RELATIVE CONTRIBUTION OF OXYGENATED HYDROCARBONS TO THE TOTAL BIOGENIC VOC EMISSIONS OF SELECTED MID-EUROPEAN AGRICULTURAL AND NATURAL PLANT SPECIES

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Abstract—Emission rates of more than 50 individual VOCs were determined for eight plant species and three different types of grass land typical for natural deciduous and agricultural vegetation in Austria. In addition to the emissions of isoprene and monoterpenes, 33 biogenic oxygenated volatile organic compounds (BOVOCs) were detected. Of these, 2-methyl-1-propanol, 1-butanol, 2-butanol, 1-pentanol, 3-pentanol, 1-hexanol, 6-methyl-5-hepten-2-one, butanal and ethylhexylacetate were observed for the first time as plant emissions. In terms of prevalence of one of the groups of emitted VOCs (isoprene, terpenes, BOVOCs) the grain plants wheat and rye, grape, oilseed rape and the decidous trees hornbeam and birch could be classified as "BOVOC"-emitters. For the grass plots examined, BOVOCs and terpenes appear to be of equal importance. The emission rates of the total assigned organic plant emissions ranged from 0.01 $\mu g\,g^{-1}\,h^{-1}$ for wheat to 0.8 $\mu g\,g^{-1}\,h^{-1}$ for oak (based on dry leaf weight). Intercomparison with available data from other studies show that our emission rates are rather at the lower end of reported ranges. The influence of the stage of growth was examined for rye, rape (comparing emissions of blossoming and nonblossoming plants) and for grape (with and without fruit). Emission rate differences for different stages of growth varied from nondetectable for blossoming and nonblossoming rye to a factor of six for the grape with fruits vs grape without fruits (emission rate based on dry leaf weight). The major decidous tree in Austria (beech) is a terpene emitter, with the contribution of BOVOCs below 5% of the total assigned emissions of 0.2 $\mu g\,g^{-1}\,h^{-1}$ for the investigations of 20°C.

Keyword index: Biogenic hydrocarbons, isoprene, monoterpenes, sesquiterpenes, NMHC, oxygenated VOC, biogenic emission rates.

INTRODUCTION

The recent interest in emission inventories of biogenic volatile organic compounds (VOCs) on the regional and global scales is due to results from atmospheric chemistry simulations, which indicate that biogenic VOC might contribute to the formation of regional (Trainer *et al.*, 1987) and global tropospheric ozone (Jacob and Wofsy, 1988).

Compared to the number of plant species in different parts of the world the available emission data of biogenic VOC are still sparse (Fehsenfeld *et al.*, 1992). Most of the work has been performed on the American continent (discussed in Winer *et al.*, 1992) and has been focused primarily on the emissions of isoprene and terpenes (Lamb *et al.*, 1993). Thus emission inventories of biogenic VOC are generally based on the plant emissions of isoprene, α-pinene and the total nonmethane hydrocarbons (NMHC) (Lamb *et al.*, 1987, 1993). Until now European emission inventories of biogenic VOC have been based on the emission rates of decidous and coniferous forest types from the U.S.A. and on the temperature dependence model used by Lamb *et al.* (1987) (Lübkert and Tilly, 1989; Orthofer and Urban, 1989; Veldt, 1991).

The weakness of this approach has been demonstrated by Anastasi *et al.* (1991) and Hewitt and Street (1992) for the biogenic VOC emissions in the

U.K. While the emission rate data for U.S. coniferous forests are derived primarily for pines and firs, which are terpene but not isoprene emitters, in the European coniferous forests spruces are the most common trees. Sitka spruce, which is the most common tree species in the U.K., is an isoprene emitter (Evans *et al.*, 1982). Accounting for the isoprene emissions from Sitka spruce and a three times higher biomass density for this species than for pine forests, annual VOC emissions for the U.K. was estimated to be 172 kt yr^{-1}, or 2.5–4.5 times higher than earlier estimates (Anastasi *et al.*, 1991; Hewitt and Street, 1992). However VOC emission data from European plant species are now slowly emerging (Isidorov *et al.*, 1985; Steinbrecher, 1989; Hewitt *et al.*, 1990; Bufler and Wegmann, 1991; Steinbrecher *et al.*, 1993).

In early studies it was assumed that the majority of NMHC emissions from plants consisted of isoprene and the monoterpenes. However it has more recently been recognized that many other compounds, especially oxygenated VOCs may also be emitted. For example Arey *et al.* (1991b) have shown that oxygenated hydrocarbons (in the further text referred to as biogenic oxygenated volatile organic compounds, "BOVOCs") may provide a major contribution to the terrestrial biogenic organic emissions.

As the biogenic emissions of isoprene and terpenes and their role in the tropospheric chemistry have been reviewed earlier (Graedel, 1979) and recently (Arey *et al.*, 1991c; Fehsenfeld *et al.*, 1992; Hewitt and Street, 1992) here an outline is given of recent developments in the field of BOVOC emissions of plants. The emission of an oxygenated terpenoid—1,8-Cineol—from a eucalyptus tree was reported by Rasmussen as early as 1972. The detection of biogenic emissions of other oxygenated terpenoids observed by other groups is discussed in Arey *et al.* (1991). Schulting *et al.* (1980) found that certain grass species emit (Z)-3-hexen-1-ol and (Z)-3-hexenylacetate, referred to as "leaf alcohol and -ester". Isidorov *et al.* (1985) identified leaf alcohol as a main component of the volatile emissions of birch, but no emission data were reported. Buttery *et al.* (1982, 1985) identified (Z)-3-hexenylacetate, (Z)-3-hexen-1-ol and (E)-β-ocimene as the major volatiles from oat, barley and wheat.

The first quantitative BOVOC screening of a variety of plant species was performed by Arey *et al.* (1991b). For certain crop species grown in central California it was shown that the emissions of (Z)-3-hexen-1-ol and (Z)-3-hexenylacetate were dominant compared to the "classic" biogenic emissions of isoprene and terpenes. In a more detailed report from the same group (Winer *et al.*, 1992), emission rates of BOVOCs in comparison to isoprene, monoterpenes, sesquiterpenes and total organics were presented for more than 30 of the most dominant plant types in California's Central Valley. There it was shown that in about one third of the examined plants BOVOCs formed the major fraction of the total assigned organic emissions.

