry weight basis exceeded 1.0 mg g^{-1} h^{-1} in only 4 of 38 species surveyed. However, the authors assumed that the emission factors were approximately an order of magnitude too low due to sparse foliation resulting from dry season senescence. The rubber tree *Hevea brasiliensis* was confirmed as a significant and light-dependent monoterpene emitter. *Wilske et al.* [2007] also studied VOC emissions in Yunnan Province, China where he investigated eight tropical tree species of SE Asia using dynamic Teflon bag branch enclosures and enclosed the branches for longer adaptation times. Emission potentials of four species were considerably different from those previously reported. Two species emitted isoprene. Six species emitted monoterpenes though with low standard emission factors between <0.1 and 0.5 µg g^{-1} h^{-1}. Four out of five species investigated at two different times of the year showed seasonal differences in emission rates and composition. Total isoprenoid emissions were generally higher with new leaf flush than with aged leaves. In accordance with *Geron et al.* [2006], even taking into account the reports about the numerous plant species from the Chinese tropical areas, we suggest that better understanding of VOC emissions from tropical species of SE-Asia requires more enclosure investigations that cover different seasons.

The most elaborate screening of Amazonian tree species is reported by *Harley et al.* [2004]. In this study, more than 100 tree species were investigated for their isoprene emission capacity using different enclosure systems. For initial screening of VOC emissions with no separation between isoprene and other VOC species, a handheld photoionization detector (Thermo Environmental Instruments, Inc.) was used. Additionally, cartridge samples were analyzed for a better resolution and identification of VOC species. In these studies, approximately 38% of 125 tree species examined at six sites in Brazilian Amazonia were found to emit isoprene. The question of how many trees emit monoterpenes and other volatiles remained open. But even with this high number of single species investigated, any upscaling of isoprene can be

problematic as far as biodiversity is concerned. The authors therefore developed a method to assign emission rates to tree species which were never measured. Such an approach is not without problems; it clearly reveals the gaps of our knowledge and underlines the necessity to continue primary emission measurements to improve our emission-rate estimates on a larger scale. This interpretation is supported by recent findings [*Wilske et al.*, 2007] demonstrating that there can be significant discrepancies between results obtained by a fast screening and data from a more intensive enclosure type investigation of a few plant species. Enclosure measurements in Amazonia with dynamic branch enclosures and adaptation time of more than one day per plant species coupled to the simultaneous determination of climatological variables and physiological parameters such as assimilation, transpiration, and stomatal conductance contributed significantly to a better understanding of the emission processes and controls. *Kuhn et al.* [2002a] investigated tree species in a secondary forest during the wet season of 1999 at a remote field site in Rondônia; *H. courbaril* was found to be a strong isoprene emitter, and *A. tibourbou* was identified to exclusively emit substantial amounts of monoterpenes in a light-dependent manner, but no isoprene. The diel emission pattern of both tree species was similar in regard to controlling environmental parameters, such as light fluctuation, and temperature. This is a clear demonstration of the now well-accepted, closely related metabolisms of isoprene and monoterpenes. A strong light dependence of biogenic monoterpene emissions may have a strong impact on estimated global flux rates for tropical regions.

Whereas extratropical regions are characterized by strong annual growth cycles, tropical regions are often regarded as exhibiting only little climatic and growth variability. However, though we accept tropical regions as a dominant trace gas source all year round, it is now well accepted that there are strong seasonal cycles which can be clearly detected by dendrochronology [*Worbes*, 1999; *Worbes and Junk*, 1999; *Schöngart et al.*, 2002, 2004]. Recently, *Myneni et al.* [2007] used remote sensing to observe a strong leaf area fluctuation in Amazonian rainforest. Similarly, changes in trace gas exchange can be expected. *Kuhn et al.* [2004a] observed leaf age-dependent seasonal differences comparing wet-to-dry and dry-to-wet transition phases. Strong seasonal differences in emission capacity were observed in these cases. The isoprene standard emission factor in the case of *H. courbaril* was about twofold at the end of the dry season with freshly developed new leaves, compared to the end of the wet season. In contrast, standardized monoterpene emission rates of *A. tibourbou* exhibited a decrease at the end of the season. Such branch emission data are in close accordance with atmospheric mixing ratios [*Kesselmeier et al.*, 2002b].

Hence, using a single standard emission factor to represent an entire seasonal cycle is no longer adequate. Furthermore, in addition to the variability of isoprene emission, considerable amounts of monoterpene emissions were detected in the period between bud break and leaf maturity of this tree at the end of the dry season [*Kuhn et al.*, 2004b]. Apparently, in addition to light and temperature, we need to invest more research into the roles of other potential factors, such as leaf developmental stage, water and nutrient status, and abiotic stresses like the oxidative capacity of the ambient air. Obviously, such factors contribute significantly to the current emission capacity during the relevant season. Within this context, it is interesting to see that a strong linear correlation between the isoprene emission capacity and the gross photosynthetic capacity was observed covering all developmental stages and seasons [*Kuhn et al.*, 2004b]. Such findings may represent a valuable basis on which to model the seasonal variation of isoprenoid emission capacity.

Though we learned much in the course of the LBA studies, there is still a need for a more basic understanding of the regulation of primary emissions from important plant species. This becomes evident especially in view of a growing number of publications reporting about surprising biogenic emission qualities, amounts, and regulation for vegetation species thought to have been sufficiently investigated as, for example, in the very recent case of European Beech [*Moukhtar et al.*, 2005; *Dindorf et al.*, 2006].

1.4. Plant Species Growing in Floodplain Areas Adapt to the Fluctuating Water Table

More than 300,000 km^2 in size, the Central Amazon floodplain represents one of the largest inundation areas in the world; there are up to 210 days of continuous flooding per year with an average flood amplitude of several meters [*Junk*, 1997]. Inundation of trees in these areas causes drastic changes in soil chemistry and oxygen availability to plant roots [*Parolin et al.*, 2004]. This stress affects primary plant physiology as well as secondary metabolism, for example, photosynthesis, and potentially also the isoprenoid metabolism, respectively [*Rottenberger*, 2003; *Rottenberger et al.*, 2008]. Furthermore, studies on European tree species demonstrated that leaves emit ethanol and acetaldehyde as a physiological response to anaerobic conditions in the roots [*MacDonald and Kimmerer*, 1993; *Kreuzwieser et al.*, 1999; *Holzinger et al.*, 2000], which in turn initializes alcoholic fermentation in the roots with ethanol production. The major portion of the root ethanol is transported with the transpiration stream to the leaves, where it can be re-metabolized by stepwise oxidation to acetaldehyde and acetate, mediated by the leaf enzymes ADH and aldehyde dehydrogenase

(ALDH). Through this mechanism, the plant recaptures carbon and energy which was invested into ethanol and avoids an accumulation of phytotoxic ethanol and acetaldehyde. A fraction of these compounds can be emitted into the atmosphere, a process which can be considered to be a "leak" between production and consumption of these compounds. In the atmosphere, all three C2-compounds are of high importance for tropospheric chemistry and influence the oxidative capacity of the atmosphere, the production of organic nitrates, as well as atmospheric acidity, especially in remote areas [*Carlier et al.*, 1986; *Keene et al.*, 1983; *Kesselmeier*, 2001; *Singh et al.*, 1995; *Talbot et al.*, 1990; *Thompson*, 1992].

In contrast to our knowledge of terra firme tree species [*Rottenberger et al.*, 2004, 2005], floodplain area trees are poorly investigated; however, there have been intensive investigations on the anaerobic production and metabolism of ethanol (fermentation) in roots and its transportation to the leaves (see Figure 1). Only a limited number of studies of the flooding-induced release of compounds from leaves such as ethanol and acetaldehyde, and only one pilot study for plants from Amazonia have been reported [*Rottenberger*, 2003; *Rottenberger et al.*, 2008]. Considering the vast area of inundated forest as well as the duration of flooding, the Amazonian floodplain forests represent potentially one of the most important vegetative sources of atmospheric ethanol, acetaldehyde, and acetic acid, which may have an impact on both regional as well as global atmospheric chemistry and climate.

Despite our knowledge of plant physiological processes which can be initialized by flooding, important questions remain to be investigated. Our experience is based on experiments under controlled conditions; to our knowledge, there are no field experiments. Hence, we do not know how adult trees behave. Furthermore, we do not know how trees deal with the long flood pulse. If some species switch over to fermentation, will the emissions continue over the whole flooding period? Another important question is whether the isoprenoid metabolism is affected. Can we expect changes in the emission rates of isoprene or monoterpene emitters?

If photosynthesis decreases and VOC emission is not affected, or even increases, the carbon budget of the plant would be affected. Stress effects, such as high temperatures, are known to cause such a shift. How do floodplain area adapted plants react? Do only trees with an excellent gas supply through aerenchyma or adventivous roots keep their leaves, whereas others drop all leaf material to survive? Investigations made over several seasons of the seasonal fluctuations of VOCs, including acetaldehyde as a potential marker for floodplain emissions, will help to determine the relevance for atmospheric chemistry and climate.

1.5. Exchange of Short-Chain Aldehydes and Acids in Terra Firme and Floodplain Areas: Emission and Deposition

Within the LBA project, special attention has been given to the release of isoprenoids (isoprene and monoterpenes). However, many other VOCs can be released by the biosphere in significant quantities [*Fehsenfeld et al.*, 1992; *König et al.*, 1995; *Guenther et al.*, 1995; *Kesselmeier and Staudt*, 1999]. Furthermore, it is not only trace gas emission that can be found, but also deposition which may contribute to a recycling of carbon. Among these VOC species, the short-chain oxygenated organic acids, formic acid and acetic acid, as well as their homologous aldehydes are of interest. These two acids contribute significantly to the acidity of the precipitation as discovered by *Andreae et al.* [1988] and *Talbot et al.* [1990] during the ABLE-2 campaign in central Amazonia. The short-chain aldehydes play an important role in the oxidative chemistry of the troposphere [*Carlier et al.*, 1986; *Singh et al.*, 1995, 2001; *Chebbi and Carlier*, 1996]. According to an earlier publication [*Glasius et al.*, 2000b], 80–100% of formic acid, in particular, stems from biogenic sources, whether it derives from the photochemical decomposition of other biogenic trace gases (indirect emission), or
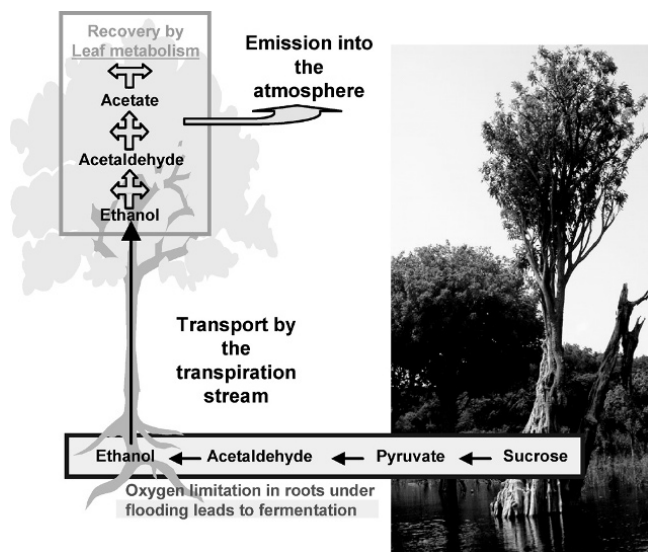
Figure 1. Fermentation processes in the roots under aerobic conditions allows the trees to overcome oxygen limitation which otherwise would prevent energy production. The ethanol can be transported into the canopy leaves where it is metabolized to acetaldehyde and acetic acid (acetate) and recaptured by plant metabolism. Due to their volatility, a part of these compounds can be lost to the atmosphere.

is produced and released directly by plants (direct emission) has not been determined. A dominating uptake as well as emission was found in the LBA studies.

Kuhn et al. [2002b] reported about the exchange of formic acid and acetic acid between vegetation and the atmosphere in the wet-to-dry season transition and the dry-to-wet season transition periods in 1999 in Rondônia. Enclosure measurements on individual branches mainly exhibited uptake of formic acid and acetic acid for all plant species in both seasons. The uptake of organic acids was found to be closely related to the ambient atmospheric mixing ratios. A bidirectional exchange could be detected, but with a very low compensation point, thus nearly excluding any emission. Generally, the forest could be regarded rather as a sink than a source for organic acids, a conclusion which was supported by concentration gradients above the canopy. Strong diel variations were found in both seasons and very high mixing ratios, caused by vegetation fires, occurred in the dry season. A substantial contribution to the atmospheric burden by direct emission was excluded. However, the chemical production by oxidation of primary biogenic reactive compounds such as isoprene and monoterpenes may be regarded as a dominant source for these acids during the wet season. Dry season data were dominated by vegetation fire emissions.

Very similar behavior was reported for form- and acetaldehyde [*Rottenberger et al.*, 2004, 2005]. Branch enclosure measurements of several tree species showed more clearly a bidirectional exchange with a compensation point of 0.6 ppb. Thus emission as well as deposition was observed, though exchange was clearly dominated by deposition. Deposition velocities and the compensation point increased during the dry season. Uptake occurred through the stomata under clean-air conditions in the wet-to-dry transition period, whereas deposition to the leaf surface was estimated to be substantial for the dry-to-wet period when biomass burning activities and atmospheric mixing ratios were high. Diel courses and concentration gradients above the canopy support the conclusion of a photochemical oxidation of biogenically or pyrogenically emitted precursor compounds acting as sources for these aldehydes which can be taken up by vegetation again.

However, the exchange of trace gases as mentioned above is not always limited to deposition with some emission depending on the current ambient mixing ratios and the compensation point. Special environmental conditions such as flooding and inundation of plants, which is a typical feature of large areas of the Amazonian floodplains might change the picture [*Junk*, 1997; *Parolin et al.*, 2004]. This caused some concern about trace gas emissions from partly flooded tree species which thus suffered from anoxic conditions of their root system.

