

ABSTRACT

The Treatability of Seven Acid Herbicides with VTX Catalyst

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The purpose of this project is to determine the treatability and percent reduction, if any, of an acid-herbicide mix added to soil and treated with a proprietary catalyst (VTX) and hydrogen peroxide.

Acid herbicides present a substantial environmental problem, and are often found above the Environmental Protection Agency's (EPA) Maximum Residue Limit (MRL).

A known amount of fortified solution was added to six 25.00g soil samples. Three samples were used as controls and three were treated with VTX and 35% hydrogen peroxide for each of seven pesticides including Dicamba, 2,4-D, Triclopyr, Silvex, 2,4,5-T, Bentazon and Picloram. All samples were extracted using a modified EPA method on a Shimadzu GC14-A gas chromatograph then analyzed. It was found that four of the seven herbicides (2,4-D, Silvex, Bentazon and Picloram) were reduced substantially to less than the EPA MRL tolerances. The three others (Dicamba, Triclopyr and 2,4,5-T) were reduced significantly, but

levels were still found above the MRL. It is probable that a less than adequate dose rate of VTX catalyst and peroxide was applied for these three pesticides.

Introduction: The use of organic pesticides is an important tool to the agricultural, landscaping and nursery industries. Pesticides prevent an approximate 9 billion dollar annual revenue and crop loss every year in the United States (Encarta 95).

One of the negative issues associated with herbicide use is pollution. Pesticide related environmental pollution can lead to human and wildlife health problems, ecosystem damage, acid rain, and other undesirable occurrences. In situations where pesticides are being used, there are tolerance levels established by the government and harsh penalties associated with failure to observe these laws. Spills and negligent usages of pesticides have resulted in numerous situations where the environment has been adversely affected.

Herbicide use accounts for 60% of the volume of pesticides used annually on U.S cropland. Approximately 460 million pounds of active ingredient are used per year. Herbicides are very widely used today. Nearly 100% of the nations corn and soybean acreage use are treated. Corn and soybean acreage accounts for about 2/3 of the 460 million pounds of herbicides used annually. (Gianessi, 1)

Acid herbicides, also known as phenoxy herbicides, are derivatives of phenoxyalkane carboxylic acids; these phenoxy herbicides act as plant growth regulators. They were the first selective herbicides discovered and are still widely used today. These herbicides work by stimulating natural hormones resulting in uncoordinated plant growth. Their action is selective in that they are toxic to dicotyledons, but safe to monocotyledonous plants (IPMRC, 2002). The amount of herbicide use is increasing with human population growth, as there is a greater need to feed the planet's increasing population. These chemicals are continuing to escape into ground water. A major concern is that these compounds are being incorporated into the ecosystems food-chain by means of bio-magnification.

Acid herbicides are known to cause acute intoxication, Parkinson's disease, peripheral neuritis, Alzheimer's disease, acute and chronic encephalopathy, non-Hodgkin lymphoma, Hodgkin's lymphoma, multiple myeloma, soft-tissue sarcoma, leukaemias and cancers of the brain, prostate, stomach, pancreas and testicles (Meyers, 64).

A common method today for the removal of toxins in a soil matrix is to put soil into a rotary kiln and burn off unwanted products. While effectively reducing target chemicals, the amount of partially oxidized contaminants escaping into the air makes the rotary kiln a less-than-

perfect approach to this problem. Additionally, burning of pesticide residues to extremely expensive.

A catalytic process, named VTX and developed by Advanced Oxidation Technology, Inc., has been used in the treatment of a wide variety of organic contaminants but has not been used successfully for the treatment of pesticides.

The VTX catalytic process is a treatment option for a variety of different compounds including benzene, phenol, TCE, PCE and methyl tert-butyl ether (MtBE). The catalyst works by creating hydroxyl radicals when combined with hydrogen peroxide. Hydroxyl radicals are very powerful oxidants. Much more powerful than hydrogen peroxide alone. However, past studies have shown that not all pesticides respond to this treatment. For example in a preliminary study, Bis(p-chlorophenyl)-2,2,2-trichloroethane (DDT) was not treatable by this technique. Presence of DDT in soil was tested using ortho-para and para-para DDD, DDE and DDT standards. There was no reduction found in any of these compounds to any significant degree. However, given the success of treating a host of recalcitrant chemicals, it is speculated that the VTX catalytic process could be used to treat a variety of acid herbicides.

