AIR POLLUTION AND THE SMELL OF CUT GRASS

Wayne Kirstine[1], Ian Galbally[2] and Martin Hooper[1]
[1] School of Applied Sciences, Monash University, Churchill, Vic 3842, Australia
[2] CSIRO Division of Atmospheric Research, Aspendale, Vic 3195, Australia

Summary

Recently we have demonstrated that grass and cut grass are important sources of volatile organic compound (VOC) emissions into the atmosphere. The production of these VOCs can be traced back to plant growth, maintenance and wound defence mechanisms. The gases emitted as part of these wound defence mechanisms are responsible for the smell of freshly cut grass, and are also highly photochemically reactive. These emissions from grass and cut grass are not currently included in urban and global emissions inventories. Our preliminary estimate is that, within an urban airshed, during the growing season, about one third of the emissions of photochemically reactive VOCs come from grass and cut grass. These grass emissions should be included in models of urban photochemical pollution so that accurate smog predictions can be obtained.

Keywords: VOCs, grass, cut grass, hexenyl compounds, oxygenated hydrocarbons, emissions inventories, air pollution, photochemical smog.

1. Introduction

Until recently, the volatile organic compound (VOC) emission flux from grass had been misjudged both to be negligible in magnitude and to have a composition comparable to the emissions from trees (Placet *et al.* 1990, Lamb *et al.* 1993). Kirstine *et al.* (1998), in a study of the emissions of VOCs from grass pasture in south-eastern Australia, discovered that the emissions from pasture were principally light oxygenates. Kirstine *et al.* (1998) also showed that the VOC profile for grass clippings was significantly different from that for normal grass emissions. There was approximately a hundred-fold increase in emissions following cutting and the subsequent drying of cut grass, with most of the increase in VOC emissions coming from the production of C_6-oxygenates. These oxygenated compounds are know to be responsible for the characteristic 'green odour' associated with freshly cut grass and leaves of other plants (Hatanaka 1993). These emissions from cut grass are not included in inventories of emissions of VOCs from plants (Guenther *et al.* 1995), and may constitute a significant omission. These C_6-compounds are highly reactive with hydroxyl radicals and ozone, are potent precursors to ozone formation, and in urban areas will contribute to the formation of photochemical smog.

2. Emissions from Grass

Kirstine *et al.* (1998), in a study of the emissions of VOCs from grass pasture in south-eastern Australia, discovered that the emissions from pasture were principally light oxygenates, including methanol, ethanol, acetaldehyde, and acetone. Together, these four compounds formed 61% of the total emissions from the grass pasture. See Figure 1. The combined emissions of isoprene and monoterpenes, which are predominant emissions from trees, made up only about 6% of the VOCs emitted from grass. Similar results were obtained in a study conducted by Fukui and Doskey (1998) on grasslands in the northern United States.

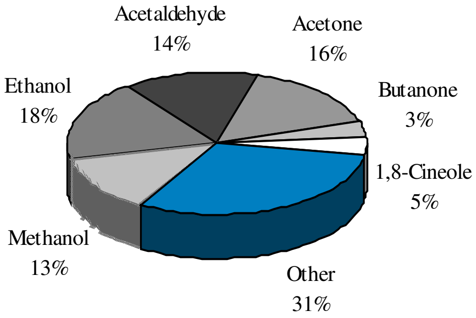

Figure 1. Approximate composition of VOCs from grass pasture as a percentage of total carbon (Kirstine *et al.* 1998).

The best estimate of Kirstine *et al.* (1998) for the VOC emission rates (covering C_2-C_{10} hydrocarbons and oxygenates) for grasslands in warm, sunny conditions was approximately 600 $\mu g(C)\ m^{-2}\ h^{-1}$. This rate, when referenced against the amount of biomass in the sampling chamber, expressed as dry matter (dm), is equivalent to 0.4 $\mu g(C)\ g(dm)^{-1}\ h^{-1}$. Similar flux estimates have been obtained from additional measurements conducted by Fukui and Doskey (1998) and Warneke *et al.* (1999). Integrated over a typical growing season, these emission rates are approximately 1.3 mg(C)/g(dm). Given that grassland ecosystems occupy about one-quarter of the Earth's land surface and contribute about 25-30% of the global net primary production (Guenther *et al.* 1995), the global emissions from grasslands and pastures could amount to 30-35 Tg(C)/y of VOCs. This emission rate is small compared to the 821 Tg(C)/y that Guenther *et al.* (1995) estimated for the global emissions from trees, but about one-third of the emission rate of anthropogenic non-methanic hydrocarbons as determined by Müller (1992).

