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# Clomazone Residues in Soil and Runoff: Measurement and Mitigation

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Movement of pesticides in runoff is influenced by the pesticide chemical properties, application methods, soil type, crop management, and environmental conditions. Ground covers in agricultural systems can alter the amount of runoff and pesticide loss from the soil surface (Antonious and Byers 1997; Antonious 1999). In Kentucky, there exist at least 635 surface water bodies and 48 groundwater sources impacted by non-point source (NPS) pollution. Agricultural activity is the leading NPS pollution statewide which affects 89% of the streams surveyed (KNR/EPC 1994). Clomazone (Figure 1), known as Command[R], is a pre-emergence herbicide used at rates ranging from 0.6 to 1.1 kg A.I./ha (Vencill et al. 1990) for the selective control of many grass and broadleaf weeds.

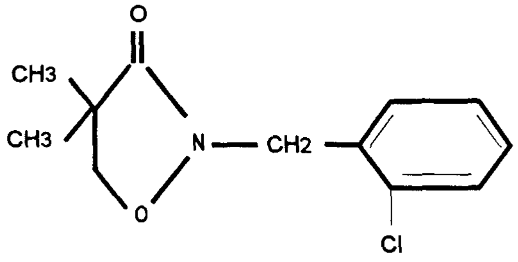



Figure 1. Chemical structure of clomazone [2-[(2-chlorophenyl) methyl]- 4,4-dimethyl-3-isoxaolidinone].

Clomazone, a soil applied herbicide, shows promise for all season weed control in selected vegetable crops and is currently registered for use on pepper and pumpkins in Kentucky (Anonymous 1999). Clomazone is taken up by plant roots and shoots and moves in the xylem to plant leaves. It inhibits the biosynthesis of chlorophyll and carotenoid pigments, causing a bleached appearance in susceptible plant species producing white, yellow or light-green plants (Duke and Paul 1986). Like other pesticides, clomazone may move from the site of application into runoff and infiltration water following field application. The high water solubility of clomazone (1.1 g/L) and its vapor pressure ($1.44 \times 10^{-4}$ mm Hg) (Carlson 1985) are good indicators of its possible off-site movement into runoff. No information is available on clomazone movement by runoff water following irrigation or natural rainfall. Due to geographic conditions, many Kentucky farmers operate on highly erodible land. The increasing concern about agricultural chemicals and their impact on surface and groundwater quality has made this a national issue. Ground cover associated with cropping systems may alter runoff and pesticide loss from the soil surface. The goals of this study were: 1) to evaluate the impact of three soil treatments, grass strips (GS), black plastic (PB) mulch, and a bare soil (no mulch, NM) as well as two vegetable crops (pepper vs. pumpkin) on clomazone residues in runoff water and sediment following natural rainfall incidents; and 2) to determine the impact of soil covers and cropping systems on clomazone vertical movement in the soil profile.

## MATERIALS AND METHODS

The study was conducted on a Lowell silty loam soil (2% organic matter, pH 6.7) located at Kentucky State University Research Farm, Franklin County, KY. Runoff plots (universal soil loss equation (USLE) standard plots) of 22 x3.7 m (n=18), on a soil of 10% slope were established. Plots were separated using 16 cm plastic edging (Warp's Easy Edge, Wrap Bros., Chicago, IL, USA). Clomazone analytical standard grade (92.8% purity) and its formulation (Command 4EC, 47.1% A.I.) were obtained from FMC Corporation (Agricultural Chemical Group, Princeton, NJ, USA). Command was applied to soil surface as a pre-emergence herbicide at the recommended rate of 1.1 kg/ha using a 4-gallon portable backpack sprayer (Solo) equipped with one conical nozzle operated at 40 psi (275 kPa).

