The Disappearance of Chlorobromuron in Ensilage

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Chlorobromuron, 3-(4-bromo,3-chlorophenyl)-1-methoxy-1-methylurea is a preemergent and postemergent herbicide used for the control of many annual broadleaf weeds and grasses in field corn and soybean production. Both corn and soybeans are very common forage crops used for ensilage production and feeding to farm animals.

The ensilage process involves a fermentation wherein the aerobic organism utilize quickly the available oxygen in the silo causing the atmosphere to become anaerobic allowing the fermentation and subsequent acid production to proceed. Hence the procedure is a preservative measure minimizing putrefication.

In practice, corn plants, including stalk, leaves and ears, or mixtures of corn plants, legumes, soybeans or other grasses are chopped and packed into air-tight silos. The period of 48-72 hours is one of great fermentive activity with the production of considerable heat and pressure. The organisms responsible for the fermentation are streptococci and lactobacilli producing lactic acid, butyric, propionic and acetic acid with small amounts of alcohol. A pH of 5.2 or less is generally necessary to prevent decomposition of the ensilage.

As is common with most, if not all chemicals used in crop production, small but measurable amounts of herbicides and/or their metabolic products are present as residues in plant materials. Because of the great importance in assessing the potential for the production of hazardous substances or unwanted residues, a study of the stability of chlorobromuron in the ensilage process was undertaken.

Materials

Field corn (Zea mays L.), N.J. No. 9, was grown at the experimental farm at Adelphia, New Jersey. Maloran as a 50% W.P. was applied as a preemergent herbicide at the rate of 4.0 lbs chlorobromuron/acre. The corn plant, leaves, stalk and ear were harvested at the ensiling stage. The corn plants in the treated plots were cut at ground level and chopped in a Hobart Food Chopper for ensiling.

The chopped whole corn plants from the treated plots were packed tightly in taped screw-top jars capable of containing 250

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grams of the chopped corn. The jars were closed and the tops sealed with paraffin. Separate jars were prepared for each day of the 28-day experiment. Similarly blank chopped corn was incubated in a parallel 28-day experiment. Each day a sample and a blank were removed and placed in a freezer at 20°C and stored until analyzed. Incubations were performed at 27°C.

Analytical Methodology

The procedure for the analysis of chlorobromuron residues was basically that of Pease (1) which was first described by Bleidner (2), Bleidner and co-workers (3) and Dalton and Pease (4). The procedure was modified by using 50% sodium hydroxide instead of 20% sodium hydroxide, a 4-hour digestion instead of the 12-hour digestion and by using 1-naphthylamine hydrochloride in place of N-(1-Naphthyl)ethylenediaminedihydrochloride as the coupling reagent in the diazotization reaction. With this reagent, a 1-hour color development period was required for maximum color intensity. The cellulose column to remove interferences from the dye developed from diazotized 4-bromo, 3-chloroaniline and 1-naphthylamine was 6 inches in length. The column required a 250 ml wash with 1N hydrochloric acid to remove any color interferences from plant materials. Elution of the color from the column is accomplished with 1:1 v/v 1N hydrochloric acid : glacial acetic acid and discarding the eluate prior to the color complex being eluted. A total of 45 ml of color containing eluate is collected in a 50 ml volumetric flask which is then brought to volume for colorimetric analysis. The wave length of maximum absorbance was 545 mμ. Absorbance measurements were performed using a Beckman DB spectrophotometer and 4 cm cells. A standard curve between 5 and 50 ug was developed.

