Volatile organic compound emissions in relation to plant carbon fixation and the terrestrial carbon budget

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Received 19 October 2001; revised 12 March 2002; accepted 22 July 2002; published 11 December 2002.

[1] A substantial amount of carbon is emitted by terrestrial vegetation as biogenic volatile organic compounds (VOC), which contributes to the oxidative capacity of the atmosphere, to particle production and to the carbon cycle. With regard to the carbon budget of the terrestrial biosphere, a release of these carbon compounds is regarded as a loss of photosynthetically fixed carbon. The significance of this loss for the regional and global carbon cycles is controversial. We estimate the amount of VOC carbon emitted in relation to the CO_2 taken up, based on our own enclosure and micrometeorological flux measurements of VOC emissions and CO_2 exchange within the Mediterranean area and the tropical rainforest in Amazonia and on literature data. While VOC flux estimates are small in relation to net primary productivity and gross primary productivity, the amount of carbon lost as VOC emissions can be highly significant relative to net ecosystem productivity. In fact, VOC losses are of the same order of magnitude as net biome productivity. Although we must assume that large amounts of these reemissions are recycled within the biosphere, a substantial part can be assumed to be lost into longer-lived oxidation products that are lost from the terrestrial biosphere by transport. However, our current knowledge does not allow a reliable estimation of this carbon loss. *INDEX TERMS:* 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 1615 Global Change: Biogeochemical processes (4805); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; *KEYWORDS:* carbon cycle, volatile organic compounds (VOC)

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

1. Introduction

[2] Terrestrial ecosystems are thought to be the most substantial global carbon sink besides the oceans. Around 120 Pg C a^{-1} (Pg = 10^{15} g) are fixed by the photosynthetic carbon dioxide assimilation of green vegetation; this overall amount is termed the gross primary production (GPP). Of this total carbon, about half is released back to the atmosphere through plant respiration (autotrophic respiration, R_a), leaving a net primary production (NPP) of about 60 Pg C a^{-1}, of which 50 Pg C a^{-1} returns to the atmosphere via decomposition of plant matter and soils [*Intergovernmental Panel on Climate Change* (*IPCC*), 2001] (heterotrophic respiration, R_h). The remaining ca. 10 Pg C a^{-1} is the net amount of biomass carbon referred to as the net ecosystem production [NEP; *IPCC*, 2001]. The absolute amount of NEP depends on the delicate balance between GPP, R_a, and R_h. However, additional carbon is also lost through fires, by dissolved organic and inorganic carbon in rivers, harvesting and other forest clearing, which ultimately results in the net land uptake of carbon termed the net biome production (NBP). NBP is estimated to range around 0.2 ± 0.7 Pg C a^{-1} for 1980–1989 and 1.4 ± 0.7 Pg C a^{-1} for 1989–1998. Intensive research is ongoing to attribute this net residual sink to different biomes and to reduce the uncertainties associated with its estimates. Due to the small ultimate residual sink, each flux of carbon into and out of terrestrial ecosystems needs to be investigated and accounted for to allow reasonable estimates for the processes involved in carbon sequestration in the biosphere. A substantial amount of carbon is reemitted as volatile organic compounds (VOC) by terrestrial vegetation [*Fehsenfeld et al.*, 1992; *Guenther et al.*, 1995; *Kesselmeier and Staudt*, 1999], with the dominant class of emitted compounds being isoprenoids.

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0886-6236/02/2001GB001813

The amount of carbon emitted by plants as isoprene, probably the most substantial fraction of isoprenoid emission, accounts for up to 2% of NPP in most cases, but can reach higher values (15–50%) under special conditions [*Sharkey et al.*, 1991a, 1991b, 1996; *Sharkey and Loreto*, 1993; *Harley et al.*, 1999]. However, the production and release of organic carbon by VOC emission have rarely been considered in carbon budget calculations. The likely reasons for this omission are the great variability in the emission patterns of the diverse plant species and vegetation types as well as the insufficient knowledge about the number and amount of different VOC species emitted. In particular, the release of compounds other than isoprenoids has not been examined extensively, although other compounds, which are often emitted in response to several stress effects (e.g., wounding, flooding), are getting more and more attention [*Kimmerer and Kozlowski*, 1982; *Kimmerer and MacDonald*, 1987; *De Gouw et al.*, 1999; *Fall et al.*, 1999; *Heiden et al.*, 1999; *Kreuzwieser et al.*, 1999; *Wilske and Kesselmeier*, 1999; *Kesselmeier*, 2001]. Nevertheless, current knowledge suggests that isoprenoid emissions form the dominant part of VOC emissions. In order to assess the impact of biogenic VOC emissions on the uptake of carbon by the terrestrial vegetation and its relation to the global carbon budget, we compared the VOC carbon emissions with the net ecosystem carbon gain.