Studies on European tree species demonstrated that leaves emit ethanol and acetaldehyde as a physiological response to anaerobic conditions in the roots [*MacDonald et al.*, 1989; *Kreuzwieser et al.*, 1999; *Holzinger et al.*, 2000], which initializes alcoholic fermentation with ethanol production. The major portion of the root ethanol is transported with the transpiration stream to the leaves, where it can be re-metabolized by stepwise oxidation to acetaldehyde and acetate, mediated by the leaf enzymes ADH and aldehyde dehydrogenase (ALDH). This mechanism allows the plant to recapture carbon and energy invested into ethanol and to avoid an accumulation of phytotoxic ethanol and acetaldehyde. A fraction of these compounds can be emitted into the atmosphere, a process which can be considered to be a "leak" between production and consumption of these compounds. In the atmosphere, all three C2-compounds are of high importance for tropospheric chemistry influencing the oxidative capacity of the atmosphere, the production of organic nitrates, as well as the atmospheric acidity, especially in remote areas [*Carlier et al.*, 1986; *Keene et al.*, 1983; *Kesselmeier*, 2001; *Singh et al.*, 1995; *Talbot et al.*, 1990; *Thompson*, 1992].

In contrast to investigations on the production and metabolism of ethanol in roots and its transportation to the leaves, only a limited number of studies of the flooding-induced release of compounds, such as ethanol and acetaldehyde, have been reported, and only one pilot study for plants from Amazonia is reported [*Rottenberger*, 2003; *Rottenberger et al.*, 2008]. In contrast to the slight deposition of acetaldehyde and acetic acid under nonflooded conditions, flooding of the roots caused leaf emissions of ethanol and acetaldehyde by all tree species investigated. Those plant species exhibiting the highest ethanol and acetaldehyde emission also emitted acetic acid. Of special interest were emission bursts of all three compounds in the morning, which can be understood as an accumulation during the night and a sudden release as soon as the stomata opened in the morning. Emission rates varied substantially among tree species, with maxima differing by up to two orders of magnitude (3–200 nmol m^{-2} min^{-1} for ethanol and 5 and 500 nmol m^{-2} min^{-1} for acetaldehyde). Acetic acid emissions reached 12 nmol m^{-2} min^{-1}. Differences between tree species can be understood as a consequence of different kinds of adaptation strategies to overcome oxygen deficiency in the roots, i.e., development of morphological root anatomy and morphology allowing for enhanced root aeration. The pronounced differences in the relative emissions of ethanol to acetaldehyde and acetic acid indicate that not only the ethanol production in the roots but also the metabolic conversion in the leaf is an important factor determining the release of these compounds to the atmosphere. In most cases, emissions initially increased

during the first 3 days of the flooding period, and then declined after 3 to 7 days. Some plant species which were not dramatically affected by the flooding obviously adapted to the anoxic situation. Others with strong physiological symptoms of injury degenerated.

The effects of root anoxia reported above were only investigated under controlled conditions using young tree species. But the results indicate that there may be an important trace gas source to be better understood. The Amazonian floodplain forests thus potentially represent one of the important vegetative sources of atmospheric ethanol, acetaldehyde, and acetic acid, which may have an impact on both regional as well as global atmospheric chemistry and climate. Nothing is known about the behavior of adult trees under field conditions and about how trace gas emissions adapt to long-term flooding, which is characteristic of the Amazonian floodplains. We therefore recommend studies of the effect of flooding on the exchange of the metabolically related compounds, ethanol and acetaldehyde, between the forests and the atmosphere in the Amazonian floodplain areas.

1.6. Primary Emissions Can Be Affected by Plant-Plant or Plant-Insect Relations

Plants attacked by herbivores or pathogens may react by producing volatile compounds used for direct or indirect defense. Directly affecting toxic volatiles may cause a fast defense, whereas signaling compounds may indirectly contribute by activating a symbiotic chain by, for example, calling herbivore predators. Thus, plants may be alarmed by volatile organic compounds released by herbivore-attacked neighbors and activate defenses to avoid being attacked themselves. There are numerous reports in the literature [*Baldwin et al.*, 2006; *Dicke et al.*, 2003; *Schulze et al.*, 2006], but investigations in tropical forests are rare.

1.7. Primary Emissions Affect the Carbon Budget

The carbon balance of the world's terrestrial ecosystems is uncertain and the carbon balance of Amazonia especially is a matter of ongoing debate [see *Houghton et al.*, this volume; see also *Chou et al.*, 2002; *Araújo et al.*, 2002; *Carswell et al.*, 2002; *Houghton*, 2003; *Baker et al.*, 2004]. However, it has become well accepted that the tropics appear to be a nearly neutral, or small net source of carbon. As reported very recently by *Lloyd et al.* [2007], estimates based on regional surface fluxes using ABL budgeting techniques for evaluating airborne data clearly suggested a close to neutral Amazon carbon balance. It is then of special interest to carefully check the contribution of volatile organic carbon to sinks and sources, especially as reactive carbon fluxes are very sensitive to land cover and climate change and may vary significantly due to future perturbations [*Guenther*, 2002].

The role of vegetation as a source of volatile carbon was discussed by Frits Went and coworkers for the first time 50 years ago [*Went*, 1955, 1960a]. The amounts of these compounds were even regarded to be one of the sources of petroleum [*Went*, 1960b]. Today, our estimates of biogenic carbon released from terrestrial vegetation is above 1000 Tg a^{-1} [*Guenther et al.*, 1995]. Compared to the gross primary productivity of vegetation in the range of 120 Pg a^{-1}, this is only a small contribution equivalent to one percent and consequently VOC emissions from vegetation are rarely included in estimates of global carbon fluxes. However, this picture changes as soon as we look a little closer and relate the VOC release to net primary productivity (NPP), net ecosystem productivity (NEP), or net biome productivity (NBP) [*Geron et al.*, 2002; *Guenther*, 2002; *Kesselmeier et al.*, 2002a]. Based on such studies, it can be assumed that with regard to the carbon budget of the terrestrial biosphere, a release of VOC carbon is a significant loss of photosynthetically fixed carbon. *Kesselmeier et al.* [2002a] estimated the amount of VOC carbon emitted in relation to the CO_2 taken up at a leaf or branch level to range up to a few percent of the photosynthetically assimilated CO_2. Based on numerous enclosure and micrometeorological flux measurements of simultaneous VOC emission and CO_2 exchange in the Mediterranean area, and the tropical rainforest in Amazonia, they demonstrated that VOC flux estimates are small in relation to NPP and gross primary productivity (GPP). However, the amount of carbon lost as VOC emissions can be highly significant relative to NEP. Carbon losses on a GPP basis were estimated to be equivalent to 0.45% for temperate and 0.54% for tropical forests. As pointed out by *Kesselmeier et al.* [2002a], the VOC loss of 0.45% of a GPP of 120 Pg a^{-1} accounted for 0.54 Pg C for the total isoprenoids, a number very close to the modeled estimate of the global isoprene emission of about 0.5 Pg C [*Guenther et al.*, 1995]. Compared to the range of current estimates of NEP, a loss of 3.5–39% of the NEP carbon was calculated. Ranges for global and tropical scenarios were very similar with 3.5–36% and 3.4–27%, respectively. Compared to NBP, the VOC carbon loss was even found to be equivalent, a clear demonstration of the necessity to take VOC fluxes into account for discussions on carbon exchange. Furthermore, the authors noted that such a contribution may increase if data for other VOC species are used in addition to the better-described isoprenoid emissions. The main uncertainty with these estimations was the fate of such reactive compounds. How much is converted to CO_2 (and CO) bypassing terrestrial respiration. How much is returned to the terrestrial biosphere, with or without chemical transformation into other organic compounds? Is this simply

an internal recycling of organic carbon within the terrestrial carbon pool? And how much is finally escaping the forest ecosystems by a transfer from the terrestrial to the marine biosphere, for example? As we know about deposition of some potential oxidation products (see section 1.5.), such as organic acids and aldehydes, we can assume that substantial amounts of these carbon emissions are recycled within the biosphere. Nevertheless, a substantial part can be assumed to be lost into longer-lived oxidation products that are lost from the terrestrial biosphere by transport. Such a conclusion was recently confirmed by *Naik et al.* [2004] who integrated surface emission algorithms using a dynamic global ecosystem model, the integrated biospheric simulator (IBIS), to simulate biogenic fluxes of isoprenoids as a component of the climate-vegetation dynamics. In this simulation, increasing CO_2 levels caused an increase of VOC emissions as a result of increases in foliar biomass. The authors came to the conclusion that the increases in biogenic emissions could have significant impacts not only on regional and global atmospheric chemistry, but also on the global carbon budget.

Suntharalingam et al. [2005] have recently demonstrated that the importance of accounting for biogenic VOC and other reduced carbon emissions in CO_2 inversion analyses is far greater than that expected based solely on its small contribution to the total carbon flux. This is because the usual assumption that the CO_2 source from atmospheric oxidation of these compounds is released at the surface produces a bias in the inversion modeling technique used for estimating regional carbon fluxes. They found that including reduced carbon emissions as a CO_2 source distributed in the atmosphere, rather than emitted at the surface, resulted in considerable differences in estimates of regional CO_2 fluxes. This included a reduction in the northern hemisphere carbon sink and the net carbon emission from tropical landscapes.

2. LOCAL TO REGIONAL SCALE BIOGENIC VOC FLUX MEASUREMENTS AND MODELING

The first measurements of biogenic VOC (BVOC) in the Amazonian atmospheric boundary layer were made during a 1979/1980 aircraft research program in Brazil [*Greenberg and Zimmerman*, 1984; *Crutzen et al.*, 1985]. This research effort was focused on biomass burning but included measurements of background conditions that characterized BVOC emitted from the tropical forest. *Greenberg and Zimmerman* [1984] report an average isoprene mixing ratio of 2.27 ppb and monoterpene mixing ratio of >5 ppb for heights between treetop and 2 km. *Crutzen et al.* [1985] concluded that there are large biogenic organic emissions from the tropical forest and that the emissions were responsible for both an enhancement of CO and depletion of ozone in

the boundary layer. They assumed an OH concentration of at least 5×10^5 molecules cm^{-3} and estimated that an isoprene flux of at least 2 mg m^{-2} h^{-1} was required to maintain the observed isoprene mixing ratio. During aircraft flights over Guyana in 1984 and Brazil in 1985, widespread boundary layer isoprene mixing ratios of ~2 ppb were observed confirming that isoprene was emitted from Amazonian tropical forests in large quantities [*Gregory et al.*, 1986; *Rasmussen and Khalil*, 1988].

Landscape average BVOC fluxes have been estimated from above canopy observations in Peru and in the Brazilian states of Pará, Amazonas, and Rondônia. Studies conducted at six tower sites, ten tethered balloon launching locations, and three aircraft studies are listed in Table 1. The seven different flux estimation approaches used for estimating BVOC fluxes include indirect approaches, based on budgets and concentration gradients, and eddy flux techniques including direct eddy covariance measurements. An additional approach, combining enclosure BVOC emission measurements with tree biomass and species composition data, has been used to characterize fluxes at four of the sites in Table 1 and at additional sites in Ecuador [*Harley et al.*, 2004].

The 1985 GTE ABLE2A study at the Reserva Ducke near Manaus included measurements of mixed layer height and vertical profiles of trace gas concentrations within and above the boundary layer [*Zimmerman et al.*, 1988, *Jacob and Wofsy*, 1988]. These observations provided an improved data set for characterizing the surface fluxes required to balance losses from boundary layer oxidant concentrations. *Zimmerman et al.* [1988] used an estimate for daytime OH of 8.3×10^5 molecules cm^{-3} [*Jacob and Wofsy*, 1988] and observed isoprene (median = 2.03 ppb) and total monoterpene (median = 0.23 ppb) mixing ratios to calculate daily total emissions of 25 mg m^{-2} of isoprene and 5.6 mg m^{-2} of monoterpenes. Estimated isoprene emission peaked at 4 mg m^{-2} h^{-1} around noon and averaged about 3.1 mg m^{-2} h^{-1} between the hours of 0800 to 1600. *Jacob and Wofsy* [1988] using the same observations but a different analysis approach reported a daily total emission that is ~10% lower and a maximum emission that is ~50% higher than the Zimmerman et al. estimates. *Davis et al.* [1994] used these same tethered balloon data to estimate fluxes from the vertical concentration gradient and arrived at isoprene fluxes that were about 30% higher than the Zimmerman et al. estimates.

