

Biogenic Volatile Organic Compounds (VOC): An Overview on Emission, Physiology and Ecology

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Abstract. This overview compiles the actual knowledge of the biogenic emissions of some volatile organic compounds (VOCs), i.e., isoprene, terpenes, alkanes, alkenes, alcohols, esters, carbonyls, and acids. We discuss VOC biosynthesis, emission inventories, relations between emission and plant physiology as well as temperature and radiation, and ecophysiological functions. For isoprene and monoterpenes, an extended summary of standard emission factors, with data related to the plant genus and species, is included. The data compilation shows that we have quite a substantial knowledge of the emission of isoprene and monoterpenes, including emission rates, emission regulation, and biosynthesis. The situation is worse in the case of numerous other compounds (other VOCs or OVOCs) being emitted by the biosphere. This is reflected in the insufficient knowledge of emission rates and biological functions. Except for the terpenoids, only a limited number of studies of OVOCs are available; data are summarized for alkanes, alkenes, carbonyls, alcohols, acids, and esters. In addition to closing these gaps of knowledge, one of the major objectives for future VOC research is improving our knowledge of the fate of organic carbon in the atmosphere, ending up in oxidation products and/or as aerosol particles.

Key words: nonmethane hydrocarbons, volatile organic compounds, terpenes, isoprene, oxygenated compounds, alkanes, alkenes, carbonyls, acids, esters, emission, physiology, ecology, emission inventories, review.

1. Introduction

The term *biogenic volatile organic compounds* (biogenic VOCs) includes organic atmospheric trace gases other than carbon dioxide and monoxide. Focusing on hydrocarbons but excluding methane, the term nonmethane hydrocarbons (NMHCs) is used, while VOCs without methane are termed nonmethane VOCs (NMVOCs). Hence, large numbers of groups of saturated, unsaturated, and oxygenated derivatives are included within VOCs. Biogenic VOCs include the isoprenoids (isoprene and monoterpenes) as well as alkanes, alkenes, carbonyls, alcohols, esters, ethers, and acids. Emission inventories show isoprene and monoterpenes as the most prominent compounds. Alcohols and carbonyls follow the isoprenoids as the most predominant groups. The release of compounds other than isoprenoids has

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Table I. Comparison of nonmethane volatile organic compound (NMVOC) categories (Goldan *et al.*, 1993; Guenther *et al.*, 1995; Neeb *et al.*, 1997; Singh *et al.*, 1994)

Name	Chemical lifetimes ^a		Example	Atmospheric concentrations
	Day	Night		
Isoprene	3 hrs	1.5 hrs	isoprene	ppt to several ppb
Monoterpenes	2–3 hrs	5–30 min	α -pinene; β -pinene, sabinene	ppt to several ppb
	40–80 min	5–20 min	limonene, t- β -ocimene, myrcene	
	15–20 min	<1 min	terpinolene, α -phellandrene	
	<5 min	<2 min	α -terpinene	
Sesquiterpenes	<4 min	<2 min	β -caryophyllene	not detectable due to high reactivity
ORVOC	<1 day		2-methyl-3-buten-2-ol	1–3 ppb
OVOC	>1 day		methanol, acetone	2–30 ppb

^a Lifetimes are estimated in relation to $[\text{NO}_3] = 10$ ppt, $[\text{O}_3] = 20$ ppb for night; and to $[\text{OH}] = 10^6$ molecules/cm³, $[\text{O}_3] = 20$ ppb for daylight conditions.

been poorly investigated; gaps in knowledge exist for factors controlling emission, for example, developmental stage, stress such as injuries and air pollution, and even the ‘simple’ factors light and temperature. One of the consequences of the heterogeneity of VOC is the large variety of acronyms, each defining a special class of VOCs, such as BOVOC (biogenic oxygenated VOC), ORVOC (other reactive VOC), BVOC (biogenic VOC) versus AVOC (anthropogenic VOC), and finally OVOC (other VOC) for the rest. The last acronym is still open for new ideas.

The high diversity of VOC, sometimes also falsely summarized in the subgroup nonmethane hydrocarbons (NMHC), points to one of the main problems in VOC research: the large number of different compounds is coupled to an equivalent number of problems with sampling and analysis techniques, understanding the biological metabolisms and the biological emission/deposition regulations, and describing and modeling the exchange as well as the atmospheric chemistry of all these compounds. Furthermore, for a better knowledge of the production and the fate of all these compounds in the atmosphere, we need a better description of the exchange processes on a local and regional scale (especially in the tropics where our knowledge is worst) and a better understanding of the factors influencing the release of VOC from different biogenic sources. These sources can be highly variable owing to stress effects, e.g., experimental influences, injuries, parasites, or atmospheric pollutants such as ozone (Kimmerer and Kozłowski, 1982; Kimmerer and MacDonald, 1987; Arey *et al.*, 1991a; Loreto and Sharkey, 1993a; Juuti *et al.*, 1993; Parusel, 1996; Wedel, 1997; Bertin and Staudt, 1996; Staudt, 1997; Kesselmeier *et al.*, 1998a).

Atmospheric concentrations of nonmethane biogenic VOCs range between a few ppt and several ppb (Table I). Isoprene, monoterpenes, sesquiterpenes, and also some other VOCs can be quite reactive under atmospheric conditions, as reflected by their chemical lifetimes which range between some minutes and hours (Table I). Measured concentrations reflect the diverse factors influencing atmospheric NMVOCs, such as anthropogenic and biological sources or sinks, as well as the more physical and chemical influences like meteorology, chemical reactivity, and deposition. Isoprene and monoterpenes, in particular, as well as their reaction products are involved in tropospheric chemistry, fueling (directly or indirectly) the production of air pollutants and greenhouse gases, such as ozone, carbon monoxide, and methane, and increasing acidity as well as the production of aerosols (Graedel, 1979; Altshuller, 1983; Yokouchi and Ambe, 1985; Trainer *et al.*, 1987; Chameides *et al.*, 1988; Warneck, 1988; Kotzias *et al.*, 1989; Atkinson, 1990b; Brasseur and Chatfield, 1991; Pandis *et al.*, 1991; Fehsenfeld *et al.*, 1992; Andreae and Crutzen, 1997).

This article gives an overview of our current knowledge of the biogenic emissions of nonmethane VOCs with special emphasis on the biological background of natural VOC emissions. We point out problems and deficits from a biological point of view with influence on the assessments of emission inventories and global budgets.

2. Monoterpenes and Isoprene

2.1. GENERAL REMARKS

Isoprene and monoterpenes belong to the biochemical class of isoprenoids (or terpenoids), whose carbon skeletons are composed of characteristic C₅ units (McGarvey and Croteau, 1995). According to the number of C₅ units, they are subdivided into hemiterpenes (C₅, e.g., isoprene, prenylresidue of cytokinene), monoterpenes (C₁₀, e.g., α -pinene, menthol, camphor), sesquiterpenes (C₁₅, e.g., β -caryophyllene, abscisic acid), diterpenes (C₂₀, e.g., gibberellins, phytol, tocopherol, retinol), triterpenes (C₃₀, e.g., sterols, saponins), tetraterpenes (C₄₀, e.g., carotenoids), and prenols and polyterpenes (>C₄₅, e.g., plastochinone, ubiquinone, india rubber). This subdivision gives an impression of the multiplicity of terpenoids present within all life forms. However, of importance for atmospheric chemistry are mainly the more volatile compounds isoprene and monoterpenes. Sesquiterpenes appear to be of minor importance, though some studies report emission rates on the order of those known for monoterpenes (Koenig *et al.*, 1995; Winer *et al.*, 1992; Schuh *et al.*, 1997). Usually these compounds are strong smelling, hardly water-soluble, and found in plants as well as in animals and microorganisms. The group of monoterpenes comprises acyclic, and mono-, bi-, and tricyclic structures; they may exist as hydrocarbons with or without the inclusion of oxygen in compounds such as menthol, camphor, linalool, and geraniol. Oxygenated monoterpenes and

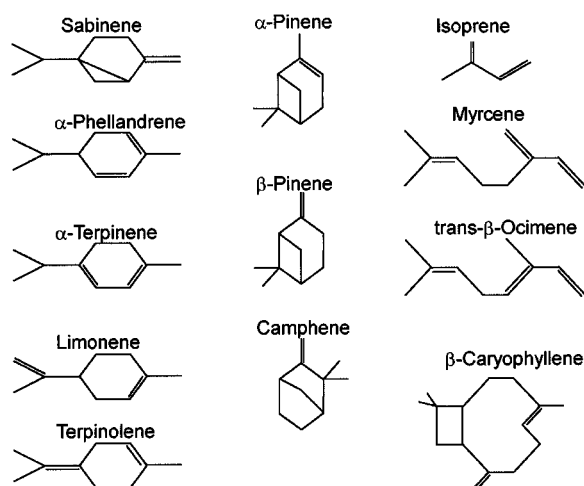


Figure 1. Molecular structures of the volatile hydrocarbons isoprene (C_5), some monoterpenes (C_{10}) and the semivolatile sesquiterpene β -Caryophyllene (C_{15}).

their derivatives are often summarized as monoterpenoids. Some examples of the dominant biogenic isoprenoids are given in Figure 1.

2.2. BIOSYNTHESIS

According to the Ruzicka rule (Ruzicka *et al.*, 1953; cf. McGarvey and Croteau, 1995), all isoprenoids are synthesized via a common C_5 precursor, the isopentenyl pyrophosphate (IPP), called 'active isoprene'. IPP can be reversibly transformed to its isomer dimethylallyl pyrophosphate (DMAPP), which is the substrate for isoprene synthase, a chloroplastic enzyme producing isoprene by cleaving pyrophosphate (Silver and Fall, 1991, 1995; Monson *et al.*, 1992; Kuzma and Fall, 1993; Schnitzler *et al.*, 1996; Wildermuth and Fall, 1996, 1998). Isoprene synthase is regarded to be active only in mature chloroplasts (Kuzma and Fall, 1993). By adding another IPP unit to DMAPP, the monoterpene geranylpyrophosphate (GPP) is formed, which is the starting unit for other monoterpenes as well as the origin for a further addition of IPP units to produce sesqui- and diterpene species (farnesylpyrophosphate, FPP; geranylgeranylpyrophosphate, GGPP). Based on the activities of different monoterpene cyclases, different types of monoterpenes will be synthesized (Croteau *et al.*, 1988). Isoprenoid synthesis by plants is ruled by several control mechanisms (cf. Gershenzon and Croteau, 1990). It is generally accepted that the production of monoterpenes takes place within the plastids, whereas sesquiterpenes are synthesized within the cytosol (Carde *et al.*, 1980; Gleizes *et al.*, 1983; Kleinig, 1989; Soler *et al.*, 1992; McCaskill and Croteau, 1995).

The synthesis of the basic isoprenoid precursor IPP can be explained by two different biochemical pathways (Figure 2): the classical *mevalonate pathway* according to the characteristic intermediate compound mevalonic acid (Sharkey *et*

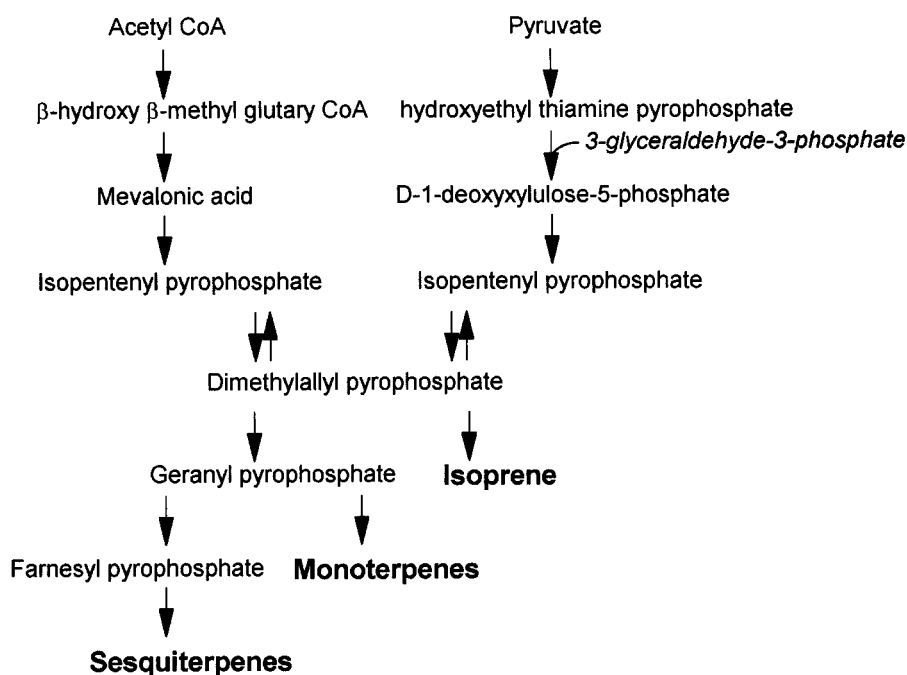


Figure 2. Schematic compilation of the biosynthesis of the volatile and semi-volatile isoprenoids: isoprene, monoterpenes and sesquiterpenes in plants. Upper left part describes the classical acetate/mevalonate pathway, whereas the upper right part summarizes the recently described novel pathway via pyruvate by introducing 3-glyceraldehyde-3-phosphate (GAP), both leading to the key compound isopentenyl pyrophosphate.

al., 1991; McGarvey and Croteau, 1995; Chapell, 1995; Bach, 1995) and the novel mevalonate-independent pathway also known as the *Rohmer pathway* (Flesch and Rohmer, 1988; Rohmer *et al.*, 1993, 1996; Bach, 1995). The novel mevalonate-independent pathway was first discovered in procaryotic organisms, and recent studies give evidence that it also exists in chloroplasts of higher plants. By delivering IPP, it is also responsible for the formation of isoprene, carotenoids, and other isoprenoids in higher plants (Schwender *et al.*, 1996; Lichtenthaler *et al.*, 1997; Zeidler *et al.*, 1997). A schematic compilation of both biosynthetic pathways leading to isopentenyl pyrophosphate and finally to isoprene is given in Figure 2. Principally, both pathways for IPP synthesis require phosphorylation energy (ATP) and reduction power (NADPH, NADH) plus a carbon substrate like pyruvate, glyceraldehyde 3-phosphate, or acetate. However, the consumption of reduction power is higher for the novel pathway, while the mevalonate track involves more steps to CO₂ formation and therefore entails additional carbon losses. Another major difference is that the novel pathway bypasses the plastidic acetyl-CoA pool used for synthesis of fatty acids and certain amino acids.

2.3. OCCURRENCE AND MAGNITUDE OF EMISSION

Table II compiles a number of emission factors for isoprene and monoterpenes organized according to basic botanical systematics. Emission factors (E_S) are given in relation to leaf biomass and time and describe the release of a trace gas species under standard conditions of temperature (30 °C) and light (1000 $\mu\text{mol m}^{-2} \text{s}^{-1}$ photosynthetically active radiation (PAR)). Both factors, temperature and light, are known to influence emissions instantaneously (see 4.2). This compilation does not include all potentially available data. For instance, emission factors that are exclusively reported on a leaf area basis were not considered. Nevertheless, the table delivers an overview of emission variability among species and reflects the high number of investigations which have already been performed in this field of research. It also shows important intraspecies variability as many plant species were studied several times by different investigators.

It should be noted that the reliability and the comparability of the reported emission factors are biased by the diverse experimental conditions used in the studies. The emission factors of the sum of monoterpenes reported by diverse authors for the same plant species may include a different number of identified compounds, though usually comprising the quantitatively most important ones. Another shortcoming is that emissions were not always determined under standard light and temperature, but under other conditions, and were afterwards adjusted by using universal algorithms describing the light and temperature influences on emissions (see 4.2). This adjustment procedure may yield emission factors with an error comparable to the deviation of the actual light and temperature influences of the regarded emission from applied algorithms. Errors, however, should be relatively small, since emission rates are usually measured close to standard conditions.