2. Results and Discussion

[3] Considering the physiological significance of the release of volatile organic compounds, the amount of the lost carbon in relation to the CO_2-carbon as assimilated and metabolized has gained interest for decades. Table 1 reviews data on total carbon emitted as isoprenoids related to the photosynthetically fixed carbon, given as net photosynthesis, NPP or NEP. Already *Went* [1959, 1960a, 1960b] proposed a first estimate of 5% based on NEP estimates for a shrubland ecotype. This number still fits today into a larger set of regional estimates as published for a few ecotypes. Numerous investigations on single plant species resulted in numbers based on the actual rate of photosynthesis and some based on NPP in cases where a 24 hour cycle could be taken into consideration. Overall, the reported ranges of carbon loss are in reasonable accordance with the first estimates made by *Went* [1959]. However, stress effects can lead to a significant increase by an order of magnitude (see Table 1).

[4] During the last decade, we have performed numerous studies of plant/atmosphere VOC exchange in relation to plant primary metabolism, and have collected data from different plant species using dynamic branch enclosures (cuvettes) within several field studies taking cycles of 24 hours or more into account. We relate VOC release to net photosynthetic uptake of CO_2 by branches within the cuvette (net photosynthesis, i.e. net primary production, $NPP_{cuvette}$). Based on 24 hour measurements including the dark and night period, $NPP_{cuvette}$ at the branch level can be regarded as analogous to the NPP of a whole forest ecosystem, which is the difference between the total amount of carbon taken up by plants (i.e. the gross primary production (GPP)) and the amount given back to the atmosphere through autotrophic plant respiration (R_a). However, it has to be noted that $NPP_{cuvette}$ does not include stem or root respiration or storage. On a broader scale, micrometeorological flux measurements at the forest canopy level (i.e., on an ecosystem level) include considerable carbon loss by heterotrophic soil respiration (R_h). Subtraction of this carbon loss from the net primary production (NPP) yields the net ecosystem productivity (NEP). As the canopy flux measurement approach cannot distinguish between plant and soil respiration processes, the total CO_2 flux data cannot be directly compared with carbon assimilation data from enclosure measurements.

[5] To better compare cuvette and flux data, we propose to use GPP as a common basis for the branch/leaf level and the ecosystem level approaches. As a first approximation, we can assume that for both R_a and R_h, there is no difference between the day and night values. In this case, a simulated daytime GPP (GPP_{sim}) can be calculated by adding the observed daytime flux values (NEP) to the observed amount of nighttime respiration (which we assume in a first approximation the same as daytime respiration). For micrometeorological canopy flux measurements, the nighttime respiration includes that of both soil and plants, whereas for the enclosure measurements, only the nighttime activity of the branch is taken into account.

[6] Table 2 compiles VOC emissions and CO_2 assimilation as observed by enclosure studies of six different tree species. The data were derived from our earlier studies in the Mediterranean area and very recent ones in the Amazonian rainforest. Data sources are given in the table caption. The table shows $NPP_{cuvette}$- and GPP_{sim}-related data as well. Given the large ecological and taxonomic differences between the two regions, the data sets of the Amazonian and Mediterranean trees are quite similar. The coniferous tree species *Pinus pinea* (Italian stone pine) and the Amazonian deciduous broad leafed *Apeiba tibourbou* both showed a very low organic carbon loss, whereas all other investigated trees emitted substantial amounts of VOC carbon relative to the assimilated carbon reaching up to 3% of NPP (isoprenoids only). The range presented here is in good agreement with values reported in the literature [*Harley et al.*, 1999; *Zimmerman et al.*, 1988; *Harley et al.*, 1994; *Street et al.*, 1996; *Bertin et al.*, 1997; *Cao et al.*, 1997; see Table 1] and with the amount of CO_2 that is used by plant metabolism for producing isoprene [*Sharkey et al.*, 1991a, 1991b]. New results obtained in the course of our studies in Amazonia indicate a quite significant seasonal behavior for tropical rainforests. While these regions show generally less seasonal behavior than temperate forests, we did observe a doubling of isoprene emission during the dry season in the case of *Hymenaea courbaril* (Table 2). Such an observed increase is of particular interest for tropical VOC emissions and agrees with our recent observations of a doubling of atmospheric concentrations of isoprene during the dry season in Amazonia [*Kesselmeier et al.*, 2002]. In addition to temperature effects, these higher emission rates may also reflect special physiological conditions, such as drought stress. From Table 2, we obtain an arithmetic mean of 1.2% as an estimate for the GPP-normalized VOC carbon loss for forest tree species. Obviously, given the small

