THE POTENTIAL CONTAMINATION OF SURFACE WATERS BY HERBICIDES

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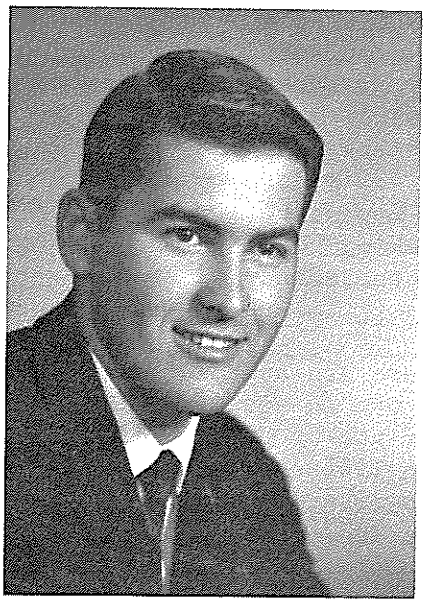
Biographical Sketch



Born at Lethbridge, Alberta, Canada, June 29, 1945 - son of William James and Dorothy Leora Wocknitz; married Joanne Wilde December 27, 1967; two children -- Cheri and Sandra.

Attended Magrath Elementary and High Schools graduating in 1963; received the Bachelor of Science degree with a major in Agronomy from Brigham Young University in 1970; presently a Masters of Science candidate at Utah State University under the direction of Dr. John O. Evans.

Professional Experience: Summers and weekends of high school and undergraduate assisting father on farm. The summer of 1969 I operated an 800-acre farm in partnership with my father's operation.

Abstract. The present demand for maintaining high quality water has created considerable interest in the role of pesticides in water pollution. In addition, there are increased pressures on farmers to return irrigation water without lowering its quality. Prior to 1940 few herbicides existed; at present, there are over 100 herbicides registered. With nearly 400,000,000 pounds of herbicides used annually on cropland and rangeland there is considerable potential for contamination of water sources with these materials. It is imperative that we understand the behavior of herbicides and their degradation products in the environment; particularly those herbicides have proven to be extremely toxic to plant or other living organisms in a water environment. Degradation products also may be more detrimental to aquatic life than the parent material. Picloram in extremely small quantities is toxic to most plants. The movement and the persistence of picloram and its degradation products in water has been studied over a two-year period. Photolytic decomposition occurs with picloram resulting in degradation products. An analytical and a quantitative procedure has been worked out for these products, and will be reported. In addition, the extension of these procedures to study the movement of other herbicides in the environment will be discussed.

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The demand for high quality water has created considerable interest in the role of pesticides in water quality. Although pesticides have increased food and fiber production enormously, there is an increasing concern of these compounds affecting the welfare of non-target organisms. Historically, there has not been a great deal of concern of the impact of pesticides on the environment except by a few individuals; at present we are experiencing the reverse trend, where many individuals or groups of individuals are involved in the decision making processes which may result in drastic and damaging curtailment of the use of agricultural chemicals. It is true that many of the most active opponents base their actions on personal emotion rather than on reputable data. In their opinion, agricultural chemicals are an uncontrolable detriment to the balance of nature and all the same, so consequently we should stop using them. Research has shown that each chemical behaves in the environment in a unique and predictable fashion. If we are to use them effectively and insure that we have control of their movement we must consider each new chemical independently from the rest. By taking this approach it is possible to use agricultural chemicals and to insure the safety of aquatic life, plants, animals and man.