The goal of this present study was to perform a screening of the biogenic VOC emissions of the major agricultural crops and native tree species grown in Austria with the focus on an assessment of the relative importance of the emissions of oxygenated VOCs compared to the "classical" biogenic VOC species, isoprene and terpenes, for mid-European plant species. Eight plant species were chosen for the study, including four deciduous tree types, two grain species, oilseed rape, grape and three specimens of grassland. Coniferous trees were not considered as they are under investigation in another project (EUROTRAC subproject "BIATEX") in the Bavarian Forest (Enders *et al.*, 1992). Emphasis was placed on the detection of unidentified lower molecular weight species as addressed by Winer *et al.* (1992) and Lamb *et al.* (1993).

In addition to the list of compounds reported by Winer *et al.* (1992) we identified and quantified other BOVOCs as important contributions to the total VOC emission of certain crops, e.g. butanone from grape, 2-pentanone from wheat and 2-methyl-1-butanol from blossoming rye. MacDonald and Fall (1993) reported recently about considerable emission rates of methanol from plants. Methanol emissions were not quantified in our and the other studies mentioned above as the analytical procedures applied were not suitable to determine methanol.

EXPERIMENTAL

Plant enclosure chambers

A portable dynamic flow-through enclosure system with a volume of approximately 15 ℓ was used to sample VOC emissions from agricultural and natural plant species. The enclosure chamber was constructed from a 50 μm Teflon film cylindrically suspended from an external aluminum frame with a top formed by a Teflon disk. The approximate diameter of the cylinder is 0.25 m with a length of 0.3 m. The top bears a small stirring fan and has several ducts for the carrier gas supply and sampling lines. The design followed closely that of the system described by Street *et al.* (1993). Stirring was performed in such a way to cause little movement of the leaves in order to prevent enhanced emissions caused by mechanical damage (Juuti *et al.*, 1990). Ventilation of the chamber was performed by pumping charcoal-filtered ambient air at a flow rate of about 4–6 ℓ min^{-1} into the enclosure. Gas flows were measured with calibrated mass flow meters and calibrated rotameters. During all measurements the air temperature in the enclosure system and of the ambient air were measured.

After introduction of the plants into the enclosure purified air flowed for 20 min through the system (which approximately corresponds to five air exchanges in the chamber) before the first samples were taken to allow the system to achieve steady state. By using carbon monoxide as a tracer Winer *et al.* (1992) verified that biogenic emissions were within ~10% of their steady-state value after three air exchanges in a plant chamber.

For the determination of the emission rates of grassland a second enclosure system was constructed. It consisted of a PVC framework, 0.4 m wide, 0.6 m long and 0.4 m high in

which the 50 μm PTFE foil was suspended. For the introduction of ventilation air and the withdrawal of analytical samples, the enclosure was equipped with inlet and outlet ports. The chamber was operated in the same manner as described above except that this enclosure did not have a mixing fan. The design followed that of the system described by Winer *et al.* (1992).

Two samples were always taken simultaneously, one of the inflowing air downstream of the charcoal filter before the chamber and the second at the outlet port of the enclosure. In this way the difference in the concentrations of each substance between the inflowing and the chamber air could be determined, so allowing calculation of emission rates. As rough handling of plants may cause dramatic increases in emission rates, great emphasis was given to the careful introduction of the plants into the enclosure (Juuti *et al.*, 1990). All measurements were made outdoors under ambient light conditions.

Analytical procedures

Gas samples of 1–3 ℓ were collected at a rate of 0.1–0.2 ℓ min^{-1} onto Tenax TA cartridges with a little amount of Carbotrap downstream of the Tenax. The cartridges were glass tubes, length 150 mm, inner diameter 3 mm. The length of the Tenax filling was 100 mm, the one of the Carbotrap filling was 20 mm. Silanized glass wool was used to keep the sorption phases in place. Carbotrap, which is hydrophobic (Ciccioli *et al.*, 1993) was used instead of Carbosieve II (Arey *et al.*, 1991b, c) for quantitative collection of isoprene and lower molecular weight alcohols and aldehydes. These cartridges were thermally desorbed and cryofocused for simultaneous compound identification by gas-chromatography–mass-spectrometry (GC–MS) and quantification by GC with flame ionisation detection (GC–FID).

For the simultaneous operation of the two detectors a GC–MS–FID system with a pre-column splitter and two identical analytical columns (J&W DB5-MS 50 m × 0.2 mm × 0.33 μm) was used. The system was based on a Hewlett-Packard 5890 series II GC with an FID and a Hewlett-Packard 5971 A mass-selective-detector. Thus a total ion chromatogram (TIC) and a FID chromatogram were obtained simultaneously for each sample, with the FID data used for quantification and the MSD data for peak identification from full mass spectra (19–250 amu). The different operating pressures of the two detectors caused different column flows, giving a slight shift in retention times between the two chromatograms. Relative GC–MS retention times were used to identify GC–FID peaks.

All calibration and sample analyses were performed at the same initial temperature since the split ratio varies with temperature as an effect of gas viscosity.

A home-made thermo desorption and cryofocusing injection system was used for sample introduction (Lanzerstorfer and Puxbaum, 1990). The Tenax-TA/Carbotrap samples were thermally desorbed at 250°C via a six port valve into a cryo loop. The direction of the flow through the cartridges during desorption was reversed from that during sample collection so that only the most volatile compounds (such as isoprene) for which breakthrough occurred on the Tenax-TA were collected and hence subsequently desorbed from the Carbotrap. During the 20 min allowed for desorption the cryo loop was cooled with liquid nitrogen (−196°C). After switching the valve to the injection position the loop was heated with boiling water so that all the desorbed substances passed via the six port valve directly onto the column. All transfer lines from the tube to the valve and to the cryo loop were electrically heated to 70°C to avoid any condensation of high boiling substances. After injection the column temperature was held at 15°C for 8 min and then heated to 250°C at a rate of 3°C min^{-1}. Hold time at 250°C was 10 min.

Standards of isoprene, nine monoterpenes, selected hydrocarbons and 27 oxygenated compounds were used. Identifications were made by matching both the retention time and the mass spectra with those of the reference compound. Quantification was carried out by using the FID data and individual response factors for each compound, as determined by calibration experiments carried out during the study period. For a few peaks overlap of two substances was detected by GC–MS. For such substances quantification was performed by integrating peaks of characteristic single ions of the substances using response factors determined with reference substances. The reproducibility of this method is in the order of 20% relative standard deviation. Prior to the plant experiments, calibration, recovery and cartridge breakthrough tests were performed. A detailed report on these experiments and the determination of the response factors of the FID for the oxygenated compounds is given in Brunda (1994). For substances where no standards were available, response factors were taken from Dietz (1967).

