

# Short-chain oxygenated VOCs: Emission and uptake by plants and atmospheric sources, sinks, and concentrations

Roger Seco\*, Josep Peñuelas, Iolanda Filella

*Unitat d'Ecofisiologia CSIC-CEAB-CREAF, Centre de Recerca Ecològica i Aplicacions Forestals (CREAF), Edifici C, Universitat Autònoma de Barcelona, 08193 Bellaterra (Barcelona), Catalunya, Spain*

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## Abstract

Emissions of volatile organic compounds (VOCs) have multiple atmospheric implications and play many roles in plant physiology and ecology. Among these VOCs, growing interest is being devoted to a group of short-chain oxygenated VOCs (oxVOCs). Technology improvements such as proton transfer reaction-mass spectrometry are facilitating the study of these hydrocarbons and new data regarding these compounds is continuously appearing. Here we review current knowledge of the emissions of these oxVOCs by plants and the factors that control them, and also provide an overview of sources, sinks, and concentrations found in the atmosphere.

The oxVOCs reviewed here are formic and acetic acids, acetone, formaldehyde, acetaldehyde, methanol, and ethanol. In general, because of their water solubility (low gas–liquid partitioning coefficient), the plant-atmosphere exchange is stomatal-dependent, although it can also take place via the cuticle. This exchange is also determined by atmospheric mixing ratios. These compounds have relatively long atmospheric half-lives and reach considerable concentrations in the atmosphere in the range of ppbv. Likewise, under non-stressed conditions plants can emit all of these oxVOCs together at fluxes ranging from 0.2 up to 4.8  $\mu\text{g}(\text{C})\text{g}^{-1}(\text{leaf dry weight})\text{h}^{-1}$  and at rates that increase several-fold when under stress.

Gaps in our knowledge regarding the processes involved in the synthesis, emission, uptake, and atmospheric reactivity of oxVOCs precludes the clarification of exactly what is conditioning plant-atmosphere exchange—and also when, how, and why this occurs—and these lacunae therefore warrant further research in this field.

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\*Corresponding author. Tel.: +34 93 581 3420; fax: +34 93 581 41 51.

*E-mail address:* roger@creaf.uab.cat (R. Seco).

## 1. Introduction

Over the last few years great emphasis has been placed on emissions of volatile organic compounds (VOCs) by plants. Their presence in the air affects atmospheric chemistry: reactions with OH radicals and  $\text{NO}_x$  produce ozone (Atkinson, 2000), a secondary oxidant pollutant in the troposphere. Furthermore, VOCs also react with ozone to form OH radicals and can form aerosol particles (Matsunaga et al., 2003; Goldstein et al., 2004; Holzinger et al., 2005) that can act as cloud condensation nuclei (Kavouras et al., 1998) with climatic implications (Peñuelas and Llusà, 2003).

Emitted VOCs can represent up to 10% of the carbon fixed by plants (Llusà and Peñuelas, 2000; Peñuelas and Llusà, 2004) and their multiple roles in plant physiology have been widely studied. They seem to provide protection against high temperatures (Singsaas and Sharkey, 1998; Peñuelas and Llusà, 2002), high irradiation (Peñuelas and Munne-Bosch, 2005), and oxidation stress (Velikova et al., 2005). As well, they also act as herbivore deterrents, as attractants of pollinators and the enemies of herbivores (Pichersky and Gershenzon, 2002), as plant–plant communication cues (Peñuelas et al., 1995), and as plant ‘safety valves’ (Rosenstiel et al., 2004). The release of VOCs by plants after wounding or stress and, specially, the release of methanol and hexenals in connection with lipooxygenase activity (Fukui and Doskey, 1998; Fall et al., 1999; Heiden et al., 2003; Peñuelas et al., 2005) are currently widely under study.

Most of the interest in VOCs has to date been focused on isoprenoids (isoprene, monoterpenes, and sesquiterpenes), and less studies have dealt with short-chain oxygenated compounds (oxVOCs) such as formaldehyde, acetaldehyde, acetone, methanol, ethanol, and formic and acetic acids. These compounds were formerly grouped together under the generic name of ‘other VOCs’ and were thus split into two categories: (i) other reactive VOCs with lifetimes of less than one day (including formaldehyde and acetaldehyde) and (ii) other less reactive VOCs with lifetimes of more than one day (including methanol, ethanol, formic acid, acetic acid, and acetone) (Guenther et al., 1995).

Emissions of many of these oxygenated compounds, because there are analytical difficulties associated with their sampling and analysis, were identified only recently, and many of them were previously thought to have only a limited role in atmospheric chemistry (Fall, 1999). Nowadays, however, growing importance is being attached to the study of these compounds. A large amount of carbon ( $150\text{--}500\text{ Tg C y}^{-1}$ ) fluxes from the Earth’s surface into the atmosphere in the form of oxygenated species. There is evidence of the presence of highly abundant global sources of oxVOCs, although their origin is not as yet exactly clear (Singh et al., 2001, 2004). These sources are either direct—primary—or indirect—secondary—and can be either biogenic or anthropogenic.

Some analytical problems have been solved with the use of proton transfer reaction-mass spectrometry (PTR-MS) (described by Lindinger et al., 1998). This technique allows for real-time or on-line (without preconcentration) monitorization of emissions at concentrations as low as pptv (1 pptv = 1 part in  $10^{12}$  by volume) and so the responses of plant emissions to environmental changes can be detected almost instantaneously. It has been used in measures of direct leaf emissions (Fall et al., 1999; Karl et al., 2002a; Peñuelas et al., 2005) and atmospheric mixing ratios (Sanhueza et al., 2001; Warneke et al., 2003; Filella and Peñuelas, 2006), as well as coupled to micrometeorological techniques like eddy covariance (Karl et al., 2001a, b), proving to be a powerful tool.

In this paper we review current knowledge of emissions of oxVOCs by plants and the factors that control them (Fig. 1), and also provide an overview of sources, sinks, and concentrations found in the atmosphere. These are areas of study that are still not fully understood and are yet to be fully deciphered. The exchange of oxVOCs between plants and the atmosphere has been studied (i) in various plant species or communities, (ii) using different approaches and objectives, (iii) with different sampling and analytical techniques, and (iv) under wide-ranging field and laboratory conditions. The papers cited in our review reflect the whole spectrum of situations that have led authors to reach conclusions that in some cases may seem

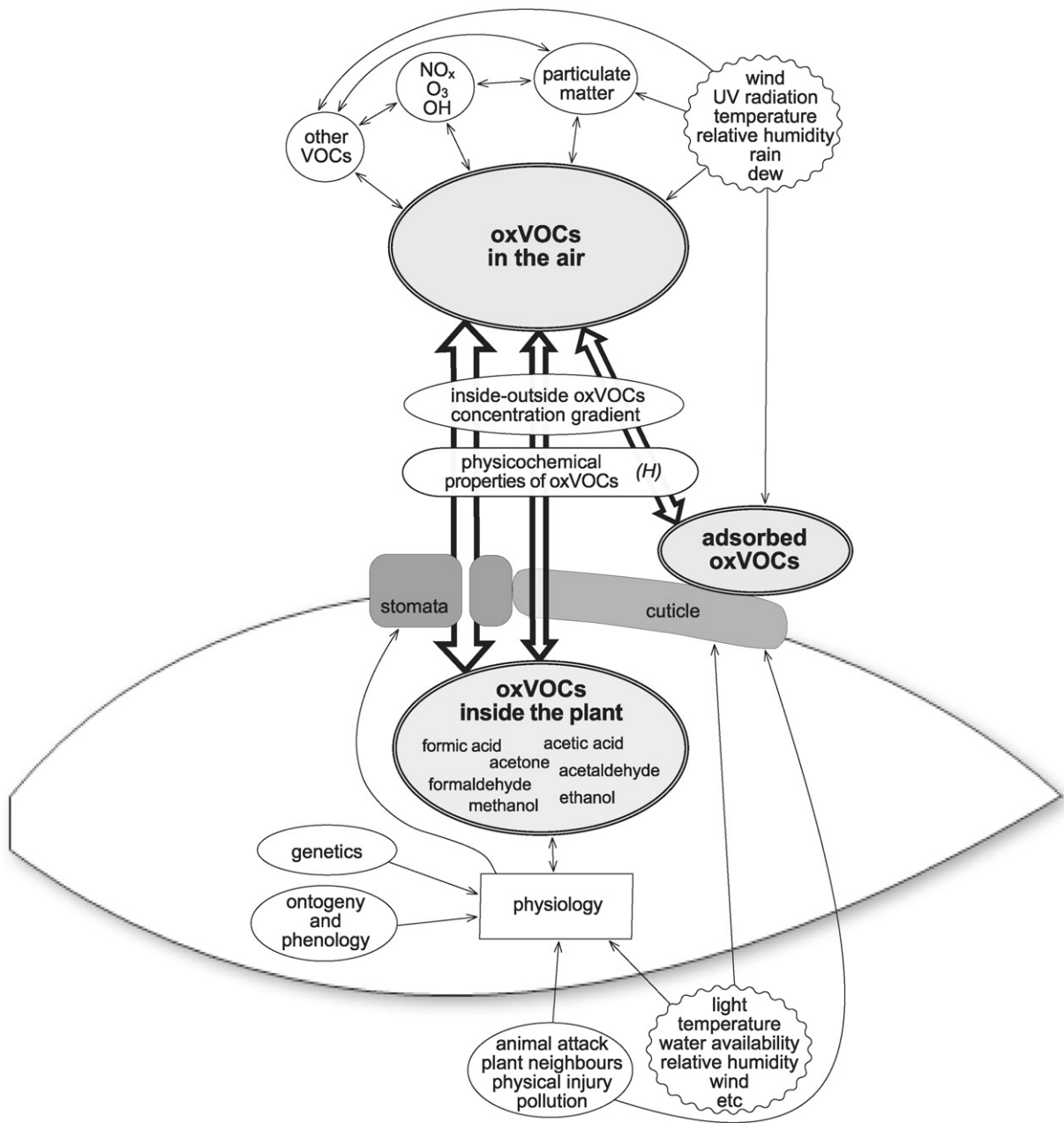


Fig. 1. Schematic diagram showing the factors driving the emission and uptake of short-chain oxVOCs.

even to be contradictory. For instance, some authors have proposed that oxVOCs emissions are mainly physiologically controlled, while others consider that the principal control mechanisms are physicochemical. In fact, control by physicochemical processes does not preclude biochemical control (or vice versa) and it is very likely that both mechanisms are involved. However, the lack of knowledge regarding processes involved prevents us

from clarifying exactly what is conditioning the exchange of a certain compound and when, how, and why it is doing so.