Table II. Reported normalized emission rates (i.e., emission factors for standard conditions of 1000 $\mu\text{mol m}^{-2} \text{s}^{-1}$ and 30 °C PAR and temperature, respectively): Isoprene and monoterpene emissions from trees and shrubs sorted according to family, genus, species following Mabberley (The Plant-Book 1997), Elsevier' Dictionary of Botany (1979), Engler (Syllabus der Pflanzenfamilien 1964), and additional literature on Mediterranean and African vegetation

Family	Species, trivial name	Isoprene	Monoterpenes	Ref. (#)
		[$\mu\text{g g(LDW)}^{-1} \text{h}^{-1}$]		
Aceraceae (Compositae)				
	<i>Acer floridanum</i> , Florida maple	+	2.0	1
	<i>Acer rubrum</i> , red maple	-	3.5	2
	<i>Acer platanoides</i> , Norway maple	<0.04		38
	<i>Acer saccharinum</i> , silver maple	-	2.2	3
	<i>Acer saccharinum</i> , silver maple		3.5	4
	<i>Chrysothamnus nauseosus</i> , rubber rabbit brush	<1	>3	27

Table II. (Continued)

Family	Species, trivial name	Isoprene [$\mu\text{g g(LDW)}^{-1} \text{h}^{-1}$]	Monoterpenes	Ref. (#)
	<i>Dittrichia viscosa</i> , aromatic inula		0.03	45
	<i>Holocarpha</i> spp., tarweed	0	3.1	9
Anacardiaceae				
	<i>Pistacia lentiscus</i> , pistachio		0.41	50
	<i>Pistacia vera</i> , kerman pistachio	0	9.0	14, 41
	<i>Rhus leptodictya</i> , sumac	54	1.1	39
	<i>Rhus ovata</i> , sugar sumac	+	+	1
	<i>Schinus molle</i> , California pepper	–	3.7	5
	<i>Schinus molle</i> , California pepper	–	–	1
	<i>Schinus terebinthifolius</i> , Brazilian pepper	–	1.3	5
	<i>Schinus terebinthifolius</i> , Brazilian pepper	+	10.4	1
	<i>Sclerocarya birrea</i> (<i>S. caphra</i>), Maroala plum	<0.5	<0.5	39
Apocynaceae				
	<i>Carissa macrocarpa</i> , Natal plum	+	+	1
	<i>Nerium oleander</i> , oleander	+	+	1
	<i>Nerium oleander</i> , oleander	–	–	2
Aquifoliaceae				
	<i>Ilex cassine</i> , Dahoon holly	–	–	2
Apiaceae				
	<i>Daucus carota</i> , carrot	0	1.1	14
Areaceae (Palmae)				
	<i>Elaeis guineensis</i> , palm oil tree	172.9		6
	<i>Phoenix dactylifera</i> , date palm	15.8	+	1
	<i>Sabal palmetto</i> , cabbage palmetto	4.7	0.4	2
	<i>Serenoa repens</i> , saw palmetto	8.9	+	2
	<i>Washingtonia filifera</i> , California fan palm	9.9	+	1
	<i>Xylosma congestum</i> , shiny xylosma	6.8	+	1
Asteraceae				
	<i>Artemisia californica</i> , California sagebrush	0.0	47.0	7
	<i>Artemisia californica</i> , California sagebrush	+	9.6	1
	<i>Artemisia tridentata</i> , big sagebrush	<1	<0.2	27
	<i>Carthamus tinctorius</i> , safflower	0	0.04	14, 41
	<i>Chrysanthemum praecox</i> , daily		0.51	45
	<i>Helianthus annuus</i> , sunflower	<0.1	0.7	26
	<i>Helichrysum stoechas</i> , everlasting flower		4.8	45
Berberidaceae				
	<i>Mahonia</i> spp., Oregon grape	10–40	<0.2	27
	<i>Nandina domestica</i> , sacred bamboo	25.1	+	1

Table II. (Continued)

Family	Species, trivial name	Isoprene [$\mu\text{g g(LDW)}^{-1} \text{h}^{-1}$]	Monoterpenes	Ref. (#)
Betulaceae				
	<i>Alnus rubra</i> , red alder	0.02		52
	<i>Betula pendula</i> , birch	0	0.19	36
	<i>Betula pendula</i> , birch	0	5.4	46
	<i>Carpinus betulus</i> , hornbeam	0	0.04	36
Bignoniaceae				
	<i>Catalpa</i> spp.	<1	<0.2	27
	<i>Jacaranda mimosifolia</i> , jacaranda		+	5
	<i>Jacaranda mimosifolia</i> , jacaranda	-	-	1
	<i>Tecomaria capensis</i> , cape-honeysuckle	+	+	1
Brassicaceae (Cruciferae)				
	<i>Brassica napus</i> , winter rape	0	0.1	36
Caprifoliaceae				
	<i>Sambucus simonii</i> , elderberry	-	+	2
	<i>Symphoricarpos occidentalis</i> , snowberry	<1	<0.2	27
	<i>Viburnum rufidulum</i> , snowball	-	0.2	2
Caesalpiniaceae (Leguminosae)				
	<i>Cercis canadensis</i> , eastern redbud	0.0	-	3
	<i>Burkea africana</i> , red syringa	36	<0.5	39
	<i>Colophospermum mopane</i> , mopane	<0.5	52	39
Chenopodiaceae				
	<i>Atriplex canescenz</i> , saltbush	<1	>3	27
Cistaceae				
	<i>Cistus incanus</i> , rockrose		0.3	45
	<i>Cistus salvifolius</i> , salvia rockrose		0.34	45
Combretaceae				
	<i>Combretum apiculatum</i> , myrobolan family	<0.5	<0.5	39
	<i>Combretum molle</i> , myrobolan family	<0.5	<0.5	39
	<i>Terminalia prunoides</i> , myrobolan family	<0.5	3.9	39
	<i>Terminalia sericea</i> , myrobolan family	<0.5	1.3	39
Cupressaceae				
	<i>Cupressus forbesii</i> , tecate cypress	0.0	1.7	7
	<i>Cupressus sempervirens</i> , Italian cypress	0.0	0.1	1
	<i>Juniperus chinensis</i> , Chinese juniper	0.0	0.6	1
	<i>Juniperus oxicedrus</i> , prickly juniper	0.08	0.96	45
	<i>Juniperus phoenicea</i> , Phoenician juniper		0.77	45
	<i>Thuja plicata</i> , western red cedar, giant thuya	0.02 \pm 0.01	0.07 \pm 0.05	52

Table II. (Continued)

Family	Species, trivial name	Isoprene [$\mu\text{g g(LDW)}^{-1} \text{h}^{-1}$]	Monoterpenes	Ref. (#)
Ericaceae				
	<i>Arbutus unedo</i> , strawberry tree		0.12	45
	<i>Arctostaphylos glandulosa</i> , peninsular manzanita	0	0	7
	<i>Arctostaphylos glauca</i> , bigberry manzanita	+	+	1
	<i>Erica multiflora</i> , heath	2.0	0.03	45
	<i>Erica arborea</i> , tree heath	20.3		45
	<i>Erica arborea</i> , tree heath	6.4		50
	<i>Kalmia latifolia</i> , mountain laurel	<1	<0.2	27
	<i>Vaccinium uliginosum</i> , bog bilberry, blueberry	0.009		52
Euphorbiaceae				
	<i>Hevea brasiliensis</i> , par rubber tree	7.5	0.5	6
	<i>Macaranga triloba</i> , macaranga	45.3	0.7	6
	<i>Mallotus paniculatis</i> , mallotus		0.8	6
	<i>Securinega virosa</i> , securinega	81	4.7	39
Fabaceae (Papilionaceae)				
	<i>Cytisus sp.</i> , broom	26.9		45
	<i>Glycine max</i> , soy bean	0.0	0.0	3
	<i>Medicago sativa</i> , alfalfa	0	0.2	14, 41
	<i>Mucuna pruriens</i> , velvet bean	317		38
	<i>Phaseolus vulgaris</i> , bean	0	0	14
	<i>Pueraria lobata</i> , kudzu bean	9.6	0.0	3
	<i>Pueraria lobata</i> , kudzu bean	10–40	0.2–1	27
	<i>Robinia pseudoacacia</i> , black locust	13.5	4.7	4
	<i>Robinia pseudoacacia</i> , black locust	10.1	0.0	1
	<i>Spartium junceum</i> , Spanish broom	6.4	0.53	45
Fagaceae				
	<i>Castanea dentata</i> , American chestnut	<1	<0.2	27
	<i>Fagus sylvatica</i> , European beech	0	0.3	2
	<i>Fagus sylvatica</i> , European beech	<0.01	0.25–0.5	36
	<i>Quercus agrifolia</i> , Calif. coast live oak	35.3	+	1
	<i>Quercus agrifolia</i> , Calif. coast live oak	35.6		17
	<i>Quercus alba</i> , white oak	7.8	1.5	4
	<i>Quercus alba</i> , white oak	38		33
	<i>Quercus alba</i> , white oak	50–120		16
	<i>Quercus alba</i> , white oak	30–60		47
	<i>Quercus borealis</i> , Northern red oak	19.7	0.0	3
	<i>Quercus borealis</i> , Northern red oak	40.4		8
	<i>Quercus calliprinos</i> , Palestina oak	0.1	3.1	42

Table II. (Continued)

Family	Species, trivial name	Isoprene [$\mu\text{g g(LDW)}^{-1} \text{h}^{-1}$]	Monoterpenes	Ref. (#)
	<i>Quercus canariensis</i> , Canary oak	11.3	1.0	42
	<i>Quercus cerris</i> , Turkish oak	0.1	0.0	42
	<i>Quercus cerris</i> , Turkish oak		3.1	45
	<i>Quercus chrysolepis</i> , Canyon live oak	11.7	0.1	42
	<i>Quercus coccifera</i> , kermes oak	0.1	18.7	20
	<i>Quercus coccinea</i> , scarlet oak	20.1	3.2	4
	<i>Quercus coccinea</i> , scarlet oak	40–130		16
	<i>Quercus douglasii</i> , blue oak	8.7	0.0	9
	<i>Quercus dumosa</i> , California scrub oak	5.0	0.0	7
	<i>Quercus dumosa</i> , California scrub oak	54.4	+	1
	<i>Quercus faginea</i> , Portuguese oak	111	0.5	42
	<i>Quercus frainetto</i> , Hungarian oak	134	0.0	43
	<i>Quercus gambelii</i> , gambel oak	151		38
	<i>Quercus garryana</i> , Oregon white oak	59.2		4
	<i>Quercus ithaburiensis</i>	0.1	13.9	42
	<i>Quercus ilex</i> , Holm (holly) oak	<0.1	6–58	44
	<i>Quercus ilex</i> , Holm (holly) oak	+	15.7	17
	<i>Quercus ilex</i> , Holm (holly) oak	+	16.7	18
	<i>Quercus ilex</i> , Holm (holly) oak	+	19.9	21
	<i>Quercus incana</i> , bluejack oak	45.6	0.2	2
	<i>Quercus laevis</i> , scrub oak	24.3	0.8	2
	<i>Quercus laurifolia</i> , laurel oak	10.4	0.2	2
	<i>Quercus libani</i> , Lebanon oak	3.2	0.1	42
	<i>Quercus lobata</i> , Californian valley oak	3.4	0.0	14, 41
	<i>Quercus macrolepis</i> , valonia oak	0.2	0.7	42
	<i>Quercus mexicana</i> , Mexican oak	14.4	0.1	42
	<i>Quercus myrtifolia</i> , myrtle oak	15.2	0.2	2
	<i>Quercus nigra</i> , water oak	24.6	+	2
	<i>Quercus petrea</i> , durmast oak	0.61	0.12	36
	<i>Quercus phellos</i> , willow oak	32.2	–	2
	<i>Quercus prinus</i> , swamp chestnut oak	6.5	1.5	4
	<i>Quercus prinus</i> , swamp chestnut oak	56		33
	<i>Quercus prinus</i> , swamp chestnut oak	40–90		16
	<i>Quercus pubescens</i> , pubescent oak	90.7		43
	<i>Quercus pubescens</i> , pubescent oak	45.3		17
	<i>Quercus pyrenaica</i> , Pyrenean oak	59	0.3	42
	<i>Quercus robur</i> , English oak	76.6		10
	<i>Quercus rotundifolia</i>	0.2	14.6	42
	<i>Quercus rubra</i> , red oak	14.8	1.8	4

Table II. (Continued)

Family	Species, trivial name	Isoprene [$\mu\text{g g(LDW)}^{-1} \text{h}^{-1}$]	Monoterpenes	Ref. (#)
	<i>Quercus rubra</i> , red oak	45–61		32
	<i>Quercus serrata (acutissima)</i>	15–30		34
	<i>Quercus suber</i> , cork oak	<0.1	<0.1	43
	<i>Quercus trojana</i> , Macedonian oak	0.2	0.2	42
	<i>Quercus velutina</i> , black oak	18.9	1.0	4
	<i>Quercus velutina</i> , black oak	59	1.0	33
	<i>Quercus velutina</i> , black oak	60–100		16
	<i>Quercus virginiana</i> , Virginia live oak	30.9		11
	<i>Quercus virginiana</i> , Virginia live oak	9.5	0.3	2
	<i>Quercus wislizeni</i> , interior live oak	16.6	0.0	42
	<i>Quercus wislizenii</i> , interior live oak	12.0	0.0	7
Ginkgoaceae				
	<i>Ginkgo biloba</i> , ginkgo	–	3.0	5
	<i>Ginkgo biloba</i> , ginkgo	<1		27
Hamamelidaceae				
	<i>Hamamelis virginiana</i> , common witch hazel	<1	<0.2	27
	<i>Liquidambar styraciflua</i> , sweetgum	34	3.5	5
	<i>Liquidambar styraciflua</i> , sweetgum	17.8	2.9	3
	<i>Liquidambar styraciflua</i> , sweetgum	3.5	51.5	2
	<i>Liquidambar styraciflua</i> , sweetgum	63–99		37
Hippocastanaceae				
	<i>Aesculus flava</i> , yellow buckeye	<1	<0.2	27
Juglandaceae				
	<i>Carya aquatica</i> , water hickory	–	0.7	2
	<i>Juglans regia</i> , English walnut	0	1.8	14, 41
Lamiaceae (Labiatae)				
	<i>Rosmarinus officinalis</i> , rosemary		2.2	50
	<i>Salvia mellifera</i> , black sage	0.0	5–27	7
	<i>Salvia mellifera</i> , black sage	+	11.7	1
	<i>Trichostema lanatum</i> , woolly blue curls	0.0	17.7	1
Lauraceae				
	<i>Cinnamomum camphora</i> , camphor tree	–	0.03	5
	<i>Cinnamomum camphora</i> , camphor tree	–	0.0	1
	<i>Persea americana</i> , American avocado	+	+	1
	<i>Persea borbonia</i> , red bay	–	1.2	2
Lythraceae				
	<i>Lagerstroemia indica</i> , common crape myrtle	–	–	5
	<i>Lagerstroemia indica</i> , common crape myrtle	–	–	1

Table II. (Continued)

Family	Species, trivial name	Isoprene [$\mu\text{g g(LDW)}^{-1} \text{h}^{-1}$]	Monoterpenes	Ref. (#)
Magnoliaceae				
	<i>Liriodendron tulipifera</i> , tulip tree	4.1		4
	<i>Magnolia grandiflora</i> , magnolia	+	5.9	1
Malvaceae				
	<i>Gossypium hirsutum</i> , cotton	0	0.4–0.8	14, 41
Mimosaceae (Leguminosae)				
	<i>Acacia farnesiana</i> , sweet acacia	–	4.7	2
	<i>Acacia nigrescens</i> , African akazia	110	0.7	39
	<i>Acacia tortilis</i>	<0.5	8.8	39
	<i>Albizia julibrissin</i> , silk tree	10–40	<0.2	27
Moraceae				
	<i>Ficus fistulosa</i> , fig	27.0	0.2	6
	<i>Morus rubra</i> , red mulberry	–	1.6	2
Myrtaceae				
	<i>Callistemon citrinus</i> , bottlebrush	16.0	+	1
	<i>Eucalyptus globulus</i> , blue gum eucalyptus	57.0	9.2	3
	<i>Eucalyptus globulus</i> , blue gum eucalyptus	28.0	+	19
	<i>Eucalyptus globulus</i> , blue gum eucalyptus	15–49	0,7–4	48
	<i>Eucalyptus viminalis</i> , ribbon gum	8.0	+	1
	<i>Eugenia grandis</i> , eugenia	12.1		6
	<i>Myrtica cerifera</i> , southern wax myrtle	–	1.1	2
	<i>Myrtus communis</i> , true Myrtle	34.0	+	1
	<i>Myrtus communis</i> , true Myrtle	136.7	0.3	45
	<i>Myrtus communis</i> , true myrtle	25.2		50
Ochnaceae				
	<i>Ochna puchra</i> , ochnea	32	<0.5	39
Oleaceae				
	<i>Fraxinus caroliniana</i> , Carolina ash	–	–	2
	<i>Fraxinus uhdei</i> , evergreen ash	+	+	1
	<i>Ligustrum lucidum</i> , glossy privet	+	+	1
	<i>Olea europaea</i> , common olive	+	0.5	1
	<i>Olea europaea</i> , common olive	0	0.1	14, 41
	<i>Phillyrea angustifolia</i> , narrowed leaved Ph.		0.47	45
Pinaceae				
	<i>Abies lasiocarpa</i> , fir	<0.1	3	2
	<i>Cedrus deodara</i> , deodar cedar	–	0.3	5
	<i>Cedrus deodara</i> , deodar cedar	+	0.9	1
	<i>Picea abies</i> , Norwegian spruce		1.2	12
	<i>Picea abies</i> , Norwegian spruce		0.2–3.0	31