3. Emissions of VOCs from Cut Grass

Mechanical injury of plant leaves, whether through herbivore attack, unintentional rough handling, cutting or mowing, results in a significant increase in the emission of VOCs, including a set of eight related C_6-oxygenated hydrocarbons and associated esters (Ohta 1984, Arey *et al.* 1991, König *et al.* 1995, Mayland *et al.* 1997, Paré and Tumlinson 1997). These C_6-oxygenated hydrocarbons include the isomers of hexenol and hexenal, as well as the saturated compounds, hexanal and hexanol. Hatanaka (1993) describes the emissions of these compounds and their contribution to the smell of cut grass.

The fractional composition of the emissions from cut grasses varies somewhat among the available studies. Mayland *et al.* (1997) analysed the headspace volatiles from freshly cut samples of *Festuca arundinacea* (tall fescue) one hour after cutting. On average, 81.5% of the VOCs consisted of (Z)-3-hexenyl acetate, 8.9% (Z)-3-hexen-1-ol, 1.0% (Z)-3-hexenal, 0.6% (E)-2-hexenal, 0.4% (E)-3-hexenal, 0.3% (E)-2-hexenyl acetate and 0.1% (Z)-2-hexenal. Three of these hexenyl-type compounds were also enhanced in the emissions of mown grassland as determined by König *et al.* (1995).

Kirstine *et al.* (1998) showed that the VOC profile for cut pasture grass was different from that for normal grass emissions. As shown by the pie chart in Figure 2, most of the increase in VOC emissions from cut grass came from the production of C_6-oxygenates. Together, these C_6-hexenyl compounds constituted 69% of the volatile emissions of the cut grass. The most abundant species, which made up about 40% of the total, was (Z)-3-hexenyl acetate. Hexenals and hexenols accounted for 20% and 9% of the emissions, respectively, while the only saturated C_6-compound, hexanal, contributed 2%. Methanol made up about 9%, while acetaldehyde and acetone accounted for about 4% and 2% of the total emissions, respectively. Isoprene and monoterpenes accounted for less than 0.5% of the emissions from cut grass.

The cutting or grazing of pastures induces both the production of traumatic acid that stimulates the formation of new leaf cells at the wound site to close the wound, and also a suite of hexenyl-type alcohols, aldehydes and esters that function as antibiotics at the wound site to prevent bacterial infection and inhibit fungal growth (Major *et al.* 1960, Croft *et al.* 1993). In addition to these roles, certain of these C_6-compounds may act as volatile signalling molecules that induce production of defence-related compounds such as lignin and cell wall proteins in un-wounded sites in the same or an adjacent plant (Sharkey 1996, Bate and Rothstein 1998).

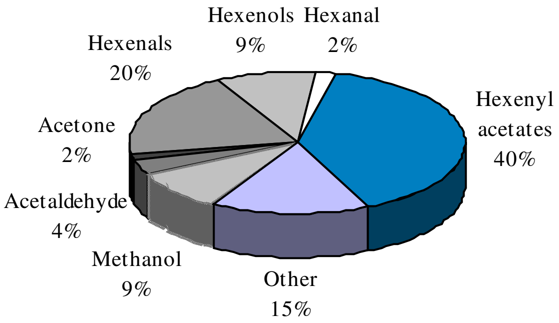

Figure 2. Approximate composition of VOCs from slashed pasture grass as a percentage of total carbon (Kirstine *et al.* 1998).

The mechanism for the production of these C_6-compounds from the oxidative cleavage of C_{18}-fatty acids in the presence of oxygen and an enzyme system was originally elucidated by Hatanaka *et al.* (1978). The biosynthesis and regulation of these compounds has been the subject of a number of recent reviews (Hatanaka 1993, Hatanaka *et al.* 1995, Sharkey 1996, Blée 1998, Grechkin 1998, Fall 1999), and is summarised in Figure 3.

Through the action of enzymes and oxygen, the plant lipids (that contain fatty acids) are transformed to C_6-aldehydes, C_6-alcohols and the growth stimulant, traumatic acid, which is structurally similar to 12-oxo-(Z)-9-dodecenoic acid (Croft *et al.* 1993). The production of hexenyl acetate is thought to occur in the damaged tissue through the action of the enzyme, acetate transferase (Fall *et al.* 1999).

