ISSN 2348-1218 (print)
International Journal of Interdisciplinary Research and Innovations ISSN 2348-1226 (online)
Vol. 3, Issue 4, pp: (96-99), Month: October - December 2015, Available at: www.researchpublish.com

# The Detection of Chlorinated Herbicides at Lake Woodruff Wildlife Refuge and Their Effects on Waterfowl

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***Abstract:*** **Chlorinated herbicides are some of the most common types of pesticides used to control unwanted plants while allowing the desired fauna to grow and prosper. At Lake Woodruff Wildlife Refuge in DeLeon Springs, Florida, these chlorinated herbicides are used to cover vast acres of protected marsh to create strong living environments for migrating waterfowl. However, in recent years, the amount of waterfowl visiting the refuge has steadily declined. During a comprehensive test of the water quality of the Lake Woodruff Wildlife Refuge, large amounts of Triclopyr (a commonly used chlorinated herbicide) were found in the impoundments. These quantities of Triclopyr were found to be at potentially harmful levels to fish and macroinvertebrates at the refuge. This could lead to a lack of food for waterfowl, making Lake Woodruff Wildlife Refuge a less desirable place for migration.**

***Keywords:*** **Chlorinated herbicides, DeLeon Springs, Florida, Lake Woodruff Wildlife Refuge.**

## 1. INTRODUCTION

Compared to the expansive populations in the 1970s, there are currently critically low numbers of waterfowl migrating to Lake Woodruff Wildlife Refuge in DeLeon Springs, Florida each year (U.S. Fish and Wildlife Service, 2012). It is not yet possible to pinpoint the exact cause of this decline; however, climate change could allow migratory birds to live in northern states for the winter, unaffected by the cold that could previously harm them. The effects of chlorinated herbicides on the environment, namely Triclopyr, and how that could impact the livelihood of migratory waterfowl that once thrived in Lake Woodruff Wildlife Refuge are topics worth investigating.

Triclopyr, a molecule in the pyridine group, is a commonly used chlorinated herbicide (Extonet, 1993). Its structure allows it to be used for control of woody and broadleaf plants. However, pyridines express movement throughout plants and soil (Davis, n.d.). This easily allows for Triclopyr to travel through the species it is sprayed on into the connecting water supply. Triclopyr is effective in killing plants, as it mimics auxin, or the plant respiration hormone, causing an overdose up to one thousand times the normal auxin amount (Thoreby, 2011). This disrupts the coordination of plant growth, and eventually causes mutations and the prevention of new cells. Auxins in high concentrations can also be identified as harmful to human beings (New World Encyclopedia, nd.).

Triclopyr can appear in two forms: the Triclopyr triethylamine salt (TEA) and the Triclopyr butoxyethyl ester (TBEE). TEA and TBEE both have high mobility in soil, and half-lives of 139 and 39 days, allowing plenty of time to poison the water supply. The degradation of Triclopyr in the environment is illustrated in Figure 1 below. Both forms of Triclopyr rapidly convert to Triclopyr acid in water (Ganapathy, 1997). Triclopyr acid is slightly toxic to birds, and moderately to highly toxic to fish and other marine species (Thoreby, 2011). With less fish and macroinvertebrates for the waterfowl to feed on, it is less likely that they will continue to migrate to Lake Woodruff Wildlife Refuge or other refuges that consistently use Triclopyr as an herbicide. Our study was conducted to see if the Triclopyr sprayed on invasive species is in fact invading the water supply of the refuge.

## 2. FIELD-SITE DESCRIPTION

A 22,000 acre refuge located in central Florida, Lake Woodruff Wildlife Refuge hosts many species of migratory bird and waterfowl. Established in 1964 by the U.S. Fish and Wildlife Service, it exhibits a wide variety of habitats, such as freshwater marshes, rivers, impounded wetlands, and upland shrubs and forests (U.S. Fish and Wildlife Service, 2012). It is bordered by the largest river in Florida, the St. Johns River, and is located twenty-five miles west of Daytona Beach in Volusia County. Protected by the St. Johns River Water Management District, Lake Woodruff takes pride in its pure waters ("Watershed", n.d.). Despite its water hardness, the refuge sports quality water, with a median temperature of 22.52 degrees Celsius and a slightly alkaline pH of 7.46. This data would suggest healthy aquatic life and water purity ("Watershed", n.d.).