Prior to 1940 few herbicides existed; at present, there are over 100 herbicides registered. Of these, many are registered for use in aquatic weed control including canal and ditchbank weed control. The use of herbicides during the period 1965-1968 increase by 54 percent (14). In 1965 thirteen states reported treatment of 84,000 acres of ponds, lakes, and reservoirs with herbicides, and they reported a need to treat considerable additional acres of waterways (2). As more effective herbicides are developed, it will increase the number of herbicides being used, and also increase the area treated. The potential for contamination is obvious unless we become aware of the conditions for movement and persistence of these chemicals into water and it might be impossible to use them without polluting our waterways. Canal and ditchbank weed control has also been increasing. Since these are applied very near the surface of water, the potential for contamination of water sources is very high. With nearly 170,000 miles of irrigation canals, 190,000 miles of drainage canals, and 21.5 million acres of small lakes and reservoirs in the United States, many of which are treated once, twice or three times annually, there exists a potential for contamination (12). In addition, about 400,000,000 pounds of herbicides are used annually on cropland and rangeland, some enters the irrigation waters and streams by surface runoff and erosion (2).

It is important that we understand the behavior of herbicides and their degradation products in the environment; particularly those herbicides that are used where they may get into water channels. Molecular structure, formulation and dosage rate play an important role in governing the movement of herbicides into water and their persistence. Recent research data has indicated that herbicides do not tend to accumulate in soil or water even under conditions of repeated applications. Frank and Comes (6) could not detect 2,4-D after 55 days when 1.33 ppm was placed in a pond and Faust and co-workers (5) were not capable of detecting 2,4-D within four days of applying a high rate of 20 lb/A to surface waters. Residues do exist for varying periods of time after treatment with most herbicides but are usually of little practical concern since they fall within the allowable tolerances set for the herbicides. Considerable effort is being made to insure that chemicals of high toxicity

to aquatic life do not enter waterways. For example trifluralin in water is extremely toxic to fish, but it is applied to the soil and its movement is nearly non-existant because it is strongly adsorbed onto the soil colloid (11). The maximum allowable tolerances for herbicides in water are set by the federal government. A limit of 0.1 ppm has been established for 2,4-D, 2,4,5-T and Silvex (2,4,5-TP) in surface waters (15). Studies involving the control of aquatic weeds indicate that 2,4-D does not persist in high enough concentrations to cause injury to crops. In Oregon, Tarrant and Norris (13) after spraying forest land observed the detectable level of 2,4-D in surface runoff waters to drop to a level of 0.2 ppb in two days. It appears that herbicides do not seriously affect our municiple waters when applied at recommended rates.

Some herbicides have proven to be extremely toxic to plants but safe to most desirable aquatic organisms in a water environment. Diquat, an herbicide for aquatic weed control, is reported to persist in the hydrosoils for a number of years controlling the weeds, but having no affect on the fish (3). The herbicide 2,4-D is used extensively for the control of some undesirable aquatic plants. At recommended rates no serious affects from 2,4-D have been reported.

Picloram is an important herbicide because of its toxicity in small quantities to most plants. It is especially phytotoxic to most broadleaved plants and many natural weedy plants along ditchbanks or on range watersheds. The movement of picloram into water, however, may be especially undesirable due to its extreme toxicity to some plant life. There is also considerable concern in using water containing picloram for subsequent crop irrigation (1).

The movement and persistence of picloram has been studied over a two-year period in Utah. Two experimental watersheds were selected to study the surface movement of picloram (4-amino-3,5,6-trichloropicolinic acid) and 2,4-D (2,4-dichlorophenoxyacetic acid) in runoff waters. One watershed located in Wasatch county, Utah, consisting of a mixed grass sward on a loam soil, was divided into two half-acre plots. One plot was treated with ½ lb/A picloram (formulated as the potassium salt of picloram) and the remaining plot was treated with 2 lb/A (ai) 2,4-D (formulated as alkanolamine salt of 2,4-D).

The second watershed was located in Northern Utah in Cache county and consisted of a sparce cover of native grasses and woody shrubs with discontinuous infestations of perennial broadleaved weeds. The predominant soil at the site was a loam. The area was divided and treated in a manner described above for the Wasatch county site. Both watersheds had a slope of 15 to 25 percent and the areas were delineated so that no surface or subsurface flow waters entered the area.