Short-chain oxVOCs can be emitted or taken up by plants. The direction of the exchange is thought to be at least partly determined by the atmospheric mixing ratios, since gases move along the concentration gradient between the inner part and the outside part of the leaf. Another physicochemical

property that influences oxVOC atmospheric exchange is solubility. These compounds all have in common high water solubility, as shown by their Henry's law constants ( $H$ ) that range in magnitudes from  $10^{-2}$  (formic acid) to  $10^1$  (acetaldehyde)  $\text{Pa m}^3 \text{mol}^{-1}$  under standard conditions. These figures are low in comparison with those of highly volatile isoprene and monoterpenes, both of which have constants in the order of  $10^3 \text{Pa m}^3 \text{mol}^{-1}$  (Sander, 1999). In highly water-soluble compounds exchange is more affected by stomatal conductance, with the degree of stomatal sensitivity varying with  $H$  (Niinemets and Reichstein, 2003b). Thus, physicochemical characteristics such as low volatility or diffusion of some VOCs may also control emissions and interact with physiological limitations (Niinemets and Reichstein, 2003a, b; Niinemets et al., 2004).

Aside from stomatal regulation, the exchange of oxVOCs can also be physiologically controlled by metabolic activity rates and both of these processes are affected by internal (genetic traits, developmental stage, phenology, water content, etc.) and environmental (light, temperature, relative humidity, herbivory, and pollution stresses, wind speed, etc.) conditions. The oxVOCs formation mechanisms within the plant are known in some cases, although often our knowledge of these processes is not as detailed as would be desirable. Furthermore, unknown processes contributing to the VOC pool within the plant might be at work. The metabolic pathways working in the opposite direction, that is, those that determine the fate of the uptaken oxVOCs within plants, also warrant further study.

Uptake can occur by means of the absorption of gas-phase oxVOCs through the stomata into the mesophyll or via adsorption into the cuticle as a result of dry (gas-phase) or wet (liquid-phase) deposition. Although entry through the stomata is the most commented upon, studied, and—possibly—important way of absorption of short-chained oxVOCs, the diffusion of adsorbed oxVOCs through aqueous pores of the cuticle may also play an important role in absorption, as has been described recently for inorganic and organic ions (Schreiber, 2005; Schönherr, 2006). This could happen, for example, after rain, on dew-wetted leaves, or by means of the transpired water vapour recondensed on the leaf surface (Burkhardt et al., 1999). On the other hand, if not absorbed, the oxVOCs adsorbed on the cuticle may be revolatilized, for example with the evaporation of dew in

the morning, as a result of a decrease in atmospheric concentration caused by photochemical activity or through the action of air turbulence (wind). As well, oxVOCs may react with other atmospheric chemical species on the cuticle itself.

In addition to adsorbed and absorbed oxVOCs, in certain studies uptake estimates may include oxVOC scavenging resulting from the reactions of the oxVOCs with other reactive VOCs freshly emitted by plants. This would specially be the case in measurements carried out within canopies or above communities, although the low reactivity of the short-chained oxVOCs may render this process quantitatively unimportant and ozone chemistry may turn out to be the main factor responsible for scavenging newly emitted reactive VOCs such as isoprenoids (Goldstein et al., 2004; Holzinger et al., 2005).

The emission of oxVOCs from within the leaf may occur along the same pathways as the uptake, that is, via the stomata and the cuticle, the former being again the most studied pathway and probably the most important in quantitative terms. However, more research is needed to elucidate the importance of each pathway and their respective roles and mechanisms in both the release and the deposition of oxygenated VOCs.

Emitted and revolatilized oxVOCs enter the atmospheric compartment in which they can react with ozone molecules, OH radicals, other VOCs, and nitrogen oxides. Otherwise, they may be degraded by ultra-violet (UV) radiation. Such transformations, however, are slow due to the low reactivity of short-chain oxVOCs, a fact that is illustrated by their relatively long half-lives ranging from a few hours (aldehydes) to 15 days (acetone). A long-range transport of oxVOCs on the wind is thus likely to occur and hence influence the atmospheric chemistry of distant regions.

The low reactivity of these compounds is derived from the fact that short-chained oxVOCs are themselves products of photolysis and the chemical reactions of a vast diversity of other VOCs present in the atmosphere. Currently, this secondary photochemical production from VOCs is thought to be the main atmospheric source of oxVOCs. Another related issue that needs further investigation is the balance between biogenic emission and photochemical production: sometimes the maximum reported emissions of oxVOCs take place when secondary atmospheric production is likely also to be at a maximum, e.g. at midday or in the afternoon when

stomatal conductance, photosynthetic rate, transpiration, irradiation, and temperatures are high, and thus plant metabolic activity and oxVOCs volatilization are also high. However, if atmospheric mixing ratios control the gas exchange, and photochemical production increases the mixing ratios, then oxVOCs emissions should be hindered. Photochemical destruction of oxVOCs may partly offset photochemical production, although the long lifespan and low reactivity of oxVOCs may in fact ensure that this effect is of little import. These processes are not well understood and future research may well unravel some of these uncertainties.

In general, plants synthesize C<sub>1</sub> oxVOCs during many growth and developmental processes such as seed maturation, cell expansion, cell wall degradation, leaf abscission, and senescence of plant tissues. C<sub>2</sub> oxVOCs seem mainly related to responses to changes in the environment, above all during periods of stress (Kreuzwieser et al., 1999b). In this detailed overview, we will group the short-chained oxVOCs into acids, acetone, aldehydes and alcohols. Usually, the compounds within each group—especially aldehydes and acids—have been studied together due to the similarities in the sampling and analytic techniques involved.

## 2. Acids

Formic (HCOOH) and acetic (CH<sub>3</sub>COOH) acids are the most prominent organic acids emitted by vegetation (Kesselmeier and Staudt, 1999). In C<sub>3</sub> plant leaves in the light, formic acid can be generated in its deprotonated form—formate—by the non-enzymatic decarboxylation of glyoxylate formed in photorespiration (Igamberdiev et al., 1999; Kesselmeier and Staudt, 1999; Hanson and Roje, 2001). In the dark, in nonphotosynthetic tissues and in C<sub>4</sub> species its origin is not clear. In these cases, formic acid may be produced through the oxidation of methanol and formaldehyde, 10-formyl-tetrahydrofolate cleavage, or the direct reduction of CO<sub>2</sub> to formate, as reported in potato tubers (Igamberdiev et al., 1999; Hanson and Roje, 2001). Acetic acid is mainly found in its activated form acetyl-CoA, which participates in multiple metabolic processes, and is the main product of the decomposition of carbohydrates and fats (Kesselmeier and Staudt, 1999).

Formic and acetic acids have been reported to be both deposited and emitted. Studies in a remote tropical forest site in Amazonia detected predomi-

nantly the uptake of these acids at branch level as a function of the atmospheric mixing ratios (Kuhn et al., 2002) and in a tropical rain forest canopy in Costa Rica these acids were also mainly deposited (Karl et al., 2004). In the Valencia region, high concentrations in ambient air promoted acid deposition on orange trees (*Citrus sinensis*) (Staudt et al., 2000). These authors stated that both acetic and formic acids exhibited similar emission time-series, which suggests that the exchange of acids is mainly controlled more by physicochemical than biochemical processes, since these compounds do not usually share the same metabolic pathways.

After uptake, organic acids may be transferred from the apoplast to the symplast and thereby enter the plant metabolism, thereby maintaining the concentration gradient between the interior and the exterior of the plant that permits continuous uptake. Once in the symplast, acetic acid may be converted to acetyl-CoA and enter general metabolism pathways such as the TCA (TriCarboxylic Acids) cycle; formic acid may participate in the transfer of methyl and hydroxymethyl groups for the synthesis of other molecules (see Kesselmeier and Staudt, 1999; Kuhn et al., 2002, and references therein) or may be oxidized into CO<sub>2</sub> in mitochondria, specially when under stress (Igamberdiev et al., 1999; Hanson and Roje, 2001).

On the other hand, other studies have reported emission of these acids (Tables 1 and 2). Aside from physicochemical control, some authors have observed that short-chain acid emissions are controlled physiologically. Light triggers emission (Kesselmeier et al., 1997, 1998; Staudt et al., 2000; Kesselmeier, 2001) and release is generally correlated with transpiration (Kesselmeier et al., 1997, 1998; Gabriel et al., 1999) and temperature (Kesselmeier et al., 1997; Staudt et al., 2000), although Martin et al. (1999) found poor correlation with temperature in New Mexico. Stomatal conductance is a further important factor in the emission of acids (Kesselmeier et al., 1997, 1998; Kesselmeier, 2001; Niinemets and Reichstein, 2003b). The high solubility of these acids explains the correlation between emission and both transpiration and stomatal conductance, which allows for bursts of emissions after stomatal opening (Niinemets and Reichstein, 2003a, b).

