MODIFICATIONS OF SOIL ECOLOGY BY VOLATILE ORGANIC COMPOUNDS FROM PLANT RESIDUES

J.M. Bradow[1], W.J. Connick, Jr.[1], and P.J. Bauer[2]

ABSTRACT: Throughout decomposition, dicot plant residues release mixtures of low molecular-weight, volatile compounds that have marked negative effects on seed germination and seedling root growth. Structure-activity studies indicate that C_6 through C_9 aldehydes and methyl ketones have the highest physiological activity and that unsaturated bonds in the carbon chains increase retardation of germination and seedling growth. Chain branching and substitution decrease the biological activity of the volatiles. These volatiles exhibited similar structure-activity relationships as promoters of sporulation in pathogenic soil fungi and as insect semiochemicals. The additive effects of plant-residue volatile emissions have been implicated in reductions of crop field establishment and yield, and these emissions represent a significant factor in any cropping system in which large amounts of winter legume or fallow cover are incorporated immediately prior to crop planting.

INTRODUCTION: Under warm, moist soil conditions and intense sunlight, soil-incorporated residues of the prolific weed, Palmer amaranth, *Amaranthus palmeri*, (AMAPA), severely inhibited root growth of carrot and onion and seedling growth of sorghum and cotton in Weslaco, TX (20). Phytotoxicity occurred within two weeks after residue incorporation and dissipated after 10 to 12 weeks. Toxicities associated with weed and crop residues were also recognized as reducing seedling survival and, consequently, yield in conservation-tillage and green-manuring systems (1,11,13). This report is a synopsis of the identification and structure-activity characterizations of the low molecular weight organic components of plant-residue [weed and cover crop] volatile emissions.

MATERIALS AND METHODS: The chemical characterizations of water-soluble allelo-chemicals released by AMAPA residues have been described (4,5,16). No water-soluble natural product allelochemicals were extracted from either AMAPA residues or the soil containing those residues (5). However, the volatile emissions, both from AMAPA residues and soil containing those residues, were potent inhibitors of seed germination (5), and the emissions from winter cover legumes inhibited cotton seedling root growth (8). The components of the volatile emissions [primarily C_4 through C_9 alkanones, alkanals, and alkanols] from six amaranth species (14,15) and three cover crop legumes (9) were identified by GC/MS, and the relative bio-inhibitory potentials and structure-activity relationships were determined through a series of seed germination and seedling growth bioassays (5,6,7,8,9,10,12,13,15).

RESULTS AND DISCUSSION: The volatile emissions from residues of amaranth species, crimson clover, Berseem clover, and hairy vetch were mixtures of 2-alkanones, straight and branched-chain alkanols, alkenals, alkanes, esters, terpenes, and furans (9,14,15). Excepting the terpenes, all the compounds identified and tested contained fewer than 11 carbon atoms. These low molecular-weight inhibitors were highly volatile at ambient temperatures and were most potent in the vapor phase (5). Major components of the volatile emission mixtures from amaranth species and cover crop legumes and relative inhibitory activities as seed germination inhibitors are listed in Table 1. Not all decomposing plant residues assayed emitted every volatile listed, but the most active 2-alkanones were found in all the volatile emissions mixtures characterized (5,9,14,15). Most apparent inhibitions of seed germination proved to be *retardations* since seed germination proceeded after the volatiles dissipated (6,7,9,10). There were also differences among species in sensitivity to the various volatile emission components.

When more than 90 volatile organic compounds emitted by plant residues were surveyed for germination inhibitory and allelochemical potential, significant structure-activity correlations among substituent groups, carbon-chain lengths, and degree of carbon-chain branching and/or unsaturation were found (6,7,9,10). Germination-retarding activity depended primarily upon the chemical class and carbon-chain length. Among the chemical classes, the activity series was: 2-alkenals > 2-alkanones ≥

[1]USDA, ARS, Southern Regional Res. Center, POB 19687, New Orleans, LA 70179

[2]USDA, ARS, Coastal Plains Soil and Water Res. Center, POB 3039, Florence, SC 29502

n-alkanals ≥ 2-alkanols >> *n*-alkanoic acids ≥ *n*-alkanes (6,7,9,10). Onion seeds were sensitive to esters that did not affect carrot and tomato seed germination (9). Within the 2-alkanone class, the relationship between carbon-chain length and bioactivity inhibition followed the activity series: $C_8 = C_9 > C_{11} > C_7 > C_6 > C_4$ (6). In general, the C_7 and C_8 compounds were the most inhibitory within a class of volatiles. The high inhibitions obtained in the seed bioassays of C_7 and C_9 alkadienals, which were not detected in the volatile emissions mixtures, validated the hypothesis that increasing carbon-chain unsaturation was directly related to increased inhibitory activity (10).