Table 1. Total Carbon Emitted as Isoprenoids (Isoprene and Monoterpenes) Related to the Photosynthetically Assimilated Carbon[a]

	Percentage of C_{fixed}	ASS	NPP	NEP	ENCL	FLUX	UPS	MOD	Reference
				Ecotype, Region					
Shrub land (*Artemisia tridata*)	5			X			X		*Went* [1959]; estimated on Haagen-Smit (personal communication)
U.S.A.	0.7		X				X		*Zimmerman et al.* [1978]
Tropical forests	2.0		X				X		*Zimmerman et al.* [1988]
Different ecosystems	0.1–4.0		X					X	*Guenther et al.* [1995]
Global mean	2.4		X					X	*Guenther et al.* [1995]
Oak/pine forest	1–2			X		X			*Valentini et al.* [1997]
				Plant species					
Salvia mellifera	0.06	X			X				*Tyson et al.* [1974]
Quercus agrifolia	1–2	X			X				*Tingey et al.* [1979]
Populus tremuloides	1–8	X			X				*Monson and Fall* [1989]
Quercus rubra	1.4–2.1	X			X				*Loreto and Sharkey* [1990]
Quercus rubra	7.2	X			X				*Sharkey and Loreto* [1993]
Populus tremuloides	5.3	X			X				*Sharkey et al.* [1991a, 1991b]
Quercus rubra	3.8	X			X				*Sharkey et al.* [1991a, 1991b]
Populus tremuloides [young-old leaves (average)]	0.18–2.8 (1.15)	X			X				*Fehsenfeld et al.* [1992]
Quercus alba	3.9–13.7	X			X (f)				*Sharkey et al.* [1996]
Picea sitchenis	0.01–0.27	X			X(f)				*Street et al.* [1996]
Several plant species	0.2–2.0	X			X				*Harley et al.* [1999]
Rosmarinus officinalis	0.04–0.09	X			X(f)				*Hansen et al.* [1997]
Pistacia lentiscus	0.01–0.02	X			X(f)				*Hansen et al.* [1997]
Myrtus communis	0.2–0.5	X			X(f)				*Hansen et al.* [1997]
Erica arborea	0.32	X			X(f)				*Hansen et al.* [1997]
Pinus pinea (May)	0.1–0.26		X		X(f)				*Staudt et al.* [1997]
Pinus pinea (August)	2.5–7.6		X		X(f)				*Staudt et al.* [1997]
Quercus ilex (*shade*)	5.8–12.4		X		X(f)				recalculated from *Kesselmeier et al.* [1996]
Quercus ilex	0.7–1.9	X			X(f)				*Kesselmeier et al.* [1997]
Quercus ilex	0.8–2.2		X		X(f)				*Kesselmeier et al.* [1997][b]
Quercus ilex	1.0–2.7	X			X(f)				*Kesselmeier et al.* [1998]
Quercus ilex	1.1–3.0		X		X(f)				*Kesselmeier et al.* [1998][b]
Quercus pubescens	0.6–1.8	X			X(f)				*Kesselmeier et al.* [1998]
Quercus pubescens	0.7–2.0		X		X(f)				*Kesselmeier et al.* [1998][b]
Quercus agrifolia (young potted plant)	0.4–0.6	X			X				*Kesselmeier et al.* [1998]
Pinus pinea (May)	0.12	X			X(f)				*Kesselmeier et al.* [1997]
Pinus pinea (May)	0.14		X		X(f)				*Kesselmeier et al.* [1997][b]
Quercus ilex (30–45°C)	0.5–6.0	X			X				*Staudt and Bertin* [1998]
Quercus ilex	0.5–2.3	X			X				*Holzinger et al.* [2000]
Hymenaea courbaril (wet season)	1.5–1.7		X		X(f)				*Kuhn et al.* [2002b]
Hymenaea courbaril (dry season)	3.0–3.5		X		X(f)				Kuhn et al. (in preparation)
Apeiba tibourbou (wet season)	0.09–0.11		X		X(f)				*Kuhn et al.* [2002b]
Apeiba tibourbou (dry season)	0.07–0.11		X		X(f)				Kuhn et al. (in preparation)
				Stress					
Pueraria lobata, 30°C, water stress, 35°C	20	XX			XX				*Sharkey and Loreto* [1993]
	67								*Sharkey and Loreto* [1993]
Quercus ilex 2–3 days at 45°C	20	X			X				*Staudt and Bertin* [1998]

[a]All enclosure data are given as weight% of (a) carbon assimilated during the measurements (net photosynthesis; ASS), (b) twenty-four hours net primary productivity (NPP) or (c) net ecosystem productivity (NEP). NPP for enclosure measurements includes respiration losses of the branches but not losses by stems and roots (see $NPP_{cuvette}$ in the text). Further information is given about the estimation base, such as enclosure measurements (enclosure), larger scale flux studies (flux), upscaled from short term measurements (UPS) or modeled (MOD). *F* added to enclosure column, field measurements.
[b]Data recalculated on a NPP basis.

number of species investigated and the limited seasonal range covered, this value cannot be generalized. But it agrees well with the few previous measurements from which NPP- and/or GPP-normalized VOC emission has been estimated (see Table 1). Tropical forests are likely to have somewhat higher mean annual emission due to the absence of a dormant period for a majority of the plant species.