Table II. (Continued)

Family	Species, trivial name	Isoprene [$\mu\text{g g(LDW)}^{-1} \text{h}^{-1}$]	Monoterpenes	Ref. (#)
	<i>Picea abies</i> , Norwegian spruce	0.34	3,1	49
	<i>Picea abies</i> , Norwegian spruce	0.5–1,8	0,6–7,8	51
	<i>Picea engelmannii</i> , engelmann spruce	16.3	3.4	3
	<i>Picea engelmannii</i> , engelmann spruce	9.5	4.3	40
	<i>Picea engelmannii</i> , engelmann spruce	16	+	49
	<i>Picea glauca</i> , white spruce	7–15	1.4	49
	<i>Picea mariana</i> , black spruce	15	+	49
	<i>Picea pungens</i> , blue spruce	12	1.0	49
	<i>Picea rubens</i> , red spruce	1.1	+	49
	<i>Picea sitchensis</i> , sitka spruce	4.0	1.1	3
	<i>Picea sitchensis</i> , sitka spruce	1.8	1.1	40
	<i>Pinus canariensis</i> , Canary island pine	–	1.7	5
	<i>Pinus canariensis</i> , Canary island pine	+	2.6	1
	<i>Pinus clausa</i> , sand pine	–	11.5	2
	<i>Pinus densiflora</i> , red pine		0.15	13
	<i>Pinus ellotii</i> , slash pine	–	6.9	3
	<i>Pinus ellotii</i> , slash pine	–	5-6.2	11
	<i>Pinus ellotii</i> , slash pine	–	3.2	2
	<i>Pinus halepensis</i> , Aleppo pine		0.2	5
	<i>Pinus halepensis</i> , Aleppo pine	+	0.5	1
	<i>Pinus halepensis</i> , Aleppo pine	+	1.0	31
	<i>Pinus palustris</i> , longleaf pine	–	5.9	2
	<i>Pinus pinaster</i> , maritime pine		0.6	30
	<i>Pinus pinaster</i> , maritime pine		1.0	31
	<i>Pinus pinea</i> , Italian stone pine	–	0.4	5
	<i>Pinus pinea</i> , Italian stone pine	+	+	1
	<i>Pinus pinea</i> , Italian stone pine (spring)		1.3	18
	<i>Pinus pinea</i> , Italian stone pine (spring)		1.5	24
	<i>Pinus pinea</i> , Italian stone pine (spring)		2–3.5	23
	<i>Pinus pinea</i> , Italian stone pine (summer)		7–15	23
	<i>Pinus pinea</i> , Italian stone pine	<0.01	2.2–7.4	44
	<i>Pinus ponderosa</i> , ponderosa pine		2.5	35
	<i>Pinus radiata</i> , Monterey pine	–	0.9	5
	<i>Pinus radiata</i> , Monterey pine	+	0.7	1
	<i>Pinus sabiniana</i> , digger pine	–	0.6	9
	<i>Pinus sylvestris</i> , scots pine	–	12.1	10
	<i>Pinus sylvestris</i> , scots pine		0.8	12
	<i>Pinus sylvestris</i> , scots pine		6	31

Table II. (Continued)

Family	Species, trivial name	Isoprene [$\mu\text{g g(LDW)}^{-1} \text{h}^{-1}$]	Monoterpenes	Ref. (#)
	<i>Pinus taeda</i> , loblolly pine		5.1	4
	<i>Pseudotsuga macrocarpa</i> , bigcone douglas fir	0.0	1.1	7
	<i>Pseudotsuga menziesii</i> , coastal douglas fir	1.5 ± 1.6	2.3 ± 1.4	52
	<i>Tsuga mertensiana</i> , mountain hemlock	0.03 ± 0.01	0.4 ± 0.2	52
Pittosporaceae				
	<i>Pittosporum tobira</i> , Chinese pittosporum	+	+	1
	<i>Pittosporum undulatum</i> , orange berry pittosporum	+	+	1
Platanaceae				
	<i>Platanus occidentalis</i> , American sycamore	27.5	–	3
	<i>Platanus racemosa</i> , western sycamore	10.9	+	1
Poaceae				
	<i>Arundo donax</i> , giant reed	38.6		25
	<i>Chusquea</i> spp., giant chusqua	>40	<0.2	27
	<i>Oryza sativa</i> , rice	0	0	14
	<i>Phragmites mauritianum</i> , reed	35	0.6	39
	<i>Secale cereale</i> , rye	0	0.03–0.11	36
	<i>Sorghum bicolor</i> , sorghum	0	0.04	14, 41
	<i>Triticum aestivum</i> , wheat	0	0	14
Podocarpaceae				
	<i>Podocarpus gracilior</i> , fern pine	+	+	1
Polygonaceae				
	<i>Eriogonum fasciculatum</i> , California buckwheat	+	+	1
	<i>Polygonum sachalinense</i> , Sakhalin knotweed	0.005		52
Rhamnaceae				
	<i>Ceanothus crassifolius</i> , hoaryleaf ceanothus	+	+	1
	<i>Ceanothus leucodermis</i> , chaparral whitehorn	0	5.4	14, 41
	<i>Ceanothus spinosus</i> , greenbark	0.0	1.8	7
	<i>Rhamnus californica</i> , California buckthorn	29.3	–	3
	<i>Rhamnus crocea</i> , redberry	54.4	+	1
Rosaceae				
	<i>Adenostoma fasciculatum</i> , common chamise		–	7
	<i>Adenostoma fasciculatum</i> , common chamise	–	–	1
	<i>Adenostoma fasciculatum</i> , common chamise	0	0.4	14, 41
	<i>Amelanchier alnifolia</i> , serviceberry	<1	<0.2	27
	<i>Cerocarpus betuloides</i> , birchleaf mountain mahogany	–	–	7
	<i>Cercocarpus montanus</i> , true mountain mahogany	<1	<0.2	27
	<i>Cotoneaster pannosus</i> , cotoneaster	+	+	14

Table II. (Continued)

Family	Species, trivial name	Isoprene [$\mu\text{g g(LDW)}^{-1} \text{h}^{-1}$]	Monoterpenes	Ref. (#)
	<i>Crataegus</i> spp., hawthorn	<1	<0.2	27
	<i>Malus domestica</i> , apple	<1	0.2–1	27
	<i>Prunus armeniaca</i> , blenheim apricot	0	0.1	14, 41
	<i>Prunus avium</i> , bing cherry	0	0.1	14, 41
	<i>Prunus domestica</i> , santa rosa plum	0	0	14
	<i>Prunus dulcis</i> , nonpareil almond	0	0.0	14
	<i>Prunus persica</i> , peach	0	0.1	14
	<i>Prunus persica</i> , peach	0	0.3	41
	<i>Prunus persica</i> , nectarine	0	<0.01	14
	<i>Pyrus kawakamii</i> , evergreen pear	+	+	1
	<i>Rhaphiolepis indica</i> , India hawthorne	+	+	1
	<i>Rubus fruticosus</i> , shrubby blackberry		0.03	45
	<i>Rubus ursinus</i> , loganberry, blackberry	0.08		52
	<i>Sorbus scopulina</i> , mountain ash	<1	>3	27
Rutaceae				
	<i>Citrus limon</i> , Lisbon lemon	–	3.2	15
	<i>Citrus limon</i> 'Meyer', meyer lemon	+	+	1
	<i>Citrus sinensis</i> , navel orange	0	1.8	14, 41
	<i>Citrus sinensis</i> 'Valencia', Valencia orange	0	0.9	14, 41
Salicaceae				
	<i>Populus deltoides</i> , eastern poplar	37.0	–	3
	<i>Populus balsamifera</i> , balsam or southern poplar	100 ± 46	0.3 ± 0.1	52
	<i>Populus tremula</i> , European or trembling aspen	51	4.6	46
	<i>Populus tremuloides</i> , quaking aspen	50.2	–	3
	<i>Populus tremuloides</i> , quaking aspen	86	–	22
	<i>Salix babylonica</i> , weeping willow	115.0	–	1
	<i>Salix caroliniana</i> , coast plain willow	12.5	+	2
	<i>Salix nigra</i> , black willow	25.2	–	3
	<i>Salix phylicifolia</i> , tea leafed willow	32	0.33	46
Sapindaceae				
	<i>Cupaniopsis anacardioides</i> , carrotwood	49	–	5
Solanaceae				
	<i>Lycopersicon esculentum</i> , tomato	0	20–60	14
	<i>Lycopersicon esculentum</i> , tomato	0	13–21	41
Taxodiaceae				
	<i>Metasequoia</i> spp., metasequoie	<1		27
	<i>Taxodium spec.</i> , cypress	–	8.5	2

Table II. (Continued)

Family	Species, trivial name	Isoprene [$\mu\text{g g(LDW)}^{-1} \text{h}^{-1}$]	Monoterpenes	Ref. (#)
Thelypteridaceae				
	<i>Thelypteris decursive-pinnata</i> , maiden fern	24.5	0.0	3
Tiliaceae				
	<i>Tilia americana</i> , American linden	1–10		27
	<i>Grewia flavescens</i> , grewia	<0.5	0.5	39
Ulmaceae				
	<i>Ulmus americana</i> , American elm	+	+	1
	<i>Ulmus americana</i> , American elm	–	–	2
	<i>Ulmus parvifolia</i> , Chinese elm	+	+	1
Vitaceae				
	<i>Vitis vinifera</i> , European grape	0	0	14, 41
	<i>Vitis vinifera</i> , European grape	0	0–0.03	36

References (#). 1: Winer *et al.* (1983); 2: Zimmerman (1979); 3: Evans *et al.* (1982); 4: Lamb *et al.* (1983); 5: Corchnoy *et al.* (1992); 6: Cronn and Nutmagul (1982); 7: Arey *et al.* (1995); 8: Flyckt (1979); 9: Tanner and Zielinska (1994); 10: Isidorov *et al.* (1985); 11: Tingey *et al.* (1979); 12: Janson (1993); 13: Yokouchi and Ambe (1984); 14: Winer *et al.* (1992); 15: Winer *et al.* (1989); 16: Harley *et al.* (1997); 17: Kesselmeier *et al.* (1998b); 18: Kesselmeier *et al.* (1997a); 19: Pio *et al.* (1996); 20: Hansen and Seufert (1996); 21: Bertin *et al.* (1997); 22: Monson and Fall (1989); 23: Staudt *et al.* (1997); 24: Pio *et al.* (1993); 25: Hewitt *et al.* (1990); 26: Schuh *et al.* (1997); 27: Guenther *et al.* (1996a); 28: Guenther *et al.* (1994); 30: Simon *et al.* (1994); 31: Staudt (1997); 32: Pier (1995); 33: Dilts (1993), Dilts *et al.* (1994); 34: Ohta (1986); 35: Lerdau *et al.* (1994); 36: König *et al.* (1995); 37: Harley *et al.* (1996a); 38: Harley *et al.* (1996b); 39: Guenther *et al.* (1996b); 40: Evans *et al.* (1985); 41: Arey *et al.* (1991c); 42: Csiky and Seufert (1999); 43: Steinbrecher *et al.* (1997); 44: Street *et al.* (1997b); 45: Owen *et al.* (1997); 46: Hakola *et al.* (1998); 47: Pier and McDuffie (1997); 48: Street *et al.* (1997a); 49: Kempf *et al.* (1996); 50: Hansen *et al.* (1997); 51: Steinbrecher (1994).

Moreover, emission studies under controlled light and temperature conditions are often performed in the laboratory on young potted plants, whereas those under nonenvironmental controlled conditions are often performed in the field on mature plants of natural stands.

Thus, there is an experimental uncertainty associated with emission factors reported in the literature. This might be partly responsible for the apparent intraspecies variability of E_S values, but they cannot explain it totally. In some cases, a significant E_S variability was observed by the same author under similar experimental conditions. For instance, the emission rates of adult spruces and pines grown in five different regions of central and northern Europe differ up to a factor of 50 (Janson, 1993). This range is unlikely to result from experimental shortcomings.

Monoterpenes are known to constitute the main fraction of 'terpenic oils' or 'essential oils' that are produced and stored in plant secretory organs like glandular

trichomes and resin ducts. Within the plant families, their occurrence is reported in numerous studies on coniferous plants as well as on members of the families *Lamiaceae*, *Apiaceae*, *Rutaceae*, *Myrtaceae* and *Asteraceae*, (Guenther, 1952; Dell and McComb, 1978; Dev *et al.*, 1983; Gershenson and Croteau, 1990; Riba and Torres, 1997; Steinbrecher, 1997; see also Table II). Usually, monoterpene-storing plants were also found to be monoterpene emitters; and for some coniferous species, a correlation could be observed between leaf concentration and leaf emission (Simon *et al.*, 1994; Lerda *et al.*, 1994; Yatagai *et al.*, 1995). In other cases, this correlation was less evident (Schindler and Kotzias, 1989; Yatagai *et al.*, 1995; Staudt *et al.*, 1997). For example, orange foliage contains high amounts of sabinene and limonene, but mainly emits the sesquiterpene β -caryophyllene (BEMA, 1997). In contrast, some oak species emit high amounts of monoterpenes, but do not store them (Staudt *et al.*, 1993; Loreto *et al.*, 1996a; Csiky and Seufert, 1999).

Isoprene is never stored in plants after its production, but is rapidly lost by volatilization. Isoprene-emitting species occur in many plant taxa throughout many functional types (Table II), but they are more often found in woody plant species than in herbs and crops. They are particularly common in the families *Salicaceae*, *Fagaceae*, and *Palmae* as well as in the genus *Picea* (spruces) and diverse ferns (Sharkey, 1996b; Tingey *et al.*, 1987). However, there are also important exceptions. For example, within the group of evergreen oaks growing under Mediterranean climate, some species (*Quercus agrifolia*, California life oak) emit exclusively isoprene and others (*Quercus ilex*, European holm oak; *Quercus coccifera*, European kermes oak) exclusively monoterpenes, whereas *Quercus suber* (European cork oak), ignoring some trace emissions, emits neither isoprene nor monoterpenes (Staudt *et al.*, 1993; Pio *et al.*, 1993, 1996; Staudt and Seufert, 1995; Seufert *et al.*, 1995; Hansen and Seufert, 1996; Steinbrecher *et al.*, 1997; Kesselmeier *et al.*, 1996, 1997a, 1998b; Bertin *et al.*, 1997; Staudt and Bertin, 1998). This example points out the limits of assigning emission factors to noninvestigated plant species by taxonomical approaches as proposed by Benjamin *et al.* (1996).

3. Other Nonmethane Volatile Organic Compounds

3.1. ALKANES AND ALKENES

Ethane, propane, and butane with atmospheric background concentrations of 1–3 ppb originate from natural gas sources in the range of 6 Tg yr⁻¹ (Rudolph, 1995; Lindskog, 1997). A further significant source is biomass burning with ethane emissions of 6.4 Tg yr⁻¹ (Rudolph, 1995). Calculations of the southern hemispheric budgets for ethane and propane predict 2.7 and 2.1 Tg yr⁻¹, respectively, released by biomass burning (Clarkson *et al.*, 1997). Further anthropogenic sources discussed are for butane: namely, evaporation and incomplete combustion of fuel (traffic and other combustion processes are regarded to be of minor importance) (Lindskog, 1997). Terrestrial biogenic sources of C₂–C₄ alkanes are trees, crops, and grass- and marshland (Zimmerman, 1979; Altshuller, 1983) with a possible

bidirectional exchange for ethane and propane (Hahn *et al.*, 1991; Steinbrecher *et al.*, 1992). However, according to Guenther *et al.* (1994), the global contribution of terrestrial vegetation to the atmospheric budget is low. Lichens, mosses, and heather are discussed as potentially relevant sources (Isodorow *et al.*, 1994) and might be of importance for some remote areas without a dominant higher vegetation. Van Cleemput *et al.* (1991) reported low production rates for ethane and propane in soil samples, which is in accordance with soil studies within a wheat field by Hahn *et al.* (1991) and Steinbrecher *et al.* (1992). A biogenic marine contribution is also discussed, although without sufficient knowledge of marine biogenic production. Bonsang *et al.* (1988) estimate the marine global emissions of ethane, propane, and butane to be around 30 Tg yr⁻¹. Recent budget estimates by Plass-Dülmer *et al.* (1995) reach only 1 Tg yr⁻¹.