Plots were planted with green bell pepper *(Capsicum annuum)* "Lady Bell" transplants and pumpkin *(Cucurbita pepo)* "Big Moon" seeds. Pepper transplants and pumpkin seeds were planted by hand into bare ground or holes punched into the black polyethylene mulch at the rates of 10 plants of pepper and 2 seeds of pumpkin per 3.7 m of row. Plots contained 10 rows oriented along the contour of the slope and each plot contained one of the three soil management practices. The soil management practices were grass *(Festuca sp.*., Kentucky 31) strips placed between every cropping row (GS), black plastic mulch (BP) placed between every cropping row, and no mulch (NM) treatment (roto-tilled bare soil). GS of 30 cm wide (Elkorn Springs, Georgetown Road, Frankfort, KY, USA) and BP mulch (Holland Mulch Layer, Model 1275, Holland, MI) of 0.1 mm thick and 90 cm wide, as well as vegetable rows (pepper vs. pumpkin) were used as repeated barriers to runoff, The experimental design was a 2 x 3 factorial with main factors including the two crops and three soil management practices.

Following natural rainfall events, runoff (soil-water suspension) was collected in 4 L amber borosilicate glass bottles and quantified at the lower end of each plot using tipping-bucket runoff metering apparatus (Department of Agricultural Engineering, University of Kentucky, Lexington, KY, USA). Runoff water and sediment samples were transported to the laboratory on ice in coolers and stored at 4°C for extraction and analysis. Sediment loss, dependent on natural rainfall, was determined by weighing the sediments collected from 1 L of runoff water. Sediment (g/L) was converted to kg/ha based on total runoff water lost per runoff event, per each 0.008 ha plots. Clomazone in a 300 mL aliquot of the runoff water sample was transferred quantitatively to a Buchner funnel and passed through a Whatman 934-AH glass microfibre filter (Fisher Scientific, Pittsburgh, PA, USA) using vacuum filtration. Clomazone in a 100 mL of the filtered water sample was extracted three times by liquid-liquid partition with 100, 60, and 40 mL of n-hexane. The hexane fractions (top layers) were combined and dried over anhydrous $Na_2CO_4$.

Sediment (20 g) samples were dried and refluxed with 250 mL of 0.25 N HCl for 3 h in a Soxhlet apparatus to extract clomazone residues. Soil samples (3 cores per plot) were collected bimonthly to a depth of 18" (46-cm) from the experimental plots during the growing season using a soil core sampler equipped with a plastic liner tube (Clements Associates, Newton, IA, USA) of 2.5 cm i.d. for maintenance of sample integrity. Soil samples (50 to 100 g) were air-dried, sieved to a size of $\leq 2$ mm. Twenty g soil were refluxed with 250 mL of 0.25 N HCl for 3 h. Clomazone residues were extracted from the aqueous acid solution by liquid-liquid partition with n-hexane using the same procedure described for runoff water samples. The hexane portion was then washed with 25 mL of a saturated sodium bicarbonate ($NaHCO_3$) solution and the $NaHCO_3$ wash was then discarded (Anonymous 1986). Hexane extracts were then dried over anhydrous $Na_2SO_4$ and concentrated by rotary vacuum (Buchi Rotavapor Model 461, Switzerland) and $N_2$ gas stream evaporation to 1 mL final volume for quantification.

Clomazone residues were detected and quantified by gas-liquid chromatography (GLC) (HP Model 5890, Hewlett Packard Co., Palo Alto, CA, USA) equipped with a nitrogen-phosphorus detector (NPD) and a HP-l, 15 m x 0.53 mm i.d., megabore column (Hewlett Packard Co. Palo Alto, CA, USA). Injector, oven and detector temperatures were 250, 180, and 250 °C, respectively. Helium (He) was used as the carrier gas and the flow was set at 17 mL/ min. Under these conditions clomazone retention time was 2.58 ± 0.04 min. Standards ranging from 0.25 to 1.0 ng/µL were prepared in n-hexane and were used to spike soil and water samples for evaluating the efficiency of the analytical procedure used. Recovery values (means ± SD) using fortified samples were 92.0 ± 2.5, 88.3 ± 2.0, and 85.9 ± 1.8% for clomazone in runoff water, runoff sediment, and soil samples, respectively. All clomazone residue data have been adjusted for efficiency of recovery. Clomazone residues detected in soil, sediment, and runoff water were reported in µg/g, and related to crop and soil management technique, and statistically analyzed by SAS procedure (SAS Institute 1991) using analysis of variance (ANOVA) and least significant differences (Snedecor and Cochran 1967) for mean comparisons.