Vertical profiles of isoprene and monoterpenes have been measured at ten additional Amazonian locations in Peru and the Brazilian states of Rondônia, Pará, and Amazonas using tethered balloon [*Helmig et al.*, 1998; *Greenberg et al.*, 2004] and aircraft samplers [*Kuhn et al.*, 2007; *Karl et al.*, 2007]. While *Zimmerman et al.* [1988] collected 25 vertical profiles (18 daytime and 7 at night) consisting of 106 sam-

Table 1. Amazonian Field Measurements That Have Been Used to Estimate Above Canopy Isoprene and Monoterpene Fluxes

Approach	Platform	Season and Year	Year	Location	References
Budget	aircraft	dry	1979, 1980	between Manaus and Humaita, Brazil	*Crutzen et al.* [1985]
Budget; mixed layer gradient	tethered balloon	early dry	1985	Reserva Ducke: Forest 10 km north of Manaus, Brazil	*Jacob and Wofsy* [1988] *Zimmerman et al.* [1988] *Davis et al.* [1994]
Budget; mixed layer gradient	tethered balloon	early dry	1996	forest 500 km west of Iquitos, Peru	*Helmig et al.* [1998]
Budget	tethered balloon	wet	1998	Balbina: four forest locations about 150 km NE of Manaus Brazil	*Greenberg et al.* [2004]
Budget	tethered balloon	wet	1999	Fazenda Nossa Senhora: pasture 280 km SE Porto Velho, Brazil	*Greenberg et al.* [2004]
Budget	tethered balloon	wet	1999	Jaru Reserve: forest 270 km SE Porto Velho, Brazil	*Greenberg et al.* [2004]
Budget	tethered balloon	wet	2000	Tapajos: forest 50 km south of Santarem, Brazil	*Greenberg et al.* [2004]
DEA; EC	tower	early dry	2000	Tapajos: forest 50 km south of Santarem, Brazil	*Rinne et al.* [2002]
REA	tower	wet, early dry	2000	Caxiuana: forest 330 km west of Belem, Brazil	Pegoraro et al. (unpublished data)
REA	tower	early wet, early dry, wet	2000, 2001, 2002	Cuieiras Reserve: forest 60 km north of Manaus, Brazil	Stefani et al. (unpublished data)
EC	tower	wet, early dry, late dry	2001	Tapajos: forest 50 km south of Santarem, Brazil	Potosnak et al. (unpublished data)
Budget	tethered balloon	early dry	2001	Balbina: forest 150 km NE of Manaus Brazil	Greenberg et al. (unpublished data)
Mixed layer gradient	aircraft	early dry	2001	Cuieiras Reserve: forest 60 km north of Manaus, Brazil	*Kuhn et al.* [2007]
REA; Surface layer gradient	tower	early dry	2001	Cuieiras Reserve: forest 60 km north of Manaus, Brazil	*Kuhn et al.* [2007]
EC	tower	late dry	2004	Cuieiras Reserve: forest 60 km north of Manaus, Brazil	*Karl et al.* [2007]
Mixed layer gradient; variance	aircraft	late dry	2004	forest, wetlands and croplands regions between 10 and 150 km, north and east of Manaus, Brazil	*Karl et al.* [2007]

ples at different heights, the data sets for most of the other sites are considerably smaller and consist of less than ten profiles. The median daytime mixed layer isoprene mixing ratios from the 11 sites ranges from 0.6 to 6.7 ppb. Median daytime total monoterpene mixing ratios varied from 80 to 690 ppt and were positively correlated with isoprene with a typical ratio of ~ 0.1. Note that this is nearly 20% when expressed on a mass basis due to the higher molecular weight of the monoterpenes. The dominant monoterpene at all sites was α-pinene, which typically comprised about half of the total monoterpenes. *Helmig et al.* [1998] observed relatively low median isoprene mixing ratios (1.39 ppb), but report one of the highest isoprene flux estimates (8.1 mg m^{-2} h^{-1}). This is due to their choice of a relatively high OH concentration (4.5×10^6 molecules cm^{-3}). Helmig et al. also estimated fluxes from vertical concentration gradients, but due to the small sample size ($n = 5$) and the large uncertainties associated with individual estimates from this technique, these estimates cannot be used to validate the higher OH estimate. However, recent observations by *Kuhn et al.* [2007] and

Karl et al. [2007] suggest that earlier studies [i.e., *Crutzen et al.*, 1985; *Jacob and Wofsy*, 1988; *Greenberg et al.*, 2004] may have underestimated OH by a factor of 5 or more. Such interpretations were supported by the recent reports about an OH recycling process by isoprene oxidation which may explain such high OH levels [*Lelieveld et al.*, 2008]. These findings give rise to new discussions about the interactions of biogenic emissions and atmospheric chemistry [*Guenther*, 2008] and to isoprene and monoterpene flux estimates which may be underestimated by at least a factor of five.

The tower-based measurement approaches listed in Table 1 include surface layer gradients (SLG), relaxed eddy accumulation (REA), disjunct eddy accumulation (DEA), and eddy covariance (EC). The labor-intensive SLG, REA, and DEA techniques used in these studies have resulted in small data sets, typically less than 20 measurements, and because the samples were transported to laboratories in Europe and the United States, uncertainties associated with sample storage were introduced. Additional uncertainties are associated with the assumptions that are required with these techniques. The continuous measurements of an EC system can provide much larger data sets and more accurate results. Midday average fluxes from all of the tower campaigns listed in Table 1 range from 1.5 to 8.3 mg m^{-2} h^{-1} for isoprene and from 0.2 to 1.7 mg m^{-2} h^{-1} for total monoterpenes. The mean isoprene and monoterpene fluxes from these studies are positively correlated, and total monoterpene emissions tend to be 10% to 20% of the isoprene mass flux. Tower measurement systems are particularly useful for measuring diurnal and seasonal variations in BVOC fluxes. *Karl et al.*'s [2007] eddy covariance measurements show that emissions of isoprene, total monoterpenes, methanol, and acetone are all controlled by both light and temperature. There have been no attempts to continuously measure BVOC fluxes throughout a year, but several of the data sets shown in Table 1 include some information on seasonal variations. These limited data suggest that emissions in the dry season, especially in the later part, are considerably higher than in the wet season. This is in agreement with the ambient isoprene concentration measurements of *Kesselmeier et al.* [2002b] and *Trostdorf et al.* [2004]. An increase in emissions during the dry season has been reported, due to higher sunlight and leaf temperature, but phenology [*Kuhn et al.*, 2002a] may also have an important role.

Karl et al. [2007] measured BVOC concentrations above various land cover types (wetlands, soybean fields, mixed agriculture, primary forest) north and east of Manaus using an airborne fast response proton transfer reaction mass spectrometer (PTRMS). These measurements were made on only two flights because the main focus of the study was on biomass burning, which was primarily occurring south of Manaus. Their aircraft measurements did not include fast response vertical wind fluctuations, required for eddy covariance measurements, but they were able to estimate fluxes from concentration variations. This limited study has provided the first data for characterizing BVOC emission variations over relatively large scales (25 to 10,000 km^2). Isoprene emissions varied over about an order of magnitude (1 to 10 mg m^{-2} h^{-1}) after emissions were adjusted to account for variations in temperature and light. The observed emission variations corresponded with differences in land cover types.

Rasmussen and Khalil [1988] scaled up a constant emission rate, similar to that reported by *Zimmerman et al.* [1988], to estimate annual isoprene fluxes of 60 Tg of isoprene for a 5 × 10^6 km^2 area of Amazonia. *Guenther et al.* [1995] extrapolated *Zimmerman et al.*'s [1988] emission rate using variable temperature, light, and leaf area and estimated an annual emission of 96 Tg isoprene and 14 Tg monoterpenes for a 4.33 × 10^6 km^2 area representing all tropical rainforests. The Guenther et al. estimate used a land cover data set that classified much of the Amazon basin as seasonal tropical forest and other land cover types. *Guenther et al.* [2006] incorporated some of the additional data shown in Table 1 and estimated isoprene emissions that ranged both higher and lower than *Guenther et al.*'s [1995] estimates depending on the weather and land cover data used to drive emissions. *Shim et al.* [2005] used satellite CH_2O observations and a global chemistry and transport model to constrain global isoprene distributions. Their estimates of global isoprene emissions were about 13% higher than *Guenther et al.* [1995], but their estimate for South America was about 35% lower.

3. ATMOSPHERIC CHEMISTRY OVER AMAZONIA: PRODUCTION OF OZONE FROM BIOGENIC HYDROCARBONS, NO$_x$ AND THE ROLE OF OH

In the absence of anthropogenically induced pollution, intensive tropical atmospheric chemistry and physics in Amazonia is dominated by the biosphere. Biogenic emissions of volatile organic compounds contribute to particle formation (see section 4) as well as oxidative chemistry in the rainforest environment. This is a complex chemistry driven by light, OH radicals, ozone, and NO$_x$. Within this context, reactive volatile organic compounds can be involved in both ozone production, as well as ozone consumption. The net effect of VOC on ozone is governed by the amount of available NO$_x$ (NO and NO$_2$). For a more detailed discussion, see relevant literature [i.e., *Carter and Atkinson*, 1996; *Sanhueza et al.*, 1996; *Jacob and Wofsy*, 1988; *Jacob et al.*, 2002; *Neeb et al.*, 1997a, 1997b; *Williams*, 2004]. In the following section, we will concentrate on the oxidation chemistry of isoprene,

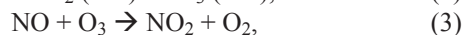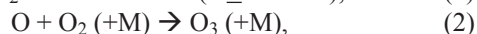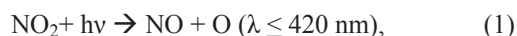since it is thought to be the main compound released from tropical vegetation.

Simplified schemes are used here to help to understand the basic reactions. The atmospheric oxidation of VOC initiated by OH as well as O_3 is described by the following reaction scheme. A subsequent sequence of reactions of the resulting peroxy radical (RO_2) leads to stable products such as alcohols, carbonyls, and acids.

Oxidant consumption

VOCs + OH, O_3 → oxidation products (i.e., alcohols, aldehydes, acids, ketones).
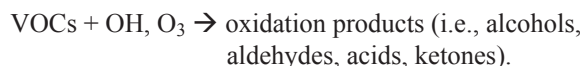
Ozone, NO_2, and NO coexist in the atmosphere in a photostationary equilibrium. NO destroys ozone in reaction 3, but the ozone reforms through reactions 1 and 2, which also regenerates NO. In the presence of VOCs, the RO_2 can convert NO to NO_2 without destroying ozone, leading to production.

Photostationary equilibrium

$$NO_2 + h\nu \rightarrow NO + O \ (\lambda \leq 420 \ nm), \quad (1)$$
$$O + O_2 \ (+M) \rightarrow O_3 \ (+M), \quad (2)$$
$$NO + O_3 \rightarrow NO_2 + O_2, \quad (3)$$
$$RO_2 + NO \rightarrow RO + NO_2. \quad (4)$$

An OH-initiated and NO_x-catalyzed oxidation of a VOC species leads to the formation of many intermediates and is tightly coupled to the conversion of NO to NO_2 [see *Jenkin et al.*, 2002; *Derwent et al.*, 2007].

Ozone production potentials have been related to NO_x/VOC ratios for different sites, ranging from remote to polluted areas [*Chameides et al.*, 1992]. The relation between O_3, NO_x, and VOC has been shown to be driven by complex nonlinear photochemistry. These relations dramatically change in Amazonia from the wet to the dry season. Dry season conditions with higher temperatures lead to substantial higher emission rates of biogenic VOC species from the forest, even though leaf area indices can decrease due to the adaptation strategies of some tree species of dropping their leaves under drought conditions. The most prominent changes are caused by anthropogenic influences such as slash and burn techniques to change forest ecosystems into pasture. Not only is NO_x released by these vegetation fires and further additional anthropogenic sources, but VOC emission is also significantly increased by fires [see also *Longo et al.*, this volume]. This is best reflected by emission ratios of VOC species to other fire emissions as reported by *Andreae and Merlet* [2001]. On the other hand, natural

climate changes from the wet to dry season can also have a significant impact on VOC emissions [*Guenther et al.*, 1999; *Serça et al.*, 2001; *Kesselmeier et al.*, 2002b; *Kuhn et al.*, 2002a, 2004a]. The impact of climatic factors has been also clearly demonstrated by *Sanderson et al.* [2003] who illustrated the impact of climate change on both isoprene emissions and ozone levels. Global isoprene emissions are predicted to increase on a carbon basis from 484 Tg a^{-1} for the 1990s to 615 Tg a^{-1} for the 2090s, as a result of climate and vegetation distribution changes; the authors calculated an ozone increase of 10–20 ppb in some locations. They also noted that these changes in ozone levels were closely linked to changes in isoprene surface fluxes in regions such as the eastern United States or southern China. However, this effect was much less marked over Amazonia and Africa because of lower levels of nitrogen oxides. The VOC/NO_x ratios change due to anthropogenically induced land use change.

A closer look into the OH/Ozone chemistry directs our view to the oxidation products methyl vinyl ketone (MVK) and methacrolein (MACR) [*Kesselmeier et al.*, 2002b; *Kuhn et al.*, 2007]. Under remote environmental conditions over Amazonia during wet season conditions, the only known source of MVK and MACR is isoprene oxidation. This is a nice tool for evaluating the oxidation conditions as the ratio (MVK + MACR)/isoprene can provide an indication of the extent of oxidation. The instantaneous ratio (MVK + MACR)/isoprene is not purely photochemically driven, but is also influenced by the isoprene emission rate, the proximity to emission sources, as well as by atmospheric mixing [*Montzka et al.*, 1995]. For NO_x levels between 0.2 and 0.5 ppb as reported for the different seasons [*Andreae et al.*, 2002], the (MVK + MACR)/isoprene ratios agreed extremely well with the relationship shown in the work of *Biesenthal et al.* [1998].

The ratio of MVK/MACR is also useful in examining the oxidant conditions during the day. This ratio depends on the yields of MVK and MACR from isoprene oxidation and on the relative reaction rates of isoprene, MVK, and MACR with both OH and ozone. OH-induced isoprene oxidation leads to MVK and MACR with respective yields of 32% and 23% [*Tuazon and Atkinson*, 1990]. But MACR is removed more quickly through further OH oxidation than MVK, thus shifting the MVK/MACR ratio to higher values. In the dry season, the daytime ratios were typically in the range of 1.3–1.5 [*Kesselmeier et al.*, 2002b], which is quite close to the relative OH production yield of 1.4 reflecting a relatively high O3/OH ratio [*Starn et al.*, 1998], i.e., a relatively low oxidation capacity due to OH concentrations. Interestingly, the corresponding wet season data showed higher MVK/MACR values, but were difficult to discuss

due to higher individual uncertainties of the data as stated by the authors. In a very recent paper, *Kuhn et al.* [2007] discussed the oxidation capacity in the tropical convective boundary layer (CBL) in an early dry season (July 2001). On the basis of (MVK + MACR)/isoprene and MVK/MACR ratios, they concluded that OH must be much higher than previously assumed. Based on observed vertical gradients of isoprene and its primary degradation products MVK and MACR, they estimated a range of OH during the daytime of $3–8 \times 10^6$ molecules cm^{-3}. This number is an order of magnitude higher than estimates by current state-of-the-art atmospheric chemistry/transport models. Only such high estimates were able to reconcile VOC fluxes derived from an airborne mixed layer gradient (MLG) approach. These results clearly demonstrate that the influence of VOCs on the oxidation capacity in models has high uncertainties [*Lelieveld et al.*, 2004] and that we need many more field measurements in order to understand these chemical processes in the atmosphere. This becomes even more clear when comparing model estimates and measurements of other oxygenated species (acetaldehyde, methanol, formic, and acetic acid), indicating severe gaps in our understanding of the present budgets of these species [*von Kuhlmann et al.*, 2003]. The chemical processes within the oxidation scheme obviously are not fully understood. Recently, *Lelieveld et al.* [2008] reported about an OH recycling process by isoprene which may explain high OH levels in a pristine atmosphere. The authors propose that natural VOC oxidation, notably of isoprene, contributes to an efficient recycling of OH in low-NO_x air through reactions of organic peroxy radicals. Thus, emission of such reactive trace gases might enhance the cleansing capacity of the atmosphere in remote areas like the Amazonian rainforest.