To test for water purity in the form of herbicide concentrations, we took our samples from Pools, otherwise known as impoundments, One, Two, and Three. These pools are manmade embankments upheld by dikes from the St. Johns River. We also took three more samples for testing from the South Marsh, West Marsh, and Spring Garden Run Marsh. These specific locations are marked on the map below.

## 3. METHODS

To isolate Triclopyr in our water samples, we measured 0.5L of sample and poured it into a 1L separatory funnel. We then weighed 125g NaCl and added it to the separatory funnel. We shook the solution until all the NaCl dissolved. We then added 6M HCl dropwise, shaking between drops, until the pH of our solution was less than 2. We then added 100mL diethyl ether and extracted the organic components from our water (“EPA”, 1996). We saved both phases, then repeated the extraction once more. After both extractions were complete, we combined the organic phases and dried them with sodium sulfate for 15 minutes. We poured the extract through a funnel with cotton for filtration. We then reduced the volume of the diethyl ether solution using a rotary evaporator. After preparation of our samples, we loaded 0.1µL into a gas chromatograph, along with samples of the Triclopyr herbicide sprayed on the plants at the refuge.

We ran the GC at a column temperature of 170 °C and a split temperature of 250°C. From the chromatograms, we identified strong peaks matching the retention time of our triclopyr sample. We integrated the peaks and converted the area ratio to parts per million of our original sample (.500L of collected water.) To make sure that the molecule detected was triclopyr, we set different parameters (190 °C column and 270°C split) and obtained a second set of matched retention times.

## 4. RESULTS

We found a significant amount of Triclopyr (154 ppm) in Pool 1 of Lake Woodruff Wildlife Refuge and smaller amounts in the other two pools (Pool 2 - 47 ppm and Pool 3 - 25 ppm) as seen in Table I below. This suggests that the spraying of chlorinated herbicides at the refuge infiltrate the water supply, and in turn, damage the wildlife in and around the pools.

## 5. DISCUSSION

Between the three pools, there is a wide range of Triclopyr concentration. This could be due to its relatively fast degradation and the rotation of herbicide spraying done at Lake Woodruff (on an as-needed basis.) Triclopyr Acid, the most common degradation of TBEE and TEA, can be toxic at levels very close to what was seen in Pool 1. Pool 1’s toxicity is already over the LD50 for sunfish and water fleas, and trout, as shown in Table II. Thus, it is a significant factor to the health and population of fish and macroinvertebrate species in Lake Woodruff. These animals’ (which are prey for migratory waterfowl) reduced populations may contribute to a food scarcity for birds in Lake Woodruff and thus lead to reduced bird populations.

## ACKNOWLEDGEMENTS

We would like to thank the Stetson University Chemistry department, along with professors Dr. Harry Price and Dr. Ramee Indralingam for allowing us access to their lab equipment. We also extend gratitude to Candice Stevenson at Lake Woodruff Wildlife Refuge and Stetson student Alexis Korotasz and Stetson professor Dr. Kirsten Work for assisting in macro invertebrate research.

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## APPENDIX

**Table I.**

| | Concentration (ppm) |
|---|---|
| Triclopyr Sample | 21,100 |
| Triclopyr peak in Pool 1 | 154 |
| Triclopyr peak in Pool 2 | 47 |
| Triclopyr peak in Pool 3 | 25.2 |

**Table II. Toxicity of Triclopyr Acid. (Ganapathy, 1997)**

| Triclopyr Acid | |
|---|---|
| Rat (oral, acute) | $LD_{50}$ 713mg/kg |
| Mallard Duck (oral, acute) | $LD_{50}$ 1,698mg/kg |
| Mallard Duck 8-day (oral) | $LC_{50}$ >5,000 ppm |
| Bobwhite Quail 8-day (oral) | $LC_{50}$ 2,934 |
| Bluegill Sunfish (96 hrs) | $LC_{50}$ 148 ppm |
| Rainbow Trout (96 hrs) | $LC_{50}$ 117 ppm |
| *Daphnia Magna* (48 hrs) | $LC_{50}$ 132 ppm |