## RESULTS AND DISCUSSION

Runoff water collected from pepper plots was 1527, 10735, and 12129 liter/ha in GS, BP, and NM treatments, respectively. No significant differences ($P$>0.05) were found

Figure 2. Runoff water (upper graph) and runoff sediment (lower graph) collected at the lower end of USLE standard plots under two cropping systems and three soil management strategies:
grass filter strips placed between every cropping row; black plastic mulch placed between every cropping row; and no mulch treatment, a bare soil. Statistical comparisons were done between the three soil treatments for each cropping system. Bars accompanied by the same letter are not significantly different (E-0.05; Duncan's multiple range test).

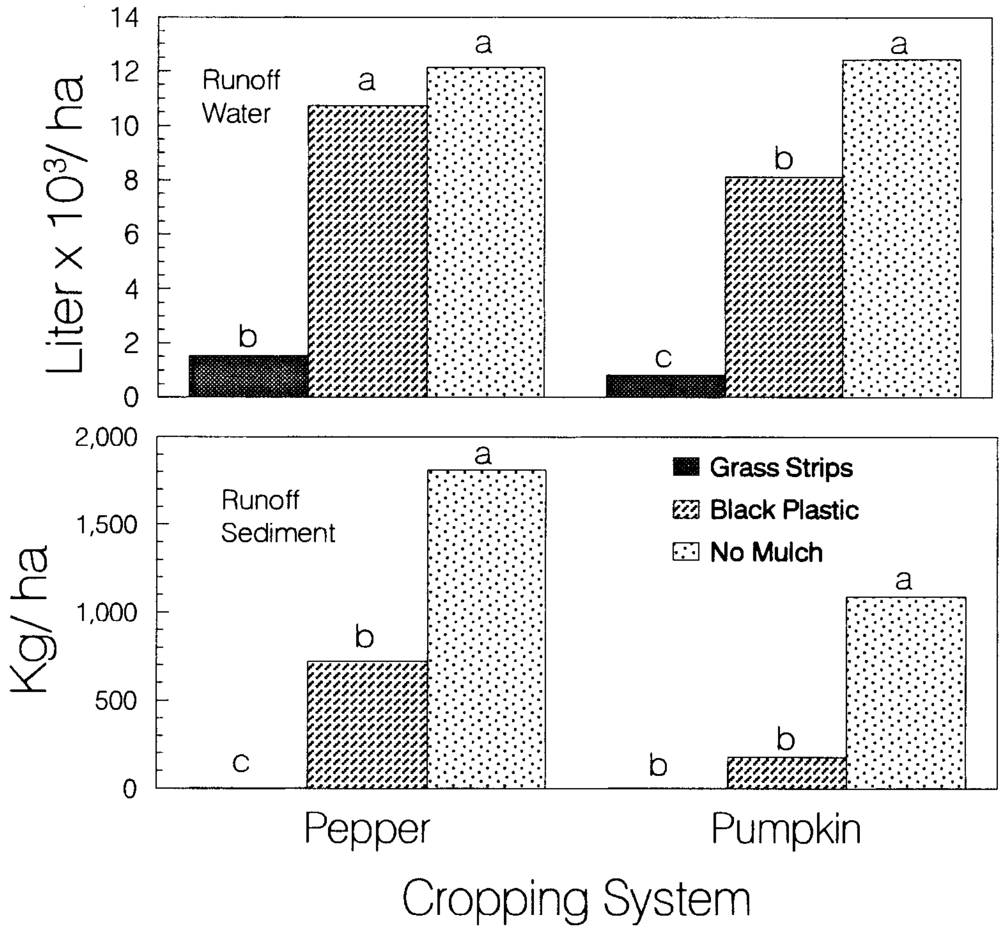
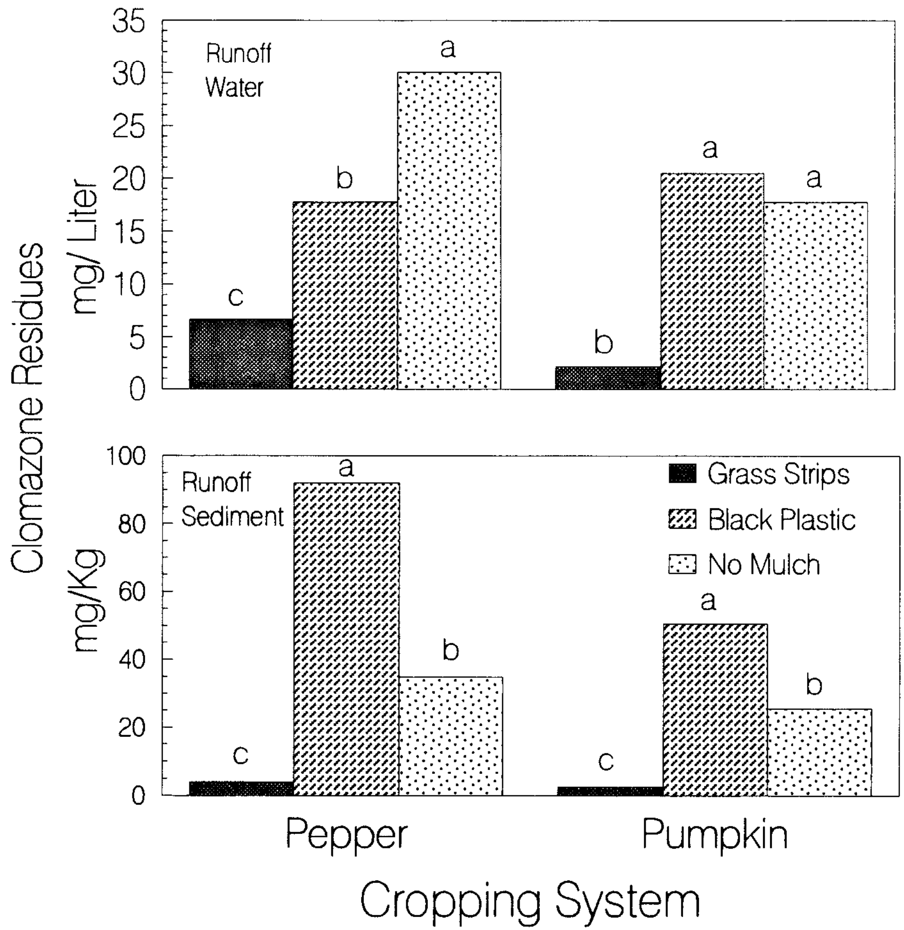