The herbicides were applied to both areas in early May 1969 and the subsequent movement of the herbicides were followed during the succeeding 18-month period. Samples were collected four times during the season immediately following periods of natural precipitation. Each plot was equipped with a catchment device to monitor the movement of the herbicides. A Varian Aerograph Model 1800 gas chromatograph equipped with an electron capture detector was used to quantitate the movement of the compounds. Low limits of detection of picloram

in water was 0.1 ppb; for 2,4-D the low limit was 1.0 ppb. Following the application of the herbicide, sampling stations were established at points 10, 100, 1,000 and 10,000 meters below the treated area. In each case the two most distant sampling locations were along a natural creek-bed being fed by the watersheds. Samples were acidified and refrigerated immediately after collection and were analyzed within two days after collection.

Only the results of the movement of picloram will be given in this report. A total of 32 water samples were collected and analyzed for picloram from the two sites. The average picloram context of the triplicate samples taken at each site are shown in Table 1.

Table 1. Average picloram concentration at various collection points during 1969.

Site	Collection date	Precipitation after treatment	Concentration (ppb) Location (Meters from treated Area)			
			10	100	1,000	10,000
Wasatch county	May 16	0.25	28	21	0	0
	June 26	2.32	3	10	0	0
	July 20	2.80	0	T	0	0
	Aug. 17	4.08	0	0	0	0
Cache county	May 15	0.20	10	8	T	0
	June 16	1.10	0	0	0	0
	June 27	3.55	0	0	0	0
	July 8	4.04	0	0	0	0

Table 1 indicates that there was no residue problem in water with picloram since movement from soil into surface waters was very limited. The Wasatch county study shows that as distance from treated area increases, the quantity of picloram in the water decreases. As time increases the amount of picloram also decreases. At the time of the first collection, picloram concentrations of 28 and 21 ppb at the 10 meter and 100 meter collection points respectively were obtained. The concentration at the collection site nearest the treated area was 28 ppb at the time the first samples were taken, but dropped to 3 ppb on the second date of collection.

In Cache county the concentrations of picloram were somewhat less than in Wasatch county, but the trends of picloram movement was similar. Detectable levels of picloram were observed in the water sample only at the time of the first collection. Subsequent samples taken from the collection devices did not reveal detectable levels. There were no detectable levels of picloram in the runoff waters from these sites during the 1970 collection period.

The results of the above study led to a further investigation of possible degradation products from picloram and their subsequent movement. In 1967 Merkle (10) suggested that photodecomposition may be responsible for the major loss of activity of picloram. He reported that the degradation product resulting from radiation of picloram at wavelengths of 220 mu and 280 mu was a molecule in which a chlorine atom had been lost (7). Studies have been made in our laboratory to determine what particular wavelengths are the most efficient in causing picloram to decompose. Studies have also been made on the stability of the degradation products in water and on their phytoxicity. A Baird-Atomic fluorospec Model SF 100 was used to radiate the samples at a concentration of 9 ppm picloram in water. The samples were radiated at wavelengths ranging from 300 mu to 350 mu in 10 angstrom increments, each for a one hour period. The radiated samples were then spotted and developed on thin layer chromatograms. The spots were removed with 1 ml of acetone and aliquots were injected into a gas chromatograph equipped with an electron capture detector to determine the amount that degraded. The location of the peaks were compared to the peaks of a standard solution of decarboxylated picloram (4-amino-2,3,5-trichloropyridine). The retention times were exactly equal for the two. Preliminary studies indicate that decarboxylated picloram is a major degradation product. This does not rule out the possibility of a product or decarboxylated molecule having lost a chlorine atom. Studies are now in progress to determine more precisely the molecular structure of the major products. A goal will be to see if the decarboxylated picloram has lost a chlorine atom. This study was greatly aided by an analytical technique developed by Evans (17) for the detection of minute quantities of either picloram or decarboxylated picloram in water.