Reproducibilities for VOC-concentrations from parallel sampling from the enclosures from various plants ranged from 8% (hexanal) to 41% (limonene) R.S.D. with an average value of around 20% for the main components (emission rates $> 10\ ng\ g^{-1}\ h^{-1}$). Minor components (emission rates $< 10\ ng\ g^{-1}\ h^{-1}$) showed a larger scatter with reproducibilities up to 100% R.S.D. Thus emission data reported for the minor components have to be considered as semiquantitative information only (Brunda, 1994).

The recovery of test samples of selected terpenes and BOVOCs for the complete analytical procedure was shown to be > 90% provided that transfer lines, even when very short, were heated to 70°C. International calibration experiments between the participating laboratories confirmed the validity of the applied procedure.

Chemicals

The Tenax-TA (60–80 mesh) porous polymer and Carbotrap (20–40 mesh) graphitized carbon black were purchased from Chrompack and Supelco, Inc., respectively. Isoprene, and the terpenes α-terpinene, γ-terpinene, β-pinene, tricyclene, trans-caryophyllene and most of the saturated and unsaturated HC were purchased from FLUKA Chemical Corporation. α-Pinene, camphene, myrcene, limonene, and Δ^3-carene were gifts of KREMS Chemie Austria. The BOVOCs hexanal, (Z)-3-hexen-1-ol, and (Z)-3-hexenylacetate were from SIGMA. Linalool, pulegone, geraniol and 1,8-cineol were received from Lancaster University. The oxygenated compounds 3-methyl-2-buten-1-ol, 3-methyl-3-buten-1-ol, 4-penten-1-ol, 2-methyl-1-butanol, 1-pentanol, 1-heptanol, 1-octanol, methylvinylketone, methylpentylketone, caprylic aldehyde, and 1-heptaldehyde were purchased from FLUKA Chemical Corporation. 1-Propanol, 2-propanol, 2-methyl-2-propanol, 2-butanone, 1-butanol, 3-pentanone, 4-methyl-2-pentanone, ethylacetate and isobutylacetate were from MERCK.

Dry biomass determinations

After each set of emission samples from a plant the investigated parts were harvested for dry weight determination. From woody plants the whole branch that had been enclosed within the Teflon chamber was cut off. Herbaceous plants were cut off as close as possible to ground level. In all cases the dry leaf weight was determined, except for the three agricultural crops, rye, rape and wheat, where a separation of leaves and stems was not possible. As a result, only the total dry weight of these plants was determined. Emission rates of the grape-vine were determined for total dry weight (including the grapes) and dry leaf weight to enable a subsequent calculation of the emission rates of the grapes and the leaves separately.

Emission rates were calculated assuming a steady state concentration of the emissions in the flow through chamber and are reported as an emission rate per gram biomass ($\mu g\,h^{-1}\,g^{-1}$), with the biomass data reported as dry leaf weight or total dry weight (Corchnoy *et al.*, 1992).

Normalization of the emission rates

The following equation was used for the normalization of the terpene emission rates to 30°C (Arey *et al.*, 1991):

$$\text{monoterpene emission rate} = Ae^{BT}$$

with the exponent $B = 0.060$ for the monoterpenes and $B = 0.040$ for isoprene (Tingey, 1980). Guenther *et al.* (1993) reported that the exponent B was in the range of 0.057–0.144 for different monoterpenes emitted by different coniferous trees. It was also shown that the emission rate of isoprene depends strongly on light intensity and temperature.

Guenther *et al.* (1991) showed that the exponent B for α-pinene and for 1,8-cineol in eucalyptus emissions was 0.094, respectively, 0.100. Therefore the temperature dependence of BOVOCs was tentatively assumed to be identical to the behaviour of monoterpenes.

Plant species

The study was conducted in eastern Austria and the suburban areas of Vienna using plant species typical of Austria. The selection of plant species was based on acreages reported by the forestry and agricultural crop inventories of Austria (Bundesministerium f. Land- und Forstwirtschaft, Jahresbericht 1991). Table 1 lists the major forestry plant and agricultural crop species grown in Austria.

We chose examples which we considered to be typical for the most abundant plants in Austria: grasses, beech (fagus sylvatica), oak (quercus petrae), birch (betula pendula) and hornbeam (carpinus betulus) (for the decidous trees). Wheat and rye (as examples of grain plants) rape (as the major oil seed plant in Austria) and grape (*Vitis vinifera* (chardonnay)) (as major agricultural species in eastern Austria). As mentioned before, conifer trees were not included in our study. The area coverage of the examined species in Austria is about 33% with grassland and pastures as predominant species with an area coverage of 24%. Major species not tested were maize/corn for which we had no appropriate enclosure chamber at hand and barley which was assumed to have similar emissions as wheat (Buttery *et al.*, 1985).

Preliminary laboratory tests with young plants grown in a greenhouse from seedlings (oak, hornbeam, beech, birch) yielded very low emission rates and completely different VOC emission patterns when compared to naturally growing plants under natural light conditions. Thus we report here only the results which were obtained for the naturally growing plants. Table 2 lists sampling dates, sites, time of the day, mean ambient temperatures and the stage of growth.

Table 1. Land use inventory of Austria (1991) [values as percentage of the total area (83,855 km^2)] (from Bundesministerium f. Land- und Forstwirtschaft, Jahresbericht 1991)

Coniferous forest	**29.9**
Spruce	23.9
Fir	2.8
Larch	1.9
Pine	1.0
Others	0.3
Decidous forest	**7.8**
Beech	3.8
Oak	0.7
Other hardwood	2.0
Softwood	1.4
Bush/shrub	**0.7**
Grassland	**11.7**
Pasture	**12.0**
Cropland	**17.0**
Wheat	3.2
Barley	3.5
Rye	1.0
Oat	0.7
Maize/corn	3.5
Sugarbeet	0.6
Oilseed rape	0.5
Others	4.0
Vine	**0.7**
Not productive	**9.9**

RESULTS AND DISCUSSION

Over 50 individual organic compounds were identified as emissions from the eight agricultural and natural plant species and the grass plots investigated in the current study. These compounds are listed by chemical classes in Table 3. In addition to isoprene and the monoterpenes a number of sesquiterpenes, alcohols, ketones, aldehydes, ethers and esters were observed. Emission rates of some low boiling alcohols (2-methyl-1-propanol, 1-butanol, 2-butanol, 1-pentanol, 3-pentanol and 1-hexanol), ketones (6-methyl-5-hepten-2-one), aldehydes (butanal) and ethers (ethylhexylacetate), which to our knowledge have not previously been reported, were also determined. Sesquiterpenes were observed to be emitted from two plant species (birch and hornbeam) and in both cases the emission rates of sesquiterpenes were almost as high as the monoterpene emission rates. Such high sesquiterpene emissions were previously reported for peach, safflower, olive, cherry and grape (French Columbard) (Arey *et al.*, 1991b; Winer *et al.*, 1992). The unsaturated hydrocarbon 1-dodecene was present in the emissions of rape, rye, hornbeam and birch.