Significant biogenic sources are known for ethene, propene, and butene, released at rates of 2.63, 1.13, and 0.41×10^{10} molecules cm⁻² s⁻¹, respectively, from a forest (Goldstein *et al.*, 1996). These values suggest that biogenic emissions of propene and butene exceed anthropogenic ones in the Northeast of the U.S.A. and, in contrast, that biogenic ethene is equivalent to 50% of the anthropogenic contribution. Hakola *et al.* (1998) have reported seasonal fluctuations of ethene, propene, and butene emissions by two boreal tree species in the range of 0.5–2 μg g⁻¹ (LDW, leaf dry weight) h⁻¹. Such data point to terrestrial vegetation as the most important source, where agriculturally used crops obviously show a higher percentage of ethene and propene emissions to nonmethane hydrocarbon emissions than forest trees with emission of a large amount of isoprenoids (Parusel, 1996). Sufficient understanding of the plant physiological production is, however, only available for the synthesis of ethene. The formation of ethene proceeds from the amino acid methionine via two intermediates (S-adenosylmethionine and aminocyclopropane carboxylic acid, ACC). To regenerate methionine, the by-product 5'-methylthioadenosine (MTA) of the abovementioned synthesis undergoes a reaction chain called Yang or methionine cycle. During this cycle, formic acid and MTA are released in equivalent amounts (Abeles *et al.*, 1992). Stimulation of ethene production is observed after injury, under arid conditions or extreme temperatures, or following high pollution episodes and other stresses (Bucher, 1981; Kimmerer and Kozlowski, 1982; Yang and Hoffman, 1984). This is the reason why ethene is called a 'stress hormone'. However, presumably all plant tissues produce ethene under normal conditions. Global extrapolation of emissions from vegetation is a matter of debate. For ethene, Ehalt and Rudolph (1984) discuss a low emission around 1 Tg yr⁻¹. Sawada and Tutsuka (1986) estimate 12.9 Tg yr⁻¹, while Hough (1991) reports about 20 Tg yr⁻¹. A recent compilation made by Rudolph (1997), however, comes up with a more moderate estimation in the range of a few Tg yr⁻¹. Soils are also regarded as sources of ethene (Hahn *et al.*, 1991, 1992; Smith and Cook, 1979; Ramon and Van Cleemput, 1990; Van Cleemput and Vermoesen, 1991, 1993) and both ethene and propene (Parusel, 1996). Global estimates for soil emissions are 3.7 (Sawada and Tutsuka, 1986) and 2.6 Tg yr⁻¹ (Warneck, 1988).

Another significant source of C₂–C₄ alkenes is the oceans. According to Rudolph (1997), alkenes are not directly produced by marine organisms, but are formed by the photochemical degradation of dissolved organic carbon (DOC). DOC is released to a considerable extent by algae during growth or decay; and thus, oceanic alkene emissions are indirectly related to biological processes in the ocean, with a maximum of 5 Tg yr⁻¹ being released into the atmosphere. Some limited data indicate that soils and vegetation can also act as a sink for light alkenes (Abeles, 1971; Hahn *et al.*, 1991, 1992; Steinbrecher, 1993).

3.2. ORGANIC ACIDS

Organic acids are found in several geochemical compartments including the atmosphere, biosphere, soils, and hydrosphere (Graedel and Weschler, 1981; Keene and Galloway, 1988). These compounds are relevant to atmospheric chemistry, as they not only have a dominant impact on the acidity within the precipitation in remote areas, but also significantly influence the acidity in industrial regions (Keene *et al.*, 1983; Keene and Galloway, 1984; Andreae *et al.*, 1988). The acidification in remote areas is mainly due to formic and acetic acids, although some other species are also involved (Lunde *et al.*, 1977; Likens and Galloway, 1983; Norton *et al.*, 1983; Kawamura *et al.*, 1985; Kawamura and Kaplan, 1986; Andreae *et al.*, 1987, 1988; Hofmann *et al.*, 1997). In more polluted areas, sulfuric and nitric acid dominate rainwater pH. In addition to the existence in and on aerosol particles (Ketseridis *et al.*, 1976; Grosjean *et al.*, 1978; Andreae *et al.*, 1988; Ludwig and Klemm, 1988; Hofmann *et al.*, 1997), organic acids are not only found in the liquid, but also in the gas phase. Due to their high partial pressure, formic and acetic acids are particularly regarded as the more important species in the gas phase. A large data set for atmospheric concentrations over the European continent with mixing ratios for formic and acetic acids between 0.1–11 ppb, but typically 1–3 ppb, can be found in the works of Puxbaum and co-workers (Puxbaum, 1987; Puxbaum *et al.*, 1988; Winiwarter *et al.*, 1988). Investigations by Hartmann *et al.* (1989) and Hartmann (1990) come up with very similar numbers, as do those reported for the North American continent (Dawson *et al.*, 1980; Farmer and Dawson, 1982; Dawson and Farmer, 1988; Talbot *et al.*, 1988). Over an agricultural region in the Rhine valley, Hoffmann *et al.* (1997) demonstrated the occurrence of formic, acetic, propionic, and oxalic acids, with oxalic acid mainly bound to particles. Several authors reported decreasing concentration from the continents to the marine environment (Farmer *et al.*, 1988; Schultz-Tokos and Duce, 1989; Hartmann, 1990) and also for the transition from the boundary layer to the free troposphere (Hartmann *et al.*, 1989; Helas *et al.*, 1992; Talbot *et al.*, 1990). Data of tropical regions are given for Amazonia during the dry (Andreae *et al.*, 1988) and the wet season (Talbot *et al.*, 1990). Helas *et al.* (1992) report concentrations over equatorial Africa which are, outside times of biomass burning, similar to those over the European continent. A short overview of atmospheric concentrations is given in Table III. The high vari-

ability of organic acids points to the relatively short atmospheric lifetimes, which are bound to the atmospheric water cycle and do not exceed 7–9 days (Pruppacher and Klett, 1980).

Potential sources of organic acids are still under investigation. Anthropogenic indirect sources are discussed in view of the production of formic and acetic acids during the oxidation of ethene and propene by ozone (Calvert and Stockwell, 1983; Puxbaum *et al.*, 1988; Horie and Moortgat, 1991; Grosjean, 1992; Neeb *et al.*, 1994). Emissions from automobile exhaust, industrial combustion processes, and biomass burning represent significant contributions, but are discussed as being of minor importance for global budgets (Keene and Galloway, 1986; Talbot *et al.*, 1988, 1995). Investigations by Sanhueza and Andreae (1991) show evidence that soils may represent a source of both formic and acetic acids. However, biogenic emissions from vegetation, directly or indirectly, must play a dominant role within the budget of tropospheric organic acids (Keene and Galloway, 1986; Andreae *et al.*, 1988; Berresheim *et al.*, 1988; Helas *et al.*, 1992; Hartmann *et al.*, 1989). With regard to the indirect emission from vegetation, isoprene was discussed as one of the most important compounds which can be oxidized to deliver formic and pyruvic acids (Duce *et al.*, 1983; Jacob and Wofsy, 1988; Andreae *et al.*, 1987). Other authors assume the production of formic and acetic acids by the oxidation of formaldehyde and acetaldehyde in the liquid phase (Chameides and Davis, 1983; Jacob, 1988; Keene and Galloway, 1986). In addition, Madronich *et al.* (1990) describe gas-phase oxidation of NMHC as a potential source of acetic acid. Talbot *et al.* (1995), however, find it unlikely that decomposition of isoprene or other nonmethane hydrocarbons can be a dominant source of these acids in the midlatitude continental atmosphere. With this understanding, it is of great interest that there is growing evidence that formic acid as well as acetic acid is directly emitted by vegetation (Talbot *et al.*, 1990; Kesselmeier *et al.*, 1991; Schäfer *et al.*, 1992, 1995; Bode, 1994; Bode *et al.*, 1996; Ciccioli *et al.*, 1997b). Recently published extensive studies of forest trees and agricultural crops (Kesselmeier *et al.*, 1998a) show that trees are generally regarded as direct emitters of both formic and acetic acids, whereas crops were found to act as a significant sink. Rough estimates of global annual emissions range between 1 to 6 Tg formic acid and 0.6 to 2 Tg acetic acid. Such numbers reflect a 15–30% contribution by direct forest emissions to the European continental organic acid budget (Kesselmeier *et al.*, 1998a). An overview of sources discussed for these two acids is given in Table IV.

As discussed above, the most prominent volatile organic acids emitted by the vegetation are formic and acetic acids. Therefore, the following paragraphs will give an overview of the potential pathways for synthesis within plant metabolism. A schematic overview of the likely pathways for the formation of formic and acetic acids is given in Figure 3. Generally, formic acid is used in plants via activation with tetrahydrofolic acid for numerous metabolic pathways. This so-called C₁ metabolism (see textbooks on biochemistry or plant physiology) also includes the transfer of hydroxymethyl and methyl groups and is an important pathway for

Table III. Gas-phase concentrations (ppb) of organic acids in some regions

<i>Acid species:</i>	Formic	Acetic	Propionic	Pyruvic
Mainz (univ. campus) ^a	1.1–2.1	1.1–2.2	0.07–0.21	
Bellheim (Rhine valley) ^a	0–4.0	0–3.8	0.00–0.12	
Central-Germany (free troposphere) ^b	0.9 ± 1.4	0.9 ± 1.2		
Austria (rural) ^c	1.6 ± 0.6	1.0 ± 0.4		
Virginia ^d	1.9 ± 1.2	1.3 ± 0.9		
Pacific Ocean ^e	0,03–1,7	0,05–1,9		
Amazonia (dry season) ^f	1,3–2,9	1,0–3,0		
Amazonia (wet season) ^g	0, 43 ± 0, 23	0, 34 ± 0, 16		0, 025 ± 0, 015
Tropical savannah (dry season) ^f	1.8	1.25		
(wet season) ^f	1.0	0.7		
South-west U.S.A. (rural/urban) ^h	0,7–3,0	0,6–4,0		
Los Angeles, U.S.A. ⁱ	0,1–3,0	0,3–3,9		
Los Angeles, U.S.A. ^j	1,3–13	1,9–16		
Schenectady (semiurban) ^k	0,8–2,5	0,6–5,4		
Above deciduous forest in Pennsylvania (summer) ^l	0,1–9,8	0,1–6,5		0,01–0,1
Deciduous forest (crown region), Italian coast, near Rome ^m	0,3–2,2	0,1–1,4		
Eastern U.S.A. (rural) ⁿ	0,5–21,4	0,2–6,3		0,04–0,27
Nagoya (urban air) ^o	0,84–2,93		0,04–0,26	
Tallahassee, Florida ^p				0,008–0,16
Charlottesville, Virginia ^p	0,34–2,8			0,04–0,11
Western North Atlantic ^p				0,024–0,048
Ducke Reserve, Manaus (dry season) ^p	1,2–2,9			0,08–0,4
Kleiner Feldberg, Germany ^q	0,09–0,63	0,15–0,6	0,01–0,05	<0,01
India, semiurban ^s	1.3 ± 1.4	1.7 ± 1.6		

^a Hofmann *et al.* (1997); ^b Hartmann *et al.* (1989); ^c Puxbaum *et al.* (1988); ^d Talbot *et al.* (1988);
^e Arlander *et al.* (1990); ^f Andreae *et al.* (1988); ^g Talbot *et al.* (1990); ^h Dawson and Farmer
(1988); ⁱ Kawamura *et al.* (1985); ^j Grosjean (1989); ^k Khwaja (1995); ^l Martin *et al.* (1991);
^m Schäfer *et al.* (1995); ⁿ Talbot *et al.* (1995); ^o Hoshika (1982); ^p Andreae *et al.* (1987); ^q Beck *et al.*
(1997); ^r Sanhueza *et al.* (1996a); ^s Kumar *et al.* (1996).

Table IV. Continental sources for atmospheric formic and acetic acids

Source	Formic acid	Acetic acid
	[Gmol/y]	
Biomass burning ^a	55 ... 202	182 ... 650
Vegetation ^b	14 ... 256	9 ... 94
Forests ^c	20 ... 130	10 ... 33
Savannah soils ^a	36	24
Ants ^a	10	–
Traffic ^a	0.4	1.3
Ruminants ^a	–	2.5

^a Helas and Kesselmeier (1993); ^b Bode *et al.* (1997);
^c Kesselmeier *et al.* (1998a).

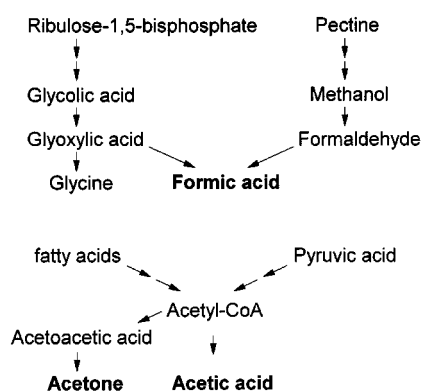


Figure 3. Simplified scheme of pathways for formic acid and acetic acid production, enclosing also methanol and acetone production.

the synthesis of purines, pyrimidines, and alkaloids as well as amino acids. Additionally, formic acid can be formed as a by-product during the synthesis of ethene, a plant hormone, and by oxidation of methanol derived from pectine demethylation during cell wall growth and expansion (Fall and Benson, 1996).

Photorespiration is discussed by Kesselmeier (1992), Kesselmeier and Bode (1997), and Bode *et al.* (1997) as a further possible source of formic acid emission. As a minor reaction in the peroxisomes, the intermediate glyoxylate decays to formate and carbon dioxide (Halliwell and Butt, 1974; Grodzinski, 1978, 1979; Somerville and Ogren, 1981). While this pathway normally makes up only a few percent of respiratory CO₂ emission, the decay is assumed to be enhanced if the consumption pathways for glyoxylate are inhibited (Halliwell and Butt, 1974; Grodzinski, 1978; Amory and Cresswell, 1986). Such a blockade could be due to an inadequate availability of nitrogen so that not enough glycine can be formed (Oliver, 1981 II). The once-produced formate may then either be further oxidized or

emitted after protonation. Only 0.1–0.3% of this pool would be sufficient to match measured emission rates of formic acid (Bode *et al.*, 1997), but this assumption has not been experimentally proven.

Acetic acid is mainly found in its activated form acetyl-CoA. Acetyl-CoA plays a major role in anabolic as well as catabolic processes. Acetyl-CoA is the main product after decomposition of carbohydrates and fats. It is channeled into the citrate cycle, a central cycle in cellular processes, and thus serves in many other processes, including energy production. Furthermore, so-called acetate units serve for the synthesis of fatty acids, carotenoids, and, for example, terpenes. Additionally, the direct loading of acetate with CoA by the enzyme acetyl-CoA synthetase is possible (Richter, 1988), presumably inside the chloroplasts, using the acetate set free by mitochondria. This process serves to activate the acetate for further use in fatty acid synthesis (Libbert, 1987; Harwood, 1988). As the inner mitochondrial membrane is impermeable for acetyl-CoA, this compound has to be hydrolyzed for transport from the mitochondria to the chloroplasts across the cytosol. Inside the chloroplasts, it is used for fatty acid synthesis which takes place only (or mainly) inside plastids (Harwood, 1988; Lawlor, 1990). Additionally, plants use free acetate for many anabolic pathways. In experiments with tissue and cell cultures, it was possible to transfer the carbon of labeled acetic acid to lipids and other organic acids (Fletcher and Beevers, 1970; Gupta *et al.*, 1976, 1979; Groeneveld *et al.*, 1991; Igamberdiev and Rodlonova, 1991). Hop plants were observed to consume labeled acetic acid for the production of fatty acids and steroids (Drawert and Beier, 1974). However, it is not yet possible to discuss any close relationship between these metabolic processes and emissions.