The picloram was also decarboxylated with the aid of the sublimation unit illustrated on page 125. Water samples can be analyzed rapidly with this unit. A liter of water is collected, acidified with HCl to pH2 and extracted with two separate portions of diethyl ether in a separatory funnel. The picloram, now in solution in ether, is placed on the flash evaporator at 40°C. and taken to dryness. The flask is then placed in a heating mantle and the temperature is taken to 190° - 200°C. for 15 minutes with cold water circulating and vacuum being applied to the sublimation unit. After the apparatus cools the unit is removed from the flask and the decarboxylated picloram is washed from the unit with acetone. It can then be injected into the G.L.C. and quantitatively measured. A similar procedure as used for picloram may be used for other herbicides. The benzoic acid herbicides may also be quantitated by a similar procedure.

Following a study with 2,4-D Butler (4) concluded that herbicides are less toxic than most other pesticides. The literature does not produce any evidence that there is a biological magnification with herbicides. Government studies show very little residues in the water. Some parts of the year showed no residues. The report also indicates that no residues were found in excess of the permissible limits (9).

SUBLIMATION UNIT

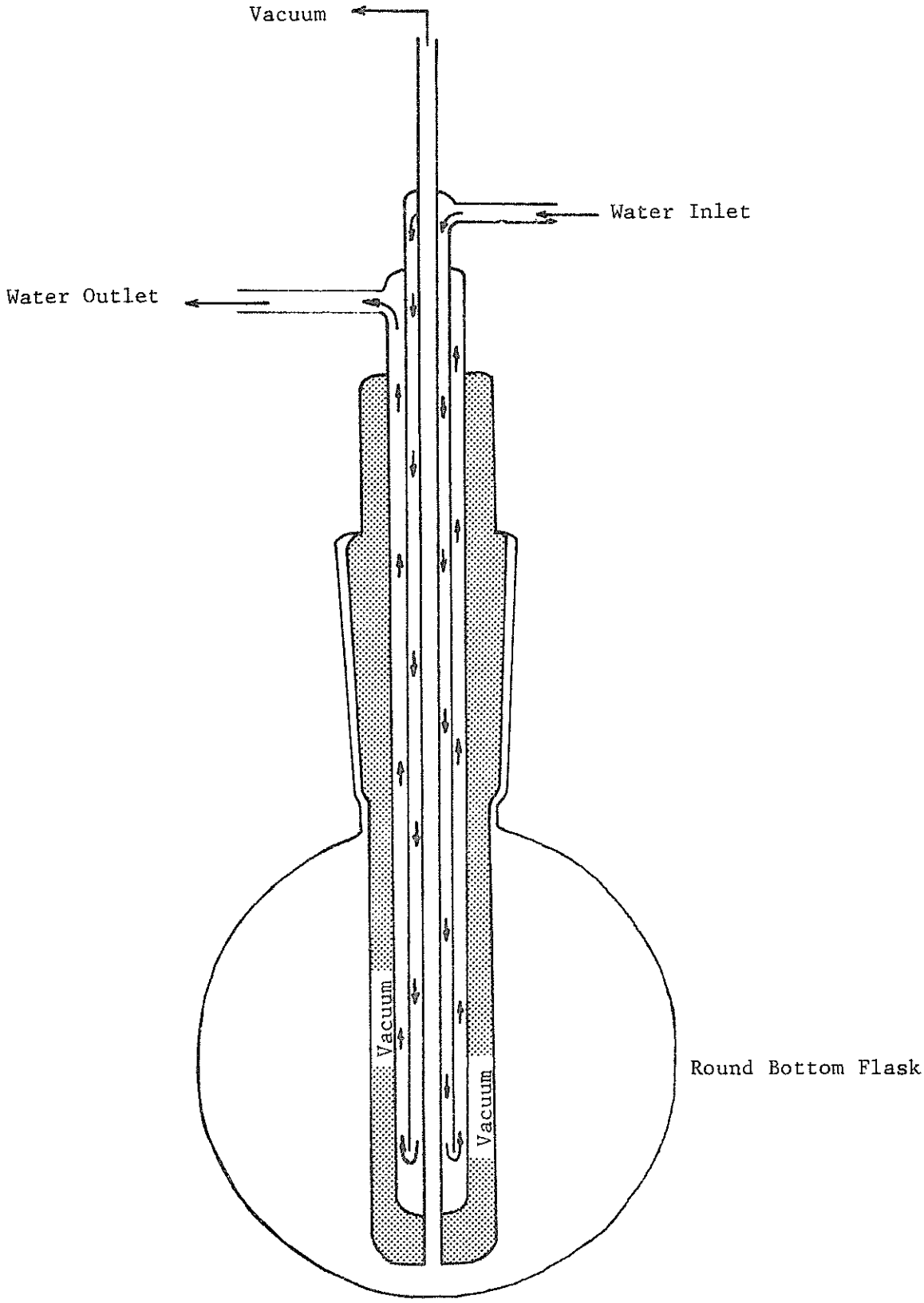

Figure 1. Schematic of Sublimation Unit for Degrading Picloram.

REFERENCES

1. Alley, H. P. 1965. A promising future for control of perennial weeds. Down to Earth 21(1-2): 8-10.

2. A Survey of Extent and Cost of Weed Control and Specific Weed Problems. 1965. (Joint Report) Agr. Res. Ser. and Fed. Ext. Ser. U.S.D.A. ARS 34-102. 70 pp.

3. Beasley, P. G., J. M. Lawrence, and H. H. Funderburk, Jr. 1965. The adsorption and distribution of C^{14}-labelled diquat in the goldfish (Carossius airratus L.). Proc. So. Weed Conf. 18: 581.