Staudt et al. (2000) detected emission at noon and in the afternoon and deposition at night and morning in orange trees, observations that agree with the findings of Gabriel et al. (1999) in holm oak

Table 1  
Foliar emissions and atmospheric mixing ratios of formic acid (HCOOH)

Formic acid					
<i>Foliar emissions</i> <sup>a</sup>					
Species	Emission rates		Location	Period	Reference
	nmol m <sup>-2</sup> s <sup>-1</sup>	ng g <sup>-1</sup> dw h <sup>-1</sup>			
<i>Quercus ilex</i>		221–434 <sup>c</sup>	Castelporziano (Italy)	May 1994	Kesselmeier et al. (1997)
<i>Pinus pinea</i>		320–345 <sup>c</sup>	Castelporziano (Italy)	May 1994	Kesselmeier et al. (1997)
<i>Populus fremontii</i>		310 ± 300 <sup>c</sup>	New Mexico (USA)	Summer 1997	Villanueva-Fierro et al. (2004)
<i>Pinus ponderosa</i>		210 ± 210 <sup>c</sup>	New Mexico (USA)	Summer 1997	Villanueva-Fierro et al. (2004)
diverse		15–916 <sup>d</sup>	New Mexico (USA)	Summer 1996	Martin et al. (1999)
<i>Quercus ilex</i>	0.03–0.86		Castelporziano (Italy)	May, August 1994	Gabriel et al. (1999)
<i>Quercus ilex</i>	0.04 <sup>c</sup>		Laboratory		Kesselmeier et al. (1998)
<i>Citrus sinensis</i>	0.3		Burriana (Spain)	June 1997	Staudt et al. (2000)
<i>Citrus sinensis</i>	0.08 <sup>c</sup>		Laboratory	November–December 1997	Staudt et al. (2000)
<i>Fraxinus excelsior</i>	0.06–0.49 <sup>c</sup>		Laboratory		Kesselmeier et al. (1998)
<i>Fagus sylvatica</i>	0.02 <sup>c</sup>		Laboratory		Kesselmeier et al. (1998)
<i>Picea abies</i>	0.02 <sup>c</sup>		Laboratory		Kesselmeier et al. (1998)
<i>Betula pendula</i>	0.11 <sup>c</sup>		Laboratory		Kesselmeier et al. (1998)
Crop plants	(–4.25*)–(–0.01*) <sup>d</sup>		Laboratory		Kesselmeier et al. (1998)
<i>Atmospheric mixing ratios</i> <sup>b</sup>					
Site	Mixing ratio (ppbv)		Location	Period	Reference
Rain forest	(0.75–2.5)		Amazonia (Rondonia, Brazil)	wet season 1999	Kesselmeier et al. (2002)
Rain forest	(4–17)		Amazonia (Rondonia, Brazil)	dry season 1999	Kesselmeier et al. (2002)
Tropical rain forest	0.51–1.3		Costa Rica	April (dry season) 2003	Karl et al. (2004)
Savannah	2		Venezuela	January–February 2000	Sanhueza et al. (2001)
Remote forested site	0.6 ± 0.5		Langmuir (NM, USA)	Summer 1997	Villanueva-Fierro et al. (2004)
Forested site	1.05–2.5 <sup>d</sup>		diverse (America)	diverse	Villanueva-Fierro et al. (2004)
Rural ambient	1.7 ± 1.5/0.4–4.4		Gopalpura (India)	Monsoon 1995, 1996	Khare et al. (1997)
Rural ambient	0.7 ± 0.9		Socorro (NM, USA)	Summer 1997	Villanueva-Fierro et al. (2004)
Rural ambient	0.2–5.6 <sup>d</sup>		diverse (world)	diverse	Khare et al. (1997)
Rural ambient	0.6–0.7		Germany	diverse	Granby et al. (1997)
Semi-rural ambient	0.6 ± 0.3/0.2–1.5		Denmark	February 1994	Granby et al. (1997)
Semi-rural ambient	0.1–3.8		diverse (Europe, USA)	diverse	Granby et al. (1997)
Urban ambient	0.7 ± 0.3/0.3–1.5		Copenhagen (Denmark)	February 1994	Granby et al. (1997)
Urban ambient	3.6 ± 1.6/0.9–8.5		Brussels (Belgium)	June 1993	Granby et al. (1997)
Urban ambient	4.36 ± 2.70		São Paulo (Brazil)	July (winter) 1996	Souza et al. (1999)
Urban ambient	1.7–9.3 <sup>d</sup>		diverse (USA)	diverse	Villanueva-Fierro et al. (2004)
Urban ambient	0.02–19.8		diverse (N.America, Japan)	diverse	Khare et al. (1997)
Urban ambient	0.2–10.5		diverse (world)	diverse	Granby et al. (1997)
Marine air	0.02–1.7		Pacific, Indian oceans	diverse	Khare et al. (1997)
diverse	0.03–40		diverse (world)	diverse	Chebbi and Carlier (1996)

\*Negative values represent uptake.

<sup>a</sup>Foliar emissions measured with enclosure chambers. Displayed values are means or range of observed emissions. Rates are referred to leaf area (m<sup>2</sup>) or leaf dry weight (dw).

<sup>b</sup>Atmospheric mixing ratios reported in the literature. Displayed values are mean mixing ratios and/or range of observed values. Numbers between brackets represent maximum mixing ratios.

<sup>c</sup>Normalized standard emission rate at 303 K and 1000 μmol m<sup>-2</sup> s<sup>-1</sup> PAR (photosynthetic active radiation) flux, fitted according to equations developed by Guenther et al. (1993, 1995).

<sup>d</sup>Range of means.

(*Quercus ilex*). Gabriel et al. (1999) also propose that the pH is a factor that controls the solubility of acids in the apoplastic solution. Turgor maintenance mechanisms in leaves lead to lower pH

levels of the apoplast, which in turn helps acids to leave the aqueous phase and enter the gaseous phase. They also found that formic acid has more cuticular permeability than acetic acid so this acid

Table 2  
Foliar emissions and atmospheric mixing ratios of acetic acid (CH<sub>3</sub>COOH)

Acetic acid					
<i>Foliar emissions</i> <sup>a</sup>					
Species	Emission rates		Location	Period	Reference
	nmol m <sup>-2</sup> s <sup>-1</sup>	ng g <sup>-1</sup> dw h <sup>-1</sup>			
<i>Quercus ilex</i>		36.6–289 <sup>c</sup>	Castelporziano (Italy)	May 1994	Kesselmeier et al. (1997)
<i>Pinus pinea</i>		182–190 <sup>c</sup>	Castelporziano (Italy)	May 1994	Kesselmeier et al. (1997)
<i>Populus fremontii</i>		470 ± 540 <sup>c</sup>	New Mexico (USA)	Summer 1997	Villanueva-Fierro et al. (2004)
<i>Pinus ponderosa</i>		170 ± 180 <sup>c</sup>	New Mexico (USA)	Summer 1997	Villanueva-Fierro et al. (2004)
diverse		52–1275 <sup>d</sup>	New Mexico (USA)	Summer 1996	Martin et al. (1999)
<i>Quercus ilex</i>	0.02–0.75		Castelporziano (Italy)	May, Aug. 1994	Gabriel et al. (1999)
<i>Quercus ilex</i>	0.33		Laboratory	June 2001	Holzinger et al. (2000)
<i>Quercus ilex</i>	0.03 <sup>c</sup>		Laboratory		Kesselmeier et al. (1998)
<i>Citrus sinensis</i>	0.15		Burriana (Spain)	June 1997	Staudt et al. (2000)
<i>Citrus sinensis</i>	0.035 <sup>c</sup>		Laboratory	November–December 1997	Staudt et al. (2000)
<i>Fraxinus excelsior</i>	0.02–0.13 <sup>c</sup>		Laboratory		Kesselmeier et al. (1998)
<i>Fagus sylvatica</i>	0.02 <sup>c</sup>		Laboratory		Kesselmeier et al. (1998)
<i>Picea abies</i>	0.01 <sup>c</sup>		Laboratory		Kesselmeier et al. (1998)
<i>Betula pendula</i>	0.03 <sup>c</sup>		Laboratory		Kesselmeier et al. (1998)
Crop plants	(–0.035*)–0.004 <sup>d</sup>		Laboratory		Kesselmeier et al. (1998)
<i>Atmospheric mixing ratios</i> <sup>b</sup>					
Site	Mixing ratio (ppbv)		Location	Period	Reference
Rain forest	(0.75–2.5)		Amazonia (Rondonia, Brazil)	Wet season 1999	Kesselmeier et al. (2002)
Rain forest	(2–12)		Amazonia (Rondonia, Brazil)	Dry season 1999	Kesselmeier et al. (2002)
Tropical rain forest	0.8–1.01		Costa Rica	April (dry season) 2003	Karl et al. (2004)
Savannah	1		Venezuela	January–February 2000	Sanhueza et al. (2001)
Remote forested site	1.7 ± 2.0		Langmuir (NM, USA)	Summer 1997	Villanueva-Fierro et al. (2004)
Forested site	2.0–2.6 <sup>d</sup>		diverse (America)	diverse	Villanueva-Fierro et al. (2004)
Rural ambient	2.7 ± 3.8		Socorro (NM, USA)	Summer 1997	Villanueva-Fierro et al. (2004)
Rural ambient	1.6 ± 1.6/0.2–4.0		Gopalpura (India)	Monsoon 1995, 1996	Khare et al. (1997)
Rural ambient	0.2–2.2 <sup>d</sup>		diverse (world)	diverse	Khare et al. (1997)
Rural ambient	1.2–7.5		Germany	diverse	Granby et al. (1997)
Semi-rural ambient	1.0 ± 0.5/0.4–2.0		Denmark	February 1994	Granby et al. (1997)
Semi-rural ambient	0.1–3.4		diverse (Europe, USA)	diverse	Granby et al. (1997)
Urban ambient	1.2 ± 0.5/0.4–2.8		Copenhagen (Denmark)	February 1994	Granby et al. (1997)
Urban ambient	4.0 ± 2.0/1.3–8.1		Brussels (Belgium)	June 1993	Granby et al. (1997)
Urban ambient	3.66 ± 2.63		São Paulo (Brazil)	July (winter) 1996	Souza et al. (1999)
Urban ambient	3.8–8.8 <sup>d</sup>		diverse (USA)	diverse	Villanueva-Fierro et al. (2004)
Urban ambient	0.2–17.8		diverse (N.America, Japan)	diverse	Khare et al. (1997)
Urban ambient	0.1–9.5		diverse (world)	diverse	Granby et al. (1997)
Marine air	0.05–1.9		Pacific, Indian oceans	diverse	Khare et al. (1997)
diverse	0.05–7.3		diverse (world)	diverse	Chebbi and Carlier (1996)

\*Negative values represent uptake.

<sup>a</sup>Foliar emissions measured with enclosure chambers. Displayed values are means or range of observed emissions. Rates are referred to leaf area (m<sup>2</sup>) or leaf dry weight (dw).

<sup>b</sup>Atmospheric mixing ratios reported in the literature. Displayed values are mean mixing ratios and/or range of observed values. Numbers between brackets represent maximum mixing ratios.

<sup>c</sup>Normalized standard emission rate at 303 K and 1000 μmol m<sup>-2</sup> s<sup>-1</sup> PAR (photosynthetic active radiation) flux, fitted according to equations developed by Guenther et al. (1993, 1995).

<sup>d</sup>Range of means.

escapes not only through stomata but also in an uncontrolled fashion through plant membranes and the cuticle.

Kesselmeier et al. (1997) found convincing evidence that acid emissions in *Quercus ilex* follow the isoprene algorithm for the light-and-tempera-

ture-dependent release developed by Guenther et al. (1993, 1995). Filella et al. (2007) found that acid emission by the Norway spruce (*Picea abies*) increased with temperature, but reached saturation at 30 °C.