The relative proportion of C_6-compounds that occur in wound-induced emissions is variable. Changes in the amounts of specific C_6-compounds occur during plant development, seasonally and with the composition of the fatty acids within the plant tissue (Hatanaka *et al.* 1978, Hatanaka 1993, Zhuang *et al.* 1996).

4. The Rates of VOC Emissions from Cut Grass

Kirstine et al. (1998) measured VOC emission rates from grass or clover clippings by placing small quantities of coarsely chopped grass or clover in a sampling chamber

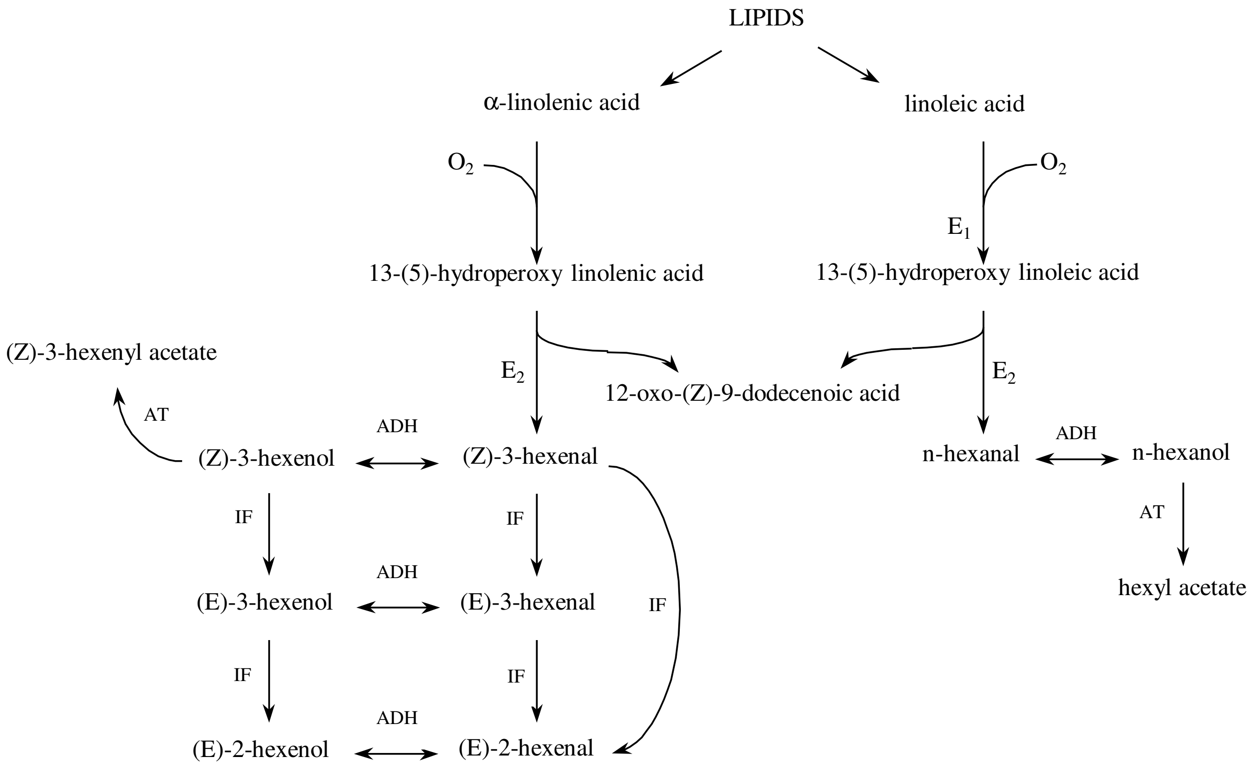

Figure 3. Biochemical production of C_6-volatiles in green plants (Hatanaka *et al.* 1995, Fall *et al.* 1999). IF = isomerisation factor; E_1 = lipoxygenase; E_2 = hydroperoxide lyase; ADH = alcohol dehydrogenase; AT = acetyl transferase.

immediately after cutting. They obtained emission rates about 80 times the maximum emission rate observed for undamaged clover, and about 180 times the maximum rate for undamaged grass under similar conditions of temperature and light intensity. Emission rates ranged from 33 µg(C) $g(dm)^{-1}$ h^{-1} to as high as 830 µg(C) $g(dm)^{-1}$ h^{-1}. Unlike the normal emissions from undamaged grass or clover, the emissions from the cut material were short-lived and decreased exponentially with time. The initial emission rate increased with temperature and with the degree of maceration, but the decay rate was relatively constant with an average value of 0.3 per hour, the emission rate approximately halving every 2 hours.

