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STABILITY TEST OF BENTAZON AND DICAMBA IN WATER

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ABSTRACT

A reduction in pesticide effectiveness, in general, may be due to hydrolysis. The rate of hydrolysis is dependent on pH, pesticide chemistry, length of time in the spray tank and water temperature in the spray tank. The exposure of the spray tank to sunlight will also impact the rate of hydrolysis. The present work describes stability test of bentazon and dicamba in water under different conditions, such as pH, presence or absence of sunlight and different temperatures. Stability of bentazon and dicamba aqueous solution was assessed by exposing aqueous samples to different temperatures, different pH (4, 7 and 10) and presence or absence of sunlight. The stability study under laboratory conditions revealed high stability of both compounds in aqueous solution pH 10, when exposed to sunlight or darkness. Dicamba was stabile at pH 7, while in aqueous solution pH 3 degraded 30% of initial concentration of dicamba. Bentazon degraded more that 50% after two weeks at pH 4 and 7.

INTRODUCTION

When a pesticide fails to control or regulate a pest's population, there is a common tendency to blame it on resistance. However, there are a number of other factors that may be responsible – poor coverage, waiting too long between applications, using the wrong pesticide, using the wrong label rate, improper timing (applying pesticides when susceptible life stages aren't present), using an old pesticide and lastly, the pH of the water or spray solution (Cloyd, 2009).

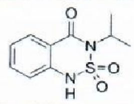
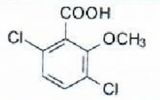
The pH of the water that goes into spray tank makes a difference in how effectively the pesticide works. A reduction in pesticide effectiveness, in general, may be due to hydrolysis, which is a chemical process whereby molecules are cleaved into several smaller components by the addition of water molecules. The rate of hydrolysis is dependent on pH, pesticide chemistry, length of time in the spray tank and water temperature in the spray tank. The exposure of the spray tank to sunlight will also impact the rate of hydrolysis. It should be noted that even tank mixes or combining two or more pesticides together may lead to an increase in a pesticides' susceptibility to decomposition (McKie and Johnson, 2002).

Also, water quality is very important for pesticide fate and behavior in the environment. Different water conditions can influence on presence or absence of pesticide and/or their transformation products in water environment. The fate of pesticide in surface and ground water depends upon many different factors including photodegradation, volatilization, chemical degradation, adsorption.

The present work describes stability test of bentazon and dicamba in different water conditions, such as pH, presence or absence of sunlight and different temperatures.

Bentazon and dicamba are selective agricultural herbicides which are widely use in agriculture for control the growth of different unwanted weeds species in crops. Very often, bentazon and dicamba are formulated in together. Physico–chemical properties of analized herbicides are shown in table 1.

Table 1. Physico–chemical properties of bentazon and dicamba herbicides

Common name/ molecular formula/CAS No.	Chemical name (IUPAC)	Structural formula	p*Ka*	Aqueous solubility (mg/l)	logK_{ow}
Bentazon $C_{10}H_{12}N_2O_3$ (25057-89-0)	3-isopropyl-1*H*-2,1,3-benzothiadiazin-4(3*H*)-one 2,2-dioxide		3.3	500	3.81
Dicamba $C_8H_6Cl_2O_3$ (1918-00-9)	3,6-dichloro-2-methoxy-benzoic acid		1.9	4500	2.21

MATERIALS and METHODS

Materials and reagents

The analytical standard of bentazon and dicamba were provided by Dr Ehrenstorfer (Germany). Stock solutions of pesticide mixtures were prepared in acetonitrile immediately before each analysis. The calibration standards solutions ranging from 0.0125–0.1 mg/ml were prepared also in acetonitrile. Analytical HPLC grade acetonitrile was obtained from J.T. Baker (Darmstadt, Germany). Deionised water was prepared through the NANOpure water system.

Equipment

Aqueous solutions of bentazone and dicamba were analyzed by liquid chromatograph HPLC (Agilent 1100 Series), coupled with a DAD (UV–Vis) detector. Analytical column Zorbax Eclipse XDB-C18 (50 mm x 4.6 mm x 1.8 µm) was used. The pH was measured using a pH meter Consort C830.

Analytical procedures

Stability of bentazon and dicamba aqueous solution was assessed by exposing aqueous samples to different temperatures, different pH (4, 7, and 10) and presence or absence of sunlight (Zabar et al., 2011). Samples containing selected pesticides were dissolved in deionised water and stored under different laboratory conditions in 200 ml flasks, with an initial concentration of 0.05 mg/ml for all analytes. One set of flasks was kept on the laboratory desktop exposed to sunlight at room temperature 25 °C and the second set of flasks was refrigerated in the dark, at a temperature of 4 °C. During the period of 28 days, the concentration of solutions and the pH were monitored.

RESULTS

HPLC-DAD results and calibration curves

The best separation of bentazon, dicamba and 2.4-D in aqueous solutions was achieved on a Zorbax Eclipse XDB-C18 (50 mm x 4.6 mm x 1.8 µm) analytical column with gradiente elution at a constant flow rate of 1 ml/min. A binary mobile phase with a gradient programme was used, combining solvent A (0.05% solution of H_3PO_4) and solvent B (acetonitrile) as follows: linear gradient of 20% to 70% B at 9 min, 70% to 60% B at 10 min, 60% to 20% B at 11 min, then 1 min under the same conditions. The injection volume was 5 µl. Suitable wavelength for all analytes included in this study was 225 nm. For quantification purposes a calibration curve in the range from 0.0125–0.1 mg/ml was prepared. The retention times for HPLC-DAD chromatograms were 5.491 min for bentazon and for 4.907 min dicamba. The HPLC-DAD chromatogram for analyzed active ingredients is presented in Figure 1.