In a study with various species of trees and crop plants, Kesselmeier et al. (1998) found that all tree species turned out to be acid emitters, while all crop plants showed uptake of acids but no emissions. These authors consider that forests should be seen as sources of acids and agricultural sites as sinks, although their use of purified air with trees could have interfered in their results and produced higher emissions than those expected using ambient air. This fits in well with the hypothesis of a compensation point concentration that determines the emission or the absorption of acids, as reported by Kuhn et al. (2002). Kuhn et al. (2002) also stated that tropical forests are more a sink than a source of formic and acetic acids. Similar disturbances could occur, for instance, in the emissions reported by Staudt et al. (2000) in orange trees in laboratory experiments using purified air and by Villanueva-Fierro et al. (2004) in tree experiments in New Mexico in the case not only of acids but also of other oxVOCs.

Once released from the plant, carboxylic acids have low reactivity in the atmosphere because they are terminal products of the photooxidation of hydrocarbons so dry and wet deposition are their major sinks (Chebbi and Carlier, 1996; Sanhueza et al., 1996, 2001; Granby et al., 1997). Their tropospheric residence times are over a week and appear to be strongly controlled by precipitation events (Chebbi and Carlier, 1996). Formic acid mixing ratios measured in different sites around the world range from 0.02 to 40 ppbv (1 ppbv = 1 part in 10<sup>9</sup> by volume; Table 1) and acetic acid mixing ratios from 0.05 to 17.8 ppbv (Table 2). They can be responsible for up to 60% of the precipitation acidity in remote areas and up to 30% of the acidity of wet deposition in polluted areas (Kesselmeier et al., 1998; Peña et al., 2002).

VOC emission from vegetation is the main source of atmospheric formic and acetic acids and leads to a seasonal pattern of atmospheric concentrations (Granby et al., 1997; Peña et al., 2002), either by direct or indirect—in the form of precursor hydrocarbons—release (Glasius et al., 2001). Their major precursors in the gas phase are hydrocarbons (such as alkenes, aldehydes, isoprene, and terpenes), either from biogenic or anthropogenic origin, and their

degradation products that mainly take place via photochemical oxidation (Sanhueza et al., 1996; Granby et al., 1997; Kesselmeier et al., 1998; Khare et al., 1999; Glasius et al., 2001; Peña et al., 2002; Pacheco and Sanhueza, 2004; Lee et al., 2006a, b). Soils and biomass burning are other direct sources (Chebbi and Carlier, 1996; Sanhueza et al., 1996; Khare et al., 1999; Kesselmeier et al., 2002). Their direct origin from fuel combustion and industry is minor in global terms but can be important in urban or industrialized areas (Chebbi and Carlier, 1996). Vehicle exhaust may also be locally significant (Chebbi and Carlier, 1996) although some authors report the opposite (Granby et al., 1997).

Different studies have reported lower emission rates in laboratory experiments than in field measurements, which have led some authors to postulate an indirect origin for formic and acetic acid in the field (Kesselmeier, 2001) and emphasize the importance of plant phenology (Staudt et al., 2000).

### 3. Acetone

Acetone (CH<sub>3</sub>COCH<sub>3</sub>) is the simplest existing ketone. Within plant tissues, acetone can be produced by the cyanogenic pathway (activated to deter herbivores), leading to the production of hydrogen cyanide (HCN) and—as a byproduct—acetone. Another way in which acetone may be formed is via acetoacetate decarboxylation, a well-known reaction that occurs in certain soil bacteria and animals. For a detailed description of these pathways see Fall (2003).

In direct plant emission measurements (Table 3), Janson and de Serves (2001) found acetone to be the main light carbonyl emitted by both Scots pines (*Pinus sylvestris*), accounting for between 64% and 94% of the carbon mass of emissions, and Norway spruce (*Picea abies*), with more than 80% of CH<sub>3</sub>COCH<sub>3</sub> among its emitted carbonyls. Carbonyls are compounds—like ketones and aldehydes—that are characterized by a carbonyl functional group composed of a carbon atom double-bonded to an oxygen atom. These results contrast with those of Martin et al. (1999) who found levels of below 8% of acetone in emitted carbonyls, but agree with results from both a previous study by the same authors (Janson et al., 1999) who reported that acetone/acrolein make up 79 ± 13% of carbonyls in *Pinus sylvestris* and 64 ± 20% in *Picea abies*, and a study by Filella et al. (2007) also on Norway spruce.

Table 3  
Foliar emissions, ecosystem fluxes and atmospheric mixing ratios of acetone (CH<sub>3</sub>COCH<sub>3</sub>)

Acetone					
<i>Foliar emissions</i> <sup>a</sup>					
Species	Emission rates		Location	Period	Reference
	nmol m <sup>-2</sup> s <sup>-1</sup>	ng g <sup>-1</sup> dw h <sup>-1</sup>			
<i>Pinus sylvestris</i>		1403 ± 774 <sup>c</sup> / < 32–2258	Sweden and Finland	Spring/summer 1997, 1998, 1999	Janson and de Serves (2001)
<i>Picea abies</i>		427 <sup>c</sup> / < 32–468	Sweden	May–June 1997	Janson and de Serves (2001)
<i>Populus fremontii</i>		550 ± 430 <sup>d</sup>	New Mexico (USA)	Summer 1997	Villanueva-Fierro et al. (2004)
<i>Pinus ponderosa</i>		180 ± 90 <sup>d</sup>	New Mexico (USA)	Summer 1997	Villanueva-Fierro et al. (2004)
<i>Quercus ilex</i>	0.03–0.2		Tuscany (Italy)	June, July, September 2000, 2001	Kreuzwieser et al. (2002)
<i>Quercus ilex</i>	0.71		Laboratory	June 2001	Holzinger et al. (2000)
<i>Fagus sylvatica</i>	0.66		Freising (Germany)	August 2001, 2002	Cojocariu et al. (2005)
<i>Ecosystem fluxes</i> <sup>b</sup>					
Ecosystem	Flux (mg m <sup>-2</sup> h <sup>-1</sup> )		Location	Period	Reference
Tropical rain forest	0.09 (0.36)		Costa Rica	April (dry season) 2003	Karl et al. (2004)
Ponderosa pine plantation	0.35		Sierra Nevada (CA, USA)	July–October 1998	Goldstein and Schade (2000)
Ponderosa pine plantation	0.03–0.34 <sup>f</sup> (0.4)		Sierra Nevada (CA, USA)	July–September 1999	Schade and Goldstein (2001)
Mixed hardwood forest	0.5 (1.6)		N Michigan (USA)	September–November 2001	Karl et al. (2003)
Mixed hardwood forest	0.3 (1.2)		N Michigan (USA)	April–July 2002	Karl et al. (2003)
Subalpine forest	(0.8)		Rocky Mountains (CO, USA)	July 2001	Karl et al. (2002b)
Subalpine forest	(4)		Rocky Mountains (CO, USA)	summer 1999	Baker et al. (2001)
<i>Atmospheric mixing ratios</i> <sup>c</sup>					
Site	Mixing ratio (ppbv)		Location	Period	Reference
Tropical rain forest	0.73–1.14		Costa Rica	April (dry season) 2003	Karl et al. (2004)
Savannah	1.49		Venezuela	January–February 2000	Sanhueza et al. (2001)
Mixed hardwood forest	1.2 (3.1)		N Michigan (USA)	September–November 2001	Karl et al. (2003)
Mixed hardwood forest	1.9 (5.6)		N Michigan (USA)	April–July 2002	Karl et al. (2003)
Ponderosa pine plantation	1.0–8.0		Sierra Nevada (CA, USA)	July 1997, 1998, 1999	Goldstein and Schade (2000)
Ponderosa pine plantation	0.3–11		Sierra Nevada (CA, USA)	July–September 1999	Schade and Goldstein (2001)
Remote forested site	1.2 ± 1.2		Langmuir (NM, USA)	Summer 1997	Villanueva-Fierro et al. (2004)
Hay field	1–5		Tirol (Austria)	May 2000	Karl et al. (2001b)
Rural ambient	2.4 ± 2.4		Socorro (NM, USA)	Summer 1997	Villanueva-Fierro et al. (2004)
Rural ambient	0.6–3.0		diverse (Germany, Canada)	diverse	Granby et al. (1997)
Rural and semi-rural ambients	0.4–2.3 <sup>f</sup>		diverse (Europe and N.America)	diverse	Christensen et al. (2000)
Semi-rural ambient	0.9 ± 0.4/0.2–1.7		Denmark	February 1994	Granby et al. (1997)
Semi-rural ambient	1.9/0.4–6.1		Denmark	May–July 1995	Christensen et al. (2000)

Table 3 (continued)

Atmospheric mixing ratios <sup>c</sup>				
Site	Mixing ratio (ppbv)	Location	Period	Reference
Semi-urban ambient	3.29–8.53 <sup>f</sup>	Bellaterra, Catalonia (Spain)	December 2003–October 2004	Filella and Peñuelas (2006)
Urban ambient	0.25–76.4	Athens (Greece)	June–December 2000	Bakeas et al. (2003)
Urban ambient	1.0±0.5/0.2–2.2	Copenhagen (Denmark)	February 1994	Granby et al. (1997)
Urban ambient	1.6–16 <sup>f</sup>	diverse (world)	diverse	Villanueva-Fierro et al. (2004)
Urban ambient	0.6–8.4	diverse (world)	diverse	Granby et al. (1997)
Atmosphere 0–6 km height	1.14±0.41/ 0.36–2.31	Eastern Canada	July–August	Singh et al. (1994)
Atmosphere 0–12 km height	0.44–0.64 <sup>f</sup>	Tropical Pacific troposphere	February–April 2001	Singh et al. (2004)
Atmosphere 0–12 km height	0.3–1.9 <sup>f</sup>	diverse (world)	diverse	Jacob et al. (2002)

<sup>a</sup>Foliar emissions measured with enclosure chambers. Displayed values are means or range of observed emissions. Rates are referred to leaf area (m<sup>2</sup>) or leaf dry weight (dw).

<sup>b</sup>Ecosystem fluxes measured with micrometeorological techniques. Displayed values are mean daytime emissions or range of observed values. Numbers between brackets represent daily maximum peaks of emission. Fluxes are referred to ground surface area (m<sup>2</sup>).

<sup>c</sup>Atmospheric mixing ratios reported in the literature. Displayed values are mean mixing ratios and/or range of observed values. Numbers between brackets represent maximum mixing ratios.