Figure 3. Clomazone concentration in runoff water (upper graph) and runoff sediment (lower graph) following soil application of clomazone (Command 4EC) under two cropping systems and three soil management strategies: grass filter strips placed between every cropping row; black plastic mulch placed between every cropping row; and no mulch treatment, a bare soil. Statistical comparisons were done between the three soil treatments for each cropping system. Bars accompanied by the same letter are not significantly different ($P>0.05$; Duncan's multiple range test).



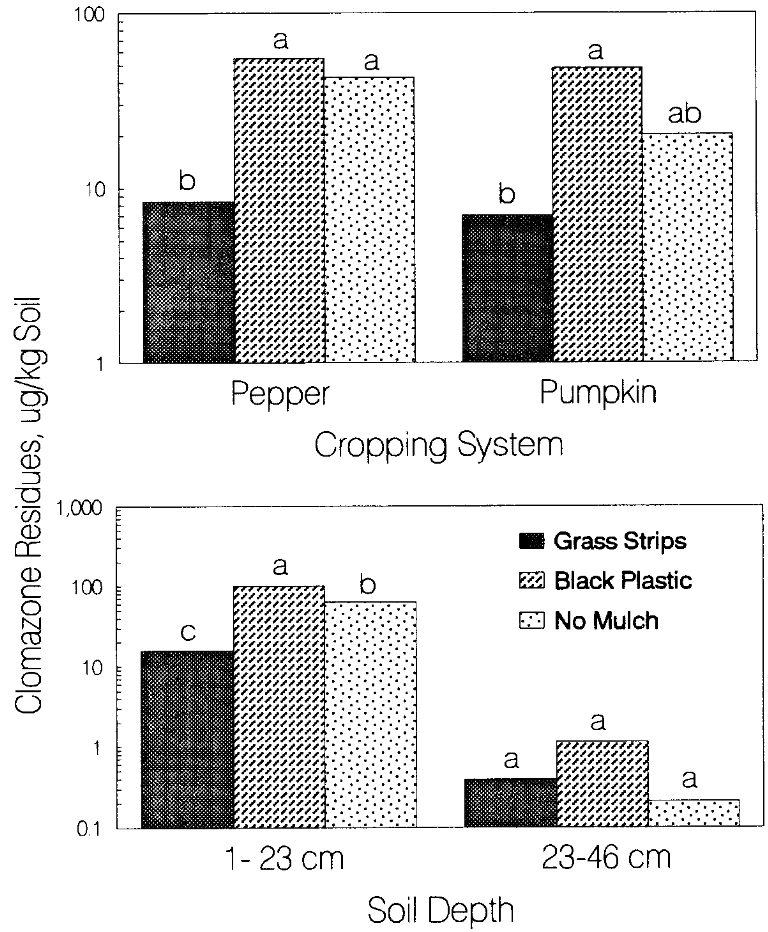



Figure 4. Clomazone residues in soil core samples collected under two cropping systems (upper graph) and from two soil depths (lower graph) during three months following soil application of clomazone (Command 4EC) in relation to three soil magement strategies: grass filter strips placed between every cropping row; black plastic mulch placed between every cropping row; and no mulch treatment, a bare soil. Statistical comparisons were done between the three soil treatments for each cropping system (upper graph) and for each soil depth (lower graph). Bars accompanied by the same letter are not significantly different (*P*>0.05; Duncan's multiple range test),

between amount of runoff water collected from BP and NM in treatments planted with pepper. However, in treatments planted with pumpkin, BP covers reduced runoff water volume compared to NM treatments (Figure 2, upper graph). This is likely due to the growth habit of pumpkin plants. Pepper has an erect growth habit, while pumpkin has a vining growth habit which in turn produced a greater soil coverage by pumpkin foliage. A significant reduction in runoff water and sediment was found in plots with GS and planted with pepper as well as plots planted with pumpkin. GS inhibited the disintegration of soil aggregates and the dispersion of clay particles down slope and consequently reduced the amount of runoff water and sediment by 85.8 and 99.7% in pepper plots and 93.4 and 99.8% in pumpkin plots, respectively compared to NM treatments (Figure 2). In NM and BP treatments, significant amounts of runoff water, sediment and sediment bound clomazone residues moved down slope following natural rainfall events (Figure 3). Previous results have indicated that the utilization of vegetative filter strips contiguous to agricultural fields resulted in a reduction of the transport of endosulfan (an insecticide) and dacthal (a herbicide) into runoff allowing for their infiltration into the vadose zone (the unsaturated water zone below the plant root) (Antonious and Byers 1997; Antonious 1999). Runoff water and sediment are frequent in sloping areas common to Kentucky where most of the arable lands are highly erodible. In addition, water solubility is one of the pesticide characteristics that controls mobility (Cohen et al. 1984). Results of this study indicated that GS can keep runoff and clomazone residues from draining into adjacent streams.

Benefits derived from the use of black plastic mulch are well documented. In addition to controlling weeds, plastic mulches can reduce leaching of nutrients and conserve moisture (Ashworth and Harrison 1983). Soil compaction is decreased, and the $CO_2$ level around the plant is increased when plastic mulch is used (Bonanno and Lamont 1987). However, BP as a management practice had little impact on reducing runoff. This could be attributed to the lack of surface roughness compared to GS that retarded runoff and trapped sediment and clomazone. GS treatments were very effective at reducing amounts of clomazone in soil at the 1 to 23-cm soil depth compared to BP and NM treatments (Figure 4, lower graph). Because clomazone is soluble in water (1.1 g/L), its vertical movement in the soil profile is therefore a function of the availability of water as the transport agent. However, following three natural rainfall events during the experimental period, clomazone residues detected at the 23 to 46-cm soil depth were in the sub-ppb ranges (Figure 4, lower graph). This may be explained by the adsorption properties of clomazone on soil and clay particles (Loux et al. 1989) as well as the degradation of clomazone by soil microbes (Mervosh et al. 1995) which include cleavage of the isoxazolidone N-C bond or complete removal of the isoxazolidone ring (Liu et al. 1996) thereby decreasing its availability in soil at lower depths.

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