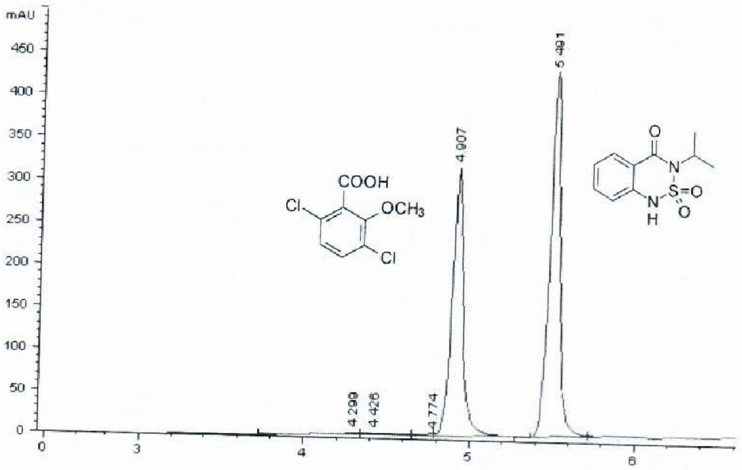


Figure 1. HPLC-DAD chromatogram of bentazon and dicamba standard solution

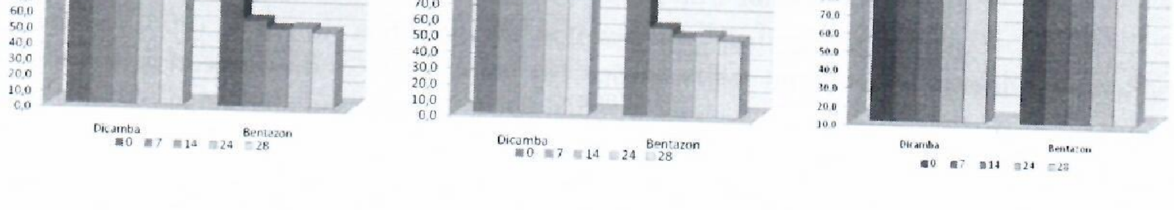
A series of bentazon and dicamba standards with the concentrations ranging from 0.0125–0.1 mg/ml were analyzed to determine linearity. The correlation coefficients (r^2) values of the regression line calculated for bentazon and dicamba were 0.999.

Stability studies under laboratory conditions

The pH of the aqueous solutions of bentazon and dicamba mixture during the period of 28 days was also observed. Seven days after adding herbicides, pH changed from starting 6.95 to 3.67 and from 10.1 to 7.02, while pH 4 did not change significantly in samples on the laboratory desk at 25 °C and in samples stored in refrigerator at 4 °C. This situation did not change at the end of experiment.

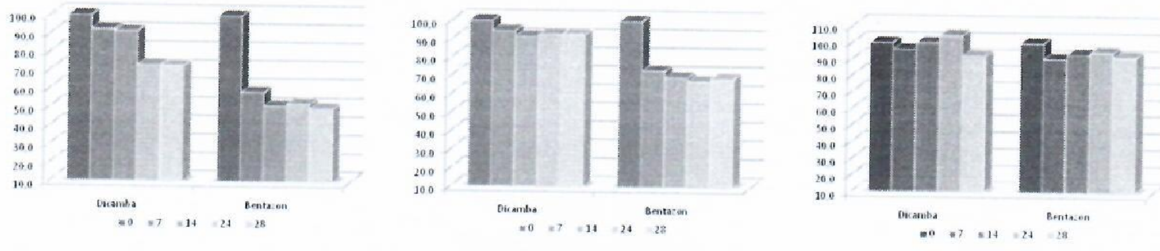
The results of the stability tests of bentazon and dicamba in deionised water under different pH, performed at room temperature (25 °C) under exposure to sunlight and in the darkness (in the refrigerator at 4 °C) are shown in Figure 2 and 3.

Figure 2. Stability test of bentazon and dicamba exposed to sunlight at 25 °C, under different pH (4, 7, 10)



The experiments performed with samples exposed to sunlight at 25 °C under pH 10 clearly indicate that the degradation or transformation is very low in case of both substances over the 28 days of experiment. However, under pH 4 and pH 7 dicamba was stabile with degradation of 20-30% of initial concentration after 24 days. Although, bentazon led to an important transformation after one week from starting experiment. Concentration of bentazon decreased for more then 50%.

Figure 3. Stability test of bentazon and dicamba stored in refrigerator at 4 °C, under different pH (4, 7, 10)



The experiments performed at 4 °C in the darkness show the degradation of bentazon under pH 4 and pH 7 (40-50 % conversion was observed), while dicamba was relatively stabile. Furthermore, the concentraction of bentazon and dicamba in aqueous solution pH 10 was stabile during 28 days.

CONCLUSIONS

- It can be concluded that the presented method can be applied for determination of bentazon and dicamba in mixture. The obtained value of r^2 indicating that achieved good linearity for bentazon and dicamba determination by HPLC/DAD.
- Water pH was changed after adding of bentazon and dicamba mixture; from starting 6.95 to 3.67 and from 10.1 to 7.02, while aqueous solution pH 4 did not change.
- The stability study under laboratory conditions revealed high stability of both compounds in aqueous solution pH 10, when exposed to sunlight or darkness.
- Bentazon was significantly degraded under pH 4 and 7, while concentration of dicamba was stabile.

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