<sup>d</sup>Normalized standard emission rate at 303 K and 1000 μmol m<sup>-2</sup> s<sup>-1</sup> PAR (photosynthetic active radiation) flux, fitted according to equations developed by Guenther et al. (1993, 1995).

<sup>e</sup>Normalized standard emission rate at 303 K, fitted according to equations developed by Guenther et al. (1993, 1995).

<sup>f</sup>Range of means.

Janson and de Serves (2001) expected physiological factors to control the emissions of carbonyls, since these compounds are not stored in the needles of conifers. Nevertheless, acetone emission levels did not correlate with CO<sub>2</sub> assimilation or H<sub>2</sub>O fluxes. The correlation between acetone emissions and relative humidity has been reported in *Picea abies* (Cojocariu et al., 2004); the same authors also report a diurnal pattern of emission under light conditions (maximal at midday) and uptake under dark conditions. Similar atmospheric diurnal patterns have been described for tropical rain forest canopies (Karl et al., 2004), with emission during the day and deposition at night, and for alfalfa (*Medicago sativa*) fields (Warneke et al., 2002) with release in the afternoon and dry deposition in the evening and morning. Villanueva-Fierro et al. (2004) also described a diurnal trend of acetone release in branch enclosures of ponderosa pine (*Pinus ponderosa*) and cottonwood (*Populus fremontii*) but found poor correlation with temperature. On the other hand, both Baker et al. (2001) in a subalpine forest in the Rocky Mountains and Schade and Goldstein (2001) in a ponderosa pine plantation found no distinct diurnal pattern of

atmospheric fluxes, although the latter authors did find temperature to be the main regulating factor in CH<sub>3</sub>COCH<sub>3</sub> emissions.

Acetone emission in alfalfa was found to be enhanced over a period of three days after cutting (Warneke et al., 2002). Similarly, de Gouw et al. (2000) observed increased emissions when wounding alfalfa and other crop species, and also when the harvested material was drying. Under stress caused by exposition to O<sub>3</sub>, emission was enhanced in beech (*Fagus sylvatica*) (Cojocariu et al., 2005) and the diurnal pattern of maximum emissions at midday was also maintained. In flooded *Quercus ilex* plants in the laboratory, acetone release almost doubled (Holzinger et al., 2000).

The lifetime of acetone in the troposphere is estimated at 15 days (Singh et al., 2004), time enough for it to be transported to remote regions of the troposphere (Atkinson, 2000). Acetone is lost by photolysis (45–64%), through reaction with OH radicals (24–30%), ocean uptake (15%) and dry deposition (10–12%) (Singh et al., 2004).

Typical measured mixing ratios are shown in Table 3 and range from 0.3 to 76.4 ppbv. Borbon et al. (2004) describe a seasonal pattern of biogenic

acetone at a rural site in France that in summer accounts for  $37 \pm 25\%$  and in winter for  $5 \pm 4\%$  of total mixing ratios. Bakeas et al. (2003) found acetone to be the third carbonyl in abundance in the urban air of Athens after formaldehyde and acetaldehyde.

Jacob et al. (2002) estimated the global source of acetone to be  $95 \text{ Tg y}^{-1}$ , in which the  $\text{C}_3\text{--C}_5$  isoalkanes (propane, isobutane, isopentane), all of anthropogenic origin, are the major atmospheric precursors ( $\sim 27 \text{ Tg y}^{-1}$ ). The oxidation of methylbutenol and terpenes of biogenic origin also contribute  $\sim 7 \text{ Tg y}^{-1}$  to the secondary acetone pool (see also Lee et al., 2006a, b). Terrestrial vegetation ( $\sim 33 \text{ Tg y}^{-1}$ ) was confirmed as a primary source along with biomass burning ( $\sim 5 \text{ Tg y}^{-1}$ ) and dead plant matter ( $\sim 2 \text{ Tg y}^{-1}$ ).

Warneke et al. (1999) described emissions from dead plant matter and proposed a potential source of  $6\text{--}8 \text{ Tg y}^{-1}$ , which Jacob et al. (2002) found to be inconsistent with the seasonal cycle observed at European sites and concluded that acetone could be consumed within the litter rather than emitted into the atmosphere. However, Karl et al. (2003) observed a fall peak in emissions and attributed this to senescing and decaying biomass in a hardwood forest in Michigan.

Soil emission has been reported by Schade and Goldstein (2001) in a ponderosa pine plantation with a Mediterranean climate in California, while Schade and Custer (2004) noted emissions from soil during a heat wave in Germany, attributing them to a biological production mechanism deep in the soil.

Calculations of absolute and relative contributions for each source and sink for acetone and all other compounds are continuously under review and greater importance now seems to be given to emission from plants. In line with the growing knowledge of the subject, the numbers reviewed here may underestimate biogenic emissions (Singh et al., 2004). For further information on acetone budget, sources, and sinks, see Singh et al. (1994, 2004) and Jacob et al. (2002).

#### 4. Aldehydes

The short-chain aldehydes emitted by plants are the  $\text{C}_1$  formaldehyde (HCHO) and the  $\text{C}_2$  acetaldehyde ( $\text{CH}_3\text{CHO}$ ). The formaldehyde origin within plants remains unclear. It seems to be a product of methanol oxidation, although its actual biochemical basis in plants is not known and other possible

origins such as 5,10-methylene-tetrahydrofolate dissociation, glyoxylate decarboxylation or oxidative demethylation reactions have been proposed (Hanson and Roje, 2001). Acetaldehyde formation is known to be caused, at least, by root metabolism in flooded plants and by sunflecks and leaf pyruvic acid decarboxylation. On one hand, in root systems ethanol production is triggered by anoxic conditions: the plant uses the classic ethanolic fermentation pathway to obtain energy by converting glucose to ethanol. Once in the leaf, under aerobic conditions, ethanol can be oxidized into acetaldehyde and further into acetate. Ethanol oxidation is mediated by alcohol dehydrogenase (ADH) and acetaldehyde emission should be seen essentially as a leak between acetaldehyde production and metabolism (Kreuzwieser et al., 2001; reviewed by Fall, 2003). On the other hand, transient acetaldehyde releases have been observed during light–dark transitions in the leaves of various tree species (Holzinger et al., 2000; Karl et al., 2002a; Graus et al., 2004; Hayward et al., 2004). To explain this phenomenon Karl et al. (2002a) proposed a pyruvate overflow mechanism that acts when cytosolic pyruvate accumulates during light–dark transitions and leads to increases in pyruvate decarboxylase activity (see Fall, 2003). Graus et al. (2004) concluded that a different biochemical pathway, unconnected to cytosolic pyruvate, must be active during such transitions and suggested that it is related to leaf response to wounding. In addition, these authors demonstrated that  $\text{CH}_3\text{CHO}$  emissions due to light–dark changes are not of quantitative significance under field conditions.

Evidence exists of the absorption of these oxVOCs by plants. Giese et al. (1994) demonstrated that formaldehyde was detoxified and metabolized by the spider plant (*Chlorophytum comosum*) and Schmitz et al. (2000) concluded that all higher plants with normal green leaves can probably metabolize HCHO. For both aldehydes, Kondo et al. (1995, 1996, 1998) stated that trees could act as an important sink, with absorption rates increasing in the following order: coniferous < evergreen broad-leaved < deciduous broad-leaved trees. Furthermore, Rottenberger et al. (2004) proposed that forests act as a sink rather than as a source for aldehydes in Amazonia. All these studies regarding the absorption of aldehydes agree that this process occurs via the stomata. Once inside the leaves, HCHO would be converted enzymatically into  $\text{CO}_2$  and thus enter the Calvin cycle (Giese et al., 1994;

Schmitz et al., 2000). The mechanism for acetaldehyde metabolism has not been studied yet although there is evidence that enzymatic pathways take  $\text{CH}_3\text{CHO}$  into the general metabolism (Rottenberger et al., 2004). According to Rottenberger et al. (2004), such metabolic pathways or the transport within the leaf tissue determine the uptake of acetaldehyde more than water solubility does. On the contrary, formaldehyde is more soluble and this characteristic accounts for most of its exchange between air and the substomatal compartment. On the basis of such observations it has been concluded that for HCHO mesophyll resistance may be of the same order as stomatal resistance (Kondo et al., 1998; Rottenberger et al., 2004). Aside from stomatal uptake, adsorption to the cuticle may also be an important sink for these aldehydes (Rottenberger et al., 2004, 2005).

Regarding emission from vegetation (Tables 4 and 5), some authors found that most of the short-chained carbonyl emissions from conifers (Cojocariu et al., 2004) and from both deciduous and coniferous trees (Martin et al., 1999) consisted of aldehydes. As stated before, according to the measurements made by Janson et al. (1999), the main carbonyl emitted by *Picea abies* and *Pinus sylvestris* is acetone. Acetaldehyde and formaldehyde make up  $26 \pm 19\%$  and  $10 \pm 16\%$  of the carbonyl flux, respectively, in *Picea abies*. In *Pinus sylvestris*, the percentages are  $11 \pm 8\%$  for acetaldehyde and  $10 \pm 12\%$  for formaldehyde.

A number of studies of *Quercus ilex* and *Pinus pinea* (Kesselmeier et al., 1997) and trees in New Mexico (Martin et al., 1999) found no clear correlation between emission and any physiological parameters; other studies conclude that fluxes of aldehydes are mostly determined by ambient mixing ratios (Kesselmeier et al., 1997; Rottenberger et al., 2004). Stomata have been seen to be the pathway for the aldehyde release (Kreuzwieser et al., 2000; Rottenberger et al., 2004), which—along with their role in uptake—means that they are the major pathway for the bidirectional exchange of aldehydes between plants and atmosphere, a process that is determined by mixing ratios and stomatal conductance.

Diurnal patterns of emission with higher rates at noon and in the afternoon than at night, when even deposition was observed, have been described for both aldehydes and for several plant species and canopy measurements (Kreuzwieser et al., 2000; Karl et al., 2004; Villanueva-Fierro et al., 2004;

Cojocariu et al., 2005). In an alfalfa field acetaldehyde emissions in the afternoon and deposition in the evening and morning have also been reported (Warneke et al., 2002).

Hayward et al. (2004) reported that acetaldehyde emissions showed exponential temperature dependence in Sitka spruce (*Picea sitchensis*) and suggested that emissions only originate from internal pools. Another suggested explanation for this behavior is that enzymatic reactions mediate the production and emission of carbonyls (Cojocariu et al., 2004).