The above mentioned new reports on higher OH concentrations in the Amazonian atmosphere than earlier expected illuminates severe gaps in our knowledge in a region, which has a particularly active photochemistry due to high solar radiation and atmospheric water vapor. Additionally, due to the strong convection in Amazonia surface emissions influence a higher part of the atmosphere than in most other regions. This tropical reactor with its biogenic sources of VOCs and nitrogen oxides is characterized by its very sensitive atmospheric chemistry. Any changes in land use will significantly affect these sources. Furthermore, additional new anthropogenic sources will occur. We have experienced such changes already when comparing wet season (undisturbed) and dry season conditions in view of ozone production as well as increase of aerosol numbers and cloud effects. Such effects on atmospheric chemistry and physics can be expected to become even stronger with increasing disturbance in the relation between biology, chemistry, and physics.

4. FORMATION OF AEROSOL PARTICLES AND CLOUD CONDENSATION NUCLEI (CCN) FROM BIOGENIC HYDROCARBONS

4.1. Introduction

Atmospheric aerosols interact both directly and indirectly with the Earth's radiation budget and climate. As a direct effect, the aerosols scatter or absorb sunlight. As an indirect effect, aerosols in the lower atmosphere can modify number and size of cloud droplets, changing how the clouds reflect and absorb sunlight, thereby affecting the Earth's radiation budget. Aerosols can also act as sites for chemical reactions to take place (heterogeneous chemistry). Hence, they play an important role in global climate and atmospheric chemistry.

The formation of aerosol particles from the oxidation of hydrocarbons is only one but an important contribution to the overall composition of atmospheric aerosols. It is well known that biogenic VOCs especially have a high aerosol formation potential. Consequently, tropical regions in particular are believed to be globally relevant source regions for these kinds of aerosol particles. In general, the volatile aerosol precursors (e.g., terpenes) are first decomposed in the gas phase by bimolecular reactions followed by the formation of products with a lower volatility. Higher functionalized compounds with hydroxyl, carbonyl, carboxyl groups, or groups containing heteroatoms are formed in an oxidizing environment, which will either condense on existing particles or even form new aerosol particles (gas-to-particle conversion). To distinguish this fraction of tropospheric aerosols from the direct input of particulate organics into the atmosphere, it is specified as secondary organic aerosol (SOA). However, although biogenic SOA is the major focus of this chapter, sources and results of field measurements of primary organic aerosol constituents will also be discussed here, especially those primary organic contributions which are linked to tropical regions.

4.2. Historical Background

The first relationship between volatile organic compounds and the formation of atmospheric particles was probably proposed by Arie Haagen-Smit at the California Institute of Technology (Caltech) in 1952 for a strongly anthropogenically influenced environment. Studying various aspects of the Los Angeles smog formation, he not only explained ozone and peroxide formation by the photochemistry of the released hydrocarbons and nitrogen oxides, but also linked the decrease in visibility during smog episodes to the condensation of aldehydes and acids formed by the oxidation of organic volatiles. In 1960, F.W. Went, director of the Missouri

Botanical Garden and former colleague of Haagen-Smit at Caltech, published an extensive article in Nature titled "Blue hazes in the atmosphere." Based on his observations when staying at a countryside site and everyday experiences, as well as his knowledge about secondary plant products, he also connected the occurrence of the natural phenomena with the volatilization and gas phase oxidation of terpenes released from terrestrial vegetation.

4.3. General Source Processes for Atmospheric Particles

Particles in the atmosphere are often divided into the categories of primary and secondary particles according to their formation processes. Primary particles are released directly into the atmosphere, whereas secondary particles are produced within the atmosphere as a consequence of the conversion of volatile precursors into low or nonvolatile substances. Formation processes of primary particles are basically mechanical production (abrasion, suspension) and production during combustion processes (condensation of hot vapors or formation inside flames as described for soot particles) [*Seinfeld and Pandis*, 1998]. In general, mechanical processes create coarse particles (>2.5 μm), whereas combustion processes create fine particles which might coagulate right after production (e.g., chain aggregates of soot particles). Secondary atmospheric particles also belong to the fine particle fraction. The low volatile compounds formed from the oxidation of the precursor compounds (e.g., VOCs, reduced sulfur compounds) can either form new atmospheric particles (homogeneous nucleation), or they can condense onto preexisting particles leading to increased particle size and mass and to an alteration of the chemical composition.

Aerosol particles from biogenic VOCs contribute to the carbonaceous aerosol fraction. The term "carbonaceous aerosols" includes all aerosol constituents which are based on carbon, i.e., the variety of different organic compounds produced from VOC oxidation or combustion processes; however, elemental carbon, bioaerosols, and a few inorganic carbon constituents are also included. The concentration of inorganic carbon, essentially as carbonate, is on average negligible, at least when considering submicrometer particles.

4.4. Molecular Composition of Organic Aerosols

The organic fraction of atmospheric particulate material can contain a large number of diverse molecular species. The composition is mainly dependant on the aerosol source with possible modifications during atmospheric transport. The organic mixture ranges from nonpolar hydrocarbons (alkanes) to highly polar and water-soluble components, such as short dicarboxylic acids or sugars, to macromolecular organics.

Therefore, it is useful to characterize the different sources (or source types) of organic aerosols in terms of their individual chemical composition. Selected source specific compounds can then be used as tracers for the origin of aerosols or to estimate the contribution of the different source types to the measured aerosol.

There are a variety of biogenic and anthropogenic sources of primary organic aerosol constituents. Although exact numbers are missing, globally the input from natural sources is believed to be prominent. However, for the aerosol composition on the local or regional scale, even weak sources can be important [*Schauer et al.*, 1996]. The following sources belong to the most important sources of primary organic aerosols that have been characterized in tropical regions: (1) biomass burning, (2) plant abrasion, and (3) suspension and release of bioaerosols.

Biomass burning is a strong source for atmospheric aerosols, producing about four times more than fossil fuel burning [*Kuhlbusch*, 1998]. A main product and a general tracer used for biomass burning is levoglucosan (1,6-anhydro-β-D-glucopyranose), an anhydro-sugar derived from the thermal degradation of cellulose during the combustion process [*Simoneit*, 1999]. Anhydro-sugars seem to be the most abundant compounds produced during the combustion process of plant material. Other major compound groups identified in smoke particles from biomass burning are alkanes, alkenes, alkanoic acids, di- and triterpenoids, monosaccharides, methoxyphenols, and PAHs [*Simoneit*, 2002]. Some of these constituents are derived from thermally altered plant material (like anhydro-sugars); others are unchanged ingredients (like some wax alkanes). Especially lignin pyrolysis products like vanillic acid can be used as tracers for certain plant species.

Plant abrasion is mainly induced by wind driven mechanical force, like the rubbing of leaves against each other [*Rogge et al.*, 1993]. Identified substances in aerosols from plant abrasion (green and dead leaves) are mainly constituents of the epicuticular plant waxes: *n*-alkanes, *n*-alkanals, *n*-alkanols, *n*-alkanoic acids (fatty acids). These compound groups are not very specific for biological sources, but due to their biosynthesis, specific patterns in carbon numbers of plant-derived wax components can be observed. Leaf wax alkanes have a strong odd carbon number predominance with dominant carbon numbers C29, C31, and C33, whereas alkanoic acids, alkanals, and alkanols are dominated by even carbon numbers. Fossil fuel constituents show no predominance in carbon numbers. Therefore, it is possible to use these specific patterns to identify contributions of plants to atmospheric aerosols [*Simoneit et al.*, 1988].

Bioaerosols are primary organic aerosols with diameters from ~10 nm to 100 μm that are either alive, carry living

organisms or are released from living organisms like bacteria, fungi, algae, viruses, pollen, spores (e.g., from ferns), cell debris, biofilms, etc. [*Ariya and Amyot*, 2004]. Generally, the size of bacteria is around 1 μm, pollen grains are mostly larger than 10 μm, and viruses are in the nanometer range. Each of these "particles" is usually itself a complex mixture of various molecules. Bacteria may spread diseases, can act as cloud condensation nuclei and ice nuclei. They have been found even at high altitudes in the atmosphere and remote regions. Bacteria and fungi can be suspended from soil or plants by wind and from water surfaces by bubble-bursting processes or sea spray. They can also be released by anthropogenic sources like farming, waste, and wastewater treatment. Bacteria can even live and grow in atmospheric water droplets like fog [*Fuzzi et al.*, 1997] or even super cooled cloud droplets [*Sattler et al.*, 2001]. The importance of bioaerosols for atmospheric aerosol content is very unclear. Some authors report bioaerosols as being major components, whereas other studies report only insignificant contributions from bacteria to the atmospheric particulate material. In Amazonian aerosols, the nocturnal increase of coarse size particle mass (PM10-PM2) was attributed to fungi [*Graham et al.*, 2003a, 2003b]. During the wet season, biogenic particles accounted for 55–92% of the fine particle mass and for 65–95% of the coarse particle mass sampled in the Amazonian basin [*Artaxo et al.*, 1988, 1990]. For Russia (Lake Baikal) and Germany (Mainz), contributions of primary biological aerosol particles (including plant fragments, pollen, etc.) to total atmospheric particles (>0.2 μm) were reported to be in the range of 20% to 30%, respectively [*Jaenicke*, 2005].

4.5. Sources and Composition of Secondary Organic Aerosols

As introduced above, secondary organic aerosols (SOAs) are produced (1) by gas-phase oxidation of volatile organic compounds that can either form new particles, or condense onto preexisting particles, (2) by heterogeneous reactions on particle surfaces, or (3) by in-cloud processing. Precursors of organic SOA are mostly volatile reactive biogenic (e.g., terpenes), or anthropogenic (e.g., aromatics) hydrocarbons. Products formed can be relatively low volatile organics, which convert almost completely to the particle phase, or semivolatile organics, which partition between the gas and particle phase. This gas-particle partitioning of semivolatile (and also low volatile) compounds can be described by gas-particle partitioning models [*Pankow*, 1994; *Odum et al.*, 1996], in which the dependence of the concentration of an individual organic compound, i, in the particle phase, on the available absorbing organic aerosol mass (MO), the parti-

tioning coefficient of compound i and the concentration of i in the gas phase has the relationship:

$$c_{aer} = c_{gas} \times \text{Kom} \times \text{MO}, \tag{5}$$

where Kom is the partitioning coefficient of i (m³ μg⁻¹) (temperature dependent), c_{aer} is the concentration of compound i in the absorbing organic particle phase (ng m⁻³), c_{gas} is the concentration of i in the gas phase (ng m⁻³), and MO is the concentration of the absorbing organic phase in the aerosol (μg m⁻³).

Although the underlying equations are rather simple, the estimation of SOA mass is complicated for certain locations and atmospheric conditions, as well as for use in regional and global SOA modeling, the strong temperature dependence of the partitioning coefficient also adds to the complication [*Takekawa et al.*, 2003].

During the first years of SOA-research, attention was paid just to the rather low volatile or semivolatile oxidation products, which directly contribute to the particle phase by gas-to-particle conversion. More recent studies also show that volatile carbonylic products formed in the gas phase oxidation of organics may contribute over a longer period of time to the SOA mass by the formation of low volatile oligomers, for example, via acid catalyzed reactions of aldehydes or ketones on the particle surfaces or inside the particles (aldol reaction/condensation, acetal formation). These processes result in increased particle mass and a lower volatility. This might be the case for both biogenic and anthropogenic precursors [*Jang et al.*, 2002, 2004; *Gao et al.*, 2004; *Iinuma et al.*, 2004; *Kalberer et al.*, 2004]. There is also evidence for the direct formation of oligomeric products by heterogeneous reactions of unsaturated gas phase compounds (e.g., isoprene) on particle surfaces [*Limbeck et al.*, 2003]. Several groups speculate that these oligomeric products formed from gaseous precursors could represent a substantial fraction of the so-called "humic-like substances" (HULIS) often identified in atmospheric aerosols. HULIS is a collective term for a group of particle phase compounds unidentified at the molecular level, which add to the water-soluble organic carbon.

This generation of new particle phase products from gas phase constituents during the atmospheric lifetime of aerosols is part of the so-called atmospheric ageing of organic particles, a process that is currently not well characterized. Besides the incorporation of reactive gas phase species into the organic aerosol fraction by oligomer formation, ageing also includes the degradation or chemical modification of particle phase constituents by atmospheric oxidants. Since these chemical modifications will result in alterations of the physical (volatility, light absorption, light scattering) and

physicochemical properties (water solubility, CCN-activity) of atmospheric aerosols, the investigation of these processes has to be addressed in future research on organic aerosols.

The incorporation of SOA formation into atmospheric models is not an easy task, since a variety of chemical and physicochemical processes influence the SOA particle mass in the ambient atmosphere. A sensitivity analysis of SOA production and transport modeling [*Tsigaridis and Kanakidou*, 2003] showed an uncertainty factor of about 20 in predicting SOA production when considering the different influences of partitioning, ageing, and MO, excluding the uncertainties of precursor emissions and individual oxidation pathways. This results in an annual global production of SOA of 2.55 to 47.12 Tg of organic matter per year. Another study showed SOA production using the partitioning method and the bulk yield method (ignoring the partitioning mechanism) to be 15.3 and 24.6 Tg per year [*Lack et al.*, 2004], respectively.