Terpenes

The most abundant terpenes in the emissions of the investigated plant species were α-pinene, limonene and sabinene. Terpinolene, β-ocimene and camphene were only emitted by one of the examined plant species. β-Pinene, sabinene, β-phellandrene and limonene were the predominant VOC emissions from beech. The examined grassland plots emitted α-pinene, β-pinene and sabinene as major species. In emissions from rape, sabinene and limonene were among the three most predominant species. The monoterpene 2-carene which was identified as a principal emission from tomatoes (Winer *et al.*, 1992) was not detected in emissions from plants examined in this study. Five species of plants emitted compounds identified only as monoterpenes by the appearance of masses 93, 105 or 107, 121 and 136 in their spectra, but for which positive identification was not possible. These are listed as "other terpenes" in Table 3. In the case of birch, only

Table 2. Summary of sampling protocols

	Date	Sampling site	Sampling time	Samples	Meteorology	Comments
Wheat	16.06.93	Laxenburg	9.00–9.30–11.00–11.45–13.30–14.15–15.00	7	Sun; 24°C	Three days after blossoming; blossoms washed off by rain
Rape						
Blossoming	12.05.93	Essling	10.00; 16.00	2	Sun; 23°C	Blossoming
After blossoming	20.05.93	Essling	11.00; 14.45	2	Sun; 30°C	Some blossoms left; fruits already visible
Rye						
Before blossoming	12.05.93	Essling	15.00; 15.30	2	Sun; 23°C	About 5–6 d before blossoming
Blossoming	20.05.93	Essling	12.15; 13.30	2	Sun; 30°C	Blossoming
Grape						
	15.08.93	Rust	11.00–11.30–12.10–13.40	4	Sun; 28°C	Green leaves
With fruits	15.08.93	Rust	14.00–14.45	2	Sun; 28°C	Fruits two weeks before ripness
Beech						
20°C	30.08.93	Jägerwiese	13.30–14.00–14.40–15.15–15.45	4	Some clouds; 20°C	All leaves green; tree top about 20 m above ground
15°C	07.09.93	Jägerwiese	11.30–12.00–12.40–13.10–13.45–14.25–15.00	7	Some clouds; 15°C	All leaves green; tree top about 20 m above ground
Birch	12.05.93	Lobau	11.30; 12.30	2	Sun; 23°C	No blossoms
Hornbeam	12.05.93	Lobau	13.30	1	Sun; 23°C	No blossoms
Oak	28.09.93	Silberwald	9.30–10.05–10.45	2	Some clouds; 15°C	Some discoloured leaves
Grass land						
i-I	28.09.93	Silberwald	10.05–10.50	2	Clouds;*15°C	Under the oak forest;
i-II	16.09.93	Straßhof	13.30–14.00	2	Sun; 25°C	No flowers; height 35 cm
i-III	16.09.93	Straßhof	10.50–11.20–11.50	2	Sun; 25°C	Some flowers; 25 cm
i-III-m	16.09.93	Straßhof	12.30	1	Sun; 25°C	i-III mowed

*Only during the second sample short sunny periods.

Table 3. Emission rates (ng $g^{-1} h^{-1}$) of all organic compounds in volatile emission of the investigated natural and agricultural species

Compound	Plant species															
	a	a*	a**	b	b*	c	c*	d	e	e15°C	f	g	h	i-I	i-II	i-III	i-III-m
Alcohols																	
2-Methyl-1-propanol						21.3	6.8								0.4	3.7	
1-Butanol					7.4	11.3	17.0			3.9	3.3	6.9			1.6	8.4	2.1
2-Butanol												13.7					
3-Methyl-1-butanol						11.1	13.4										
2-Methyl-1-butanol							9.0				5.1	6.4					1.1
3-Methyl-3-buten-1-ol						6.7	2.3										
3-Methyl-2-buten-1-ol							1.7										
1-Pentanol				0.2			8.8										
3-Pentanol				5.6	3.5												6.1
1-Penten-3-ol				17.4	22.0	4.8	5.9								1.9		37.7
2-Penten-1-ol				0.2			1.9										
1-Hexanol						58.2	31.1										
Cis-3-hexen-1-ol		29.0	2.4	20.1	20.3	33.9	11.8	0.8		0.5	31.5	48.4	6.8	0.8	6.1	7.5	23.6
1-Octanol						16.6	15.0										
1-Octen-3-ol							9.0										
Linalool				8.9	1.0	5.2	2.9				20.5	33.0					
Menthol												61.9					
Ketones																	
Butanone	19.9	44.8	3.7									9.1			4.1	4.3	5.1
2-Pentanone								2.2									
3-Pentanone															2.1	4.4	29.1
6-Methyl-5-heptan-2-one												24.9					
Menthone												32.9					
Camphor																0.5	1.1
Aldehydes																	
Butanal															2.8	3.6	3.1
Hexanal	7.3	25.3	2.1	10.4	26.9	19.2	7.3	2.8	6.4	4.8	6.3	22.2	13.6	1.0	3.1	2.1	4.6
Trans-2-hexenal													8.7			0.8	8.9
Heptanal													2.0	0.2			
Octanal													1.0				
Nonanal													1.8	0.1			

Esters																
Cis-3-hexenylacetate	10.9	114.1	9.4	37.5	117.3		11.1	5.1	3.4	4.1	50.9	95.0	5.4	1.8	13.8	13.1	29.6
Hexylacetate				10.1			21.2					33.5					
Ethylhexylacetate							17.4										
Ethers																	
1,8-Cineol				16.5	13.4						1.8	3.5			1.1	13.0	21.9
Alkenes																	
Isoprene	1.5	5.1	0.4						2.0	1.3		2.5	614.4	0.2	1.0	1.7	1.6
1-Dodecen				X	X	X	X				X	X					
Monoterpenes																	
α-Pinene				7.9	7.4	8.1	1.3		10.9	4.9	1.1	15.9	5.4	3.9	0.5	9.6	19.9
α-Thujene				8.7	10.0				2.9	2.6						1.2	3.8
Camphene																2.7	6.0
Limonene	1.0	12.5	1.0	21.7	30.6	17.6	8.2		12.2	5.7	3.9	22.7	104.9	0.2	3.3	8.6	12.3
Myrcen				9.1		16.9	1.8										
Sabinene				21.6	39.9	7.1			39.5	30.1	2.6	34.3			1.8	8.8	22.0
β-Ocimene																1.0	10.7
β-Phellandrene	0.5	9.2	0.8			10.8	10.0		25.2	6.4	11.3	27.1					
β-Pinene				5.6	20.8				57.9	3.3	2.3			1.1	2.5	11.1	12.2
Terpinolene									2.0								
γ-Terpinene									14.5	1.8					0.3	2.2	4.0
Other terpenes						16.9	4.3		27.5	8.0		1.1	11.2	1.0	0.3	7.7	35.7
Sesquiterpenes																	
Trans-caryophyllene											20.3	X					
Other sesquiterpenes												61.2					