Table 1. Seed germination inhibition at 72 h, based on % of control germination, by plant-residue volatiles [volatile concentration = 34.4 μM/L head space][1].

Compound	Onion	Carrot	Tomato
2-Butanone	+	+	++
2-Me-1-Propanol	++	+++	+++
3-Me-2-Butanone	++	+	++++
3-Me-2-Butanol	++++	+++	+++
3-OH-2-Butanone	+	NS	+++
2-Pentanone	+	+	+++++
2-Pentanol	++	++	+++
3-Pentanone	+	+++	+++++
n-Hexane	+	+	+
1-Hexenal	+++	++	++
2-Hexanone	++	++	+++++
2-Heptanone	+++	+++++	+++++
2-Heptanol	++++	+++++	+++++
n-Octane	++	NS	+++
2-Octanol	+++	+++++	+++++
n-Nonane	++	NS	NS
2-Nonanone	+++	++++	+++++
2-Undecanone	++	++	++++

[1]Volatile mixture compositions and inhibitory activities from references 6,7,9,10,14,15. Inhibitory rankings: NS:>70% control; +:>50% control; ++:>30% control; +++:>10% control; ++++:>1% control; +++++:<1% control.

The more potent plant-residue volatiles characterized in the seed-germination studies were emitted by aerial portions of cover crop legumes recommended for use before cotton in reduced-tillage and green-manure systems (9). The residues also emitted compounds reported to reduce cotton seedling root elongation (8), stimulate fungal growth (17,18) and act as insect attractants (19). Therefore, the impacts of weed and cover legume residues on cotton emergence, stand establishment, and yield were investigated in a reduced tillage cropping system in Florence, SC (1,2,3).

Winter weed or crimson clover residues were soil-incorporated 7 or 14 days before planting 'Coker 315' cotton (11,13). Soil samples were collected immediately after residue incorporation and at 7, 14 and 28 days after residue incorporation, and the soil samples were tested for inhibitory activity in a greenhouse cotton-seedling growth assay that employed sterile greenhouse soil mix as the control. The clover cover crop dry weight was 3.3 times that of the winter weeds, and the weed mixture contained significant amounts of redroot pigweed, *Amaranthus retroflexus*, the residues of which emit many of the same inhibitory volatiles associated with AMAPA (15).

In that field study, cotton stand establishment was greater following weeds than clover, and the yield differences between weed and clover treatments were significant only when planting occurred seven days after residue incorporation (10,13). In the greenhouse seedling-growth assays of soil containing weed or clover residues, both the weed and clover treatment soils inhibited root elongation [>50% inhibition] when the soil had been collected on the day of residue incorporation or a week following incorporation. Soil collected on the day of incorporation also inhibited cotton shoot elongation [>25%] and cotyledon expansion [>20%]. The inhibitory effects of both the weed and clover residue treatments decreased over time after residue incorporation. There was no evidence of cotton seedling disease complex in any of the residue-treated or control soils.

The effects observed in cotton seedlings grown in soil containing decomposing residues of winter weeds and crimson clover were emulated in the greenhouse by injecting sterile and non-inhibiting soils with known volumes [1.5 or 2.0 $\mu L/cm^3$ soil] of C_4 through C_9 alkanones previously identified as inhibitory in the seed germination assays and growing Coker 315 seedlings in the injected soil (12,13). The ketones assayed were 2-butanone [4ONE], 3-methyl-2-butanone [3ME4ONE], 3-pentanone [35ONE], 2-heptanone [7ONE], 2-octanone [28ONE], 3-octanone [38ONE], 5-methyl-2-heptanone [3ME7ONE], and 2-nonanone [9ONE]. The effects of these alkanones on cotton seedling root elongation, cotyledon expansion, and shoot elongation are shown in Figure 1.