Precursors of biogenic SOA in the continental environment are mainly unsaturated hydrocarbons, namely, (mono-) terpenes, sesquiterpenes, and isoprene. The SOA-forming potential of terpenes is well known and has been intensively investigated, e.g., [*Went*, 1960a; *Yokouchi and Ambe*, 1985; *Zhang et al.*, 1992; *Hoffmann et al.*, 1997, 1998; *Kavouras et al.*, 1998; *Griffin et al.*, 1999; *Yu et al.*, 1999; *O'Dowd et al.*, 2002], whereas isoprene was only recently found to form low volatile secondary products [*Claeys et al.*, 2004a, 2004b]. Known products of atmospheric isoprene oxidation are polyols and acidic compounds like 2-methyltetrols and 2,3-dihydroxymethacrylic acid. It was estimated that isoprene might add about 2 Tg of polyols to atmospheric SOA.

This is a substantial amount, although terpenes may add 10 times more to SOA. The most frequently studied and most important SOA-forming reactions of terpenes are gas-phase oxidations by ozone, OH– and NO3– radicals.

The oxidation of terpenes by ozone, OH radical, and photosmog generates a variety of oxygenated gas phase [*Calogirou et al.*, 1999] and particle phase products which have been identified in chamber experiments [*Christoffersen et al.*, 1998; *Hoffmann et al.*, 1998; *Yu et al.*, 1999; *Glasius et al.*, 2000a; *Koch et al.*, 2000; *Larsen et al.*, 2001; *Jaoui and Kamens*, 2003a, 2003b, 2003c; *Winterhalter et al.*, 2003]. Known terpene oxidation products relevant for SOA production mainly contain carbonyl, alcohol, and carboxylic acid functional groups. Products bearing carboxylic acid functional groups have low volatility and are therefore especially interesting for SOA formation. Figure 2 shows some important products from monoterpene oxidation. Recently, it was proposed that peroxides could also represent a major part of the SOA formed by terpene ozonolysis [*Bonn et al.*, 2004], a suggestion which was recently confirmed by chamber studies [*Docherty et al.*, 2005]. As mentioned above, oligomer formation from (semi-) volatile oxygenated terpene oxidation products might also contribute to SOA formation from biogenic precursors.

4.6. Field Measurements

Very few measurements of the aerosol composition in forested tropical regions exist, especially those focusing on the organic aerosol fraction. Nevertheless, some dedicated studies, partly in the framework of LBA, investigated the
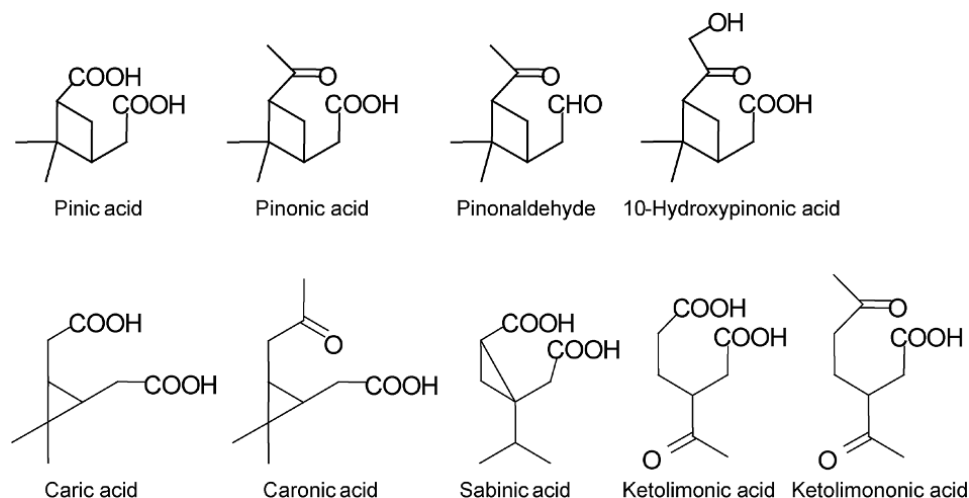
Figure 2. Important monoterpene oxidation products.

Table 2. Concentration Ranges of Some Sugars and Levoglucosan in the Atmospheric Particle Phase Measured at Different Locations[a]

Location	Description	PM	Glucose	Sucrose	Mycose	Levogluc.	Reference
			Concentration (ng m^{-3})				
Gosnan, Jeju Island, Korea	rural/marine	TSP	11–111 (50)	6–444 (86)	2.5–30 (13)	8–74	*Simoneit et al.* [2004b]
N-Pacific	marine/remote	TSP	0–4	0–1.8	0–0.2	0.2–1.3	
Amazonia, Brazil	rain-forest/remote	2.5	1.88–16.3 (7.9)	<0.06–1.9 (1.5)	4.9–12 (6.9)	7.73–32.9 (15)	*Graham et al.* [2003a, 2003b]
		>2.5	1.7–124 (48)	<0.06–77 (37)	21–90 (48)	<0.04–4.79 (1.79)	
Rondonia, Brazil	rain-forest/biomass burning	2.5	14–62 (37)	0.8–26 (7)	5–18 (9)	1182–6900 (2460)	*Graham et al.* [2002]
Santiago, Chile	urban	TSP	10–2210 (940)	15–3060 (1108)	8–1660 (477)	12–2452 (839)	*Simoneit et al.* [2004b]
Kuala Lumpur, Malaysia	urban/biomass burning	TSP				1162–33,400 (14,460)	

[a]Mean concentration is shown within parentheses.

chemical composition of organics in the particle phase. In the following paragraphs, some results of these measurements are presented, and they are put into perspective with measurement results from other regions.

Table 2 shows atmospheric concentrations of selected sugars and levoglucosan in different regions. Levoglucosan is a degradation product of cellulose and almost exclusively produced by combustion of plant material. Therefore, it is not surprising that concentrations are low in remote areas (around 1 to about 10 ng m^{-3}), higher in urban areas due to the use of wood as fuel (roughly 100 to more than 1000 ng m^{-3}), and reach highest concentrations in aerosols from massive biomass burning in tropical areas (around 1000 to more than 10,000 ng m^{-3}). Sugar concentrations also show very different concentrations from less than 1 ng m^{-3} above the oceans, but they were also observed in substantial amounts, e.g., around 1000 ng m^{-3} in aerosol samples from Chile. Usually, concentrations of glucose, sucrose, and mycose are lower than 100 ng m^{-3}. The source of sugars is believed to be mainly soil dust (including suspended microorganisms) [*Simoneit et al.*, 2004a]. Other observations in the Amazonian rainforest point to primary contributions from living plants, e.g., glucose and sucrose may derive from pollen and fern spores, or mycose may derive from fungal spores [*Graham et al.*, 2003a, 2003b]. Consequently, sugar concentrations for glucose, sucrose, and fructose were higher during the daytime, and levels of mycose (trehalose), arabitol, and mannitol were higher during the night when a strong release of fungal spores occurred. Mycose, arabitol, and mannitol are well-known constituents of fungal spores and sucrose, glucose, and fructose are known to be present in pollen grains.

Levoglucosan, sugars and the lipid constituents represent the primary fraction of organic aerosols, whereas short-chain dicarboxylic acids have primary and secondary sources.

Oxocarboxylic acids derive mostly from secondary processes, either the oxidation of VOCs or the further oxidation of carbonyls, and mono- or dicarboxylic acids. Oxalic acid (and other di- and oxocarboxylic acids) levels are rather low in marine and remote areas, although secondary production can be observed in remote arctic regions [*Kawamura et al.*, 2005]. Concentrations of oxalic acid are around 100 ng m^{-3} in natural or remote regions as shown in Table 3. Urban concentrations are in the order of a few hundred ng m^{-3}, and the highest concentrations are observed in biomass burning aerosols (more than 1000 ng m^{-3}). The same trend can be observed for malonic and succinic acid, although concentrations are substantially lower.

Particle phase constituents from the oxidation of biogenic VOCs (e.g., terpenes) are obviously of secondary origin. Therefore, it is mainly forested regions that are influenced by oxidation products from biogenic VOC. The acidic products of monoterpene oxidation add to the water-soluble OC, and therefore, they might be important for the formation of CCN. Moreover, the oxidation of terpenes has been linked to the formation of new particles above forests [*O'Dowd et al.*, 2002]. Although SOA from monoterpene oxidation seems to be very important for the global SOA budget [*Chung and Seinfeld*, 2002; *Tsigaridis and Kanakidou*, 2003], there exist only few measurements of particle phase constituents derived from monoterpene oxidation. Mostly low volatile products of α- and β-pinene, namely, pinic and pinonic acid have been measured. Table 4 shows a selection of reported concentrations. Measurements of ambient concentrations of products from other important monoterpenes, such as from limonene, 3-carene, or sabinene, are even less frequent. The concentrations of these terpene oxidation products in the particle phase vary strongly, depending on time and location. Pinic and pinonic acid concentrations can range from

Table 3. Concentrations of Different Acids and Glyoxal in the Atmospheric Particle Phase Sampled in Distinct Areas[a]

Location	Description	PM	Concentration (ng mg^{-3})							Reference
			Oxalic Acid	Malonic Acid	Succinic Acid	Glyoxylic Acid	Pyruvic Acid	Maleic Acid	Malic Acid	
Vienna, Austria	urban	TSP	340	244	117	22	63			*Limbeck and Puxbaum* [1999]
NW-Pacific	marine	TSP	3.6–430	0.1–53	0.1–37			0.1–2.5		*Mochida et al.* [2003]
Tokyo, Japan	urban	TSP	89–815	16–163	13–168	5.3–105	6.6–138	2.5–31	0–99	*Kawamura and Yasui* [2005]
Canada	Arctic	2	6.5–59 (26)	1.2–20 (7.6)	1.6–19 (7.7)	<0.01–39 (11.9)	0.37–2.76 (1.3)	0.07–1.6 (0.59)	<0.01–6.5 (1.5)	*Kawamura et al.* [2005]
Amazonia (2001)	natural rainforest	2.5	8.8–148 (57)	4.4–48 (22)	2.1–8 (4.9)			0.19–0.55 (0.37)	4.2–24 (14.5)	*Graham et al.* [2003a, 2003b]
Amazonia (1999)	rainforest (burning season)	2.5	51–691 (329)	7.4–149 (56)	3.5–76 (31)	1.6–66 (25)	1.2–28 (11)	0.6–13 (6.3)	12–146 (67)	*Graham et al.* [2002]

[a]Values are mean concentrations or concentration ranges, sometimes given with mean concentrations in parentheses.

below 1 ng m^{-3} to about 100 ng m^{-3} even at the same location. Again, very few results are reported about their atmospheric concentrations in forested tropical regions.

4.7. Summary and Research Needs

Organic contributions to the atmospheric particle phase are known to derive from primary and secondary sources. Especially in the tropics, these sources can account for the major fraction of submicrometer aerosols. Despite a series of international research projects (e.g., LBA), smog chamber studies, and model development, a quantitative understanding of the processes linking emissions and their contribution to the tropospheric particle phase still does not exist. This is especially true for tropical forests, since not only are the emissions of aerosol precursor gases poorly characterized, but very few measurements of the chemical composition of the tropical organic aerosol have been made. Another largely unknown area is the destiny of biogenic VOC oxidation products within the particle phase. Up to now, only the low-volatile products, which formed immediately during the reaction of the precursor hydrocarbon and the oxidant, were considered to contribute to aerosol formation. However, there is a growing awareness that chemical processes are also taking place within the particle phase. The atmospheric relevance of these reactions, for example, in connection with isoprene oxidation products, have to be evaluated in future studies. Moreover, there still exists a poor understanding of the influence of biogenically derived SOA components on the atmospheric water cycle (CCN or IN activity), which is potentially a significant link between the terrestrial biosphere and the atmosphere in forested tropical regions.

5. LBA CONTRIBUTIONS TO UNDERSTANDING BVOC EMISSIONS AND THEIR ROLE IN THE EARTH SYSTEM

Investigations of Amazonian BVOC began in the late 1970s and early 1980s and demonstrated that Amazonia is a major source of atmospheric BVOC and that these emissions

Table 4. Concentrations (Range or Mean) of Low Volatile Products From the Oxidation of α- and β-Pinene in Ambient Aerosols

Location	Time	Concentration (ng m^{-3})			Reference
		Pinic Acid	Pinonic Acid	Norpinonic Acid	
Tabua, Portugal	Aug 1996	0.39–83	7.1–98 (*cis-*) 1.6–43 (*trans-*)	0.14–38 (*cis-*) 0–14 (*trans-*)	*Kavouras et al.* [1999]
Nova Scotia, Canada	Jul 1996	0.48–0.59	0.13–0.39	0.04–0.24	*Yu et al.* [1999]
Pertouli, Greece	Aug 1997	0.4–4.4	1–25.7	–	[*Kavouras et al.* [1999]
Amazonia, Brazil	Jul 2001	1.1 (fine and coarse)	–	–	*Graham et al.* [2003a, 2003b]

have a substantial impact on the chemical composition of the atmosphere. Global emission, chemistry, and transport modeling studies in the 1990s provided additional evidence that Amazonian BVOC emissions are an important component of the earth system. However, they also introduced some controversy associated with reconciling the large estimates of isoprene emissions with the observed concentrations of oxidation products. Since the emission estimates were based on relatively few measurements, and because very little was known about the factors controlling these emissions, many modeling studies implemented emission rates that were considerably lower than estimates based on field observations, but were within the large range of uncertainty associated with these emission estimates.

LBA field campaigns dramatically increased the number of field studies of isoprene and monoterpenes emissions. Some LBA studies included direct flux measurements, in contrast to previous observations that only provided an indirect means of estimating terpenoid fluxes. The LBA results generally agree with earlier studies, but they also showed that there is substantial temporal and spatial variability. Additional LBA measurements provided an initial characterization of biogenic oxygenated VOC emissions. LBA studies also included improved efforts to integrate observations of chemistry, transport, and emissions. These studies provide evidence that an improved understanding of Amazonian atmospheric chemistry and cloud processes is needed and that this may explain at least some of the inconsistencies between estimates of isoprene emissions and atmospheric distributions of oxidation products.