X: no EMR calculated, a: grape (27°C), a*: grape with fruits (26°C) (DLW), a**: grape with fruits (26°C) (DW), b: rape (30°C), b*: blossoming rape (25°C), c: rye (26°C), c*: blossoming rye (28°C), e: beech (20°C), e15°C: beech (15°C), f: hornbeam (23°C), g: birch (23°C), h: oak (15°C), i-I: grass land (15°C), i-II: grass land (25°C), i-III: grass land (25°C), i-III-m: i-III after mowing.

one sesquiterpene peak was detected. By matching the retention time and the mass spectra with an authentic standard this was identified as trans-caryophyllene. In the chromatogram of the emissions of hornbeam, six resolved peaks in the retention time range of the sesquiterpenes appeared. All these peaks could be identified as sesquiterpenes from their characteristic fragmentation pattern in the MSD but an identification of the isomeres was not possible. Therefore the emission rates of these sesquiterpenes are listed as "other sesquiterpenes" in Table 3.

BOVOCs

The oxygenated compounds 3-hexen-1-ol, hexanal and cis-3-hexenylacetate were emitted by almost all the plants examined in this study. Cis-3-hexenylacetate was the predominant compound in the emissions from rape, wheat, hornbeam, birch and one of the examined grass plots and was among the major emitted species in all other plants studied except for oak and rye. 3-Hexen-1-ol was among the three major emitted VOC from rye, hornbeam, birch, oak, one of the grass plots and grapes (with fruits). 3-Hexen-1-ol and cis-3-hexenylacetate were found to be predominant emissions from several agricultural plant species grown in California's Central Valley, namely alfalfa, almond, cherry, grape, nectarine, olive and peach (Arey *et al.*, 1991b; Winer *et al.*, 1992). 3-Hexen-1-ol and cis-3-hexenylacetate were also identified as major volatile species from wheat by Buttery *et al.* (1985). Isidorov *et al.* (1985) identified cis-3-hexenylacetate and "leaf alcohol" as emissions from several European tree species, among them birch, larch and fir. "Leaf alcohol" has been quoted as a major species in the emission of birch and *n*-hexanal has been observed in emissions from alfalfa, cherry, cotton, rice, tomato, walnut and chamise (Arey *et al.*, 1991b).

A total of 17 of the 33 identified BOVOC compounds were emitted only by one of the examined plant species. For four compounds blossoming rye was the only emitter. Five of the monitored plant species (grape, beech, birch, oak and grassland) emitted isoprene but, with the exception of oak, in quantities of only 0.5–3.4% of the total assigned plant emissions (TAPE).

A major problem in the identification of the oxygenated volatile compounds was the great number of isomeric structures that exist for some of these substances. Even with the available standards of alcohols, ketones and aldehydes an unequivocal isomeric identification was not always possible. For 1-pentanol, 2-pentanol and 3-pentanol a good discrimination based on the boiling points and the quite different fragmentation pattern in the MS spectra was possible, whereas the methylbutanol-isomers posed some problems. Except for rye emissions, 2-methyl-1-butanol, which was available as an authentic standard, was always present in the samples. In the chromatogram of the blossoming rye, two peaks with a retention time difference of 0.4 min were detected. The second was positively identified as 2-methyl-1-butanol, the first tentatively as 3-methyl-1-butanol. In some of the samples we observed peaks in the range of C_4–C_7 that were generally very small which could not be identified. Since these peaks never comprised more than 1–2% of the total biogenic emission they were not evaluated.

A peculiar variety of alcohols was found in the emission of rye. Rye emissions were sampled on two days in the field. The first sampling was carried out 5–6 d before blossoming, the second during blossom. The main compound in the emissions of the blossoming and nonblossoming rye was 1-hexanol, which has not previously been reported as a plant emission and was not detected in the emissions of other plants examined in this study. Other alcohols detected from rye and not reported previously were 2-methyl-1-propanol, 1-butanol, 3-methyl-3-buten-1-ol, 3-methyl-2-buten-1-ol, 1-pentanol and 2-penten-1-ol. 1-Butanol was quite abundant in the emissions of the studied plants. It was observed in emissions from blossoming rape, beech, hornbeam, birch and two of the examined grass plots. The other alcohols found from rye have been identified as volatile emissions from wheat or oat (Buttery *et al.*, 1982, 1985). In the wheat sample in this study the only alcohol detected was cis-3-hexen-1-ol ("leaf alcohol"). The most likely reason why other alcohols were not detected in the wheat emissions is the low overall emission rate (0.01 $\mu g\, g^{-1}\, h^{-1}$) for the wheat compared to rye (0.26 $\mu g\, g^{-1}\, h^{-1}$). The large differences in the emission rates of wheat and rye are probably more a result of different stages of growth than of different plant types. Hewitt *et al.* (1992) pointed out the need for data on seasonal and interspecies variations. Emissions from mature wheat just before harvesting were essentially zero (below detection limits), compared with zero to $> 1\ \mu g\, g^{-1}\, h^{-1}$ from other studies (Winer *et al.*, 1992; Lamb *et al.*, 1993).

For grape (Chardonnay) one of the main emitted species was butanone, previously reported to be emitted from European fir, juniper, cedar, cypress and fern (Isidorov *et al.*, 1985). Butanone was also observed in the emissions from birch and two of the examined grass plots.