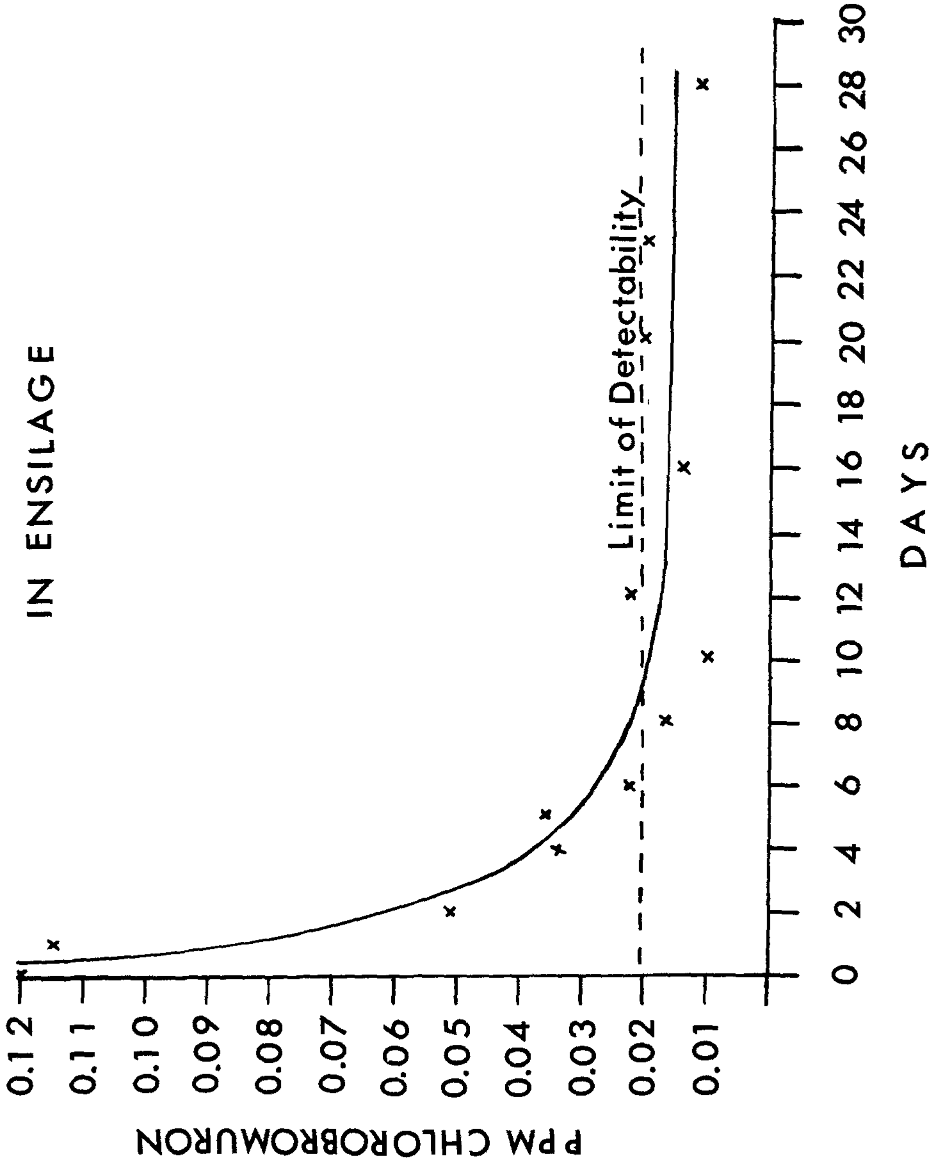
One hundred fifty gram samples of silage were used for the alkaline digestions during the first 3 days of the study and 200 gram samples were used for the remaining determinations. All aniline values were converted to the parent herbicide using a factor of 1.41.

Results and Discussion

Modification of the classical alkaline digestion procedure was necessary for several reasons. The 12 hour digestion suggested by Pease (1) was far too long for convenient analysis. The use of 50% sodium hydroxide reduced the analysis time to 4 hours or less. No additional aniline could be recovered by longer digestions. Later recovery studies indicated that 25% sodium hydroxide and a 4 hour digestion period were sufficient for quantitative recoveries.

Bleaching of color and shifts in the wave length of maximum absorbance using consecutive batches of 1-(1-Naphthyl) ethylenediaminedihydrochloride necessitated a change in coupling reagents. Since most investigators have found this reagent to be good and the one of preference, it must be concluded that batches of this

DISAPPEARANCE OF CHLOROBROMURON IN ENSILAGE



reagent require preliminary screening before use. The reagent used in this study was found to be an acceptable alternative if such problems occur elsewhere. Interference from plant materials were removed using a 6 inch cellulose column with 250 ml of 1N hydrochloric acid. The dye resulting from the aniline of the herbicide remains fixed on the surface and is easily eluted with the 1:1 v/v 1N hydrochloric acid-glacial acetic acid mixture.

The digestions revealed that chlorobromuron disappeared quite quickly during the ensilage process with a half life of approximately 2½ days with the initial residue level of 0.12 ppm dropping to the limit of detectability (5) of the analytical procedure after 8 days, Figure 1. The period of the disappearance coincides with the period of greatest fermentation activity, although complete stabilization of silage is normally considered complete after 1 month. Noteworthy is the obvious alteration of the aromatic amine nucleus in such a manner that the diazotization reaction central to the determination of the substituted urea herbicides is no longer applicable. Whether there is alteration of the ring or an actual ring cleavage is not known at the present time.

The silage produced by this procedure was of good quality from the standpoint of observation. It had a pleasant odor, was greenish in color and had no appearance of being moldy. The pH of the silage measured at the end of 28 days was 4.5. However, it is realistic to note that although acceptable, reproducible silage can be produced in small containers in the laboratory, the mass and pressure characteristics of these fermentations are not the same as occur in the field. Despite these limitations, reasonable estimates of the transformations occurring in silage-making are possible.

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