The improved logistical capabilities associated with the LBA research program provide a convenient opportunity for future investigations of BVOC emissions and their role in the earth system. Research priorities include extending efforts to integrate investigations of emissions, chemistry, transport, and cloud processes. Future studies should target a wide range of biogenic VOCs, including sesquiterpenes and oxygenated VOCs, and their products, including formaldehyde and CO (which can be observed with satellite-based remote sensing), and should investigate the impact of BVOC on oxidant and aerosol distributions and on the carbon and water cycles. Additional research priorities include investigations of the processes controlling seasonal and spatial variations and the response to a changing earth system. This can be accomplished through a combination of tower-based multiyear continuous flux measurements of temporal variations, aircraft-based direct flux measurements of regional variations, and enclosure-based process studies. Significant advances in our understanding of the processes controlling Amazonian BVOC emissions and their impact on the earth system require a continued commitment and enhancement of the international and multidisciplinary collaborations established by the LBA research program.

REFERENCES

Andreae, M. O., and P. Merlet (2001), Emission of trace gases and aerosols from biomass burning, *Global Biogeochem. Cycles*, *15*(4), 955–966.

Andreae, M. O., R. W. Talbot, T. W. Andreae, and R. C. Harriss (1988), Formic and acetic acid over the central Amazon region, Brazil: 1. Dry season, *J. Geophys. Res.*, *93*, 1616–1624.

Andreae, M. O., et al. (2002), Biogeochemical cycling of carbon, water, energy, trace gases, and aerosols in Amazonia: The LBA-EUSTACH experiments, *J. Geophys. Res.*, *107*(D20), 8066, doi:10.1029/2001JD000524.

Araújo, A. C., et al. (2002), Comparative measurements of carbon dioxide fluxes from two nearby towers in a central Amazonian rainforest: The Manaus LBA site, *J. Geophys. Res.*, *107*(D20), 8090, doi:10.1029/2001JD000676.

Ariya, P. A., and M. Amyot (2004), New directions: The role of bioaerosols in atmospheric chemistry and physics, *Atmos. Environ.*, *38*, 1231–1232.

Artaxo, P., H. Storms, F. Bruynseels, R. Van Grieken, and W. Maenhaut (1988), Composition and sources of aerosols from the Amazon Basin, *J. Geophys. Res.*, *93*, 1605–1615.

Artaxo, P., W. Maenhaut, H. Storms, and R. Van Grieken (1990), Aerosol characteristics and sources for the Amazon Basin during the wet season, *J. Geophys. Res.*, *95*, 16,971–16,985.

Ayres, J. M. (1986), White Uakaris and flooded forests, Ph.D. thesis, 338 pp., Cambridge Univ., Cambridge.

Ayres, J. M. (1993), *As Matas da Várzea do Mamirauá. MCT/CNPq*, 90 pp., Sociedade Civíl Mamirauá, Brasília.

Baker, T. R., et al. (2004), Are Amazonian forest plots increasing in biomass?, *Philos. Trans. R. Soc. London, Ser. B*, *359*, 353–365.

Baldwin, I. T., R. Halitschke, A. Paschold, C. C. von Dahl, and C. A. Preston (2006), Volatile signaling in plant-plant interactions: "Talking trees" in the genomics era, *Science*, *311*(5762), 812–815.

Biesenthal, T. A., J. W. Bottenheim, P. B. Shepson, S.-M. Li, and P. C. Brickell (1998), The chemistry of biogenic hydrocarbons at a rural site in eastern Canada, *J. Geophys. Res.*, *103*(D19), 25,487–25,498.

Bonn, B., R. von Kuhlmann, and M. G. Lawrence (2004), High contribution of biogenic hydroperoxides to secondary organic aerosol formation, *Geophys. Res. Lett.*, *31*, L10108, doi:10.1029/2003GL019172.

Braga, P. I. S. (1979), Subdivisão fitogeográfica, tipos de vegetação, conservação e inventário florístico da floresta amazônica, *Acta Amazonica, Suppl. 9*, 53–80.

Calogirou, A., B. R. Larsen, and D. Kotzias (1999), Gas-phase terpene oxidation products: A review, *Atmos. Environ.*, *33*, 1423–1439.

Carlier, P., H. Hannachi, and G. Mouvier (1986), The chemistry of carbonyl-compounds in the atmosphere—A review, *Atmos. Environ.*, *20*(11), 2079–2099.

Carswell, F. E., et al. (2002), Seasonality in CO_2 and H_2O flux at an eastern Amazonian rainforest, *J. Geophys. Res.*, *107*(D20), 8076, doi:10.1029/2000JD000284.

Carter, W. P. L., and R. Atkinson (1996), Development and evaluation of a detailed mechanism for the atmospheric reactions of isoprene and NO_x, *Int. J. Chem. Kinet.*, *28*, 497–530.

Chameides, W. L., et al. (1992), Ozone precursor relationships in the ambient atmosphere, *J. Geophys. Res.*, *97*(D5), 6037–6055.

Chebbi, A., and P. Carlier (1996), Carboxylic acids in the troposphere, occurrence, sources, and sinks: A review, *Atmos. Environ.*, *30*(24), 4233–4249.

Chou, W. W., S. C. Wofsy, R. C. Harriss, J. C. Lin, C. Gerbig, and G. W. Sachse (2002), Net fluxes of CO_2 in Amazonia derived from aircraft observations, *J. Geophys. Res.*, *107*(D22), 4614, doi:10.1029/2001JD001295.

Christoffersen, T. S., et al. (1998), *cis*-Pinic acid, a possible precursor for organic aerosol formation from ozonolysis of alpha-pinene, *Atmos. Environ.*, *32*, 1657–1661.

Chung, S. H., and J. H. Seinfeld (2002), Global distribution and climate forcing of carbonaceous aerosols, *J. Geophys. Res.*, *107*(D19), 4407, doi:10.1029/2001JD001397.

Claeys, M., et al. (2004a), Formation of secondary organic aerosols through photooxidation of isoprene, *Science*, *303*, 1173–1176.

Claeys, M., W. Wang, A. C. Ion, I. Kourtchev, A. Gelencser, and W. Maenhaut (2004b), Formation of secondary organic aerosols from isoprene and its gas-phase oxidation products through reaction with hydrogen peroxide, *Atmos. Environ.*, *38*, 4093–4098.

Crutzen, P. J., A. C. Delany, J. Greenberg, P. Haagenson, L. Heidt, R. Lueb, W. Pollock, W. Seiler, A. Wartburg, and P. Zimmerman (1985), Tropospheric chemical composition measurements in Brazil during the dry season, *J. Atmos. Chem.*, *3*, 233–256.

Crutzen, P. J., et al. (2000), High spatial and temporal resolution measurements of primary organics and their oxidation products over the tropical forests of Surinam, *Atmos. Environ.*, *34*, 1161–1165.

Davis, K. J., D. H. Lenschow, and P. R. Zimmerman (1994), Biogenic nonmethane hydrocarbon emissions from tethered balloon observations, *J. Geophys. Res.*, *99*, 25,587–25,598.

Derwent, R. G., M. E. Jenkin, N. R. Passant, and M. J. Pilling (2007), Photochemical ozone creation potentials (POCPs) for different emission sources of organic compounds under European conditions estimated with a master chemical mechanism, *Atmos. Environ.*, *41*, 2570–2579.

Dicke, M., A. A. Agrawal, and J. Bruin (2003), Plants talk, but are they deaf?, *Trends Plant Sci.*, *8*, 403–405.

Dindorf, T., U. Kuhn, L. Ganzeveld, G. Schebeske, C. Ciccioli, C. Holzke, R. Köble, G. Seufert, and J. Kesselmeier (2006), Significant light and temperature dependent monoterpene emissions from European beech (*Fagus sylvatica* L.) and their potential impact on the European volatile organic compound budget, *J. Geophys. Res.*, *111*, D16305, doi:10.1029/2005JD006751.

Docherty, K. S., W. Wu, Y. B. Lim, and P. J. Ziemann (2005), Contributions of organic peroxides to secondary aerosol formed from reactions of monoterpenes with O-3, *Environ. Sci. Technol.*, *39*, 4049.

Fehsenfeld, F., et al. (1992), Emissions of volatile organic compounds from vegetation and the implications for atmospheric chemistry, *Global Biogeochem. Cycles*, *6*, 389–430.

Fuzzi, S., P. Mandrioli, and A. Perfetto (1997), Fog droplets—An atmospheric source of secondary biological aerosol particles, *Atmos. Environ.*, *31*, 287–290.

Gao, S., et al. (2004), Particle phase acidity and oligomer formation in secondary organic aerosol, *Environ. Sci. Technol.*, *38*, 6582–6589.

Geron, C., A. Guenther, J. Greenberg, H. W. Loescher, D. Clark, and B. Baker (2002), Biogenic volatile organic compound emissions from a lowland tropical wet forest in Costa Rica, *Atmos. Environ.*, *36*, 3793–3802.

Geron, C., S. Owen, A. Guenther, J. Greenberg, R. Rasmussen, J. H. Bai, Q. J. Li, and B. Baker (2006), Volatile organic compounds from vegetation in southern Yunnan Province, China: Emission rates and some potential regional implications, *Atmos. Environ.*, *40*, 1759–1773.

Glasius, M., M. Lahaniati, A. Calogirou, D. Di Bella, N. R. Jensen, J. Hjorth, D. Kotzias, and B. R. Larsen (2000a), Carboxylic acids in secondary aerosols from oxidation of cyclic monoterpenes by ozone, *Environ. Sci. Technol.*, *34*, 1001–1010.

Glasius, M., et al. (2000b), Sources to formic acid studied by carbon isotopic analysis and air mass characterization, *Atmos. Environ.*, *34*, 2471–2479.

Graham, B., O. L. Mayol-Bracero, P. Guyon, G. C. Roberts, M. O. Andreae, S. Decesari, M. C. Facchini, P. Artaxo, W. Maenhaut, and P. Köll (2002), Water-soluble organic compounds in biomass burning aerosols over Amazonia: 1. Characterization by NMR and GC-MS, *J. Geophys. Res.*, *107*(D20), 8047, doi:10.1029/2001JD000336.

Graham, B., et al. (2003a), Composition and diurnal variability of the natural Amazonian aerosol, *J. Geophys. Res.*, *108*(D24), 4765, doi:10.1029/2003JD004049.

Graham, B., P. Guyon, P. E. Taylor, P. Artaxo, W. Maenhaut, M. M. Glovsky, R. C. Flagan, and M. O. Andreae (2003b), Organic compounds present in the natural Amazonian aerosol: Characterization by gas chromatography–mass spectrometry, *J. Geophys. Res.*, *108*(D24), 4766, doi:10.1029/2003JD003990.

Greenberg, J. P., and P. R. Zimmerman (1984), Nonmethane hydrocarbons in remote tropical, continental, and marine atmospheres, *J. Geophys. Res.*, *89*(D3), 4767–4778.

Greenberg, J. P., A. B. Guenther, G. Petron, C. Wiedinmyer, O. Vega, L. V. Gatti, J. Tota, and G. Fisch (2004), Biogenic VOC emissions from forested Amazonian landscapes, *Global Change Biol.*, *10*(5), 651–662.

Gregory, G. L., et al. (1986), Air chemistry over the tropical forest of Guyana, *J. Geophys. Res.*, *91*, 8603–8612.

Griffin, R. J., D. R. Cocker III, J. H. Seinfeld, and D. Dabdub (1999), Estimate of global atmospheric organic aerosol from oxidation of biogenic hydrocarbons, *Geophys. Res. Lett.*, *26*, 2721–2724.

Guenther, A. (2002), The contribution of reactive carbon emissions from vegetation to the carbon balance of terrestrial ecosystems, *Chemosphere*, *49*, 837–844.

Guenther, A. (2008), Atmospheric chemistry: Are plant emissions green?, *Nature*, *452*, 701–702.

Guenther, A., et al. (1995), A global model of natural volatile organic compound emissions, *J. Geophys. Res.*, *100*, 8873–8892.

Guenther, A., B. Baugh, G. Brasseur, J. Greenberg, P. Harley, L. Klinger, D. Serça, and L. Vierling (1999), Isoprene emission estimates and uncertainties for the Central African EXPRESSO study domain, *J. Geophys. Res.*, *104*, 30,625–30,639.

Guenther, A., T. Karl, P. Harley, C. Wiedinmyer, P. I. Palmer, and C. Geron (2006), Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature), *Atmos. Chem. Phys.*, *6*, 3181–3210.

Harley, P., et al. (2004), Variation in potential for isoprene emissions among neotropical forest sites, *Global Change Biol.*, *10*(5), 630–650.

Helmig, D., B. Balsley, K. Davis, L. R. Kuck, M. Jensen, J. Bognar, T. Smith Jr., R. Vasquez Arrieta, R. Rodriguet, and J. W. Birks (1998), Vertical profiling and determination of landscape fluxes of biogenic nonmethane hydrocarbons within the planetary boundary layer in the Peruvian Amazon, *J. Geophys. Res.*, *103*(D19), 25,519–25,532.

Hoffmann, T., J. R. Odum, F. Bowman, D. Collins, D. Klockow, R. C. Flagan, and J. H. Seinfeld (1997), Formation of organic aerosols from the oxidation of biogenic hydrocarbons, *J. Atmos. Chem.*, *26*, 189–222.

Hoffmann, T., R. Bandur, U. Marggraf, and M. Linscheid (1998), Molecular composition of organic aerosols formed in the α-pinene/O_3 reaction: Implications for new particle formation processes, *J. Geophys. Res.*, *103*, 25,569–25,578.

Holzinger, R., L. Sandoval-Soto, S. Rottenberger, P. J. Crutzen, and J. Kesselmeier (2000), Emissions of volatile organic compounds from *Quercus ilex* L. measured by proton transfer reaction mass spectrometry under different environmental conditions, *J. Geophys. Res.*, *105*(D16), 20,573–20,579.

Houghton, R. A. (2003), Why are estimates of the terrestrial carbon balance so different?, *Global Change Biol.*, *9*(4), 500–509.

Houghton, R. A., M. Gloor, J. Lloyd, and C. Potter (2009), The regional carbon budget, *Geophys. Monogr. Ser.*, doi:10.1029/2008GM000718, this volume.