In alfalfa and other hay-field experiments related to physical stress, enhanced emissions of  $\text{CH}_3\text{CHO}$  were reported in two phases: during the cutting of hay and while the harvested material was drying (de Gouw et al., 2000; Karl et al., 2001b; Warneke et al., 2002). These authors concluded that as a result crop harvesting may influence local air chemistry, since acetaldehyde has a short atmospheric life that does not allow for significant transportation by wind (Sanhueza et al., 2001). Similarly, in *Succisa pratensis*, acetaldehyde emissions occurred just after the plant was attacked by a herbivore (Peñuelas et al., 2005); likewise, acetaldehyde emissions of *Fagus sylvatica* increased after ozone exposition (Cojocariu et al., 2005). Stress by anoxia in the roots, usually as a result of flooding, also produces enhanced emission of acetaldehyde (up to 10–37-fold [Kreuzwieser et al., 1999a; Holzinger et al., 2000]) and this type of  $\text{CH}_3\text{CHO}$  emission is controlled by production in the leaves, which in turn is at least in part controlled by the delivery of ethanol via the transpiration stream (Kreuzwieser et al., 1999a, b, 2000, 2001; Holzinger et al., 2000; Cojocariu et al., 2004).

The lifetime of these short-chained aldehydes in summer is estimated to be in the order of a few hours (Possanzini et al., 2002). They are removed from the air by photolysis and the reaction with OH radicals, leading to the formation of photochemical oxidants such as peroxyacetyl nitrate (PAN) and ozone (Atkinson, 2000). These and subsequent reactions result in the formation of more OH radicals, which ensures that formaldehyde and acetaldehyde are important sources of free radicals (Possanzini et al., 2002).

After isoprene, formaldehyde is the most abundant VOC in the tropical forest air (Kesselmeier et al., 2000, 2002). In rural and remote sites of New Mexico and Italy (Larsen et al., 1998; Villanueva-Fierro et al., 2004) and in the urban air of Rome

Table 4  
Foliar emissions and atmospheric mixing ratios of formaldehyde (HCHO)

Formaldehyde					
<i>Foliar emissions</i> <sup>a</sup>					
Species	Emission rates		Location	Period	Reference
	nmol m <sup>-2</sup> s <sup>-1</sup>	ng g <sup>-1</sup> dw h <sup>-1</sup>			
<i>Quercus ilex</i>		382–520 <sup>d</sup>	Castelporziano (Italy)	May 1994	Kesselmeier et al. (1997)
<i>Pinus pinea</i>		519–589 <sup>d</sup>	Castelporziano (Italy)	May 1994	Kesselmeier et al. (1997)
<i>Pinus ponderosa</i>		500 ± 400 <sup>c</sup>	New Mexico (USA)	Summer 1997	Villanueva-Fierro et al. (2004)
<i>Populus fremontii</i>		4070 ± 3570 <sup>c</sup>	New Mexico (USA)	Summer 1997	Villanueva-Fierro et al. (2004)
diverse		70–1658 <sup>e</sup>	New Mexico (USA)	Summer 1996	Martin et al. (1999)
<i>Fagus sylvatica</i>	0.66		Freising (Germany)	Aug. 2001, 2002	Cojocariu et al. (2005)
<i>Atmospheric mixing ratios</i> <sup>b</sup>					
Site	Mixing ratio (ppbv)		Location	Period	Reference
Tropical forest	0.5–3		Amazonia (Brazil)	March–April (wet season) 1998	Kesselmeier et al. (2000)
Rain forest	(1.5–4)		Amazonia (Rondonia, Brazil)	Wet season 1999	Kesselmeier et al. (2002)
Rain forest	(5–25)		Amazonia (Rondonia, Brazil)	Dry season 1999	Kesselmeier et al. (2002)
Remote forested site	2.3 ± 2.4		Langmuir (NM, USA)	Summer 1997	Villanueva-Fierro et al. (2004)
Rural ambient	3.4 ± 1.4		Socorro (NM, USA)	Summer 1997	Villanueva-Fierro et al. (2004)
Rural ambient	2.61 ± 1.94		Annaka (Japan)	June 1997–March 2003	Tago et al. (2005)
Rural ambient	1.4 ± 0.8/0.3–4.2		Gopalpura (India)	Monsoon 1995, 1996	Khare et al. (1997)
Rural ambient	0.03–6.5		diverse (Germany, N.America)	diverse	Khare et al. (1997)
Rural ambient	0.4–5.0		diverse (Germany, Canada)	diverse	Granby et al. (1997)
Rural and semi-rural ambients	0.4–13.4		diverse (Europe and N.America)	diverse	Christensen et al. (2000)
Semi-rural ambient	0.9 ± 0.5/0.1–2.8		Denmark	February 1994	Granby et al. (1997)
Semi-rural ambient	1.2/0.1–4.7		Denmark	May–July 1995	Christensen et al. (2000)
Semi-rural ambient	0.63–13.4		diverse (Austria, USA)	diverse	Granby et al. (1997)
Urban ambient	7–28/18 ± 6		Rome (Italy)	Summer 1994–96	Possanzini et al. (2002)
Urban ambient	7–20/10 ± 4		Rome (Italy)	Winter 1995–97	Possanzini et al. (2002)
Urban ambient	2.6 ± 0.7/0.2–6.4		Copenhagen (Denmark)	February 1994	Granby et al. (1997)
Urban ambient	1.9 ± 0.9/0.1–4.3		Osaka (Japan)	May–December 1997	Nguyen et al. (2001)
Urban ambient	5.0 ± 2.8/1.4–9.7		São Paulo (Brazil)	February (summer) 1998	Nguyen et al. (2001)
Urban ambient	0.04–29		Athens (Greece)	June–December 2000	Bakeas et al. (2003)
Urban ambient	3.14 ± 1.87		Isesaki (Japan)	June 1997–March 2003	Tago et al. (2005)
Urban ambient	5.3–26.4 <sup>e</sup>		diverse (world)	diverse	Villanueva-Fierro et al. (2004)
Urban ambient	1.4–150 <sup>e</sup>		diverse (America)	diverse	Khare et al. (1997)
Urban ambient	4–176		diverse (world)	diverse	Granby et al. (1997)
Atmosphere 0–12 km height	0.05–0.21 <sup>e</sup>		Tropical Pacific troposphere	February–April 2001	Singh et al. (2004)
Marine air	0.12–1.0		diverse (world)	diverse	Khare et al. (1997)
diverse	0.94–17 <sup>e</sup>		diverse (world)	diverse	Nguyen et al. (2001)

<sup>a</sup>Foliar emissions measured with enclosure chambers. Displayed values are means or range of observed emissions. Rates are referred to leaf area (m<sup>2</sup>) or leaf dry weight (dw).

<sup>b</sup>Atmospheric mixing ratios reported in the literature. Displayed values are mean mixing ratios and/or range of observed values. Numbers between brackets represent maximum mixing ratios.

<sup>c</sup>Normalized standard emission rate at 303 K and 1000 μmol m<sup>-2</sup> s<sup>-1</sup> PAR (photosynthetic active radiation) flux, fitted according to equations developed by Guenther et al. (1993, 1995).

<sup>d</sup>Normalized standard emission rate at 303 K, fitted according to equations developed by Guenther et al. (1993, 1995).

<sup>e</sup>Range of means.

and Athens (Possanzini et al., 2002; Bakeas et al., 2003) it is also the prevalent carbonyl compound, being followed by acetaldehyde. HCHO is the most abundant carbonyl in the atmosphere (Muir and Shirazi, 1996) and it is reasonable to assume that CH<sub>3</sub>CHO is globally

ubiquitous and its mixing ratios are substantial (Singh et al., 2004 and references therein). See Tables 4 and 5 for examples of the measurements of the mixing ratios of these carbonyl compounds in the range of 0.03–176 ppbv for formaldehyde and 0–37.1 ppbv for acetaldehyde.

Table 5  
Foliar emissions, ecosystem fluxes and atmospheric mixing ratios of acetaldehyde (CH<sub>3</sub>CHO)

Acetaldehyde					
<i>Foliar emissions</i> <sup>a</sup>					
Species	Emission rates		Location	Period	Reference
	nmol m <sup>-2</sup> s <sup>-1</sup>	ng g <sup>-1</sup> dw h <sup>-1</sup>			
<i>Quercus ilex</i>		691 ± 214 <sup>e</sup>	Castelporziano (Italy)	May 1994	Kesselmeier et al. (1997)
<i>Pinus pinea</i>		773–1034 <sup>e</sup>	Castelporziano (Italy)	May 1994	Kesselmeier et al. (1997)
<i>Populus fremontii</i>		1190 ± 1360 <sup>d</sup>	New Mexico (USA)	Summer 1997	Villanueva-Fierro et al. (2004)
<i>Pinus ponderosa</i>		250 ± 190 <sup>d</sup>	New Mexico (USA)	Summer 1997	Villanueva-Fierro et al. (2004)
diverse		49–1122 <sup>f</sup>	New Mexico (USA)	Summer 1996	Martin et al. (1999)
<i>Fagus sylvatica</i>	0.75		Freising (Germany)	August 2001, 2002	Cojocariu et al. (2005)
<i>Picea abies</i>	0.008–1.66		Bavaria (Germany)	July–August 2001, 2002	Cojocariu et al. (2004)
<i>Quercus ilex</i>	0.23–0.75 <sup>f</sup>		Tuscany (Italy)	June, July, Sep. 2000, 2001	Kreuzwieser et al. (2002)
<i>Quercus ilex</i>	0.3		Laboratory	June 2001	Holzinger et al. (2000)
<i>Populus x canadensis</i>	0.33–0.83		Laboratory		Kreuzwieser et al. (2001)
<i>Populus x canadensis</i>	0.45	2160	Laboratory		Kreuzwieser et al. (1999a)
<i>Picea sitchensis</i>		370/30–530	Laboratory		Hayward et al. (2004)
<i>Ecosystem fluxes</i> <sup>b</sup>					
Ecosystem	Flux (mg m <sup>-2</sup> h <sup>-1</sup> )		Location	Period	Reference
Tropical rain forest	0.08 (0.2)		Costa Rica	April (dry season) 2003	Karl et al. (2004)
Mixed hardwood forest	0.3 (1.0)		N Michigan (USA)	September–November 2001	Karl et al. (2003)
Mixed hardwood forest	0.2 (0.7)		N Michigan (USA)	April–July 2002	Karl et al. (2003)
Ponderosa pine plantation	0.03–0.26 <sup>f</sup>		Sierra Nevada (CA, USA)	July–September 1999	Schade and Goldstein (2001)
Subalpine forest	0.4		Rocky Mountains (CO, USA)	July 2001	Karl et al. (2002b)
<i>Atmospheric mixing ratios</i> <sup>c</sup>					
Site	Mixing ratio (ppbv)		Location	Period	Reference
Rain forest	<1		Amazonia (Rondonia, Brazil)	Wet season 1999	Kesselmeier et al. (2002)
Rain forest	(5)		Amazonia (Rondonia, Brazil)	Dry season 1999	Kesselmeier et al. (2002)
Tropical rain forest	0.26–0.44		Costa Rica	April (dry season) 2003	Karl et al. (2004)
Savannah	0.85		Venezuela	January–February 2000	Sanhueza et al. (2001)
Remote forested site	1.0 ± 0.7		Langmuir (NM, USA)	Summer 1997	Villanueva-Fierro et al. (2004)
Mixed hardwood forest	0.4 (1.6)		N Michigan (USA)	September–November 2001	Karl et al. (2003)
Mixed hardwood forest	0.4 (2.7)		N Michigan (USA)	April–July 2002	Karl et al. (2003)
Rural ambient	1.4 ± 0.9		Socorro (NM, USA)	Summer 1997	Villanueva-Fierro et al. (2004)
Rural ambient	0.3–1.2		diverse (Germany, Canada)	diverse	Granby et al. (1997)