In the oak emission samples a range of aldehydes (C_6–C_9) was detected. Those aldehydes have been identified as potential emissions from wheat and oat (Buttery *et al.*, 1982, 1985). Trans-2-hexenal is believed to act as an antibacterial agent in the bacterial defense mechanism of plants (Croft *et al.*, 1993). The alkanals (C_4–C_{10}) have also been observed recently in ambient air (Yokouchi *et al.*, 1990; Ciccioli *et al.*, 1993) in urban and rural environments. Ciccioli *et al.* (1993) speculate that the ubiquitous occurrence of C_4–C_{10} alkanals is due to vegetative emissions and showed that alkanals are found in essential oils from various plants, fruits and blossoms. In this context it should be pointed out that alkanals may be formed by secondary reactions through ozonolysis of terpenes ad-

sorbed on Tenax traps, although the mechanism of their formation is unclear and still under investigation (König, unpublished results). Ciccioli *et al.* (1993) reported the occurrence of 6-methyl-5-hepten-2-one in air from an oak forest, but this compound was not observed in oak emissions only from birch. Finally ethylhexylacetate was detected for the first time in the emission from blossoming rye.

Importance of compound classes other than monoterpenes

The screening of nine plant species at different stages of growth showed that oxygenated compounds were dominant relative to total hydrocarbon emissions in all species except beech and oak, where the percentage of BOVOCs to the total assigned plant emission (TAPE) was below 20% (Table 4).

Based on the prevalence of one of the VOC-groups (isoprene, terpenes, BOVOCs) the grain plants wheat and rye, grape, rape, hornbeam and birch can be classified as "BOVOC"-emitters. For the examined grassland-plots the emission of "BOVOCs" was approximately equal to the emission of monoterpenes.

The most important chemical classes of BOVOCs were the alcohols and esters, which dominated the emission of oxygenated compounds in almost all the enclosure measurements. At least 16 different alcohols, mostly $> C_6$, were found to be emitted, compared with only three ethers.

Variations in emissions during different stages of growth

Previous studies showed that emission rates are affected by many seasonal variables, including the effects of temperature (Tingey *et al.*, 1980; Juuti *et al.*, 1990), light intensity (Tingey *et al.*, 1980) and phytogenic effects like leaf drop and blossoming (Arey *et al.*, 1991c). Westberg (1981) observed a dramatic increase in the emission of Δ^3-carene in the springtime from Ponderosa pine. Arey *et al.* (1991a) reported that the presence of blossoms on orange trees increased the hydrocarbon emission rate by several orders of magnitude. In contrast to this, Crape myrtle blossoms did not emit hydrocarbons at all (Corchnoy *et al.*, 1992).

In the current study the effect of blossoming was studied for two agricultural species (rape and rye) and the effect of fruits in one case (grape).

The changes of the emission rates during blossoming are shown in Tables 3 and 4. Emissions from rape were sampled during blossoming and one week after the end of blossoming. The TAPE of the blossoming rape was ~1.6 greater than from the nonblossoming plant. After normalizing the emission rates to 30°C this difference increased to ~2. The emission rates of some single substances such as β-pinene and cis-hexenylacetate were 4–5 times higher in the blossoming sample than in the sample after blossoming. The percentage of cis-hexenylacetate in the total emission increased by a factor of ~2, that of β-pinene by a factor of ~2.5, whereas the percentage of BOVOCs in the total emission rate did not significantly change. However in the emission from rape without blossoms, alcohols were the dominant chemical class of BOVOC emissions while during blossoming the esters were the most abundant compounds.

In contrast, the presence of blossoms on rye did not have any obvious influence on the total emission rate, although the GC–MS spectra showed some changes in the relative composition of the emissions. Five oxygenated substances were only present in the chromatograms of the blossoming crops and the percentage of BOVOCs in the total emission increased from 71 to 88%. The predominant compounds were the alcohols from both the blossoming and the non-blossoming crops.

The presence of fruit on grape had a clear influence on emissions. The results show distinct differences for some compounds but almost no change of the total emission rate (based on the dry weight including the fruits) and the percentage of BOVOCs. However if the emission rate calculation is based only on the dry leaf weight the total emission rate of the branch with fruits is about six times higher than the one of the fruitless branch. Moreover it was observed that the BOVOC emission of the leaves was dominated by ketones while the most important chemical class of the emissions of the branch with fruits were the esters.

For several plant specimens we observed higher emission rates for the C_6 compounds in the first emission sample during the set of 4–7 samples. In these cases we rejected the results from the first sample when averaging the emission rates. A more detailed report about handling effects is in preparation. The "handling effect" for C_6 compounds has been also observed by Arey (personal communications).

Temperature effects

For the plant species wheat, grape, grassland III and beech a sampling protocol, according to the procedure proposed by Winer *et al.* (1992), was adopted. The protocol called for at least five measurements from a given plant species over a course of several hours from mid-morning to mid-afternoon. Since the temperature changes in the enclosure were only in the range of a few degrees centigrade during the single days of measurements, no effects of temperature on the emission rates could be determined.

In the case of the beech the same branch of the tree-top was investigated on 30 August at a mean enclosure temperature of 20°C and on 7 September at a mean temperature of 15°C. As shown in Table 4 the TAPE differed by a factor ~3 whereas the percentage of terpenes in the total emission was almost constant. In contrast to this the composition of the individual terpenes was quite different for the two measurements. Only a few terpenes, such as α-pinene, limonene and β-phellandrene, had more or less constant relative emissions in both cases. However, β-pinene showed a dramatic decrease of a factor of ~5 (see Table 3).

Table 4. Summary of emission rates and relative composition of total assigned plant emissions from nine species