[7] To extend these branch-level estimates to the ecosystem scale, we examine the relation between emitted VOC carbon and assimilated carbon using micrometeorological flux data, which integrate emissions over larger areas. Two different forest ecosystems were investigated, a Mediterranean and an Amazonian forest. We relate VOC net ecosystem fluxes to simultaneous net CO_2 fluxes, which comprise both assimilation and plant and soil respiration, to calculate the GPP_{sim}. In case of the Mediterranean forest, we are now able to demonstrate the seasonal behavior of VOC fluxes as observed over 1 year. Figure 1 shows the strong seasonal

Table 2. Total Carbon Emitted as Isoprenoids Related to the Daily Photosynthetically Driven Net Primary Production of the Enclosed Branch ($NPP_{cuvette}$) and Daytime Gross Primary Production ($GPP_{sim\ (cuvette)}$)[a]

	Emitter Type	$NPP_{cuvette}$ (C) on a Leaf Area Basis, g m^{-2}	Specific Leaf Dry Weight, g m^{-2}	Percentage Emitted as Isoprenoids Based on $NPP_{cuvette}$	Percentage Emitted as Isoprenoids Based on $GPP_{sim\ (cuvette)}$
		Quercus ilex (*Site CP* [*Kesselmeier et al.*, 1996])			
8 June 1993[b]	MT	0.13	88	5.8	2.0
10 June 1993[b]	MT	0.08		12.4	2.2
		Quercus ilex (*Site CP* [*Kesselmeier et al.*, 1997])			
15 May 1994	MT	2.55	156	0.77	0.65
17 May 1994	MT	1.22		1.16	0.77
24 May 1994	MT	0.60		1.54	0.96
25 May 1994	MT	1.19		2.20	1.78
26 May 1994	MT	1.59		1.88	1.57
		Quercus ilex (*Site MP* [*Kesselmeier et al.*, 1998])			
20 June 1995	MT	2.01	199	1.43	1.28
21 June 1995	MT	1.53		1.09	0.95
22 June 1995	MT	1.16		3.02	2.54
23 June 1995	MT	1.27		2.26	2.09
		Quercus pubescens (*Site MP* [*Kesselmeier et al.*, 1998])			
20 June 1995	ISO	4.26	117	1.24	1.16
21 June 1995	ISO	3.39		0.68	0.61
22 June 1995	ISO	3.11		1.96	1.72
		Quercus agrifolia (*Site MP* [*Kesselmeier et al.*, 1998])			
10 Oct. 1995	ISO	1.91	118	0.44[c]	...
12 Oct. 1995	ISO	2.07		0.57[c]	...
		Pinus pinea (*Site CP* [*Kesselmeier et al.*, 1997])			
21 May 1994	MT	0.87	137	0.14	0.11
22 May 1994	MT	0.81		0.14	0.12
		Hymenaea courbaril (*Site RO* [*Kuhn et al.*, 2002b])			
8 May 1999	ISO	2.63	118	1.72	1.57
9 May 1999	ISO	2.94		1.52	1.40
		Hymenaea courbaril (*Site RO* (*Kuhn et al.*, *manuscript in preparation*, 2002))			
22 Oct. 1999	ISO	3.06	80	3.46	3.03
23 Oct. 1999	ISO	2.85		2.99	2.59
		Apeiba tibourbou (*Site RO* [*Kuhn et al.*, 2002b])			
4 May 1999	MT	2.42	90	0.09	0.085
5 May 1999	MT	2.61		0.11	0.105
		Apeiba tibourbou (*Site RO* (*Kuhn et al.*, *manuscript in preparation*, 2002)			
18 Oct. 1999	MT	1.55	70	0.11	0.06
19 Oct. 1999	MT	1.79		0.07	0.04