When the effects of these alkanones on root and shoot elongation, root and shoot fresh and dry weight accumulation, and cotyledon expansion were combined, the cumulative structure-activity series was: 2-octanone >> 3-octanone = 2-heptanone > 2-nonanone = 5-methyl-2-heptanone > 2-butanone > 3-pentanone > 3-methyl-2-butanone (12). The relationships between inhibitory activity and carbon-chain length in the seedling growth and seed germination assays were quite similar. Differential absorption by soil components or partitioning between rhizosphere solid, liquid, and vapor phases may account for the lower activity of 2-nonanone in the seedling growth assay, compared to the seed germination assays. The position of the carbonyl group and carbon-chain branching appeared less important in the soil/seedling system than in the germination assays *in vitro*.

The ephemeral plant-residue volatiles characterized in reports cited here have wide ecological significance. The highly bioactive alkanals, alkanones, and alkanols have been detected in volatile emissions from residues of numerous plant species (10). The structure-activity relationships dependent on carbon-chain length were similar in both seed germination and seedling growth assays (6,7,8,9,12,13). A similar structure-activity relationship has been reported in insect semiochemical studies (19). Many components of plant-residue volatile emission mixtures also promote sporulation of plant-pathogenic fungi (17,18), and C_6 to C_{10} alkenals and alkanals, the most active plant-residue volatiles in the seed germination assays, are reported to elicit plant defense response phytoalexins in crops such as cotton, corn, and peanuts (21).

These responses by rhizosphere biota to plant-residue volatiles appear to be almost universal and to follow similar structure-activity relationships that depend on molecular weight and chemical class. Dried plant residues, after rehydration, emitted detectable levels of inhibitory volatiles for more than four months after harvest, and hypoxic conditions during decomposition favored formation of the more toxic C_8 alkanones and alkanols (5). Clearly, plant-residue volatile emissions play a decisive role in the patterning of any ecosystem and the success of agricultural practices that involve incorporation and decomposition of large amounts of plant material in the soil.

Figure 1. Effects of 2-butanone, 3-methyl-2-butanone, 3-pentanone, 2-heptanone, 2-octanone, 3-octanone, 5-methyl-2-heptanone, and 2-nonanone on cotton [Coker 315] root elongation, shoot elongation, and cotyledon expansion when injected [1.5 or 2.0 uL/cc soil volume] in sterile and non-sterile soil.