Table 5 (continued)

<i>Atmospheric mixing ratios<sup>c</sup></i>				
Site	Mixing ratio (ppbv)	Location	Period	Reference
Rural and semi-rural ambients	0.2–5.0	diverse (Europe and N.America)	diverse	Christensen et al. (2000)
Semi-rural ambient	0.7±0.4/ 0.2–1.4	Denmark	February 1994	Granby et al. (1997)
Semi-rural ambient	0.8/0.2–3.6	Denmark	May–July 1995	Christensen et al. (2000)
Semi-urban ambient	1.56–3.29 <sup>f</sup>	Bellaterra, Catalonia (Spain)	December 2003–October 2004	Filella and Peñuelas (2006)
Urban ambient	2.19–24.95	Athens (Greece)	June–December 2000	Bakeas et al. (2003)
Urban ambient	3–17/10±4	Rome (Italy)	Summer 1994–96	Possanzini et al. (2002)
Urban ambient	2–7/4±2	Rome (Italy)	Winter 1995–97	Possanzini et al. (2002)
Urban ambient	1.0±0.7/ 0.2–1.8	Copenhagen (Denmark)	February 1994	Granby et al. (1997)
Urban ambient	5.4±2.8/ 1.0–10.2	São Paulo (Brazil)	February (summer) 1998	Nguyen et al. (2001)
Urban ambient	1.5±0.8/ 0.6–3.5	Osaka (Japan)	May–December 1997	Nguyen et al. (2001)
Urban ambient	3.8–37.1 <sup>f</sup>	diverse (world)	diverse	Villanueva-Fierro et al. (2004)
Urban ambient	0–35	diverse (world)	diverse	Granby et al. (1997)
Atmosphere 0–12 km height	0.06–0.2 <sup>f</sup>	Tropical Pacific troposphere	February–April 2001	Singh et al. (2004)
diverse	0.77–17.3 <sup>f</sup>	diverse (world)	diverse	Nguyen et al. (2001)

<sup>a</sup>Foliar emissions measured with enclosure chambers. Displayed values are means and/or range of observed emissions. Rates are referred to leaf area (m<sup>2</sup>) or leaf dry weight (dw).

<sup>b</sup>Ecosystem fluxes measured with micrometeorological techniques. Displayed values are mean daytime emissions or range of observed values. Numbers between brackets represent daily maximum peaks of emission. Fluxes are referred to ground surface area (m<sup>2</sup>).

<sup>c</sup>Atmospheric mixing ratios reported in the literature. Displayed values are mean mixing ratios and/or range of observed values. Numbers between brackets represent maximum mixing ratios.

<sup>d</sup>Normalized standard emission rate at 303 K and 1000 μmol m<sup>-2</sup> s<sup>-1</sup> PAR (photosynthetic active radiation) flux, fitted according to equations developed by Guenther et al. (1993, 1995).

<sup>e</sup>Normalized standard emission rate at 303 K, fitted according to equations developed by Guenther et al. (1993, 1995).

<sup>f</sup>Range of means.

These short-chained aldehydes have been recognised as having a great impact on human health given their potentially carcinogenic and mutagenic properties and their capacity for forming toxic and phytotoxic radical intermediates and stable species (Possanzini et al., 2002 and references therein). Regarding plants, although high atmospheric HCHO concentrations have been found to slightly delay budbreak and depress growth in Douglas fir (*Pseudotsuga menziesii*), the results were not statistically significant (Muir and Shirazi, 1996).

Formaldehyde and acetaldehyde are directly released into the atmosphere by vegetation and soils (specially CH<sub>3</sub>CHO; Schade and Goldstein, 2001), by industrial processes and motor exhausts (Granby et al., 1997; Possanzini et al., 2002; Bakeas

et al., 2003), and by biomass burning (Holzinger et al., 1999). In the future, if vehicles increasingly become powered by methanol and natural gas, formaldehyde emissions may predominate over secondary production (Altshuller, 1993). In Amazonia Kesselmeier et al. (2002) reported an increase up to 25 ppbv in the concentration of these aldehydes, which these authors link to the prevalence of forest fires. Emission from dead plant matter has also been proven to occur in the case of acetaldehyde (Warneke et al., 1999), Karl et al. (2003) attributed a fall peak of atmospheric CH<sub>3</sub>CHO to this phenomenon, as in the case of acetone.

Nevertheless, both aldehydes have as a major atmospheric source the indirect origin through

oxidation (via OH, NO<sub>3</sub> and O<sub>3</sub> radicals, for example) of other—biogenic or anthropogenic—hydrocarbons of higher molecular weight (Possanzini et al., 2002; Rottenberger et al., 2004; Lee et al., 2006a, b). For HCHO the main precursor hydrocarbon is thought to be isoprene, at least in the Amazon (Kesselmeier et al., 2000); other contributing hydrocarbons are methane, methanol, and acetaldehyde (Macdonald et al., 2001; Schade and Goldstein, 2001). For CH<sub>3</sub>CHO, the largest source seems to be ethane and propene oxidation (Singh et al., 2004).

## 5. Alcohols

The short-chain alcohols emitted by plants are methanol (CH<sub>3</sub>OH) and ethanol (CH<sub>3</sub>CH<sub>2</sub>OH). Methanol is a product of the demethylation of pectin during cell wall formation (biochemical details reviewed by Fall, 2003). Ethanol is produced in fermentative reactions when energy is obtained from glucose.

As in the case of acids, the high solubility of these alcohols ensures that their release is stomata-dependent (Macdonald and Fall, 1993; Nemecek-marshall et al., 1995; Schade and Goldstein, 2002) and also favors emission bursts after stomatal opening under the control of the gas–liquid phase equilibration of the alcohol within the leaf (Niinemets and Reichstein, 2003b). Similar bursts of methanol have been attributed to evaporation in the morning of the dew (Sanhueza et al., 2001; Warneke et al., 2002), given that at night methanol will probably be deposited on dew-wetted surfaces (Holzinger et al., 2001).

The emission of methanol (see Table 6) has been related to leaf development and generally declines with increasing leaf age after leaf expansion (Nemecek-marshall et al., 1995; Karl et al., 2003). A model designed by Galbally and Kirstine (2002) links plant cell growth to the global atmospheric concentration of methanol, with the ocean acting as a buffer for methanol concentration. As in the case of acetaldehyde, methanol emissions showed exponential temperature dependence in *Picea sitchensis* (Hayward et al., 2004); a similar exponential relationship between temperature and CH<sub>3</sub>OH emissions has also been observed in *Picea abies* (2007). This exponential relationship suggests that emissions may originate from an internal pool (Hayward et al., 2004) and/or that enzymatic mediation is involved, as has been

suggested for carbonyl emission by Cojocariu et al. (2004).

In measurements taken in tropical rain forest canopies, methanol was emitted by day and deposited at night (Karl et al., 2004); measurements in different forests of the USA showed no distinct diurnal patterns (Baker et al., 2001; Schade and Goldstein, 2001). In an alfalfa field, a significant methanol flux was observed from undisturbed plants. After cutting, the emission of methanol was enhanced during the three days the alfalfa was drying (Warneke et al., 2002). In the same way, two studies on crops revealed increased emissions during cutting and, above all, during drying. Thus, hay harvesting may have an influence on local air chemistry (de Gouw et al., 2000; Karl et al., 2001b). Methanol emissions in other stress situations have been also described. Studying the reaction of *Succisa pratensis* to attacks by herbivore caterpillars, Peñuelas et al. (2005) noted a great release of methanol 24 h after attack. The trigger for these caterpillar-elicited emissions seems to be the pH shift caused by the oral secretions of the larvae (von Dahl et al., 2006). In young holm oak trees subjected to flooding, emission also increased (Holzinger et al., 2000).

Methanol is the second most abundant organic gas in the atmosphere after methane (Jacob et al., 2005), with mixing ratios lying within the range 0.2–195 ppbv (Table 6). Its sources include emissions from the vegetation and soil (Fukui and Doskey, 1998; Schade and Goldstein, 2001) possibly linked to the physico-chemical degradation of soil organic matter (Schade and Custer, 2004), biomass burning (Holzinger et al., 1999; Kesselmeier et al., 2002), and dead plant matter (Warneke et al., 1999). Methanol atmospheric sinks are oxidation into formaldehyde and formic acid, dry and wet deposition and uptake by ocean. Its lifetime in the atmosphere lasts for about 10 days (Jacob et al., 2005). For more extensive considerations about methanol budget see Heikes et al. (2002) and Jacob et al. (2005).

A number of papers exist that deal with the effects of methanol on plants. Experiments testing the reaction of *Arabidopsis thaliana* when exposed to methanol showed that CH<sub>3</sub>OH affects the expression of hundreds of genes and activates multiple detoxification and signalling pathways (Downie et al., 2004). Furthermore, methanol emitted by *Nicotiana attenuata* after caterpillar attack has been reported to suppress plant defense responses to herbivores (von Dahl et al., 2006).