4. Butler, P. A. 1965. Effects of herbicides on estuarine fauna. Proc. So. Weed Conf. 18: 576-580.

5. Faust, S.D., R. R. Younger, J. T. Tucker, and O. M. Aly. 1962. Observations on the occurrence and persistence of 2,4-D and 2,4-dichlorophenol in Lake Water. Proc. No. East. Weed Contr. Conf. 16: 459-465.

6. Frank, P. A. and R. D. Comes. 1967. Herbicidal Residues in Pond Water and Hydrosoil Weeds 15: 210-213.

7. Hall, R. D., C. S. Giam, and M. G. Merkle. 1968. Photolytic decomposition of Picloram. Weed Res. 8: 293-297.

8. Herr, Donald A., E. W. Stroube, and D. A. Ray. 1966. Effect of Tordon residues on agronomic crops. Down to Earth 21 (4): 18-20.

9. Manigold, D. B. and J. A. Schulze. 1969. Pesticides in selected western streams. A Progress Report. Report Pest. Monit. J. 3:2.

10. Merkle, M. G., R. W. Bovey, F. S. Davis. 1967. Factors affecting the persistence of picloram in soils. Agron. J. 59:413-415.

11. Mullison, W. R. 1970. Effects of herbicides on water and its inhabitants. Weed Sci. 18: 738-747.

12. Principles of Plant and Animal Pest Control V. 2 - Weed Control. 1968. Nat. Academy of Sciences, Washington, D. C. 468 pp.

13. Tarrant, R. F. and L. A. Norris. 1967. Residues of herbicides and diesel oil carriers in forest water. Proc. Symp. Herb. in Veg. Mange. pp 81-88.

14. The Pesticide Review. 1969. U.S.D.A. Ag. Stabilization and Conservation Service Washington, D. C. 48 pp.

15. U. S. Dept. of Int. 1968. Report of the Committee on Water Quality Criteria. Fed. Water Poll. Contr. Admin., Washington, D. C. 234 pp.

16. Zimdahl, R. L. Pesticides - A Rational Analysis, Colorado State University, Dept. of Botany and Plant Pathology.

17. Evans, J. O. 1979. Analytical technique for the detection of Picloram and some Picloram degradation products in Water. Paper presented to the Technical Committee of the Regional Research Project W82. Dec. 2, 1970. Denver, Colorado.