[a]$NPP_{cuvette}$ is the net exchange over 24 hours. Daytime $GPP_{cuvette}$ was obtained by adding nighttime respiration rates to $NPP_{cuvette}$. All CO_2 exchange data are derived from 5-min measuring intervals. Isoprenoid data are from hourly sampling with 30–60 min of sampling time in general. Data gaps were closed by averaging between the two measured data points. MT, monoterpene type; ISO, isoprene type; CP, Castelporziano at the coast west of Rome, Italy; MP, Viols en Laval north of Montpellier, southern France; RO, south east of Rondonia, Amazonia, Brazil. Uncertainties of emission ranges [*Kesselmeier et al.*, 1997] derive mainly from estimating the isoprenoid emissions. This error ranges between 15 and 30% according to the references given. Calculation of net photosynthetic assimilation based on enclosure measurements with an infrared gas analyzer (LiCor 6262) has an uncertainty of <5%. Total propagated uncertainty for $C_{emitted}$ is around 36% and thus smaller than the day to day fluctuations. Note that isoprenoids seem to represent the main fraction (>75%) of emitted VOCs as found for *Quercus ilex* by PTR-MS studies [*Holzinger et al.*, 2000]. However, other emissions, such as methanol, may be substantial.

[b]Data are obtained with a branch growing at the side of the tree, sunlit for 3–4 hours per day only.

[c]Data for *Q. agrifolia* are based on daylight assimilation only; in this case, %C emitted may be slightly higher than if integrated over 24 hours.

pattern of VOC loss in relation to GPP_{sim} for this temperate forest, consisting mainly of holm oak (*Quercus ilex*). This monoterpene-emitting oak species is known to behave like an isoprene-emitting species in terms of light dependency and emitted isoprenoid amount. In addition to the expected and observed seasonality of carbon assimilation and VOC emission (data not shown), there was also a seasonal cycle in the ratio between VOC emission and carbon assimilation. A clear seasonal maximum is seen during the summer months, from mid-July (day 200) to early September (day 250). Figure 1 illustrates that carbon loss by VOC emission is also significant on the ecosystem scale, with peak values between 2 and 3%. Calculating the mean annual value by taking into account the total carbon fluxes (GPP and VOC emission) accumulated over the whole year, we come up with 0.45% of GPP carbon to be released as VOC from this

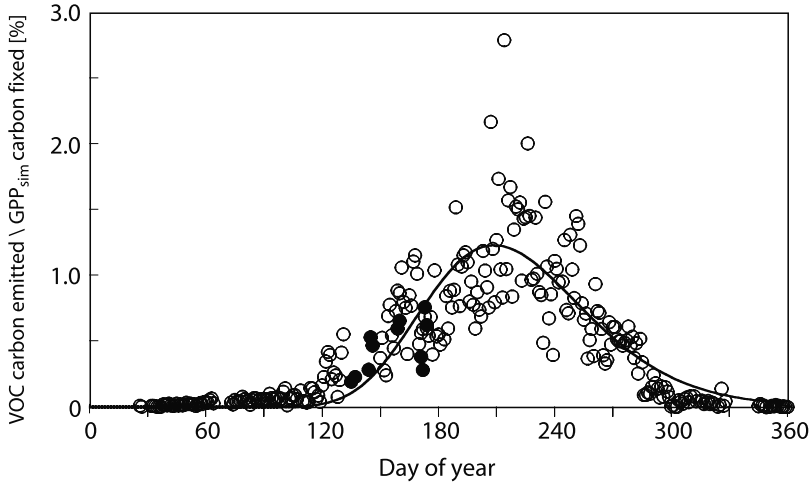

Figure 1. Seasonal pattern of VOC carbon loss in relation to the gross carbon assimilation (GPP_{sim}) of a homogenous Mediterranean holm oak (*Quercus ilex*) stand (open circles). VOC fluxes (mainly monoterpenes) were measured by trap relaxed Eddy accumulation [TREA; *Valentini et al.*, 1997] and were accompanied by eddy correlation measurements of CO_2 fluxes at Castelporziano (Italian coast, west of Rome) from February 1997 to June 1998. For comparison, VOC carbon loss data derived from enclosure measurements with *Q. ilex* (1993–1995; closed circles) are added by taking into account that a forest has only 30% emitting species and, hence, dividing the cuvette derived numbers (Table 2) by this factor. The solid line represents a mathematical approximation according to a least square regression.

forest. Our findings for this European forest and tree species highlight the importance of taking the seasonal behavior into account in any calculation of trace gas exchange for mid-latitude ecotypes.