The enhanced VOC emissions from cut grass were further studied by de Gouw *et al.* (1999), who placed samples of red fescue grass and white clover in a chamber and then re-cut the stem and leaf surfaces. A sharp increase was observed in the concentrations of C_6-compounds, including (Z)-3-hexenal, (Z)-3-hexenol and (Z)-3-hexenyl acetate. Increased emissions of formaldehyde and methanol were also observed. This initial burst of VOCs quickly began to decline, as observed by Kirstine *et al.* (1998), but after exposing the grass sample to drying air for about 200 minutes, a second, and larger, burst of VOCs was measured – this time dominated by (Z)-3-hexenal and acetaldehyde. It is likely that the VOC emissions during drying are the result of the gradual collapse of the cellular structure of the plant leaves during the drying process (Karl *et al.* 2001b).

Karl *et al.* (2001c) made on-line measurements of the VOC emissions during the mowing of lawn grass. Again, hexenyl compounds were dominant, although significant amounts of methanol, ethanol, acetic acid, butanol and butanone were also observed. Enhanced emissions of acetone from the drying grass were observed after rainfall, consistent with the production of acetone observed by Warneke *et al.* (1999) following the wetting of leaf and grass litter. The peak levels of VOCs (20-60 ppbv) obtained after mowing suggested to Karl *et al.* (2001c) that, during the mowing of a 2020 m^2 lawn area, the total biogenic VOC emission rate from the cut grass would be in the range 64-700 g/h or about 600-6000 µg(C) $g(dm)^{-1}$ h^{-1}. The approximate compositions of the available measurements of VOC emissions during the initial cutting and subsequent drying phase are shown in Table 1.

Table 1. Integrated fluxes of speciated VOC emissions from cut grass and clover. The abbreviation nf indicates that the compound was observed in significant quantities, but no integrated flux was determined.

Plant Material	Time	Integrated Production µg/g(dm)	Reference
cut grass pasture	½ hour	methanol, 149; acetaldehyde, 40; acetone, 15; hexenyls, 600	Kirstine *et al.* (1998)
cut lawn grass	12 hours	methanol, 20; hexenyls, nf; acetaldehyde, nf; formaldehyde, nf; butanone, nf	de Gouw *et al.* (1999)
cut lawn clover	8 hours	methanol, 200; acetone, 800; butanone, 700; hexenyls, nf	de Gouw *et al.* (1999)
cutting of clover	1-2 hours	methanol, 240; acetaldehyde, 3; acetone, 16; butanone, 21; hexenals, 82	de Gouw *et al.* (2000)
drying of cut clover	8 hours	Total > 1000 µg(C)/g(dm)	de Gouw *et al.* (2000)
cut pasture grasses	over drying process	methanol, 160; acetaldehyde, 20-80; acetone, 20-40; butanone, 11-80; pentenols, 15; hexenals, 100-240; hexenols and hexanal, 30-60	Karl *et al.* (2001a)
mown pasture grasses	first day after mowing	methanol, 65 ± 20; acetaldehyde, 13 ± 4; hexenyl compounds, nf, butanone, nf; pentenols, nf	Karl *et al.* (2001b)
mown lawn grass	4-5 hours	acetaldehyde, 20-80; acetone, 16-40; hexenyl compounds, 35-300, methanol, nf; ethanol, nf; butanone, nf.	Karl *et al.* (2001c)

5. Contribution of Grass and Grass Cutting to Airshed VOC Emissions

The emission rate of VOCs from grass cutting can be estimated by integrating over time the transient flux due to cutting. For an initial emission rate from cut pasture of 182 µg(C) g(dm)$^{-1}$ h^{-1} with a decay constant of 0.3 per hour, as measured by Kirstine *et al.* (1998), the integrated emission from a single cutting would be equal to about 600 µg(C)/g(dm). Measurements conducted by Karl *et al.* (2001b) suggest that an approximately equal emission of VOCs would result during the subsequent drying phase.