3.3. CARBONYL COMPOUNDS

Carbonyls play an important role in atmospheric chemistry owing to their contribution to tropospheric ozone. They are involved in photochemical reactions wherein the photolytic cleavage of aldehydes represents a significant source of free radicals in the atmosphere. Formaldehyde, for example, is regarded as the main driving force for the production of HO₂ and OH radicals (Calvert and Stockwell, 1983). The group of biogenic carbonyls includes formaldehyde, acetaldehyde, propanal, acetone, butanal, i-butanal, butenal, i-butenal, butanone-2, crotonaldehyde, pentanone-2, 2-methyl-2-pentenal, hexanal, (E)-2-hexenal, (Z)-3-hexenal, octanone-3, nonanal, benzaldehyde, citronellal, 6,6-dimethyl-bicyclo[3.1.1]-heptane-2-carboxaldehyde, methyl-isopropyl-ketone, methyl-vinyl-ketone (Graedel, 1979; Isodorow *et al.*, 1985; Buttery *et al.*, 1982, 1985; Arey *et al.*, 1991a; MacDonald and Fall, 1993a; Tanner and Zylinska, 1994; König *et al.*, 1995; Singh *et al.*, 1994; Kesselmeier *et al.*, 1997a; Kotzias *et al.*, 1997). Table V compiles the knowledge of natural sources of atmospheric relevant aldehydes and ketones and their atmospheric concentrations outside cities (Kotzias *et al.*, 1997).

Table V. Atmospheric concentrations of carbonyls outside urban areas and their natural sources (after Kotzias *et al.*, 1997)

	Concentrations [$\mu\text{g m}^{-3}$]	Sources
Formaldehyde	1–25	1, 2, 3
Acetaldehyde	1–20	1, 2, 3, 4, 5
Propanal	0.1–5.2	1, 2, 3, 4, 5
Butanal	<1	1, 2, 3
Pentanal	<1	1, 3
Hexanal	<1	1, 3
Heptanal	<1	1, 3
Octanal	3	1, 3
Nonanal	8	1, 3
Decanal	7	1
Acetone	1–25	1, 2, 3, 4, 5
Methyl ethyl ketone	<1	1, 2, 3, 5

Sources: 1: vegetation (directly or indirectly); 2: forest fires; 3: microbial processes; 4: insects; 5: vulcanoes.

Biogenic contributions to the atmospheric concentrations of aldehydes can be derived from the knowledge of direct or indirect release from vegetation. The main contribution to the atmospheric budget is seen in the secondary reactions of biogenic (or anthropogenic) hydrocarbons with radicals (OH, NO_3) and ozone as well as in photolysis. Ozonolysis occurring at vegetation surfaces, for instance, was recently recognized as a source of acetone, 4-oxopentanal, 6-methyl-5-hepten-2-one, and geranyl acetone (Fruekilde *et al.*, 1998). The most significant biogenic precursors, therefore, are some reactive terpenes and isoprene which may produce high aldehyde concentrations in vegetated regions (Lloyd *et al.*, 1983; Hov *et al.*, 1983; Altshuler, 1993; Grosjean *et al.*, 1993a, b). In addition, (Z)-3-hexene-1-ol and (Z)-3-hexenylacetate, emitted by a large number of plants, can be transformed to aldehydes, such as propanal, and in presence of OH radicals and NO_x also to formaldehyde and acetaldehyde (Atkinson, 1990b). Methanol emissions by plants (MacDonald and Fall, 1993b; Nemecek-Marshall *et al.*, 1995) also contribute to the production of formaldehyde. The ozonolysis of alkenes, in addition to the reaction with OH, plays a significant role in aldehyde production, delivering several molecules of aldehydes per molecule hydrocarbon in the case of higher NMHC (Carlier *et al.*, 1986; Atkinson *et al.*, 1995; Atkinson, 1990a, b; Neeb *et al.*, 1997). However, an estimation of the exact yield is difficult because of the numerous reaction pathways available.

Primary direct biogenic sources such as insects (Morgan and Tyler, 1977) and animal faeces (Bethea and Narayan, 1972) also exist. Ants, for example, release higher carbonyls produced for signal transfer (Hölldobler and Wilson, 1990). According to the older literature, vegetation plays only a minor role in direct emis-

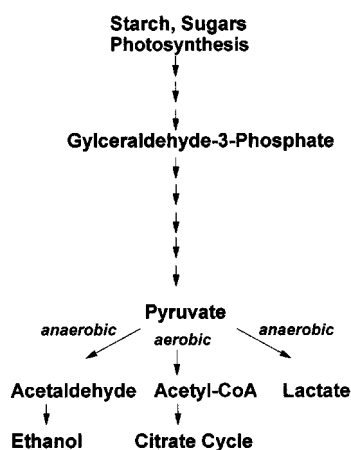


Figure 4. Simplified scheme of the biosynthesis of the volatile organic compounds acetaldehyde and ethanol.

sions (Nicholas, 1973). However, there is growing evidence that plants directly emit a large spectrum of aldehydes. Using plant enclosure techniques, Arey *et al.* (1991a) identified aldehydes higher than C₆. These findings are not surprising. Plants produce a high number of aldehydes; especially long-chain compounds (C₂₄–C₃₂) are present in the cuticular layer of leaves and fruits. Their contribution to the surface lipids depends on the plant species and reaches, for example, 5% in the case of peas (*Pisum sativum*; Schauenstein *et al.*, 1977). With regard to the low molecular compounds, C₆-aldehydes such as hexanal, cis-3-hexenal, and trans-2-hexenal ('leaf aldehyde') are often found, representing the main components derived from lipoxygenase-induced oxidative lipid decomposition that contribute to the characteristic fragrance of fresh leaves (Hatanaka and Harada, 1973; Hatanaka *et al.*, 1987; Hatanaka, 1996). Stotzky and Schenk (1976) reported the release of formaldehyde and acetaldehyde from young seedlings during the first days of germination. A stress-induced release of acetaldehyde from trees is also known (Kimmerer and Kozlowski, 1982; Kimmerer and MacDonald, 1987). Pathways contributing potentially to the release of formaldehyde and acetaldehyde are summarized in Figures 3 and 4.

Measurements by Nondek *et al.* (1992) indicate the emission of formaldehyde and acetaldehyde from forest vegetation, but they do not exclude artifacts due to adsorption and desorption processes within the enclosure. Martin *et al.* (1991) reported diurnal fluctuations of formaldehyde concentrations above a deciduous forest with maximum values in the range of 10 ppb around noon and assumed the photochemical decay of isoprene to be responsible for the high values. Recent work by Schäfer *et al.* (1995) and Kesselmeier *et al.* (1997a) shows evidence of a significant direct emission of formaldehyde as well as acetaldehyde from two Mediterranean tree species, *Quercus ilex* (Holm oak) and *Pinus pinea* (Italian stone pine). For agricultural crops only, a small number of data exists. Arey *et al.* (1991a)

Table VI. Atmospheric concentrations of C1- and C2-Aldehydes [ppb]

<i>Formaldehyde</i>		
Marine air	0.2–0.4	Lowe and Schmidt (1983)
	0.3–1.9	Zhou and Mopper (1993)
Arctic air	0.1–0.7	Deserves (1994)
Rural areas (E-Canada)	1.6–1.8	Shepson <i>et al.</i> (1991)
South west, U.S.A.	1,4	Dawson and Farmer (1988)
Tropical Savanna (Venezuela)	<2	Trapp and Deserves (1995)
		Sanhueza <i>et al.</i> (1996b)
Above deciduous forest (Pennsylvania)	4.4	Martin <i>et al.</i> (1991)
Mixed forest, crown region		
Italian coast, near Rome	0–7,5	Schäfer <i>et al.</i> (1995)
Black Forest, Germany	<4.5	Schubert <i>et al.</i> (1988)
Tanbark Flat	5.3	Grosjean (1991)
Large cities	10–100	Kern <i>et al.</i> (1996)
		Cleveland <i>et al.</i> (1977)
		Tuazon <i>et al.</i> (1978)
		Grosjean (1982, 1991)
<i>Acetaldehyde</i>		
Marine air	0.2–1.4	Zhou and Mopper (1990, 1993)
Rural areas (E-Canada)	0.5–0.6	Shepson <i>et al.</i> (1991)
	0–2.5	Schubert <i>et al.</i> (1988)
Tropical savanna	<0.7	Trapp (1995)
		Sanhueza <i>et al.</i> (1996b)
Mediterranean forest	0–7.0	Trapp (1995)
Mixed forest, crown region		
Italian coast, near Rome	0,2–6,0	Schäfer <i>et al.</i> (1995)
Black Forest, Germany	0.1–1.8	Slemr <i>et al.</i> (1996)

found the emission of n-hexanal and (E)-2-hexenal from cotton and alfalfa. Jork (1996) demonstrated a bidirectional exchange of formaldehyde and acetaldehyde for several crop species. Table VI gives an overview of atmospheric concentrations of the most frequently measured species, formaldehyde and acetaldehyde.

Biogenic sinks exist in addition to biogenic sources. Wolverton (1984) discussed plants as a general sink for formaldehyde. Recent work by Giese *et al.* (1994) shows the uptake and consumption of ¹⁴C-labeled formaldehyde by the spider plant (*Chlorophytum comosum* L.). However, this result was obtained by fumigation with extremely high gas-phase concentrations of 7 ppm, excluding a direct comparison with natural environmental conditions; nevertheless, they demon-

strated the existing capacity for an enzymatic consumption of formaldehyde. Similarly, Kondo *et al.* (1995) fumigated oleander plants (*Nerium indicum*) with unnaturally high gas-phase concentrations of 35 and 245 ppb formaldehyde and found an increase in deposition with increasing atmospheric concentrations. Furthermore, the uptake increased with light intensity. Bode *et al.* (1996) and Kesselmeier *et al.* (1997a) discussed fluctuations of exchange rates of formaldehyde and acetaldehyde as found under ambient conditions in view of variable atmospheric concentrations and concluded that a bidirectional exchange, emission as well as deposition, depends on the actual ambient concentrations of these compounds. This points out that, parallel to CO₂ for some compounds which are produced as well as taken up, a compensation point exists where the actual production balances the actual consumption and thus the exchange is zero (Kesselmeier *et al.*, 1993).

3.4. ALCOHOLS, ESTERS AND ETHERS

A high number of alcohol and ester species, initially assigned to be essential parts of flower odor, are emitted by vegetation. Graedel (1979) pointed out that these compounds are probably of minor importance when compared to the terpenoids, but the emission rates are unknown. Both Schulting *et al.* (1980) and Knoepfel *et al.* (1980) reported the emission of the so-called leaf alcohol and leaf ester, (Z)-3-hexene-1-ol and (Z)-3-hexenylacetate, respectively, and some other alcohols from plants. Other publications confirmed that leaf alcohol represents a major part of the emission spectra of several plant species (Ohta, 1984; Isodorow *et al.*, 1985). According to Arey *et al.* (1991a) and Winer *et al.* (1992), the leaf alcohol and ester represent significant parts of VOC emissions, ranging from a few percent (grape, oranges, pistachio, cotton, walnut) up to 50–100% (alfalfa, almond, apricot, nectarine, peach, plum).

Other esters and ethers have also been reported to be of biogenic nature (Graedel, 1979; Isodorow *et al.*, 1985; Buttery *et al.*, 1982, 1985; Arey *et al.*, 1991a; MacDonald and Fall, 1993; Goldan *et al.*, 1993; Nemeček-Marshall *et al.*, 1995; Tanner and Zylinska, 1994; König *et al.*, 1995; Puxbaum, 1997). In these studies, the following alcohol species were identified to be biogenically emitted in addition to the partially oxygenated monoterpenes geraniol, linalool, isopulegol, borneol, menthol, and p-cymene-8-ol: methanol, ethanol, 2-methyl-1-propanol, 1-butanol, 2-butanol, 2-methyl-2-butanol, 2-methyl-3-butene-2-ol, 3-methyl-1-butanol, 3-methyl-2-butene-1-ol, 3-methyl-3-buten-1-ol, 1-pentanol, 3-pentanol, 1-pentene-3-ol, 2-pentene-1-ol, 1-hexanol, (Z)-3-hexene-1-ol, 1-octanol, and 1-octene-3-ol. Esters identified in these studies were ethylacetate, butylacetate, methylbutyrate, methacrylonate, hexylacetate, (Z)-3-hexenylacetate, ethylhexylacetate, methylsalicylate, and bornylacetate; ether species included diethylether, p-dimethoxy-benzol, 1,8-cineol, estragol, p-methylanisol, furane, 2-methyl-furane, 3-methyl-furane, ethyl, and vinyl-furane. The emission rates of most of these compounds are low compared to the release of terpenoids (see also Table VII). How-

ever, significant influences of the plant developmental stage on emission behavior have been reported, for example, for linalool emissions by orange (Arey *et al.*, 1991b; Seufert, 1997; Torres, 1997) and pine trees (Staudt, 1997; Staudt *et al.*, 1997). Methanol is reported to be emitted from several plants in amounts between 0.3 and 17 $\mu\text{g (C) g}^{-1} \text{LDW h}^{-1}$ (MacDonald and Fall, 1993), similar to the emission rates of isoprene and monoterpenes. Pectine demethylation during cell wall growth and expansion has also been discussed as a dominant source (Figure 3; Fall and Benson, 1996; Fall, 1998).

3.5. MAGNITUDES OF EMISSION FOR NMHCS OTHER THAN ISOPRENE AND MONOTERPENES

In contrast to isoprene and monoterpenes, the emission of other biogenic NMHC has been poorly investigated. We know that alkanes, alkenes, and several oxygenated compounds are emitted from vegetation, but the data set is insufficient to support a reliable budget estimation. One of the explanations may be the problem of sampling and analysis techniques. Each group of chemical species within the VOC group needs special techniques, thus limiting the number of investigations so far. Table VII gives an overview of our recent knowledge based on only a few publications. The emission rates given within this table show that most of the compounds are emitted only in low amounts compared to isoprene and monoterpenes. The emission rates for some compounds are comparable to those of the better investigated isoprenoids. However, emissions of some compounds can be heavily influenced by stress effects (Fukui and Doskey, 1998). Recent findings on, for example, methanol emissions (McDonald and Fall, 1993) or emission of 2-methyl-3-buten-2-ol (Harley *et al.*, 1998) from plants and the plant species dependencies as reflected in the fundamental differences between forests and grassland (Kirstine *et al.*, 1998; Fukui and Doskey, 1998) encourage the investigation of new sampling and analysis techniques for the identification of compounds other than isoprene and monoterpenes.

4. Influences of Environmental Factors on VOC Emission from Vegetation

As outlined in the preceding sections, a great variability exists in the emission pattern of the diverse plant species and vegetation types. Besides the genetically predetermined biodiversity in vegetation emissions, the release of VOCs by a given plant species exhibits important temporal and spatial variations. Both have to be considered when estimating natural VOC emissions on large geographical scales (see Section 6). The variability of emissions from a plant is a result of complex interactions between the organism and its environment that are only partly understood (Monson *et al.*, 1995; Sharkey, 1996b). In particular, the release of compounds other than isoprenoids has been poorly investigated; and gaps in knowledge

Table VII. Emission of non-terpenoid hydrocarbons from vegetation. All data in [$\mu\text{g g (LDW)}^{-1} \text{h}^{-1}$] if not specified. Reports about VOC emissions other than terpenoids are limited. Experimental conditions are heterogeneous and should be checked in the primary literature. This table gives an overview about observed emission ranges

Compound	Plant species	Emission rates	Remarks
Alkanes			
Ethane	grass	0.003	Kirstine <i>et al.</i> (1998); Data as $\mu\text{g C}$
Ethane	clover	0.002	ibid.
n-Pentane	grass	0.003	ibid.
n-Pentane	clover	0.002	ibid.
Hexane	<i>Chrysanthemum praecox</i>	0.1–0.5	Owen <i>et al.</i> (1997)
	<i>Erica multiflora</i>	<0.1	ibid.
Alkenes			
Ethene	<i>Salix phylicifolia</i>	0–1.2	Hakola <i>et al.</i> (1998)
	<i>Betula pendula</i>	0–0.1	ibid.
	<i>Populus tremula</i>	0–0.1	ibid.
Ethene	grass	0.003	Kirstine <i>et al.</i> (1998); Data as $\mu\text{g C}$
	clover	0.002	ibid.
Propene	<i>Salix phylicifolia</i>	0–0.9	Hakola <i>et al.</i> (1998)
	<i>Betula pendula</i>	0–0.05	ibid.
	<i>Populus tremula</i>	0–0.06	ibid.
1-Butene	<i>Salix phylicifolia</i>	0–2.3	Hakola <i>et al.</i> (1998)
	<i>Betula pendula</i>	0–0.1	ibid.
	<i>Populus tremula</i>	0–0.1	ibid.
Alcohols			
Methanol	several tree species	2–18	McDonald and Fall (1993b)
	agricultural crops	2–50	ibid.
Methanol	grass	0.05	Kirstine <i>et al.</i> (1998); Data as $\mu\text{g C}$
Methanol	clover	0.63	ibid.
Ethanol	grass	0.08	ibid.
Ethanol	clover	0.01	ibid.
Propanol	clover	<0.01	ibid.
Propanol	grass	0.01	ibid.
2-Methyl-3-buten-2-ol	several pine species	2–50	Harley <i>et al.</i> (1998)
Z-3-Hexen-1-ol	agricultural crops	0.03– 1.3	Arey <i>et al.</i> (1991a)
	<i>Quercus lobata</i>	0.3	ibid.
	whitethorn	0.5	ibid.
	<i>Fagus sylvatica</i>	0–0.0009	Tollsten and Müller (1996)
Alcohols >C4	agricultural crops	0–0.17	König <i>et al.</i> (1995)
	several tree species	0–0.08	ibid.