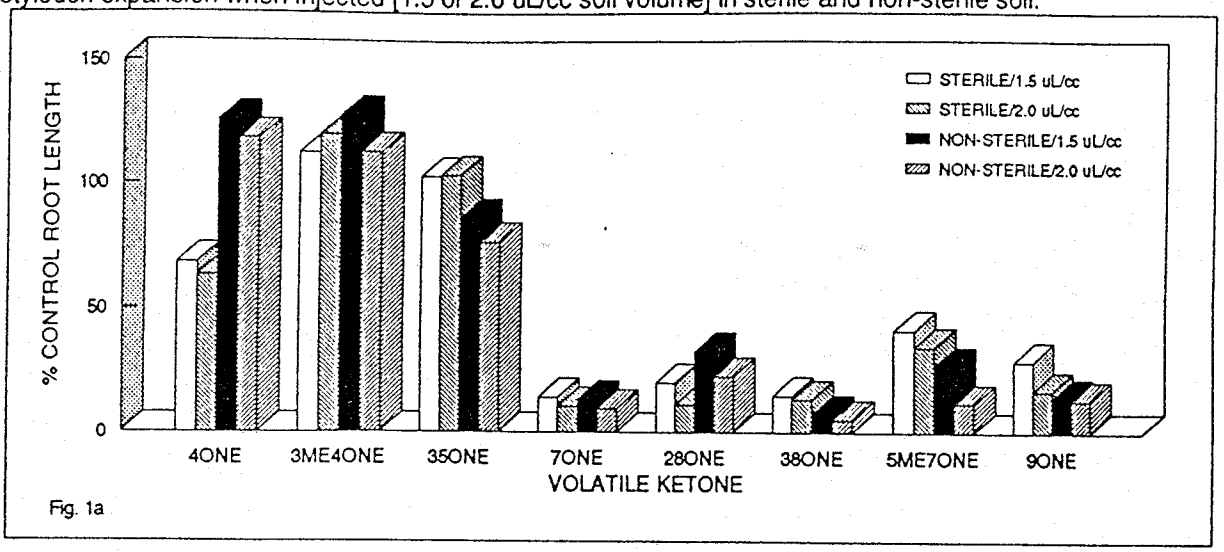

Fig. 1a

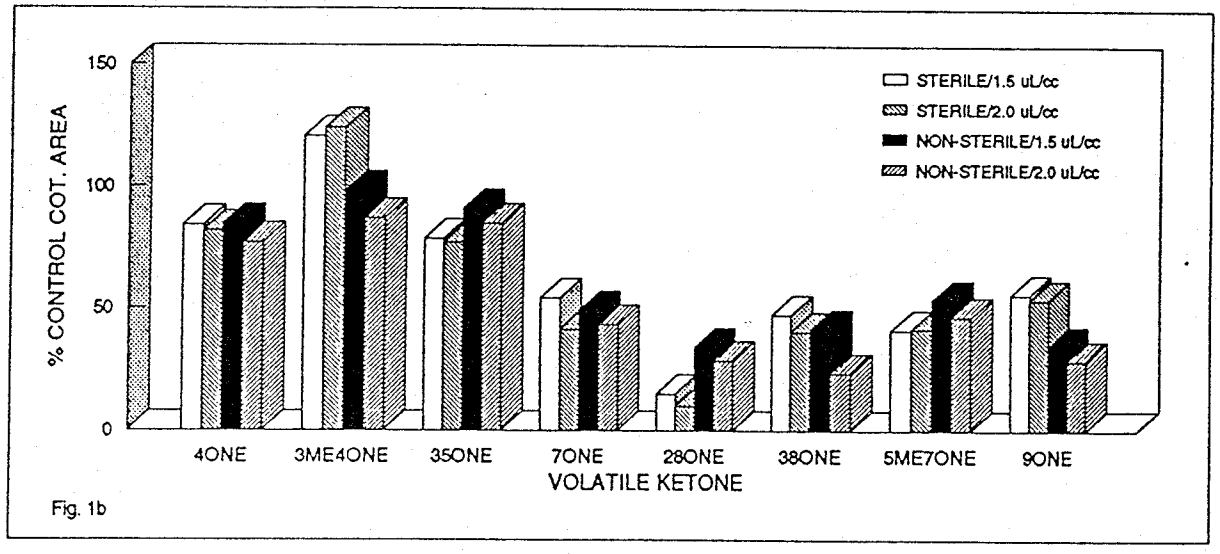

Fig. 1b

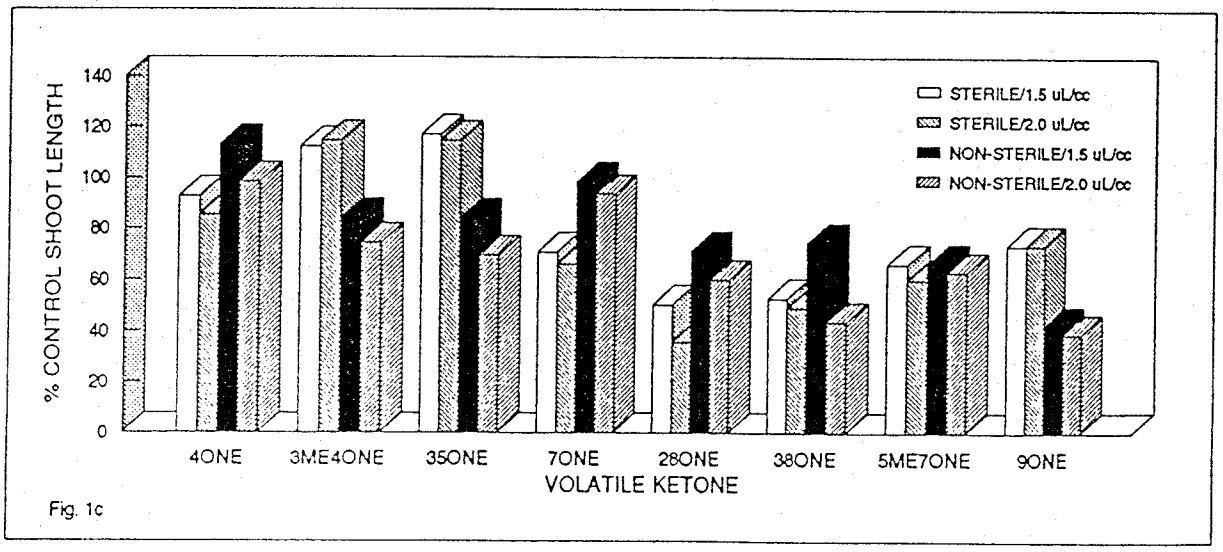

Fig. 1c

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