[8] Considering the seasonal effects and the variability of biogenic VOC emissions, the agreement between the carbon loss ratios obtained from canopy flux measurements above a *Q. ilex* stand (Figure 1) and those obtained from enclosure measurements of *Q. ilex* branches (Table 2) is quite good. Strictly speaking, of course, these measurements cannot be compared directly, since the cuvette data only represent a single species, and other plant species within a mixed forest might not emit significant amounts of VOCs. *Rasmussen and Khalil* [1988] conducted a screening of plants to determine the phylogenetic basis of isoprene emission; although the results have not been published in detail, it appeared that of the hundreds of plant species tested about 30% were isoprene emitters. Also, *Harley et al.* [1999] report that approximately one-third of all angiosperm families examined have the ability to produce significant amounts of isoprene; these are mainly woody species and a few herbaceous plant species. The proportion of isoprene-emitting species identified by screening of tropical tree species in Panama, Puerto Rico and South Africa were found to be surprisingly similar to that found in temperate forests, ranging around 28–29% [*Guenther et al.*, 1996; *Lerdau and Keller*, 1997; *Keller and Lerdau*, 1999]. We regard the monoterpene-emitting holm oak forest to be comparable with isoprene emitters in terms of amount released and the ecophysiological regulation. Hence, if we take into account that a forest has only 30% emitting species and divide the cuvette-derived numbers by this factor they fit perfectly into the flux data set (Figure 1).

[9] In addition to this study of a midlatitude forest, we have also performed micrometeorological flux studies over a tropical Amazonian forest. These canopy scale studies were performed at a tower site 50 km North of Manaus [K34 tower, Instituto Nacional de Pesquisas da Amazônia (INPA); see *Andreae et al.*, 2002] during the wet season 1999/2000. We found a GPP_{sim}-based VOC carbon loss between 0.1 and 0.6% with 0.36% as a mean value (see Figure 2), in between those derived from enclosure measurements (Table 2). The daily pattern of carbon loss exhibited a slight increase in the early afternoon, indicating some diurnal changes in the ratio of VOC emission/CO_2 uptake of the tree species (Figure 2). A strong diel course of this ratio was also reported from enclosure measurements of Amazonian tree species [*Kuhn et al.*, 2002b]. To extend this wet season flux estimate to an annual estimate, we recall the doubling of the isoprene emission of *H. courbaril* (Table 2) as well as the doubling of the atmospheric isoprene during the dry season [*Kesselmeier et al.*, 2002]. Hence, taking into account 0.36% for the wet season and a doubled value of 0.72% for the dry season, we estimate 0.54% GPP-based VOC carbon loss on an annual scale for the tropical forest.

[10] Such small carbon losses on a GPP basis (0.45% for temperate and 0.54% for tropical forests) at first appear to be insignificant. But on an ecosystem level, the total amount of emitted carbon has to be related to the net carbon gain by CO_2 exchange (NEP), which incorporates the release of carbon by respiration of the forest trees and the soil. Taking the latest IPCC estimates [*IPCC*, 2001] with a GPP of 120 Pg C a^{-1} into account, a VOC loss estimate of 0.45% GPP_{sim} for forests results in an isoprenoid emission estimate of 0.54 Pg C if all forest would be temperate and show seasonality. Using the mean of the

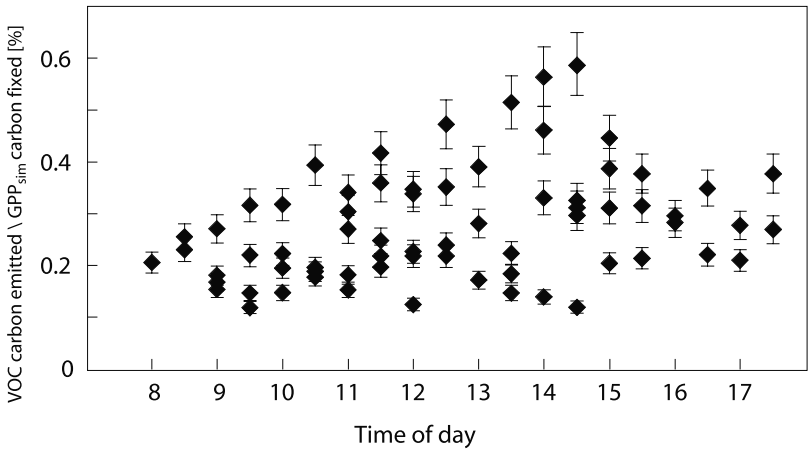

Figure 2. Pattern of VOC carbon loss in relation to the gross carbon assimilation (GPP_{sim}) of a mixed tropical rain forest north of Manaus. VOC fluxes (mainly isoprene) were measured by trap relaxed Eddy accumulation [TREA; *Valentini et al.*, 1997] and were accompanied by eddy correlation measurements of CO_2 fluxes in the beginning of the wet season in December 1999 to January 2000 (A. C. Araujo et al., Dual tower long-term study of carbon dioxide fluxes for a central Amazonian rainforest: The Manaus LBA site, submitted to *Journal of Geophysical Research*, 2002). Basic mean data for calculation were as follows: NEP 180 ± 27 μg C m^{-2} s^{-1}; GPP_{sim} 292 ± 34 μg C m^{-2} s^{-1}; Isoprene emission 0.9 ± 0.2 μg C m^{-2} s^{-1}; Monoterpene emission 0.17 ± 0.2 μg C m^{-2} s^{-1}; Mean fraction (% of GPP_{sim}) of photosynthetic carbon emitted as isoprenoids 0.36 ± 0.15.