Table VII. (Continued)

Compound	Plant species	Emission rates	Remarks
Mixtures			
Sum of Z-3-Hexen-1-ol and Z-3-Hexenyl-acetate	agricultural crops <i>Quercus lobata</i> whitethorn	0.1–4.2 <0.5 3.8	Winer <i>et al.</i> (1992) ibid. ibid.
Carbonyls			
Formaldehyde	<i>Pinus pinea</i> <i>Quercus ilex</i>	0.1–0.9 0.3–0.8	Kesselmeier <i>et al.</i> (1997a) ibid.
Acetaldehyde	<i>Pinus pinea</i> <i>Quercus ilex</i>	0.4–1.5 0.4–0.9	ibid. ibid.
Acetaldehyde	grass	0.06	Kirstine <i>et al.</i> (1998); Data as $\mu\text{g C}$
Acetaldehyde	clover	0.01	ibid.
2-Methyl-2-propenal	grass	0.005	ibid.
2-Methyl-2-propenal	clover	0.002	ibid.
3-Methyl butanal	grass	0.004	ibid.
3-Methyl butanal	clover	0.002	ibid.
Hexanal	<i>Erica multiflora</i>	<0.1	Owen <i>et al.</i> (1997)
Hexanal	grass	0.02	Kirstine <i>et al.</i> (1998); Data as $\mu\text{g C}$
Hexanal	clover	0.002	ibid.
Heptaldehyde	<i>Juniperus oxicedrus</i> <i>Phillyrea angustifolia</i>	<0.1 <0.1	Owen <i>et al.</i> (1997) ibid.
Pentanal	grass	0.004	Kirstine <i>et al.</i> (1998); Data as $\mu\text{g C}$
Pentanal	clover	0.002	ibid.
Nonanal	clover	0.002	ibid.
Nonanal	grass	0.003	ibid.
Nonanal	<i>Arbutus unedo</i> <i>Chrysanthemum praecox</i> <i>Cistus incanus</i> <i>Erica multiflora</i> <i>Helichrysum stoechas</i> <i>Juniperus oxicedrus</i> <i>Juniperus phoenicea</i> <i>Phillyrea angustifolia</i> <i>Quercus ilex</i> <i>Spartium junceum</i>	0.1–0.5 0.1–0.5 0.1–0.5 <0.1 0.5–20 <0.1 <0.1 0.1–0.5 0.1–0.5 0.1–0.5	Owen <i>et al.</i> (1997) ibid. ibid. ibid. ibid. ibid. ibid. ibid. ibid. ibid.
Decanal	<i>Arbutus unedo</i> <i>Chrysanthemum praecox</i> <i>Cistus incanus</i> <i>Erica multiflora</i> <i>Helichrysum stoechas</i>	0.1–0.5 0.1–0.5 0.1–0.5 <0.1 0.5–20	Owen <i>et al.</i> (1997) ibid. ibid. ibid. ibid.

Table VII. (Continued)

Compound	Plant species	Emission rates	Remarks
	<i>Juniperus oxicedrus</i>	<0.1	ibid.
	<i>Juniperus phoenicea</i>	0.1–0.5	ibid.
	<i>Phillyrea angustifolia</i>	0.1–0.5	ibid.
	<i>Quercus ilex</i>	0.5–20	ibid.
	<i>Spartium junceum</i>	0.1–0.5	ibid.
Benzaldehyde	grass	0.01	Kirstine <i>et al.</i> (1998); Data as $\mu\text{g C}$
Benzaldehyde	clover	0.002	ibid.
Aldehydes >C4	agricultural crops	0–0.03	König <i>et al.</i> (1995)
	several tree species	0–0.03	ibid.
Acetone	<i>Abies concolor</i>	7.4	[$\mu\text{g} / (\text{g FW h})$], buds; McDonald and Fall (1993a)
	<i>Abies concolor</i>	1.0	young needles; McDonald and Fall (1993a)
Acetone	grass	0.06	Kirstine <i>et al.</i> (1998); Data as $\mu\text{g C}$
Acetone	clover	0.25	ibid.
Butanone	grass	0.01	ibid.
Butanone	clover	0.86	ibid.
2,3-Butanedione	clover	<0.01	ibid.
2,3-Butanedione	grass	0.01	ibid.
2-Pentanone	grass	0.002	ibid.
2-Pentanone	clover	0.002	ibid.
4-Methyl-2-pentanone	clover	0.002	ibid.
4-Methyl-2-pentanone	grass	0.003	ibid.
2-Heptanone	<i>Spartium junceum</i>	<0.1	Owen <i>et al.</i> (1997)
1-Phenyl-ethanone	<i>Erica multiflora</i>	<0.1	ibid.
	<i>Juniperus oxicedrus</i>	<0.1	ibid.
	<i>Phillyrea angustifolia</i>	<0.1	ibid.
Ketones >C4	agricultural crops	0–0.05	König <i>et al.</i> (1995)
	birch	0.07	ibid.
Organic acids			
Formic acid	<i>Pinus pinea</i>	0.2–0.5	Kesselmeier <i>et al.</i> (1997a)
	<i>Quercus ilex</i>	0.1–0.5	ibid.
	<i>Quercus ilex</i>	0.02–0.05	Kesselmeier <i>et al.</i> (1998a)
	<i>Fraxinus excelsior</i>	0.05–0.1	ibid.
	<i>Fagus sylvatica</i>	0.02–0.05	ibid.
	<i>Picea abies</i>	0.03–0.04	ibid.
	<i>Betula pendula</i>	0.16–0.25	ibid.
	<i>Pinus pinea</i>	0–0.12	Staudt <i>et al.</i> (1999)
	<i>Quercus ilex</i>	0.11–0.15	ibid.

Table VII. (Continued)

Compound	Plant species	Emission rates	Remarks
Acetic acid	<i>Citrus sinensis</i>	0.12–0.18	ibid.
	<i>Aeonium glutinosum</i>	0.15–0.20	ibid.
	<i>Pinus pinea</i>	0.1–0.3	Kesselmeier <i>et al.</i> (1997a)
	<i>Quercus ilex</i>	0–0.4	ibid.
	<i>Quercus ilex</i>	0.02–0.06	Kesselmeier <i>et al.</i> (1998a)
	<i>Fraxinus excelsior</i>	0.01–0.06	ibid.
	<i>Fagus sylvatica</i>	0.02–0.04	ibid.
	<i>Picea abies</i>	0.01–0.03	ibid.
	<i>Betula pendula</i>	0.02–0.12	ibid.
	<i>Pinus pinea</i>	0–0.03	Staudt <i>et al.</i> (1999)
	<i>Quercus ilex</i>	0.03–0.06	ibid.
	<i>Citrus sinensis</i>	0.06–0.08	ibid.
	<i>Aeonium glutinosum</i>	0.07–0.12	ibid.
Esters			
Z-3-Hexenyl-acetate	agricultural crops	0.06–3.4	Arey <i>et al.</i> (1991a)
	<i>Quercus lobata</i>	0.2	ibid.
	whitethorn	3.3	ibid.
	<i>Erica multiflora</i>	0.1	Owen <i>et al.</i> (1997)
	<i>Phillyrea angustifolia</i>	<0.1	ibid.
	<i>Fagus sylvatica</i>	0–0.003	Tollsten and Müller (1996)
Esters >C4	agricultural crops	0–0.11	König <i>et al.</i> (1995)
	several tree species	0–0.14	ibid.

exist for factors controlling emission, for example, developmental stage, stress such as injuries and air pollution, and even the 'simple' factors light and temperature.

Water vapor and CO₂ exchange in leaves is controlled by the stomata located in the leaf epidermis, usually present only on the lower leaf side. Since the stomatal aperture depends on various internal and external factors (see, e.g., Mansfield, 1986), its influence on trace gas exchange is of basic interest. In the following paragraphs, we discuss first the possible role of stomata, then the short-term influences of light and temperature, and finally the effects of various other biotic or nonbiotic factors in the plant environment. The short-term effects of light and temperature are the best-described environmental influences on VOC release by vegetation, while only marginal information exists for many other potential factors. Short term means that the emission response occurs within some minutes up to one hour and should

be distinguished from long-term effects, which occur over several hours, days, or months.

4.1. RELATION BETWEEN VOC EMISSION AND STOMATAL REGULATION

A trace gas produced within leaves has to enter the atmosphere by passing the stomata if it cannot diffuse through the hydrophobic cuticle. We can discern two groups of trace gases: one stored after synthesis in special cells or organs and hence released from storage pools, and the other for which synthesis and emissions are directly interrelated. Both may underlie stomatal control in case of storage organs or synthesis within the interior of the leaves. In the case of cuticular diffusion or glands and hairs on the outside, stomatal control has no effect.

Measurements of isoprene emissions from *Quercus virginiana* (Tingey *et al.*, 1981), *Populus tremuloides* (Monson and Fall, 1989), *Eucalyptus globulus* (Guenther *et al.*, 1991), *Populus tremuloides*, *Quercus alba*, *Populus fremonii* (Fall and Monson, 1992), and *Pueraria lobata* (Sharkey and Loreto, 1993) as well as monoterpene emissions from *Pinus elliotii* (Tingey *et al.*, 1980), *Eucalyptus globulus* (Guenther *et al.*, 1991), *Quercus ilex* (Loreto *et al.*, 1996a), *Picea abies* (Steinbrecher, 1989; Staudt, 1997), and *Pinus pinea* (Staudt, 1997) showed no significant influence of stomatal conductance on emission rates. However, investigations on the localization of isoprene release from single leaves, discerning the ab- from the adaxial surface by the use of microcuvettes (*Quercus virginiana*, *Platanus occidentalis*, Tingey *et al.*, 1981; *Quercus rubra*, Loreto and Sharkey, 1990; *Eucalyptus globulus*, Guenther *et al.*, 1991; *Populus tremuloides*, *Quercus alba*, *Populus fremonii*, Fall and Monson, 1992), clearly showed that a significant isoprene emission rate was only detectable on that leaf side containing the stomatal pores. For monoterpene emission, similar experiments were reported for two plant species only. Loreto *et al.* (1996a) found a monoterpene emission only from the abaxial side of *Quercus ilex* leaves, and Guenther *et al.* (1991) reported emissions from the adaxial side of *Eucalyptus* leaves. The apparent nondependence of stomatal closure and isoprenoid emissions has been explained by the low, unsaturated VOC concentrations in the intercellular air spaces of the leaf mesophyll, which increase when stomata close. The decrease in stomatal conductance would, hence, be compensated by an increase in the concentration gradient between in- and outside the leaf (Monson *et al.*, 1991; Sharkey, 1991; Fall and Monson, 1992; Bertin and Staudt, 1996; Sharkey *et al.*, 1996; Staudt, 1997). Another possibility is that an increase in intercellular concentrations owing to stomatal closure leads to a maximized diffusion through the cuticular membrane. Monoterpenes are potentially able to permeate through cuticles, as shown by Schmid *et al.* (1992), Schmid and Ziegler (1991), and Estell *et al.* (1994), as can other gases such as CO₂, SO₂, and O₂ having a 2–3 fold higher permeability than water (Schönherr, 1982; Lenzian, 1987). Moreover, evidence exists that monoterpene emissions from leaves are strongly influenced by cuticula hydration (Croteau, 1977; Lamb *et al.*, 1985; Staudt, 1997). However, the

results obtained with isoprenoids should not be transferred to all trace gas species. Different mechanisms affecting accumulation, concentration gradients, and release of other trace gases have been reviewed by Sharkey (1991). Fall and Benson (1996) found a correlation between methanol emission rates and stomatal conductance. For carbonyl sulfide, dimethylsulfide, and ozone, stomatal conductance may also be of significance (Sharkey, 1991; Kesselmeier *et al.*, 1997b).

4.2. SHORT-TERM INFLUENCES OF TEMPERATURE AND RADIATION ON VOC EMISSION

This section deals with the short-term influence of temperature and radiation on VOC emissions, discussing the knowledge of the emission behavior of monoterpenes and isoprene as the best investigated species. Nevertheless, it has to be mentioned that further VOC species, for example, some oxygenated compounds, follow a similar emission regime and show a clearly light-triggered emission (Kesselmeier *et al.*, 1997a; Staudt *et al.*, 1998b).

All studies on the emission of isoprene and monoterpenes show a clear temperature dependence. Additionally, isoprene emissions have been shown to be triggered by light, as a result of the link between isoprene emission and synthesis from photosynthetic products. As no large isoprene pool exists, synthesis and hence emission will cease within minutes under dark conditions (Tingey *et al.*, 1981; Evans *et al.*, 1985; Guenther *et al.*, 1991; Sanadze, 1991; Sharkey *et al.*, 1991; Monson *et al.*, 1991). However, according to a recent field study, isoprene emission of CAM plants (plants belonging to a group fixing CO₂ via the Crassulacean acid metabolism in the dark) may be light-independent at least in short-term conditions (Lerdau and Keller, 1997). Generally, the emission response to radiation shows a saturation behavior similar to the light saturation of CO₂ assimilation. In contrast, temperature dependence of isoprene emission points to the necessary enzymatic production of isoprene, showing a temperature maximum and a subsequent decrease at higher temperatures owing to enzyme inactivation (Guenther *et al.*, 1991, 1993; Monson *et al.*, 1992). For a mathematical description of the temperature and light dependence of the isoprene emissions, empirically designed algorithms are used. One of the commonest algorithms is the formula

$$E = E_S \times C_T \times C_L \quad (1)$$

proposed by Guenther *et al.* (1991, 1993), where E is the actual emission and E_S is the standard emission factor (for example at a standard temperature T_s of 30 °C and a standard PAR of 1000 $\mu\text{mol m}^{-2} \text{s}^{-1}$). C_T and C_L are functions of temperature and light given by

$$C_L = \frac{\alpha C_{LI} \text{PAR}}{\sqrt{1 + \alpha^2 \text{PAR}}}$$

$$C_T = \frac{\exp \frac{C_{T1}(T - T_S)}{RT_S T}}{1 + \exp \frac{C_{T2}(T - T_M)}{RT_S T}}$$

where R ($8.134 \text{ J K}^{-1} \text{ mol}^{-1}$) is the gas constant. C_{T1} (95000 J mol^{-1}), C_{T2} ($230000 \text{ J mol}^{-1}$), T_m (314 K or $41 \text{ }^\circ\text{C}$), α (0.0027), and C_{L1} (1.066) are empirically defined parameters, derived from measurements on four isoprene-emitting temperate plant species. Hence, C_T and C_L are scaling factors allowing $T_T \times C_L = 1$ at standard conditions. The shape of each response curve depends on values of parameters that determine slopes, inflections, saturation, and optimum levels of the functions. The above parameter values suggested by Guenther and co-workers have been confirmed in several other studies (e.g. Guenther *et al.*, 1996a; Fulten *et al.*, 1998). However, there is also evidence that temperature and light responses and hence parameter values differ among plant species and can even vary among shade- and sun-adapted leaves within the canopy of an individual tree (Tingey *et al.*, 1987; Monson *et al.*, 1992; Lerdau and Keller, 1997; Harley *et al.*, 1996b, 1997; Sharkey *et al.*, 1996). Furthermore, recent investigations by Singsaas and Sharkey (1997) emphasize that the temperature response of isoprene emission depends on the rate of temperature increase applied in the experiments.