	Emission rates (ng g^{-1} h^{-1})			Percentages of TAPE										
	Terpenes	BOVOCs	TAPE	Isopr.	Mono.	Sesqui.	**BOVOCs**	Alcohols	Ketones	Aldehydes	Esters	Ethers	Temp.[a]	Samples
Agricultural														
Grape	2.9	38.2	41.1	3.5	3.5	0.0	**92.9**	0.0	48.5	17.8	26.6	0.0	27	4
DLW grape with fruits	26.7	213.2	240.0	2.1	9.0	0.0	**88.9**	12.1	18.7	10.6	47.6	0.0	26	2
DW grape with friuts	2.2	17.6	19.8	2.1	9.0	0.0	**88.9**	12.1	18.7	10.6	47.6	0.0	26	2
Rape	74.6	126.9	201.5	0.0	37.0	0.0	**63.0**	26.0	0.0	5.2	23.6	8.2	30	2
Rape blossoming	108.7	211.8	320.5	0.0	33.9	0.0	**66.1**	16.9	0.0	8.4	36.6	4.2	25	2
Rye	77.4	188.3	265.7	0.0	29.1	0.0	**70.9**	63.6	0.0	7.2	0.0	0.0	26	2
Rye blossoming	25.6	193.6	219.3	0.0	21.7	0.0	**88.3**	62.3	0.0	3.3	22.7	0.0	28	2
Wheat	0.0	10.9	10.9	0.0	0.0	0.0	**100.0**	7.3	20.2	25.7	46.8	0.0	25	7
Natural														
Beech	194.4	9.8	204.3	1.0	94.2	0.0	**4.8**	0.0	0.0	3.1	1.7	0.0	20	4
Beech	64.0	13.3	77.4	1.7	81.1	0.0	**17.2**	5.7	0.0	6.3	5.3	0.0	15	7
Hornbeam	41.4	119.4	160.8	0.0	13.2	12.6	**74.2**	37.5	0.0	3.9	31.7	1.1	23	1
Birch	164.8	391.3	556.1	0.5	18.2	11.0	**70.4**	30.6	12.0	4.0	23.1	0.6	23	2
Oak	735.9	39.3	775.2	79.3	15.6	0.0	**5.1**	0.9	0.0	3.5	0.7	0.0	15	2
Oak forest grassland 1 (i-I)	6.4	3.9	10.3	1.9	60.7	0.0	**37.4**	7.3	0.0	12.6	17.5	0.0	15	2
grassland 2 (i-II)	9.7	36.9	46.6	2.1	18.7	0.0	**79.2**	21.5	13.2	12.6	29.5	2.4	25	2
grassland 3 (i-III)	54.8	61.4	116.1	1.5	45.7	0.0	**52.8**	16.9	8.0	5.5	11.3	11.2	25	2
grassland 3 (i-IIIm)	128.1	174.0	302.1	0.5	41.9	0.0	**57.6**	23.4	11.7	5.5	9.8	7.2	25	1

[a] The temperature was measured within the branch enclosure.

If the exponential temperature dependence of monoterpene emissions (Guenther *et al.*, 1993) is assumed to be valid also for decidous trees, a maximum variation of the emission rates of a factor of about two could be expected from the temperature variation of 5°C. In addition it has to be taken into account that the investigations of Juuti *et al.* (1990) and Guenther *et al.* (1991) suggest that at any given temperature the emission rate for a single species can vary by a factor of two.

Winer *et al.* (1992) found that the ratios of the monoterpenes to one another were generally constant over the time scale of a series of measurements during one day. This is in agreement with the data of each single day of our investigations where the terpene ratios differed only up to a factor of ~1.5. Possibly the rainy weather and the large decrease in mean temperature from ~20 to ~14°C in the week between the two measurements of the beech caused the different emission pattern of terpenes.

Enclosure effects

The study of Lamb *et al.* (1987) showed a reasonable to excellent agreement of enclosure measurements with atmospheric tracer and micrometeorological gradient techniques. As shown by Juuti *et al.* (1990) and Arey *et al.* (1991b) great attention has to be payed to the handling of plants when putting them into the chamber in order not to cause any damages to the leaves which would lead to an increase in emissions. Tests in our laboratory, mainly carried out with eucalyptus trees, showed that the emission of certain BOVOCs such as 3-hexen-1-ol and cis-hexenylacetate were strongly enhanced by rough handling, so that these BOVOCs could be considered to be an indicator for rough handling. However, since these two compounds were often observed from plants during sampling, every effort was made to place the plant into the chamber gently in order to obtain representative measurements.

Comparison with literature data

Four of the plant species investigated here have been studied previously, and the present emission rate data are compared with the literature data in Table 5.

The comparison of the data for the grapes shows that the emission rates of (Z)-3-hexen-1-ol and cis-3-hexenylacetate are much smaller in this study. This may be an effect of the lower ambient temperature and the different grape varieties used. The different varieties may also explain the different pattern of monoterpenes and the lack of sesquiterpenes in our data. Arey *et al.* (1991) showed that different varieties, Thompson seedless and French Columbard, give different emission profiles of monoterpenes.

Emissions of TAPE from oak, normalized to 30°C (without considering different light intensities), are about 1.5 $\mu g\,g^{-1}\,h^{-1}$ and are within the range of the reported data for the isoprene. The emission rates of 3-hexen-1-ol and cis-hexenylacetate are after normalization to 30°C much smaller than the ones reported by Arey *et al.* (1991a) but the terpene emissions observed in this study are higher.

Our emission rate data for the European birch are within the range reported by Armelis *et al.* (1984). Moreover the emission of 3-hexen-1-ol and cis-hexenylacetate by birch trees has been reported previously (Isidorov 1985) but no emission rates were given.

Winer *et al.* (1992) reported that wheat emitted no monoterpenes, sesquiterpenes, (Z)-3-hexen-1-ol or cis-3-hexenylacetate. In their study a TAPE of 0.1 and a total carbon (TC) of 1.1 $\mu g\,g^{-1}\,h^{-1}$ was determined. The high value of the TC was caused by numerous unidentified peaks (generally $< C_6$). In the current study cis-3-hexenylacetate was found to be the main emission of the investigated species. This is in good agreement with the investigations of Buttery *et al.* (1985) who also found this volatile compound to be the most important one in wheat emissions. Moreover he reported that 2-pentanone and 3-hexen-1-ol, besides many other volatiles, were compounds of the plant emissions. 2-Pentanone and 3-hexen-1-ol were also the main emissions from wheat in our study. The total assigned plant emission rate (TAPE) for wheat was 0.011 $\mu g\,g^{-1}\,h^{-1}$. This value is much lower than the one reported by Winer *et al.* (1992). Lamb *et al.* (1993) recommend use of 0.041 $\mu g\,g^{-1}\,h^{-1}$ for emission rate inventories. The emission rate for rye in our study (0.265 $\mu g\,g^{-1}\,h^{-1}$ at 26°C) was considerably higher than that recommended for use in the U.S. biogenic emissions inventory (0.016 $\mu g\,g^{-1}\,h^{-1}$ for 30°C) by Lamb *et al.* (1993). The high emission rate was mainly due to a variety of alcohols while the terpene emission rate found here is equal to the terpene emission rate of Lamb *et al.* (1993). The reason for the large difference in the emission rates between rye and wheat as observed in our study is unclear as yet, however different stages of development might explain the differences in the observed emission rates. Rye was sampled a week before blossoming and during blossoming. Wheat was sampled 3 d after blossoming, the blossoms being washed off by heavy rain during the days prior to sampling. It might be that the emissions of alcohols in the nonblossoming rye were already a result of the development of the blossoming stage while wheat with the blossoms washed off exhibited a largely reduced emission of BOVOCs (and terpenes). It might also be that the emission of alcohols is reduced after rains due to leaching of water solubles during rainfall.