temperate and tropical forest scenarios, this value increases slightly. Such numbers are very close to the recent estimate of the global isoprene emission of about 0.5 Pg C a^{-1} obtained by modeling [*Guenther et al.*, 1995]. Compared to the range of current NEP estimates [*IPCC*, 2001] of 1.4–15.5 Pg C a^{-1}, we then calculate that 3.5–39% of the NEP carbon is re-released into the atmosphere in the form of volatile organic carbon.

[11] The carbon exchange estimates for the tropics are a matter of debate. The IPCC report 2001 [*IPCC*, 2001] gives a range of 0.7–5.9 t C ha^{-1} a^{-1} for NEP of tropical forests. We took the most recent numbers of 5.6 t C ha^{-1} a^{-1} for NEP and 36 t C ha^{-1} a^{-1} for GPP [*Malhi et al.*, 1998; *Carswell et al.*, 2002]. Using these numbers, we calculate that 0.19 t C ha^{-1} a^{-1} (0.54% of 36 t) are released as VOCs emitted into the atmosphere, representing 3.4% of NEP. Relative to an earlier published figure of NEP = 0.71 (±0.34) t C ha^{-1} a^{-1} for recent decades in tropical forests [*Phillips et al.*, 1998], the significance of VOC carbon loss increases to 27% of NEP. Thus the ranges for a global and a tropical scenario with 3.5–36 and 3.4–27%, respectively, are very similar. All these numbers are afflicted with high uncertainties, but the calculations demonstrate that the carbon lost as VOC emissions can be significant in relation to NEP. Compared to NBP, estimated to be 0.2–1.4 Pg C a^{-1} (*IPCC* [2001] for the years 1980–1998) it is in the same order of magnitude. It should be noted that this contribution may increase significantly when data for other VOC species are added to the isoprenoid emissions. Methanol, for example, is reported to be emitted from several plants in amounts similar to the emission rates of isoprene and monoterpenes [*MacDonald and Fall*, 1993]. Although a part of the atmospheric organic carbon pool is recycled through the vegetation (see below), the VOC release clearly represents a loss for NEP and NBP that must be taken into account in considerations of global carbon budgets.

[12] There are, however, unknowns within this picture. Atmospheric oxidation processes do not convert all of the emitted VOCs to CO_2, thereby returning it to the atmospheric CO_2 carbon reservoir. Fundamentally, carbon emitted VOC can have three different kinds of fate, with different consequences for the carbon cycle. First, it can be returned to the terrestrial biosphere, with or without some intermediate chemical transformation into other organic compounds. This represents simply an internal recycling of organic carbon within the terrestrial carbon pool, not much different from a leaf falling to the ground. Second, it can be transformed in the atmosphere to CO_2 by (photo)chemical reactions, in which case there is a net transfer from the terrestrial carbon reservoir to the atmospheric CO_2 reservoir, bypassing terrestrial respiration. Third, the terrestrially emitted VOC can be deposited to the oceans following atmospheric transformation to water-soluble species. This flux would be a net transfer from the terrestrial to the marine biosphere, and ultimately to the marine dissolved inorganic carbon reservoir.

[13] As shown in Figure 3, intermediate oxidation products may be redeposited into the ecosystem by chemical and physical deposition processes. VOC species can end up in oxygenated compounds, belonging to both other reactive VOC (ORVOC) and other VOC (OVOC), organic nitrates or aerosols [*Poisson et al.*, 2000; *Fuentes et al.*, 2000; *Atkinson*, 2000]. Hence some of them are recaptured by the ecosystem by dry or wet deposition, which is not taken into account in the calculations and flux measurement approaches presented above. This is obvious for some oxygenates, such as some organic acids or aldehydes, which exhibit a bidirectional exchange behavior,