Monoterpene emissions are generally regarded as light-independent, because they are compounds stored after synthesis in special organs, such as resin ducts or glands (Monson *et al.*, 1995; Lerdau *et al.*, 1997), exhibiting quite large storage pools compared to the emission rates (Schindler and Kotzias, 1989; Jüttner, 1991; Lerdau *et al.*, 1994). Hence, their emission, which is temperature-dependent and related to the vapor pressure and to the transport resistance along the diffusion path, is regarded to be a volatilization out of storage organs (Dement *et al.*, 1975; Tingey *et al.*, 1980, 1991; Evans *et al.*, 1985; Guenther *et al.*, 1991; Simon *et al.*, 1994). The emission response to temperature shows an exponential increase with temperature and is usually described using the formula by Tingey *et al.* (1980)

$$E = E_S * \exp(\beta * (T - T_S)), \quad (2)$$

where E is the emission at temperature T , β is the slope $\text{dln}E \text{ d}T^{-1}$, and E_S is the emission at a standard temperature. Slopes found in the literature range between 0.057 and $0.144 \text{ }^\circ\text{C}^{-1}$. As a generally accepted mean value, $0.09 \text{ }^\circ\text{C}^{-1}$ is used (Fehsenfeld *et al.*, 1992; Guenther *et al.*, 1993).

The postulated light independence of monoterpene emissions must, however, be questioned. Yokouchi and Ambe (1984) showed that *Pinus densiflora* changes its monoterpene emission rate under constant temperature in close relation to radiation. Jüttner and Bufler (1988) were able to show a fast ^{13}C -labeling of the monoterpenes emitted from spruce twigs (*Picea abies*) during growing and maturing of young shoots. Steinbrecher (1989) showed that the α -pinene emission from spruces is triggered positively by light. The conclusion that a part of the

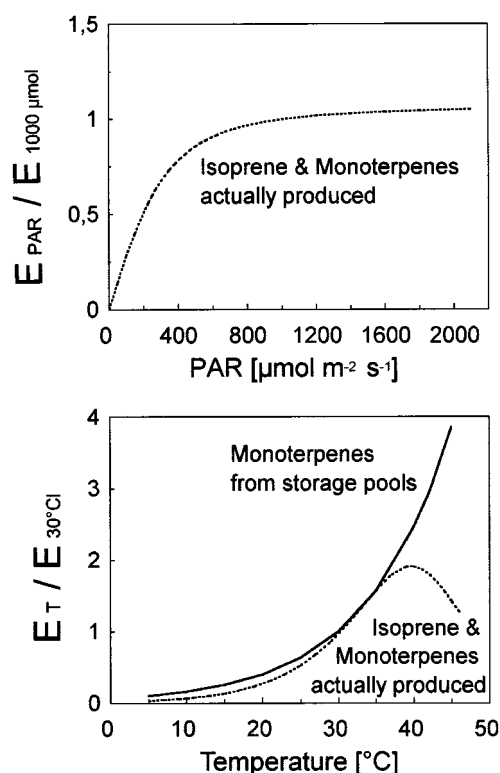


Figure 5. Generalized relative emission of isoprene and monoterpenes in relation to light (PAR) under constant temperature, and temperature under constant light as described by potential algorithms (see Equations (1) and (4) in the text). The light and temperature including algorithm (1) was used for calculation in case of actually produced compounds, the algorithm including temperature only (4) for monoterpene release from storage pools. Note the principal drop of production due to enzyme inhibition under high temperatures in the case of actually produced compounds.

emission is derived from an actual terpene synthesis was confirmed by labeling with $^{13}\text{CO}_2$ (Schürmann *et al.*, 1993). Similar effects have been reported for Italian stone pine (*Pinus pinea*) (Staudt, 1997; Staudt *et al.*, 1997; Kesselmeier *et al.*, 1997a) as well as for sunflower and beech (Schuh *et al.*, 1997), indicating that monoterpene emissions from many plants are indeed a blend of stored and recently synthesized compounds. For a better prediction, Schuh *et al.* (1997) suggested a model that combines the algorithm for light-independent monoterpene emissions from storage pools (Tingey *et al.*, 1991) with that for light-dependent isoprene emission (Guenther *et al.*, 1993). A generalized emission behavior in relation to light and temperature is given in Figure 5.

An exceptional emission behavior was found for the Holm oak (*Quercus ilex*). Diverse laboratory studies revealed that the leaves of this evergreen Mediterranean oak species release large amounts of monoterpenes but do not possess storage

pools (Staudt *et al.*, 1993; Seufert *et al.*, 1995; Loreto *et al.*, 1996a), that emissions respond to light similarly as for isoprene (Staudt and Seufert, 1995; Loreto *et al.*, 1996a; Staudt and Bertin, 1998), and that all monoterpenes are synthesized from carbon recently fixed by photosynthesis immediately prior to emission (Loreto *et al.*, 1996b, c). Data obtained during field investigations confirmed and extended these results to the emissions from mature trees in their natural habitats (Kesselmeier *et al.*, 1996, 1997a, 1998b; Bertin *et al.*, 1997; Street *et al.*, 1997b). Figure 6 gives an example showing the monoterpene emission from *Q. ilex* more closely related to the actual photosynthetic activity than to temperature, hence, underlining the laboratory results. All field data demonstrated moreover that the global model developed by Guenther *et al.* (1993) to predict isoprene emission also simulates monoterpene emission from the Holm oak (Kesselmeier *et al.*, 1997a; Bertin *et al.*, 1997), though some important deviations were recently reported by Ciccioli *et al.* (1997a) and Staudt and Bertin (1998). Ciccioli *et al.* (1997a) showed that sudden bursts of monoterpene release under naturally fast light fluctuations deviate from the algorithm-like pattern but do not contradict the overall behavior, as it can be sufficiently explained by the light-driven sudden leaf temperature increase leading to an instantaneous heating up of small monoterpene reservoirs, presumably within the apoplast. Staudt and Bertin (1998) revealed that terpene release from leaves of this thermophyllous oak species does not drop under high-temperature conditions, as predicted by the isoprene model, but further increases at least up to a temperature of 45 °C. Moreover, emission composition changes in response to high-temperature exposure with more stable monoterpene species being replaced by more reactive ones. Significant changes in emission composition are also observed during leaf development (Staudt and Bertin, 1998).

The above studies of *Q. ilex* demonstrated for the first time that the production and release of high amounts of monoterpenes by plants are not necessarily restricted to species storing essential oils in glandular organs and, moreover, that oak forests can also constitute an important source of not only isoprene but also monoterpenes. Today, there is growing evidence that other Mediterranean oak species exhibit a similar emission pattern as Holm oak (Hansen and Seufert, 1996; Csiky and Seufert, 1999; Loreto *et al.*, 1998b; see also Table II).

4.3. OTHER FACTORS INFLUENCING VOC EMISSIONS BY PLANTS

The short-term influences of factors other than temperature and light have been less extensively investigated, although some information is available about the effects of air composition, foliar moisture (leaf wetting), and mechanical stress and injury.

Relative air humidity seems to be of minor importance in controlling isoprene or monoterpene release by leaves. Yokouchi and Ambe (1984), Juuti *et al.* (1990), Janson (1993), and Guenther *et al.* (1991) conclude from their studies on pine, spruce, and eucalyptus foliage that relative humidity does not affect monoterpene emissions. Other studies, however, suggest that humidity does exert a slight posi-

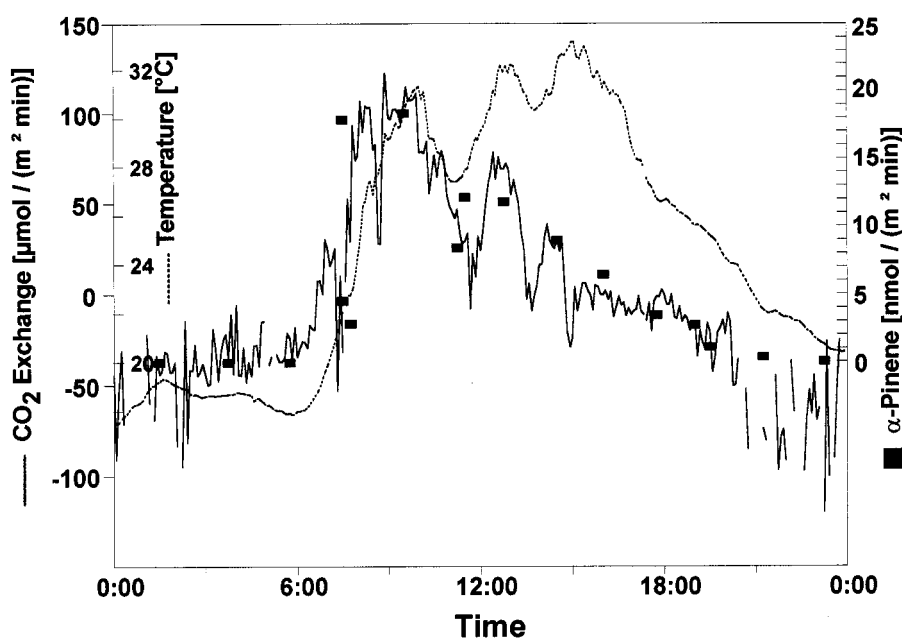


Figure 6. Emission of α -Pinene from an enclosed branch of *Quercus ilex*, related more closely to the actual photosynthetic activity than simply to temperature. This light dependent behavior points to the necessary actual production of emitted monoterpenes in the case of this oak species. Data were taken from field observations after Kesselmeier *et al.* (1996).

tive influence on emission, for example monoterpene emissions from sage, mint, and oak (Dement *et al.*, 1975; Croteau, 1977; Loreto *et al.*, 1996a) and isoprene emissions from eucalyptus and aspen (Guenther *et al.*, 1991; Monson and Fall, 1989). Significant increased monoterpene emissions were observed upon foliage wetting of diverse conifers and aromatic shrubs (Croteau, 1977; Lamb *et al.*, 1985; Janson, 1993; Street *et al.*, 1997; Staudt, 1997). This effect might be related to the hydration of the leaf cuticula (see above 4.1), although the exact mechanisms by which the apparent emission increase is triggered are not known.

The short-term response of isoprene and monoterpene emissions to changing CO_2 and O_2 concentrations was examined in several analytical gas-exchange studies (Monson and Fall, 1989; Loreto and Sharkey, 1990; Hewitt *et al.*, 1990; Loreto *et al.*, 1996a). These laboratory studies aimed to clarify the physiological linkage of VOC production to the primary carbon metabolism of leaves rather than to examine the potential impact of natural CO_2 and O_2 fluctuations in air on emissions.

Mechanical stress and injury as well as herbivore and pathogen attacks can have multiple short- and long-term impacts on VOC emissions by plants. Compounds commonly found in the emissions of any damaged leaves are C_6 -aldehydes, alcohols, and their derivatives (McCall *et al.*, 1994; Sharkey, 1996a; see also 3.3 and 3.4). Several studies on monoterpene emitters report emission bursts occurring after slight mechanical stress like the mounting of twigs or leaves in plant enclosure

systems (Juuti *et al.*, 1990; Guenther *et al.*, 1991; Arey *et al.*, 1995; Yatagai *et al.*, 1995; Staudt, 1997). This phenomenon has only been observed for plants storing monoterpenes in secretory organs and presents a potential error source when studying emission by short-term enclosures. On the contrary, isoprene emission appears to be either unaffected or inhibited by plant damages (Monson *et al.*, 1994; Loreto and Sharkey, 1993a).

Any environmental factor in plant habitat may also affect VOC emission in the long term. Long-term influences alter the amount and composition of VOC emission slowly over days, months, and years and are superimposed on short-term influences. They are hence more difficult to detect and to study. Many VOCs like monoterpenes are involved in long-term plant defense reactions against herbivore and pathogen attack. Damaging the bark of a pine tree, for instance, may enhance monoterpene release in two independent processes on different time-scales (Gershenson and Croteau, 1991): first, by the instantaneous release of resin liberated at the plant surface, and second, by the induction of a monoterpene de-novo synthesis inside the surrounding tissues which proceeds over days to weeks. Logdepole pines infected with phytopathogen fungi, however, release not only monoterpenes but also high amounts of ethanol, both primary attractants for certain pine beetles (Gara *et al.*, 1993). Other examples are ethylene and methyl-jasmonate, compounds that induce defensive reactions in the plants where they are produced and may also act as signals to other plants (Lerdau *et al.*, 1997). Numerous other studies describing VOC release within host-parasite interactions were reviewed by Harborne (1987), Gershenson and Croteau (1991) and Langenheim (1994), and emphasize the defensive role of plant VOCs attributed to them. Nevertheless, since parasite infestations occur rather as localized and temporary events, their relative importance for VOC fluxes on regional or global scales are uncertain.

Nonbiotic environmental factors can undoubtedly exert long-term influences on monoterpene and isoprene emissions from leaves. These influences are often summarized as the effect of growth conditions on emission factors in order to distinguish them from the short-term influences of temperature and light on the actual emission rate. The influence of growth conditions has been indirectly indicated in several studies reporting on the effect of canopy position or season on the leaf emission factor.

There is increasing evidence that season has a great impact on isoprenoid emissions (Guenther, 1997). In some cases, the reported seasonal effects clearly result from plant growth and phenological events, such as budding, flowering, fruiting, leaf senescence, and dormancy, and are therefore only indirectly linked to growth conditions (see, e.g., Robertson *et al.*, 1995). Hakola *et al.* (1998) demonstrated that the typical isoprene emitters *Salix phylicifolia* (tea-leafed willow) and *Populus tremula* (European aspen) also release significant amounts of monoterpenes and other alkenes during bud break and early leaf development in spring and switch over to an intensive isoprene emission only when leaves become mature in summer. Significant seasonal changes in the leaf emission capacity of diverse deciduous and

evergreen trees have also been observed for fully developed mature leaves during the main growing season (Ohta, 1986; Monson *et al.*, 1994; Pier and McDuffie, 1997; Staudt *et al.*, 1997, 1998; Yatagai *et al.*, 1995; Yokouchi *et al.*, 1984; Lerdaud *et al.*, 1995; Street *et al.*, 1996). An interesting example is *Pinus pinea* (stone pine) (Staudt *et al.*, 1997; 1998a): during the course of the year, its monoterpene emission factor drastically changes by a factor of about 20. This change in the emission amount is accompanied by characteristic changes in the emission composition as well as in the short-term response of emission to light. To summarize, seasonal variability has been observed in many cases and hence should be considered for an accurate estimation of the annual VOC release from vegetation. Some empirical approaches to predict seasonality were recently reported by Schnitzler *et al.* (1997), Pier and McDuffie (1997), and Guenther (1997), but no global mechanistic model has been proposed.

It is generally accepted that the light and temperature regime experienced by leaves can influence or even predetermine their emission capacities. In forests, sun leaves exposed to higher radiation and leaf temperature were often found to have higher emission capacities for isoprene or monoterpenes than shade-adapted leaves located inside or at the bottom of the canopy (Bertin *et al.*, 1997; Geron *et al.*, 1997; Harley *et al.*, 1996, 1997; Sharkey *et al.*, 1991b, 1996; Street *et al.*, 1997b). In laboratory studies on isoprene-emitting plants, it was shown that growth under high-light regimes results in increased emission capacities (Harley *et al.*, 1994; Litvak *et al.*, 1996; Monson *et al.*, 1995; Sharkey *et al.*, 1991b; Sharkey and Loreto, 1993). Likewise, growth under high-temperature regimes yields higher isoprene emissions; some isoprene-emitting species maintained at cool temperatures even failed to emit any isoprene until exposed to high temperatures (Kuzma and Fall, 1993; Monson *et al.*, 1992, 1994, 1995; Sharkey and Loreto, 1993). No comparable laboratory studies exist for monoterpenes or other VOCs. In an earlier study, Dement *et al.* (1975) reported that cool night temperatures increase monoterpene emission from sage.

In many ecosystems like the Mediterranean one, plant growth is partly constrained by limited water and nutrient availability. Theoretically, such resource limitations may impede VOC synthesis as they limit growth and would hence reduce emissions. On the other hand, changes in the plant metabolism induced by stress may involve additional production or higher losses of volatiles, as it is generally acknowledged for ethylene formation (Abeles *et al.*, 1992).