Iinuma, Y., O. Boge, T. Gnauk, and H. Herrmann (2004), Aerosol-chamber study of the alpha-pinene/O-3 reaction: Influence of particle acidity on aerosol yields and products, *Atmos. Environ.*, *38*, 761–773.

Jacob, D. J., and S. C. Wofsy (1988), Photochemistry of biogenic emissions over the Amazon forest, *J. Geophys. Res.*, *93*, 1477–1486.

Jacob, D. J., B. D. Field, E. M. Jin, I. Bey, Q. Li, J. A. Logan, R. M. Yantosca, and H. B. Singh (2002), Atmospheric budget of acetone, *J. Geophys. Res.*, *107*(D10), 4100, doi:10.1029/2001JD000694.

Jaenicke, R. (2005), Abundance of cellular material and proteins in the atmosphere, *Science*, *308*, 73.

Jang, M., N. M. Czoschke, and A. L. Northcross (2004), Atmospheric organic aerosol production by heterogeneous acid-catalyzed reactions, *Chemphyschem*, 5, 1647–1661.

Jang, M. S., N. M. Czoschke, S. Lee, and R. M. Kamens (2002), Heterogeneous atmospheric aerosol production by acid-catalyzed particle-phase reactions, *Science*, *298*, 814–817.

Jaoui, M., and R. M. Kamens (2003a), Gas and particulate products distribution from the photooxidation of alpha-humulene in the presence of NO_x, natural atmospheric air and sunlight, *J. Atmos. Chem.*, *46*, 29–54.

Jaoui, M., and R. M. Kamens (2003b), Gaseous and particulate oxidation products analysis of a mixture of alpha-pinene plus beta-pinene/O-3/air in the absence of light and alpha-pinene plus beta-pinene/NO_x/air in the presence of natural sunlight, *J. Atmos. Chem.*, *44*, 259–297.

Jaoui, M., and R. M. Kamens (2003c), Mass balance of gaseous and particulate products from beta-pinene/O-3/air in the absence of light and beta-pinene/NO_x/air in the presence of natural sunlight, *J. Atmos. Chem.*, *45*, 101–141.

Jenkin, M. E., S. M. Saunders, R. G. Derwent, and M. J. Pilling (2002), Development of a reduced speciated VOC degradation mechanism for use in ozone models, *Atmos. Environ.*, *36*, 4725–4734.

Junk, W. J. (1989), Flood tolerance and tree distribution in central Amazonian floodplains, in *Tropical Forests: Botanical Dynamics, Speciation and Diversity*, edited by L. B. Holm-Nielsen, I. C. Nielsen, and H. Balslev, pp. 47–64, Academic, San Diego, Calif.

Junk, W. J. (1993), Wetlands of tropical South America, in *Wetlands of the World*, edited by D. Whigham, S. Hejny, and D. Dykyjova, pp. 679–739, Springer, Boston.

Junk, W. J. (1997), *The Central Amazon Floodplain: Ecology of a Pulsing System*, *Ecol. Stud.*, vol. 126, 525 pp., Springer, New York.

Junk, W. J., P. B. Bayley, and R. E. Sparks (1989), The flood pulse concept in river-floodplain systems, in *Proceedings of the International Large River Symposium (LARS)*, *Can. Spec. Publ. Fish. Aquat. Sci.*, edited by D. P. Dodge, *106*, 110–127.

Junk, W. J., J. J. Ohly, M. T. F. Piedade, and M. G. M. Soares (2000), *The Central Amazon Floodplain: Actual Use and Options for a Sustainable Management*, 584 pp., Backhuys, Leiden, Netherlands.

Kalberer, M., et al. (2004), Identification of polymers as major components of atmospheric organic aerosols, *Science*, *303*, 1659–1662.

Karl, T., and A. Guenther (2004), Atmospheric variability of biogenic VOCs in the surface layer measured by proton-transfer-reaction mass spectrometry, *Int. J. Mass Spectrom.*, *239*, 77–86.

Karl, T., A. Guenther, R. J. Yokelson, J. Greenberg, M. Potosnak, D. R. Blake, and P. Artaxo (2007), The tropical forest and fire emissions experiment: Emission, chemistry, and transport of biogenic volatile organic compounds in the lower atmosphere over Amazonia, *J. Geophys. Res.*, *112*, D18302 doi:10.1029/2007JD008539.

Kavouras, I. G., N. Mihalopoulos, and E. G. Stephanou (1998), Formation of atmospheric particles from organic acids produced by forests, *Nature*, *395*, 683–686.

Kavouras, I. G., N. Mihalopoulos, and E. G. Stephanou (1999), Secondary organic aerosol formation vs primary organic aerosol

emission: In situ evidence for the chemical coupling between monoterpene acidic photooxidation products and new particle formation over forests, *Environ. Sci. Technol.*, *33*, 1028–1037.

Kawamura, K., and O. Yasui (2005), Diurnal changes in the distribution of dicarboxylic acids, ketocarboxylic acids and dicarbonyls in the urban Tokyo atmosphere, *Atmos. Environ.*, *39*, 1945–1960.

Kawamura, K., Y. Imai, and L. A. Barrie (2005), Photochemical production and loss of organic acids in high Arctic aerosols during long-range transport and polar sunrise ozone depletion events, *Atmos. Environ.*, *39*, 599–614.

Keene, W. C., J. N. Galloway, and J. D. Holden Jr. (1983), Measurement of weak organic acidity in precipitation from remote areas of the world, *J. Geophys. Res.*, *88*(C9), 5122–5130.

Kesselmeier, J. (2001), Exchange of short-chain oxygenated volatile organic compounds (VOCs) between plants and the atmosphere: A compilation of field and laboratory studies, *J. Atmos. Chem.*, *39*(3), 219–233.

Kesselmeier, J., and M. Staudt (1999), Biogenic volatile organic compounds (VOC): An overview on emission, physiology and ecology, *J. Atmos. Chem.*, *33*, 23–88.

Kesselmeier, J., et al. (2000), Atmospheric volatile organic compounds (VOC) at a remote tropical forest site in central Amazonia, *Atmos. Environ.*, *34*, 4063–4072.

Kesselmeier, J., et al. (2002a), Volatile organic compound emissions in relation to plant carbon fixation and the terrestrial carbon budget, *Global Biogeochem. Cycles*, *16*(4), 1126, doi:10.1029/2001GB001813.

Kesselmeier, J., et al. (2002b), Concentrations and species composition of atmospheric volatile organic compounds (VOCs) as observed during the wet and dry season in Rondônia (Amazonia), *J. Geophys. Res.*, *107*(D20), 8053, doi:10.1029/2000JD000267.

Klinger, L. F., Q.-J. Li, A. B. Guenther, J. P. Greenberg, B. Baker, and J.-H. Bai (2002), Assessment of volatile organic compound emissions from ecosystems of China, *J. Geophys. Res.*, *107*(D21), 4603, doi:10.1029/2001JD001076.

Koch, S., R. Winterhalter, E. Uherek, A. Kolloff, P. Neeb, and G. K. Moortgat (2000), Formation of new particles in the gasphase ozonolysis of monoterpenes, *Atmos. Environ.*, *34*, 4031–4042.

König, G., M. Brunda, H. Puxbaum, C. N. Hewitt, S. C. Duckham, and J. Rudolph (1995), Relative contribution of oxygenated hydrocarbons to the total biogenic VOC emissions of selected mid-European agricultural and natural plant species, *Atmos. Environ.*, *29*, 861–874.

Kreuzwieser, J., U. Scheerer, and H. Rennenberg (1999), Metabolic origin of acetaldehyde emitted by poplar (*Populus tremula x P. alba*) trees, *J. Exp. Bot.*, *50*(335), 757–765.

Kubitzki, K. (1989), The ecogeographical differentiation of Amazonian inundation forests, *Plant Syst. Evol.*, *163*, 285–304.

Kuhlbusch, T. A. J. (1998), Black carbon and the carbon cycle, *Science*, *280*, 1903–1904.

Kuhn, U., S. Rottenberger, T. Biesenthal, A. Wolf, G. Schebeske, P. Ciccioli, E. Brancaleoni, M. Frattoni, T. M. Tavares, and J. Kesselmeier (2002a), Isoprene and monoterpene emissions of Amazônian tree species during the wet season: Direct and in-

direct investigations on controlling environmental functions, *J. Geophys. Res.*, *107*(D20), 8071, doi:10.1029/2001JD000978.

Kuhn, U., S. Rottenberger, C. Ammann, A. Wolf, G. Schebeske, T. Biesenthal, S. T. Oliva, T. M. Tavares, and J. Kesselmeier (2002b), Exchange of short-chain monocarboxylic acids by vegetation at a remote tropical forest site in Amazonia, *J. Geophys. Res.*, *107*(D20), 8069, doi:10.1029/2000JD000303.

Kuhn, U., S. Rottenberger, T. Biesenthal, A. Wolf, G. Schebeske, P. Ciccioli, E. Brancaleoni, M. Frattoni, T. M. Tavares, and J. Kesselmeier (2004a), Seasonal differences in isoprene and light-dependent monoterpene emission by Amazonian tree species, *Global Change Biol.*, *10*, 663–682, doi:10.1111/j.1529-8817.2003.00771.x.

Kuhn, U., S. Rottenberger, T. Biesenthal, A. Wolf, G. Schebeske, P. Ciccioli, and J. Kesselmeier (2004b), Strong correlation between isoprene emission and gross photosynthetic capacity during leaf phenology of the tropical tree species *Hymenaea courbaril* with fundamental changes in VOC emission composition during early leaf development, *Plant Cell Environ.*, *27*(12), 1469–1485, doi:10.1111/j.1365-3040.2004.01252.x.

Kuhn, U., et al. (2007), Isoprene and monoterpene fluxes from Central Amazonian rainforest inferred from tower-based and airborne measurements, and implications on the atmospheric chemistry and the local carbon budget, *Atmos. Chem. Phys.*, *7*, 2855–2879.

Lack, D. A., X. X. Tie, N. D. Bofinger, A. N. Wiegand, and S. Madronich (2004), Seasonal variability of secondary organic aerosol: A global modeling study, *J. Geophys. Res.*, *109*, D03203, doi:10.1029/2003JD003418.

Larsen, B. R., D. Di Bella, M. Glasius, R. Winterhalter, N. R. Jensen, and J. Hjorth (2001), Gas-phase OH oxidation of monoterpenes: Gaseous and particulate products, *J. Atmos. Chem.*, *38*, 231–276.

Lelieveld, J., F. J. Dentener, W. Peters, and M. C. Krol (2004), On the role of hydroxyl radicals in the self-cleansing capacity of the troposphere, *Atmos. Chem. Phys.*, *4*, 2337–2344.

Lelieveld, J., et al. (2008), Atmospheric oxidation capacity sustained by a tropical forest, *Nature*, *452*, 737–740.

Limbeck, A., and H. Puxbaum (1999), Organic acids in continental background aerosols, *Atmos. Environ.*, *33*, 1847–1852.

Limbeck, A., M. Kulmala and H. Puxbaum (2003), Secondary organic aerosol formation in the atmosphere via heterogeneous reaction of gaseous isoprene on acidic particles, *Geophys. Res. Lett.*, *30*(19), 1996, doi:10.1029/2003GL017738.

Lindinger, W., A. Hansel, and A. Jordan (1998), On-line monitoring of volatile organic compounds at pptv levels by means of proton transfer mass spectrometry (PTR-MS) medical applications, food control and environmental research [review], *Int. J. Mass Spectrom. Ion Process.*, *173*, 191–241.

Lloyd, J., et al. (2007), An airborne regional carbon balance for Central Amazonia, *Biogeosciences*, *4*, 759–768.

Longo, K. M., S. R. Freitas, M. O. Andreae, R. Yokelson, and P. Artaxo (2009), Biomass burning in Amazonia: Emissions, long-range transport of smoke and its regional and remote impacts, *Geophys. Monogr. Ser.*, doi:10.1029/2008GM000847, this volume.

MacDonald, R. C., and T. W. Kimmerer (1993), Metabolism of transpired ethanol by eastern cottonwood (*Populus deltoides* Bartr.), *Plant Physiol.*, *102*(1), 173–179.

MacDonald, R. C., T. W. Kimmerer, and M. Razzaghi (1989), Aerobic ethanol-production by leaves—Evidence for air-pollution stress in trees of the Ohio River Valley, USA, *Environ. Pollut.*, *62*(4), 337–351.

Mochida, M., A. Kawabata, K. Kawamura, H. Hatsushika, and K. Yamazaki (2003), Seasonal variation and origins of dicarboxylic acids in the marine atmosphere over the western North Pacific, *J. Geophys. Res.*, *108*(D6), 4193, doi:10.1029/2002JD002355.

Montzka, S. A., M. Trainer, W. M. Angewine, and F. C. Fehsenfeld (1995), Measurements of 3-methyl furan, methyl vinyl ketone, and methacrolein at a rural forested site in the southeastern United States, *J. Geophys. Res.*, *100*(D6), 11,393–11,401.

Moukhtar, S., B. Bessagnet, L. Rouil, and V. Simon (2005), Monoterpene emissions from beech (*Fagus sylvatica*) in a French forest and impact on secondary pollutants formation at regional scale, *Atmos. Environ.*, *39*, 3535–3547.

Myneni, R. B., et al. (2007), Large seasonal swings in leaf area of Amazon rainforests, *Proc. Natl. Acad. Sci. U. S. A.*, *104*(12), 4820–4823.

Naik, V., C. Delire, and D. J. Wuebbles (2004), Sensitivity of global biogenic isoprenoid emissions to climate variability and atmospheric CO_2, *J. Geophys. Res. 109*, D06301, doi:10.1029/2003JD004236.

Neeb, P., F. Sauer, O. Horie, and G. K. Moortgat (1997a), Formation of hydroxymethyl hydroperoxide and formic acid in alkene ozonolysis in the presence of water vapour, *Atmos. Environ.*, *31*, 1417–1423.