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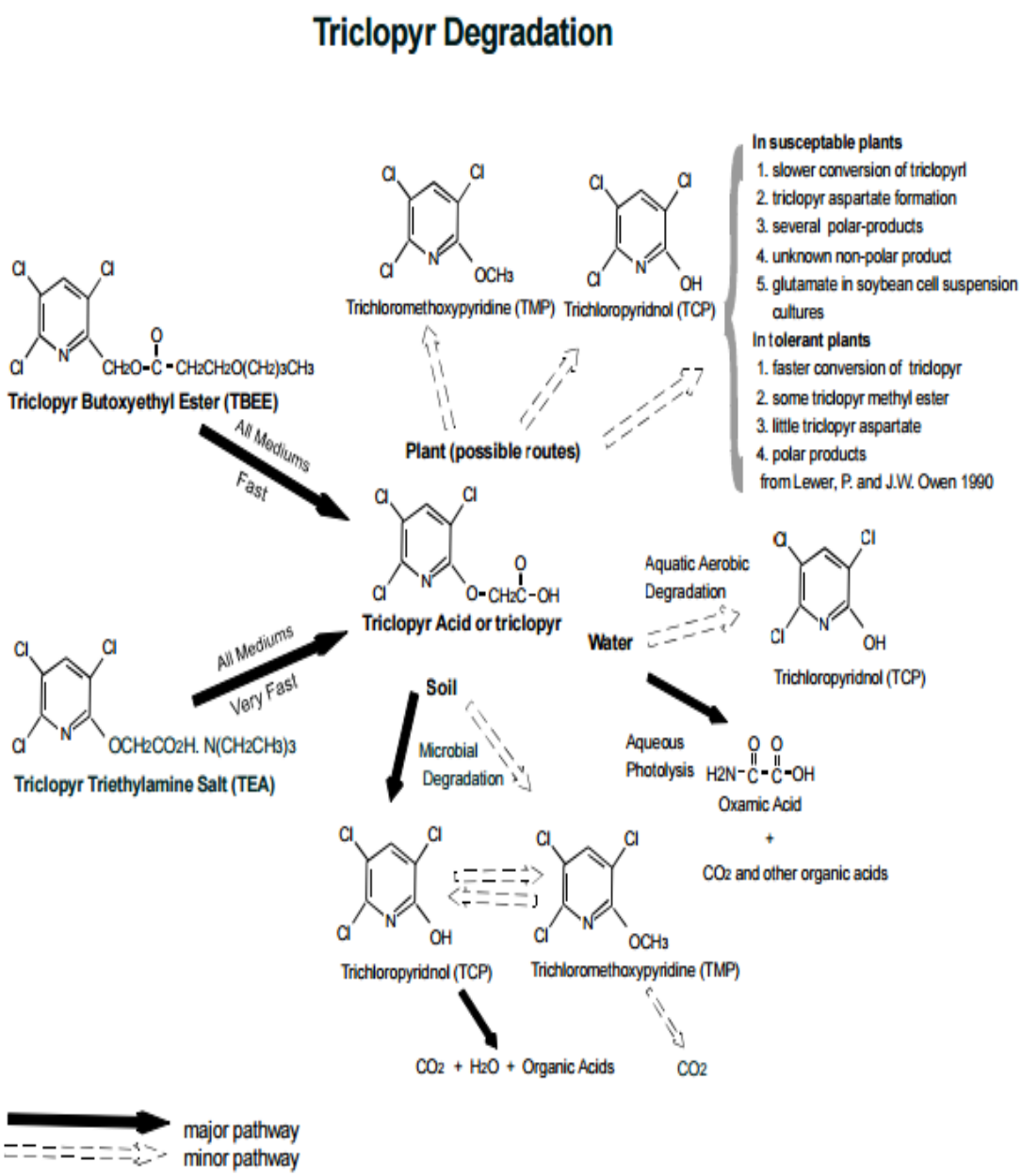


**Figure 1. Degradation of Triclopyr. (Ganapathy, 1997)**