In the emissions from drought-stressed apple leaves, Ebel *et al.* (1995) observed a significant increase in hexenal, 2-hexenal, hexanol, hexenol as well as hexylacetate and 2-hexenylacetate, all compounds that are typically related to fatty acid breakdown. Concerning isoprenoids, the impact of water stress on monoterpene emission was examined from Holm oak (Bertin and Staudt, 1996) and diverse conifers (Yani *et al.*, 1993; Staudt, 1997) and, further, on isoprene emission from live oak (Tingey *et al.*, 1981), kudzu vine (Sharkey and Loreto, 1993), and sweetgum (Fang *et al.*, 1996). Despite differences in the experimental setup, investigated

plants, and compounds, the results of these studies show similarities in the emission responses to drought. Under moderate stress conditions, when CO₂ and H₂O gas exchange declined, emissions remained rather unaffected. Under severe drought, emissions were reduced but could be largely increased after rewatering during stress recovery. All studies so far, however, have been made on young potted plants, and field investigations confirming such emission changes due to natural drought events are lacking.

The effect of nitrogen availability or leaf nitrogen concentration on isoprenoid emission is not well understood: a positive correlation between emission capacity and one of these parameters was found for most of the investigated plant material (Monson, 1994, 1995; Harley *et al.*, 1994; Litvak *et al.*, 1996; Lerdau *et al.*, 1995), although not always (Monson *et al.*, 1994; Lerdau *et al.*, 1995).

There is some controversy about the effect of air pollutants on VOC emission, depending on the pollutant and experimental conditions. Earlier studies exposing plants to higher SO₂ and ozone concentrations reported elevated ethylene and monoterpene emissions (Renwick and Potter, 1981; Bucher, 1981 and references therein). Likewise, the release of ethylene, ethane, acetaldehyde, and ethanol from diverse plant species was found to be enhanced under SO₂ exposure, anaerobic conditions, or general air pollution conditions (Kimmerer and Kozłowski, 1982, 1987; MacDonald *et al.*, 1990). On the other hand, monoterpene emissions from various conifers exposed to atmospheric ozone concentrations were not significantly influenced (Juuti *et al.*, 1990; Bufler and Wegmann, 1991; Lindskog and Potter, 1995). Finally, in a recent work, Heiden *et al.* (1999) reported the release of methyl salicylate by plants upon ozone fumigation.

There is a scarcity of emission studies which have examined the potential long-term influences of the elevated CO₂ and UV-B levels, predicted in global change scenarios of emissions. Existing information suggests that isoprene emissions are not sensitive to these events (Juuti *et al.*, 1990; Harley *et al.*, 1996a; Sharkey *et al.*, 1991b).

5. Ecophysiological Functions of VOC Productions and Emissions

Some ecophysiological functions of hydrocarbon emissions have been well described. Ripening fruits or injured tissues release ethene (ethylene, Abeles *et al.*, 1992). Harborne (1987) reviewed the large number of interrelations between plants and insects based on volatile hydrocarbons. For example, monoterpene species such as linalool are typical components of flowering fragrances attracting pollinators (Bergström, 1991; Knudsen and Tollsten, 1993). However, the dominant VOC emissions originate from green leaves, i.e., deciduous or evergreen broad leaves, or coniferous needles. Considering the ecological significance of the release from flowers and fruits, it is not easy to explain why green leaves emit these compounds. In the last few years, there has been growing evidence that microbial attack can initiate defense mechanisms by triggering the release of volatile com-

pounds. Signaling within the plants as well as between plants is receiving more and more attention. The most prominent signal compounds are jasmonic and salicylic acids, coumarins, some terpenes, and ethylene (Ennos and Swales, 1988; Kaus, 1991; Boland *et al.*, 1992; Raskin, 1992; Hopke *et al.*, 1994; Kaus *et al.*, 1994). Derivatives of jasmonic or salicylic acids are reported to act as internal signals (Malamy *et al.*, 1990; Gundlach *et al.*, 1992). According to a recent publication, the release of methyl salicylate by infected tobacco plants acts as an atmospheric signal to warn and activate other plants against the tobacco mosaic virus (Shulaev *et al.*, 1997). However, a release of methyl salicylate by plants following ozone fumigation has also been reported (Heiden *et al.*, 1999).

Isoprenoids as constituents of biological membranes, photosynthetic pigments, electron transport systems, or hormones contribute to physiologically important functions. Thus, one might assume that a small release represents an optimized loss. But 'losses' are quite high under some circumstances (see Section 2) and biological systems act economically. Therefore, it is not astonishing that some monoterpenes released from plants have an allelopathic function (Fischer, 1991; Tarayre *et al.*, 1995), i.e., limit seed germination and growth of other species nearby. Furthermore, monoterpenes are known as defense compounds against pathogens and herbivores (Gershenzon and Croteau, 1991). β -Pinene is described as an internal inhibitor of respiration (Peiser and Yang, 1979; Chen *et al.*, 1990) and might limit fungal and microbial growth within the leaf tissue by flooding the intercellular gas space. Some monoterpenes possess a deterrent odor or taste that stops herbivorous mammals from feeding (Farentinos *et al.*, 1981; Bell and Harestad, 1987; Elliott and Loudon, 1987) or protects against colonization, ingestion, and oviposition by insects (Weaver *et al.*, 1994). Some monoterpenes are only weakly toxic and are detoxicated by insects (Rhoades, 1985). A fascinating example of an indirect defense has been reported by Turlings (1990). Corn seedlings, which do not release terpenoids under normal growing conditions, emit monoterpenes when under attack by a certain caterpillar, reacting specifically to the animal's saliva. This emission signal attracts a wasp which deposits its eggs into the caterpillar. Thus, the corn seedlings defend their community against an overpopulation of their predators. A very complex function is known for monoterpenes regulating the interrelations between coniferous trees and bark beetles: the monoterpenes act as deterrents as well as attractants to bark beetles within a very complex play between trees, beetles, and their competitors (Delorme and Lieutier, 1990; Gershenzon and Croteau, 1991; Raffa, 1991). Furthermore, resin monoterpenes play an important role in an antimicrobial defense mechanism preventing the colonization of pathogens after wounding of coniferous trees (Cheniclet, 1987; Lewinsohn *et al.*, 1991a, b; Himejima *et al.*, 1992; Funk *et al.*, 1994).

For the plant organism, the emission of hydrocarbons entails a loss of carbon and energy that were previously gained in photosynthetic processes. Normally, the loss of assimilated carbon due to hydrocarbon emission ranges between a few thousandths and some percent (Fehsenfeld *et al.*, 1992; Harley *et al.*, 1994;

Sharkey, 1996b; Street *et al.*, 1996; Staudt, 1997; Hansen *et al.*, 1997; Kesselmeier *et al.*, 1997a, 1998b). In some cases, 10, 20, or even 50% loss has been reported (Sharkey and Loreto, 1993; Staudt *et al.*, 1997; Staudt and Bertin, 1998). These significant losses lead to the question whether the production and emission of these trace gases should be discussed as leakage and waste products or as physiological and ecophysiological reactions with advantages for the plant species. Indeed, the role of monoterpenes in plant defense reactions against pathogens and parasite or herbivore attack could be established in many cases (see above). No comparable function is known for isoprene (Lerdau *et al.*, 1997; Sharkey, 1996b). However, it has been hypothesized that isoprene protects the photosynthetic apparatus of leaves against nonbiotic stresses. For example, isoprene formation inside chloroplasts could serve to prevent light damage by dissipating excessive energy. Under conditions when assimilation of CO₂ is not balanced by an adequate allocation of assimilates, isoprene synthesis contributes to the regeneration of NADP⁺ and phosphate level in chloroplasts and, hence, to the protection of the photosynthetic apparatus (Osmond *et al.*, 1982; Sharkey *et al.*, 1991; Zeidler *et al.*, 1997). Other reports illuminate isoprene production as a membrane protection against heat stress (Sharkey and Singsaas, 1995; Singsaas *et al.*, 1997), a function that was also recently transferred to monoterpene production (Loreto *et al.*, 1998a).

The role of volatile isoprenoids in deleterious effects of atmospheric oxidants like ozone on plants is controversial. On one hand, the emission of reactive VOCs may help the plant cope with harmful oxidants by scavenging them in plant-surrounding air or intercellular air spaces (Sharkey and Loreto, 1993; Zeidler *et al.*, 1997; Fehsenfeld *et al.*, 1992). On the other hand, the ozone VOC reaction yields intermediate products, i.e., organic peroxides and hydroperoxides, that might be more phytotoxic and hence more responsible for plant damage than ozone itself (Salter and Hewitt, 1992; Stokes *et al.*, 1998).

6. Emission Inventories and Global Budgets of Trace Gas Fluxes

The first global estimates of biogenic hydrocarbon release were initiated more than 40 years ago by Went (1955), and 175 Tg C yr⁻¹ was considered as the first amount (Went, 1960a). Rasmussen and Went (1965) later increased the estimate to 200–400 Tg C yr⁻¹. These early investigations already pointed to the significance of biogenic emission for atmospheric chemistry (Went, 1960b), and today a large number of reports exist describing the amounts of hydrocarbon released from vegetation to the atmosphere (Table VIII). Emission inventories are based on emission factors, data on climate, land use, and/or vegetation types as well as biomass distribution. The emission factor specifies the basic emission or emission capacity of a plant species under standard conditions, usually at a temperature of 30 °C and a photosynthetically active radiation (PAR) of 1000 μmol photons m⁻² s⁻¹ (see 2.3 and Table II). The next step in building up emission inventories is the estimation of a basic emission rate for a defined landscape or vegetation

Table VIII. Global natural VOC emission rate estimates [Tg C yr^{-1}]; ORVOC, other reactive VOC; OVOC, other VOC (see Introduction and Table 1)

	Isoprene	Monoterpenes	ORVOC	OVOC	Total
Went [1960]					175
Rasmussen and Went [1965]					432
Robinson and Robbins [1968]					480
Zimmerman [1979]	350	480			
Rasmussen and Khalil [1988]	452				
Warneck [1988]					> 800
Dignon and Logan [1990]	450				
Taylor <i>et al.</i> [1990]	175	143			
Turner <i>et al.</i> [1991]	285				
Mueller [1992]	250	147			
Allwine <i>et al.</i> [1992]	420	128		279	827
Guenther <i>et al.</i> [1995]	503	127	260	260	1150

type. By combining with climate data, the emission variation in time and space for special ecotypes can be estimated. Some models cover specific climatic conditions within the vegetation canopy (Lamb *et al.*, 1993). Regional and global emission inventories for hydrocarbons include the most important monoterpenes and isoprene (Zimmerman, 1979; Lamb *et al.*, 1993; Graedel *et al.*, 1993; Guenther *et al.*, 1995; Simpson *et al.*, 1995). Estimates for the global carbon input by these compounds range between 127 and 480 Tg C yr^{-1} for monoterpenes and between 175 and 503 Tg C yr^{-1} for isoprene. Hence, they are in a similar range as discussed for methane release (ca. 500 Tg C yr^{-1} , Crutzen, 1991) and significantly higher than anthropogenic nonmethane hydrocarbon emissions (ca. 100 Tg C yr^{-1} , Singh and Zimmerman, 1992). More recently, Allwine *et al.* (cited in Fehsenfeld *et al.*, 1992) and Guenther *et al.* (1995) suggested that the amount of other VOC (OVOC) and other reactive VOC (ORVOC) released from biogenic sources is of a similar importance as isoprene or monoterpenes (Table VIII).

7. Conclusions and Outlook

Global budget estimates as described above can only be regarded as rough estimates rather than reliable numbers. The accuracy of such emission inventories is low by a factor of three (Pierce and Waldruff, 1991) and is mainly limited by the accuracy or even lack of missing emission factors. Another problem is that inventories for isoprene and monoterpene emission exclusively use models which include only a short-term influence of radiation and temperature to describe the variability of emission, the correctness and suitability of which are still a matter

of question for diverse compounds and plants. The models might be changed and adapted to recent knowledge to include, for example, plant seasonal development, water availability, or light and temperature regime (see 4.2). Such changes may have a significant influence on emission inventories. The seasonal development or the developmental stage of a plant species or the ecotype as a whole plays an important role. From bud break to a fully developed leaf, the organisms change their habitat as well as their physiology. Deciduous trees dramatically adjust their physiology during the fall and drop their leaves. According to the season, dramatic changes may occur owing to the development of flowers and fruits. Plant photomorphogenesis plays an important role, for example, in the development of sun and shade leaves, differing in emission quality and quantity as well as the reference system. Furthermore, frost, heat, nutrient deficiencies, wounding, and air pollution have to be regarded as potential triggers for physiological changes as well as trace gas emission.

Actual emission inventories still show isoprene and monoterpenes as the most prominent compounds, whereas all other VOCs seem to play a minor role (Table VIII). Nevertheless, we have to be aware that available emission data for many OVOCs are scarce and only rough estimations exist. More data are needed. Oxygenated species have recognized foliar emissions, but their biological origin and physiological role are unclear. Within this context of chemical speciation, plant species dependence is also of importance. It should be noted that the release from agricultural crops or grassland is usually found to be too low to play a significant role in the biogenic emission inventories (Simpson *et al.*, 1995; Parusel, 1996; Wedel, 1997). However, expanding the investigations to include the numerous OVOCs, grasslands have been found to emit quite substantial amounts of VOCs (Kirstine *et al.*, 1998; Fukui and Doskey, 1998).

Plant species and emission quality/quantity is still a matter of debate. Species composition of a forest, grassland, or pasture site will have significant influence on emissions. Crop plants are considered to be low emitting species. In some cases, crop plants can even be regarded as a sink for some compounds, as reported for short-chain organic acids (Kesselmeier, *et al.*, 1998a). However, there is no 'rule' without exceptions. Sunflowers emit significant amounts of monoterpenes (Wedel, 1997; Schuh *et al.*, 1997). The variabilities derive from genetic differences as well as environmental impact (Monson *et al.*, 1995; Lerda *et al.*, 1997). The North American oak *Quercus lobata* (valley oak) as well as the European species *Quercus petraea* (durmast oak) emit a significant amount of oxygenated hydrocarbons, 18% and 5%, respectively, of total VOC emissions. In contrast, the North American *Quercus douglasii* (blue oak) emits exclusively isoprene (Winer *et al.*, 1992; Tanner and Zylinska, 1994; König *et al.*, 1995). The Mediterranean Holm oak (*Quercus ilex*), which emits no isoprene but high amounts of monoterpenes (see above), also emits significant amounts of oxygenated compounds such as organic acids and aldehydes (Kesselmeier *et al.*, 1997a, 1998a). In a recent publication, oak species were regarded as genetically fixed isoprene emitters; however, the monoterpene-

emitting Mediterranean *Q. ilex* has adapted to special conditions (Loreto *et al.*, 1998b), a development which is not really understood. Further species dependencies have been reported for coniferous trees such as *Pinus ponderosa*, *Pinus sylvestris*, and *Pinus pinea* (Knoeppel *et al.*, 1980; Kesselmeier *et al.*, 1997a). The discovery that oak species emit monoterpenes (see Table I) strongly spotlights our gap of knowledge regarding the release of hydrocarbons from vegetation. Hence, assigning emission qualities and quantities to plant species not yet investigated, as recently proposed by Benjamin *et al.* (1996), could result in a misleading emissions inventory. There are important exceptions to a simple taxonomic approach, and such exceptions as within the oaks must be accounted for. Caution, therefore, should be exercised in the application of the taxonomic method, as emission rates measured in one continent or region cannot necessarily be used for another continent or region owing to evolutionary differences. Consequently, the estimation of an ozone-forming potential of trees (Benjamin and Winer, 1998), for example, may lead to numbers representing a high potential, while it is actually low (*Quercus ilex*) or even zero (*Quercus suber*).

These remarks should be considered when discussing the accuracy of estimates of the annual VOC release from vegetation. As long as we do not sufficiently understand why VOCs are released or taken up (see compensation point Section 3.3) and how this exchange is regulated, all budget estimates should be regarded as preliminary. Modeled data sets are helpful, but actual measurements, accompanied by simultaneous physiological measurements such as CO₂ exchange and transpiration, are needed especially for some regions and ecotypes of the world investigated only sporadically (e.g., tropical forests and pastures). In addition to closing these gaps, one of the major objectives for future VOC research, viewed from atmospheric chemistry, is improving our knowledge of the fate of organic carbon in the atmosphere, ending up in oxidation products and/or as aerosol particles.

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