Based on the measurements of Kirstine *et al.* (1998) and Karl *et al.* (2001c), we estimate that the VOC emissions from freshly cut grass and the subsequent drying phase total about 3 mg/g(dm). We have calculated the emissions of VOCs from uncut grass and from the freshly cut and drying phases of cut grass, and applied them to the airshed of Melbourne, Victoria (known as the Port Philip Control Region). Melbourne has a population of 3.45 million people and the airshed area is 24000 km^2. We assume that one third of the airshed area is covered by grass; 10% of the area is suburban, where the grass is cut 20 times per year; and the remaining 90% is rural, where the grass is cut twice per year. These assumptions are consistent with local knowledge and inventory information on hours of lawn mowing, etc. (EPAV 1998). The emissions are compared in Table 2 with other estimates of VOC emissions for the 1995-1996 period, as determined from the Air Emission Inventory for the Port Philip Control Region (EPAV 1998).

Table 2. VOC fluxes for the urban area of Melbourne, Australia (designated as the Port Philip Control Region), including anthropogenic emissions and those produced by grass and grass cutting.

Source of VOCs	Flux (g m^{-2} y^{-1})	% of total
Motor vehicles	2.64	31
Industrial sources	1.39	16
Domestic, commercial, and rural	2.90	34
Other mobile sources	0.09	1
Uncut grass	0.47	6
Grass cutting	1.03	12
Total	8.52	100

Thus, about 18% of the total yearly average emissions of VOCs in the Port Philip Control Region come from grasses. Because the grass emissions occur mainly during the summer months, grass emissions will constitute a greater proportion of the VOC emissions during this period, and could, at times, approach one third of the total VOC emission flux.

6. Photochemical Reactivity of the Compounds Emitted from Grass and Cut Grass

Individual VOC species have differing effects on the final production of photochemical oxidants because each reacts with a different rate and with a different reaction mechanism within the photochemical smog mixture. This is further complicated by the fact that the VOC species interact in a non-linear manner, with the oxidant-forming potential of each species depending upon the photochemical mix. Given the very complex relationship between oxidant levels and concentration of VOC precursors, it is not surprising that there is no single procedure for defining reactivity.

One approach is based on incremental reactivity, and is defined by Carter and Atkinson (1987) and Carter (1994). This reactivity measures the effect of small changes of individual precursor VOCs on the amount of smog generated by a base mixture in a given time. Unfortunately, Carter (1994), in his extensive list of reactivities, does not provide incremental reactivities for the range of hexenyl compounds considered here.

A less sophisticated measure of VOC reactivity is based on the rate constants for the reactivities of various VOCs with hydroxyl radicals, nitrate radicals and ozone. In general, the reactions of a VOC species with these compounds are important initial steps in the pathways for the generation of derived radicals involved in photochemical smog generation.

The reaction rates of the VOC species emitted from grass cutting are compared in Table 3 with those for other reactive anthropogenic pollutants.

Table 3. Rate constants (in cm^3 $molecule^{-1}$ s^{-1}) of some reactive hexenyl-type oxygenated compounds and other reactive VOCs with atmospheric oxidants at 296-298 K (Atkinson *et al.* 1995, Warneck 2000).

Species	Hydroxyl Radical	Nitrate Radical	Ozone
(Z)-3-hexen-1-ol	1.1×10^{-10}	2.7×10^{-13}	6.4×10^{-17}
(Z)-3-hexenyl acetate	7.8×10^{-11}	2.5×10^{-13}	5.4×10^{-17}
(E)-2-hexenal	4.4×10^{-11}	1.2×10^{-14}	2.0×10^{-18}
m-Xylene	2.4×10^{-11}	2.3×10^{-16}	8.5×10^{-22}
Ethylene	8.5×10^{-12}	2.0×10^{-16}	1.6×10^{-18}
Isoprene	1.0×10^{-10}	6.8×10^{-13}	1.3×10^{-17}

The hexenyl-type compounds emitted from the cut grass are more reactive than other key anthropogenic VOC pollutants such as ethylene and m-xylene, and at least as reactive as the other highly reactive biogenic compounds, such as isoprene. Overall, with respect to urban smog formation, these hexenyl emissions from cut grasses, for their weight, will contribute disproportionately more to the photochemical reactivity of the air mixture than most anthropogenic VOCs.

7. Conclusions

Emissions of VOCs from grasses, including cut grass, may contribute significantly to urban air pollution. The biological mechanisms driving these emissions are partially understood. The few measurements available indicate that these emissions may be of the order of one fifth to one third of the VOC emissions in an urban airshed averaged over a year and the growing season, respectively. Since the photochemical reactivities of the VOC emissions from grass mowing are high, there is a need to reliably quantify these emissions if urban inventories and smog forecasts are to be accurate.

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