It has to be emphasized that the comparison of emission rate (EMR) data is always very difficult because even EMR measurements on a single tree can vary by a factor of ~2 from the mean for a given temperature (Juuti *et al.*, 1990). Besides this, some studies have shown that there are significant variations (up to a factor of 10 (Tingey *et al.*, 1980)) in the emission rate values for individual trees of a given

Table 5. Volatile organic compound emission rates compared with literature data

Plant species	Emission rates ($\mu g\ g^{-1}\ h^{-1}$) 3-Hexen-1-ol	Cis-hexenylacetate	Sum of oxygenates	Isoprene	Monoterpenes	Sesquiterpenes	Sum of em TAPE	Mean temp.	Comments	Author
Grape (Thompson)	nd	0.8	0.8[a]	nd	nd	nd	2.0	34		[a]Arey *et al.* (1991b), Winer *et al.* (1992)
Grape (French C:)	0.2	0.5	0.7[a]	nd	nd	0.1	2.2	35		[a]Arey *et al.* (1991b), Winer *et al.* (1992)
Grape (French C:)				nd	nd	0.1				Arey (1991c) JGR
Grape (Chardonnay)	nd	0.011	0.038	0.002	0.002	nd	0.041	27		This study
Grape (Chardonnay)	0.029	0.114	0.213	0.005	0.027	nd	0.240	26	Fruits; DLW[b]	This study
Grape (Chardonnay)	0.002	0.009	0.018	0.001	0.002	nd	0.020	26	Fruits; DW[c]	This study
Valley Oak	0.3	0.2		2.3				27		Arey *et al.* (1991b)
Valley Oak				2.3	0.02	nd		27		Arey *et al.* (1991c) JGR
Valley Oak			< 0.5[a]	2.3	< 0.01	nd	2.8	27		Winer *et al.* (1992)
Oak (qu. robur)				1.3–36.2				15–26		Isidorov 1992 Ecological Bull. 42
Oak (qu. robur)				2.4–50.4				18–32		Armelis, Nika 1984 Fiska Atmos 9
European Oak				1.3–32.6				12–27		Isidorov Atm Env 1985, 19
Oak (quercus petrae)	0.007	0.005	0.039	0.61	0.12	nd	0.78	15		This study
Birch (bet. vericosa)							0.1–3.95	18–32		Armelis, Nika 1984 Fiska Atmos 9
Birch (betula pendula)	0.048	0.095	0.391	0.003	0.164	0.061	0.56	23		This study
Wheat	nd	nd	nd		nd	nd	0.1 (TC = 1.1)	38		Winer *et al.* (1992)
Wheat				0.02	0.08		0.041	30		Lamb *et al.* (1993)
Wheat (Capo)	0.001	0.005	0.011	nd	nd	nd	0.011	25		This study
Rye					0.08		0.016	30		Lamb *et al.* (1993)
Rye			0.188		0.08		0.265			This study

[a]Sum of cis-3-hexen-1-ol and cis-3-hexenylacetate.
[b]DLW dry leaf weight.
[c]DW dry weight.

species (Tingey *et al.*, 1980; Guenther *et al.*, 1991; Corchnoy *et al.*, 1992).

However if all these factors are taken into account the EMR data of the species compared from our study are in reasonable agreement with the data from other authors.

CONCLUSIONS

In the emissions of eight plant species and three different types of grassland tested we identified over 50 different VOCs. Of these 2-methyl-1-propanol, 1-butanol, 2-butanol, 1-pentanol, 3-pentanol, 1-hexanol, 6-methyl-5-hepten-2-one, butanal and ethylhexylacetate were observed for the first time as plant emissions. The oxygenated compounds (Z)-3-hexen-1-ol, hexanal and (Z)-3-hexenylacetate were emitted by almost all the plants investigated in our study. In terms of the prevalence of one of the groups of emitted VOCs (isoprene, terpenes, BOVOCs) the grain plants wheat and rye, the agricultural species grape and oilseed rape and the decidous trees hornbeam and birch can be classified as "BOVOC"-emitters. For the grass plots examined the emission of terpenes and BOVOCs appear to be of equal importance.

The major decidous tree species in Austria (beech) is a terpene emitter. It has long been known that oaks are isoprene emitters. The oak examined in this study emitted around 80% of TAPE as isoprene, 15% monoterpenes and 5% BOVOCs with aldehydes being the predominant class of species among the BOVOCs. The emission rates of the total assigned plant emissions (TAPE) ranged from 0.01 for wheat to 0.8 $\mu g\, g^{-1}\, h^{-1}$ for oak (calculations based on the dry leaf weight). Intercomparison with available literature data from other studies shows that our emission rates are rather on the lower end of reported ranges.

This might be due to:

(a) more careful handling of the plants during the examination,

(b) exclusion of system peaks and peaks which have already been observed in the inflowing air into the chamber from the VOC-emission evaluation,

(c) interspecies differences and intraspecies developmental differences,

(d) data used in emission inventories (e.g. Lamb *et al.*, 1993; Guenther *et al.*, 1994) are based on "leaf level" measurements. Data for isoprene from "branch level" measurements are around 60% lower than for "leaf level" measurements (Guenther *et al.*, 1994).

Variations in emissions during different stages of growth were observed for rye and oilseed rape which were studied in the blossoming and the nonblossoming stage and for grape which was studied with and without fruits.

Although emission rates of some single substances differed widely, the TAPE of rye was virtually nonaffected by blossoms, whereas the TAPE of oilseed rape was increased around a factor of two for the normalized (30°C) emission in the blossoming stage compared to the nonblossoming.

The VOC emission rate of grape with and without fruits showed a significant change of relative composition of the emitted species with the ketones predominant in the leaf emissions and the esters predominant in the emissions of the branch with fruits. If not accounting for the weight of the fruit, the emission rate based on the dry leaf weight increased by around a factor of six for the branch with fruits whereas the emission rate based on the total dry weight (stems excluded) was around 50% of the emission rate of the leaves.

The results show that BOVOCs are important compounds in the emissions of agricultural crops and of grassland. Major uncertainties still exist regarding variations in the emissions as a consequence of the stage of growth and of different plants of a single species and for the temperature dependence BOVOC emissions.

Acknowledgements—This is a contribution to project P 9118-CHE of the Austrian Science Foundation (FWF) and to the CEC project EV5V-CT91-0048 "BOVOC". We wish to thank the other members of the BOVOC project group (E. Parussel, C. Plass-Dülmer, R. Knienider) and J. Arey, A. Guenther, M. Gery, St. Smidt and R. Steinbrecher for helpful discussions.

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