Neeb, P., K. Bode, J. Beck, L. Schäfer, J. Kesselmeier, and G. K. Moortgat (1997b), Influence of gas-phase oxidation on estimated emission rates of biogenic hydrocarbons, in *Proceedings of the 7th European Symposium on Physico-Chemical Behaviour of Atmospheric Pollutants: The Oxidizing Capacity of the Troposphere*, pp. 295–299, Office for Official Publications of the European Communities, Luxembourg (EUR 17482) ISBN 92-828-0158-6.

O'Dowd, C. D., P. Aalto, K. Hameri, M. Kulmala, and T. Hoffmann (2002), Aerosol formation—Atmospheric particles from organic vapours, *Nature*, *416*, 497–498.

Odum, J. R., T. Hoffmann, F. Bowman, D. Collins, R. C. Flagan, and J. H. Seinfeld (1996), Gas/particle partitioning and secondary aerosol formation, *Environ. Sci. Technol.*, *30*, 2580–2585.

Pankow, J. F. (1994), An absorption model of the gas/aerosol partitioning involved in the formation of secondary organic aerosol, *Atmos. Environ.*, *28*, 189–193.

Parolin, P., et al. (2004), Central Amazon floodplain forests: Tree adaptation in a pulsing system, *Bot. Rev.*, *70*(3), 357–380, doi:10.1663/0006-8101(2004)070[0357:CAFFTA]2.0.CO;2.

Piedade, M. T. F., M. Worbes, and W. J. Junk (2001), Geoecological controls on elemental fluxes in communities of higher plants in Amazonian floodplains, in *The Biogeochemistry of the Amazon Basin*, edited by M. E. McClain, R. L. Victoria, and J. E. Richey, pp. 209–234, Oxford Univ. Press, New York.

Pires, J. M. (1973), Tipos de vegetação da Amazônia, *Publ. Av. Mus. Par. Emil Goeldi*, *20*, 179–202.

Pires, J. M., and G. T. Prance (1985), The vegetation types of the Brazilian Amazon, in *Amazon: Key Environments*, edited by G. T. Prance and T. E. Lovejoy, pp. 109–145, Elsevier, London.

Rasmussen, R. A., and M. A. K. Khalil (1988), Isoprene over the Amazon Basin, *J. Geophys. Res.*, *93*(D2), 1417–1421.

Rinne, H. J. I., A. B. Guenther, J. P. Greenberg, and P. C. Harley (2002), Isoprene and monoterpene fluxes measured above Amazonian rainforest and their dependence on light and temperature, *Atmos. Environ.*, *36*(14), 2421–2426.

Rogge, W. F., L. M. Hildemann, M. A. Mazurek, G. R. Cass, and B. R. T. Simoneit (1993), Sources of fine organic aerosol. 4. Particulate abrasion products from leaf surfaces of urban plants, *Environ. Sci. Technol.*, *27*, 2700–2711.

Rottenberger, S. (2003), Exchange of oxygenated volatile organic compounds between Amazonian and European vegetation and the atmosphere, Ph.D. thesis, Dept. Biology, University Mainz.

Rottenberger, S., U. Kuhn, A. Wolf, G. Schebeske, S. T. Oliva, T. M. Tavares, and J. Kesselmeier (2004), Exchange of short-chain aldehydes between Amazonian vegetation and the atmosphere at a remote forest site in Brazil, *Ecol. Appl.*, *14*(4), Suppl., 247–262.

Rottenberger, S., U. Kuhn, A. Wolf, G. Schebeske, S. T. Oliva, T. M. Tavares, and J. Kesselmeier (2005), Formaldehyde and acetaldehyde exchange during leaf development of the Amazonian deciduous tree species *Hymenaea courbaril*, *Atmos. Environ.*, *39*, 2275–2279.

Rottenberger, S., B. Kleiss, U. Kuhn, A. Wolf, M. T. F. Piedade, W. Junk, and J. Kesselmeier (2008), The effect of flooding on the exchange of the volatile C2-compounds ethanol, acetaldehyde and acetic acid between leaves of Amazonian floodplain tree species and the atmosphere, *Biogeosciences*, *5*, 1085–1100.

Sanderson, M. G., C. D. Jones, W. J. Collins, C. E. Johnson, and R. G. Derwent (2003), Effect of climate change on isoprene emissions and surface ozone levels, *Geophys. Res. Lett.*, *30*(18), 1936, doi:10.1029/2003GL017642.

Sanhueza, E., M. Santana, D. Trapp, C. de Serves, L. Figueroa, R. Romero, A. Rondon, and L. Donoso (1996), Field measurement evidence for an atmospheric chemical source of formic and acetic acids in the tropic, *Geophys. Res. Lett.*, *23*(9), 1045–1048.

Sattler, B., H. Puxbaum, and R. Psenner (2001), Bacterial growth in supercooled cloud droplets, *Geophys. Res. Lett.*, *28*, 239–242.

Schauer, J. J., W. F. Rogge, L. M. Hildemann, M. A. Mazurek, and G. R. Cass (1996), Source apportionment of airborne particulate matter using organic compounds as tracers, *Atmos. Environ.*, *30*, 3837–3855.

Schöngart, J., M. T. F. Piedade, S. Ludwigshausen, V. Horna, and M. Worbes (2002), Phenology and stem-growth periodicity of tree species in Amazonian floodplain forests, *J. Trop. Ecol.*, *18*, 581–597.

Schöngart, J., W. J. Junk, M. T. F. Piedade, J. M. Ayres, A. Huttermann, and M. Worbes (2004), Teleconnection between tree growth in the Amazonian floodplains and the El Nino-Southern Oscillation effect, *Global Change Biol.*, *10*(5), 683–692.

Schulze, B., C. Kost, G. I. Arimura, and W. Boland (2006), Signal-rezeption, biosynthese und ökologie, Duftstoffe: Die sprache der pflanzen, *Chem. Unserer Zeit*, *40*, 366–377.

Seinfeld, J. H., and S. N. Pandis (1998), *Atmospheric Chemistry and Physics*, John Wiley, Hoboken, N. J., ISBN 0-471-17815-2.

Serça, D., et al. (2001), EXPRESSO flux measurements at upland and lowland Congo tropical forest site, *Tellus, Ser. B*, *53*, 220–34.

Shim, C., Y. Wang, Y. Choi, P. I. Palmer, D. S. Abbot, and K. Chance (2005), Constraining global isoprene emissions with Global Ozone Monitoring Experiment (GOME) formalde-hyde column measurements, *J. Geophys. Res.*, *110*, D24301, doi:10.1029/2004JD005629.

Simoneit, B. R. T. (1999), A review of biomarker compounds as source indicators and tracers for air pollution, *Environ. Sci. Pol-lut. Res.*, *6*, 159–169.

Simoneit, B. R. T. (2002), Biomass burning—A review of organic tracers for smoke from incomplete combustion, *Appl. Geochem.*, *17*, 129–162.

Simoneit, B. R. T., R. E. Cox, and L. J. Standley (1988), Organic matter of the troposphere-IV: Lipids in Harmattan aerosols of Nigeria, *Atmos. Environ.*, *22*, 983–1004.

Simoneit, B. R. T., V. O. Elias, M. Kobayashi, K. Kawamura, A. I. Rushdi, P. M. Medeiros, W. F. Rogge, and B. M. Didyk (2004a), Sugars—Dominant water-soluble organic compounds in soils and characterization as tracers in atmospheric particulate matter, *Environ. Sci. Technol.*, *38*, 5939–5949.

Simoneit, B. R. T., M. Kobayashi, M. Mochida, K. Kawamura, M. Lee, H.-J. Lim, B. J. Turpin, and Y. Komazaki (2004b), Composition and major sources of organic compounds of aerosol particulate matter sampled during the ACE-Asia campaign, *J. Geophys. Res.*, *109*, D19S10, doi:10.1029/2004JD004598.

Singh, H. B., M. Kanakidou, P. J. Crutzen, and D. J. Jacob (1995), High-concentrations and photochemical fate of oxygenated hy-drocarbons in the global troposphere, *Nature*, *378*(6552), 50–54.

Singh, H. B., Y. Chen, A. Staudt, D. Jacob, D. Blake, B. Heikes and J. Snow (2001), Evidence from the pacific troposphere for large global sources of oxygenated organic compounds, *Nature*, *410*(6832), 1078–1081.

Starn, T. K., P. B. Shepson, S. B. Bertman, J. S. White, B. G. Splawn, D. D. Riemer, R. G. Zika, and K. Olszyna (1998), Ob-servations of isoprene chemistry and its role in ozone production at a semirural site during the 1995 Southern Oxidants Study, *J. Geophys. Res.*, *103*(D17), 22,425–22,435.

Suntharalingam, P., J. T. Randerson, N. Krakauer, J. A. Logan, and D. J. Jacob (2005), Influence of reduced carbon emissions and oxidation on the distribution of atmospheric CO_2: Implications for inversion analyses, *Global Biogeochem. Cycles*, *19*, GB4003, doi:10.1029/2005GB002466.

Takekawa, H., H. Minoura, and S. Yamazaki (2003), Tempera-ture dependence of secondary organic aerosol formation by photo-oxidation of hydrocarbons, *Atmos. Environ.*, *37*, 3413–3424.

Talbot, R. W., M. O. Andreae, H. Berresheim, D. J. Jacob, and K. M. Beecher (1990), Sources and sinks of formic, acetic, and pyruvic acids over central Amazonia: 2, Wet season, *J. Geophys. Res.*, *95*, 16,799–16,811.

Thompson, A. M. (1992), The oxidizing capacity of the Earths atmosphere—Probable past and future changes, *Science*, *256*(5060), 1157–1165.

Trostdorf, C. R., L. V. Gatti, A. Yamazaki, M. J. Potosnak, A. Guenther, W. C. Martins, and J. W. Munger (2004), Seasonal cycles of isoprene concentrations in the Amazonian rainforest, *Atmos. Chem. Phys. Discuss.*, *4*, 1291-1310.

Tsigaridis, K., and M. Kanakidou (2003), Global modelling of sec-ondary organic aerosol in the troposphere: A sensitivity analysis, *Atmos. Chem. Phys.*, *3*, 1849–1869.

Tuazon, E. C., and R. Atkinson (1990), A product study of the gas-phase reaction of isoprene with the OH radical in the presence of NO_x, *Int. J. Chem. Kinet.*, *22*, 1221–1236.

von Kuhlmann, R., M. G. Lawrence, P. J. Crutzen, and P. J. Rasch (2003), A model for studies of tropospheric ozone and nonmeth-ane hydrocarbons: Model evaluation of ozone-related species, *J. Geophys. Res.*, *108*(D23), 4729, doi:10.1029/2002JD003348.

Went, F. W. (1955), Air pollution, *Sci. Am.*, *192*, 63–72.

Went, F. W. (1960a), Blue hazes in the atmosphere, *Nature*, *187*, 641–643.

Went, F. W. (1960b), Organic matter in the atmosphere and its possible relation to petroleum formation, *Proc. Natl. Acad. Sci. U. S. A.*, *46*, 212–221.

Williams, J. (2004), Organic trace gases in the atmosphere: An overview, *Environ. Chem.*, *1*, 125–136.

Wilske, B., K. F. Cao, G. Schebeske, J. W. Chen, A. Wang, and J. Kesselmeier (2007), Isoprenoid emissions of trees in a tropical rainforest in Xishuangbanna, SW-China, *Atmos. Environ.*, *41*, 3748–3757.

Winterhalter, R., R. Van Dingenen, B. R. Larsen, N. R. Jensen, and J. Hjorth (2003), LC-MS analysis of aerosol particles from the oxidation of α-pinene by ozone and OH-radicals, *Atmos. Chem. Phys. Discuss.*, *3*, 1–39.

Wittmann, F., J. Schöngart, J. C. Montero, T. Motzer, W. J. Junk, M. T. F. Piedade, H. L. Queiroz, and M. Worbes (2006), Tree species composition and diversity gradients in white-water for-ests across the Amazon Basin, *J. Biogeogr.*, *33*, 1334–1347.

Worbes, M. (1997), The forest ecosystem of the floodplains, in *The Central Amazon Foodplain: Ecology of a Pulsing System*, *Ecol. Stud.*, vol. 126, edited by W. J. Junk, pp. 223–266, Springer, New York.

Worbes, M. (1999), Annual growth rings, rainfall-dependent growth and long-term growth patterns of tropical trees from the Caparo Forest Reserve in Venezuela, *J. Ecol.*, *87*(3), 391–403.

Worbes, M., and W. J. Junk (1999), How old are tropical trees? The persistence of a myth, *IAWA J.*, *20*(3), 255–260.

Yokouchi, Y., and Y. Ambe (1985), Aerosols formed from the chemical reaction of monoterpenes and ozone, *Atmos. Environ.*, *19*, 1271–1276.

Yu, J. Z., D. R. Cocker, R. J. Griffin, R. C. Flagan, and J. H. Sein-feld (1999), Gas-phase ozone oxidation of monoterpenes: Gase-ous and particulate products, *J. Atmos. Chem.*, *34*, 207–258.

Zhang, S.-H., M. Shaw, J. H. Seinfeld, and R. C. Flagan (1992), Photochemical aerosol formation from α-pinene- and β-pinene, *J. Geophys. Res. 97*, 20,717–20,729.

Zimmerman, P. R., J. P. Greenberg, and C. E. Westberg (1988), Measurements of atmospheric hydrocarbons and biogenic emission fluxes in the Amazon boundary layer, *J. Geophys. Res.*, *93*(D2), 1407–1416.

A. Guenther, National Center for Atmospheric Research, Boulder, CO 80307-3000, USA. (guenther@ucar.edu)

T. Hoffmann and J. Warnke, Institute of Inorganic and Analytical Chemistry, Johannes Gutenberg University of Mainz, D-55128 Mainz, Germany. (t.hoffmann@uni-mainz.de; warnke@uni-mainz.de)

J. Kesselmeier, Max Planck Institute for Chemistry, D-55020 Mainz, Germany. (jks@mpch-mainz.mpg.de)

M. T. Piedade, Instituto Nacional de Pesquisas da Amazônia, CEP 69060-001 Manaus, AM, Brazil. (maitepp@inpa.gov.br)