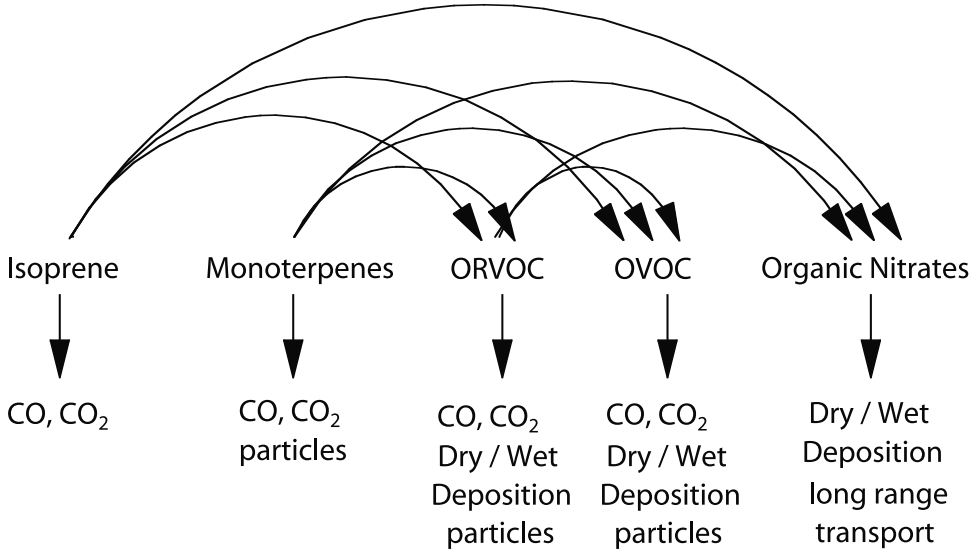

Figure 3. Once emitted, VOC species are processed in the atmosphere and can end up in CO_2 again. Others are transformed to chemical species belonging to the groups of other reactive and less-reactive VOCs (ORVOC, OVOC) or contribute to organic nitrates and aerosol production. Some of this carbon is returned to the carbon reservoir by dry or wet deposition. Another part is oxidized to the longer living species CO which, in parallel to less-reactive VOC, may be responsible for a carbon loss for the terrestrial biosphere.

i.e., which can be released, but also taken up by vegetation [*Kesselmeier*, 2001; *Kuhn et al.*, 2002a; *Rottenberger et al.*, 2002]. Furthermore, aerosols with a high organic carbon content may return to the surfaces by dry and wet deposition. At present, we are unable to predict what fraction of the emitted carbon may return by these pathways to the biosphere, to be reassimilated and eventually respired by the biota.

[14] Products with lifetimes long enough to allow a significant loss by transport pose a more complex problem. An unknown share of carbon may get lost from the terrestrial biosphere after transformation to products that are not taken up by the biosphere again and/or with atmospheric lifetimes that are long enough to allow a transport to the upper troposphere and into oceanic regions. The most important long-lived compound within this class is CO, with a mean lifetime close to 2 months [*von Kuhlmann*, 2001]. According to *von Kuhlmann* [2001], about 39% of the isoprene and of other non-methane VOC get oxidized to CO. These numbers are in close accordance with work of *Kanakidou et al.* [1991] and *Poisson et al.* [2000] on other non-methane VOC. Essentially all of this CO will be oxidized in the atmosphere to CO_2, and thus represent a transfer from the terrestrial biosphere to the atmospheric CO_2 reservoir. Another potentially relevant compound from the group of less reactive species is atmospheric acetone with significant contributions from oxidation of biogenically emitted VOC such as methylbutenol and monoterpenes [*Singh et al.*, 1994; *Goldstein and Schade*, 2000]. Chemical destruction in the atmosphere is most likely the dominant sink of this and other compounds with similar characteristics, thus representing a net loss for the terrestrial biosphere. However, we need to know more about the emission of such precursors, their chemical reaction pathways, and the fate of the oxidation products in the atmosphere in order to give an estimate in terms of carbon loss.

3. Conclusion

[15] While obviously many open questions remain, this comparison of the VOC emission fluxes with NEP and the discussion of the potential fate of the carbon within the atmosphere makes it clear that VOC emission must be regarded as a substantial loss of biologically fixed carbon from the terrestrial biosphere, significant in relation to NEP and of the same order of magnitude as compared to NBP. To obtain a more reliable estimate of this important term in the carbon budget, more broadly representative measurements of VOC fluxes in relation to CO_2 fluxes, biological process studies, and detailed model calculations on the fate of the emitted VOC are urgently needed.

[16] **Acknowledgments.** We greatly acknowledge the discussions with Jos Lelieveld, Laurens Ganzeveld (both Max Planck Institute, Mainz) and Jim Randerson (CALTECH, Pasadena). Their contributions as well as those of the unknown referees increased the value of the publication. We thank our home institutions for the continuous fundamental support and greatly acknowledge the substantial additional financial supports by the Commission of the European Communities (DG XII/D-1) in the frame of the projects "Biogenic Emissions in the Mediterranean Area" (BEMA) and "European Studies on Trace Gases and Atmospheric Chemistry as a Contribution to the Large-Scale Biosphere-Atmosphere Experiment in Amazonia" (EUSTACH-LBA).

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