Table 6  
Foliar emissions, ecosystem fluxes and atmospheric mixing ratios of methanol (CH<sub>3</sub>OH)

Methanol					
<i>Foliar emissions</i> <sup>a</sup>					
Species	Emission rates		Location	Period	Reference
	nmol m <sup>-2</sup> s <sup>-1</sup>	ng g <sup>-1</sup> dw h <sup>-1</sup>			
<i>Picea sitchensis</i>		780/20–2390	Laboratory		Hayward et al. (2004)
<i>Quercus ilex</i>	2.03		Laboratory	June 2001	Holzinger et al. (2000)
<i>Succisa pratensis</i>	3.6		Laboratory		Peñuelas et al. (2005)
<i>Ecosystem fluxes</i> <sup>b</sup>					
Ecosystem	Flux (mg m <sup>-2</sup> h <sup>-1</sup> )		Location	Period	Reference
Tropical rain forest	0.13 (0.5)		Costa Rica	April (dry season) 2003	Karl et al. (2004)
Mixed hardwood forest	0.5 (1.5)		N Michigan (USA)	September–November 2001	Karl et al. (2003)
Mixed hardwood forest	0.9 (2.0)		N Michigan (USA)	April–July 2002	Karl et al. (2003)
Subalpine forest	(1)		Rocky Mountains (CO, USA)	July 2001	Karl et al. (2002b)
Subalpine forest	(2.6)		Rocky Mountains (CO, USA)	Summer 1999	Baker et al. (2001)
Ponderosa pine plantation	0.67–2.91 <sup>d</sup> (4)		Sierra Nevada (CA, USA)	July–September 1999	Schade and Goldstein (2001)
Alfalfa field	(4–10)		Colorado (USA)	August 2000	Warneke et al. (2002)
Grassland	0.46 ± 0.07 <sup>c</sup>		Midwestern USA	Growing season (2-y period)	Fukui and Doskey (1998)
<i>Atmospheric mixing ratios</i> <sup>c</sup>					
Site	Mixing ratio (ppbv)		Location	Period	Reference
Rain forest	1–6		Amazonia (Rondonia, Brazil)	Dry season 1999	Kesselmeier et al. (2002)
Tropical rain forest	1.53–2.78		Costa Rica	April (dry season) 2003	Karl et al. (2004)
Savannah	1.54		Venezuela	January–February 2000	Sanhueza et al. (2001)
Mixed hardwood forest	4.2 (15.6)		N Michigan (USA)	September–November 2001	Karl et al. (2003)
Mixed hardwood forest	7.7 (21.0)		N Michigan (USA)	April–July 2002	Karl et al. (2003)
Ponderosa pine plantation	1.1–41		Sierra Nevada (CA, USA)	July–September 1999	Schade and Goldstein (2001)
Semi-urban ambient	4.61–12.92 <sup>d</sup>		Bellaterra, Catalonia (Spain)	December 2003–October 2004	Filella and Peñuelas (2006)
Urban ambient	34.1 ± 9.2/ 20.8–51.1		São Paulo (Brazil)	Feb. (summer) 1998	Nguyen et al. (2001)
Urban ambient	5.8 ± 3.8/ 0.3–17.3		Osaka (Japan)	May–December 1997	Nguyen et al. (2001)
Atmosphere 0–12 km height	0.51–0.86 <sup>d</sup>		Tropical Pacific troposphere	February–April 2001	Singh et al. (2004)
Atmosphere (near surface)	0.2–195 <sup>d</sup>		diverse (world)	diverse	Heikes et al. (2002)
Atmosphere (troposphere)	0.6–20 <sup>d</sup>		diverse (world)	diverse	Heikes et al. (2002)
diverse	3.6–19.6 <sup>d</sup>		diverse (world)	diverse	Nguyen et al. (2001)

<sup>a</sup>Foliar emissions measured with enclosure chambers. Displayed values are means and/or range of observed emissions. Rates are referred to leaf area (m<sup>2</sup>) or leaf dry weight (dw).

<sup>b</sup>Ecosystem fluxes measured with micrometeorological techniques. Displayed values are mean daytime emissions or range of observed values. Numbers between brackets represent daily maximum peaks of emission. Fluxes are referred to ground surface area (m<sup>2</sup>).

<sup>c</sup>Atmospheric mixing ratios reported in the literature. Displayed values are mean mixing ratios and/or range of observed values. Numbers between brackets represent maximum mixing ratios.

<sup>d</sup>Range of means.

<sup>e</sup>Static enclosure technique.

Table 7  
Foliar emissions, ecosystem fluxes and atmospheric mixing ratios of Ethanol (CH<sub>3</sub>CH<sub>2</sub>OH)

Ethanol					
<i>Foliar emissions</i> <sup>a</sup>					
Species	Emission rates		Location	Period	Reference
	nmol m <sup>-2</sup> s <sup>-1</sup>	ng g <sup>-1</sup> dw h <sup>-1</sup>			
<i>Quercus ilex</i>	0.23 <sup>c</sup>		Laboratory	June 2001	Holzinger et al. (2000)
<i>Populus x canescens</i>	0.33–0.83		Laboratory		Kreuzwieser et al. (2001)
<i>Ecosystem fluxes</i> <sup>b</sup>					
Ecosystem	Flux (mg m <sup>-2</sup> h <sup>-1</sup> )		Location	Period	Reference
Ponderosa pine plantation	0.19–0.52 <sup>d</sup> (0.6)		Sierra Nevada (CA, USA)	July–September 1999	Schade and Goldstein (2001)
<i>Atmospheric mixing ratios</i> <sup>c</sup>					
Site	Mixing ratio (ppbv)		Location	Period	Reference
Ponderosa pine plantation	0.1–9.6		Sierra Nevada (CA, USA)	July–September 1999	Schade and Goldstein (2001)
Urban ambient	176.3 ± 38.1/109.9–242.7		São Paulo (Brazil)	February (summer) 1998	Nguyen et al. (2001)
Urban ambient	8.2 ± 4.6/1.4–21.9		Osaka (Japan)	May–December 1997	Nguyen et al. (2001)
Atmosphere 0–12 km height diverse	0.02–0.03 <sup>d</sup>		Tropical Pacific troposphere diverse (world)	February–April 2001	Singh et al. (2004)
	0.25–310 <sup>d</sup>			diverse	Nguyen et al. (2001)

<sup>a</sup>Foliar emissions measured with enclosure chambers. Displayed values are means or range of observed emissions. Rates are referred to leaf area (m<sup>2</sup>) or leaf dry weight (dw).

<sup>b</sup>Ecosystem fluxes measured with micrometeorological techniques. Displayed values are mean daytime emissions or range of observed values. Numbers between brackets represent daily maximum peaks of emission. Fluxes are referred to ground surface area (m<sup>2</sup>).

<sup>c</sup>Atmospheric mixing ratios reported in the literature. Displayed values are mean mixing ratios and/or range of observed values.

<sup>d</sup>Range of means

<sup>e</sup>May be overestimated by a factor of 2.

Some authors have reported enhanced productivity in C<sub>3</sub> plants sprayed with methanol (see Fall and Benson, 1996, and the references therein). As has been reported for sycamore (*Acer pseudoplatanus*) cell cultures, plant tissues can metabolise CH<sub>3</sub>OH at a rate of 0.2 μmol h<sup>-1</sup> g<sup>-1</sup> wet weight (Gout et al., 2000).

The relationship of ethanol with acetaldehyde and root hypoxia has been reviewed in the previous section on aldehydes. However, Kreuzwieser et al. (1999a) reported higher emissions of acetaldehyde than ethanol in leaves of *Populus x canescens*, while Holzinger et al. (2000) found the contrary in leaves of *Quercus ilex*. Schade and Goldstein (2002) found an increase in ethanol emissions after high ozone deposition fluxes in *Pinus ponderosa*, supporting the

theory that ozone-induced stress may trigger fermentation processes in the leaves.

Ethanol is present in the atmosphere in mixing ratios generally below 10 ppbv (Table 7) and has an atmospheric lifetime of ~3.5 days (Singh et al., 2004). Biogenic emissions seem to be the most important source of ethanol, followed by biomass burning, the photochemical oxidation of hydrocarbons, and anthropogenic-related releases (Singh et al., 2004). This last type of emission includes motor exhausts in countries such as Brazil, where ethanol is mixed with fuel and thus reaches high concentrations (200–300 ppbv; see Table 7). Dead plant matter is also a source of ethanol (Warneke et al., 1999). Ethanol is removed from the atmosphere by oxidation into acetaldehyde (Atkinson,

2000) and other compounds. As a precursor of PAN, it may have a significant role in the long-range transportation of  $\text{NO}_x$  (Schade and Goldstein, 2001).

## 6. Final remarks

All these short-chain oxygenated VOCs have some common characteristics which set them apart from other widely studied VOCs such as isoprene and monoterpenes. For example, it is noticeable that their higher water solubility (low gas-aqueous phase partitioning coefficient,  $H$ ) partly relates their emission to transpiration and makes it sensitive to changes in stomatal conductance. Compared to isoprenoids, they have a long atmospheric lifespan and so can affect tropospheric chemistry far from where they are released. These compounds build up considerable concentrations in the atmosphere, in the range of ppbv. Likewise, under non-stress conditions plants may emit all of these oxVOCs together (adding up minimum and maximum values reported for each compound, from Tables 1–7), at fluxes ranging from 0.2 up to  $4.8 \mu\text{g}(\text{C})\text{g}^{-1}(\text{leaf dry weight})\text{h}^{-1}$ ; these rates increase several fold when under stress. These values lie within the lower part of the reported range of monoterpene [ $0.02\text{--}41 \mu\text{g}(\text{C})\text{g}^{-1}(\text{leaf dry weight})\text{h}^{-1}$ ] and isoprene [ $0.004\text{--}152 \mu\text{g}(\text{C})\text{g}^{-1}(\text{leaf dry weight})\text{h}^{-1}$ ] emission fluxes in a number of species and are comparable to fluxes in many species (Kesselmeier and Staudt, 1999). More information on the emission/uptake of these compounds is needed to correctly quantify and model biosphere–atmosphere short-chain oxVOCs exchange. Gaps in our knowledge of the metabolic reactions responsible for compound synthesis and degradation, their localization inside the cells, and, above all, the biotic and abiotic factors controlling emission or uptake are issues that should be addressed as soon as possible. The relative importance and functioning of the cuticle and stomatic pathways in every particular situation a plant faces throughout its lifetime warrants future investigation, as does the possible role of the oxVOCs in the formation and/or growth of atmospheric particulate matter, and the balance between biogenic emission and photochemical production in certain situations. In the same way, further knowledge regarding these compounds may allow us to identify physiological and ecophysiological functions of which we are currently unaware.

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