Materials and Methods: *Extraction and Clean up:* Measure out 25.00g of soil into a 120mL glass jar. Add 25.00g of pre-cleaned sand (20-30mesh) and 50g of sodium sulfate into the 120mL glass jar. There will be a 100g mixture of soil, sand, and sodium sulfate.

Mix for about 5 minutes on a rotary mixer until everything is adequately mixed together and there are no longer distinguishing layers of any of the three solids. Let the sample stand for about 30 minutes to equilibrate. Using a graduated pipette measure out one mL of spiking solution comprised of Dicamba, 2,4-D, Triclopyr, Silvex, 2,4,5-T, Bentazon and Tordon in acetone at a concentration of 4µg/mL of each. Pour the one mL spiking solution over the soil. After pouring the 1mL spiking solution over soil, pour an additional 8mL of acetone over the soil mixture. This 8mL will create the slurry needed to mix the spiking solution through the soil and allow the herbicides to adequately disperse across the matrix. Using a clean glass rod for each different jar, mix the slurry for 2 minutes, then use 1mL of acetone to rinse the soil mixture off the glass rod. There will be 10mL of acetone/spiking solution.

Mix 9mL of acetone WITHOUT spiking solution into a control jar and rinse the glass rod with an additional 1mL to remove any soil stuck to the rod.

Place the glass jars under a ventilation hood and allow them to dry completely at room temperature. After the jars are completely dry, use a pestle to break the clumps of soil that have formed from the drying process.

In the jar containing soil and spiking solution, place equal portions (3.63mL) of VTX catalyst and 35% hydrogen peroxide over the soil. Mix with a clean glass rod allowing the catalyst and peroxide mixture to adequately disperse across the matrix. Since mixing VTX and hydrogen peroxide will create bubbling and heat, proper eye protection should be worn at all times through the experiment. Rinse the glass rod and the insides of the VTX treated jars onto the soil sample with 5mL of water. Cover and place in a ventilated area and allow the soil sample to dry.

After the sample is completely dry, use a pestle to break the clumps of soil that have formed from the drying process. Add 25.00g of pre-cleaned sand (20-30mesh) and 50g of sodium sulfate into the 120mL glass jar. There will be a 100g mixture of soil, sand, and sodium sulfate. Mix for about 5 minutes on a rotary mixer until everything is adequately mixed together and there are no longer distinguishing layers of any of the three solids. Let the sample stand for about 30 minutes to equilibrate.

Place a pledget of glass wool at the bottom of a 250mL chromatographic bulb column (20mm ID). Carefully transfer the mixture to the column. Rinse the sample container with 2-3 rinsing of 10-20mL of acidified acetone. Add each rinsing to the column. Add 250mL acidified acetone (5mL, or more, 85% phosphoric acid made up to 1L with acetone-pH of 1.5 or less) (Can also use 1:4 HCL:Distilled water, to make the acidified acetone). Collect the samples in clean 500mL flasks. Adjust flow rate to 3-5mL/min. Allow column to drain to dryness (may take several hours).

Evaporate the sample to approximately 10mL on rotary evaporator. Transfer samples to 125mL separatory funnel. Rinse in with 20mL distilled water. Add 8-25mL of 4N KOH (to pH 10, keep under 11.0 pH). Wash the sample twice with 20mL ethyl ether, discarding the ether (top layer) each time. Draw the aqueous layer into a second 125mL separatory funnel. Work back and forth between the two separatory funnels. Make sample acidic with 8-25mL of 1:4 HCL:distilled water (to pH 3 or less). Extract the sample 4 times with 10mL portions of ethyl ether each time. After each extraction, draw the ether layer (top layer) through a sodium sulfate column into an unetched, unscratched, uncracked 50mL screw top tube because diazomethane has the potential to explode on rough glass surface (Merck Index). Evaporate to 2-3mL on N₂ evaporator. Add 0.5mL isooctane. Continue evaporation to 0.5mL, but try not to lose the organic layer (many of the samples will have small amounts of water at the bottom of the tube.) *Derivatization:* Add 2mL of freshly prepared diazomethane. Exercise caution when using diazomethane by wearing gloves and working under a ventilation hood. Cap tightly and let stand for at least 30 minutes. Evaporate off the diazomethane under N₂ to 0.5mL or less without going dry. Quantitatively transfer the sample to a calibrated centrifuge tube with a minimum of 10mL of hexane. Evaporate under N₂ to 2mL. Vortex and store at 4° C prior to

gas chromatography analysis. Sample may need to be further diluted based on its relation to the calibration curve.

A Shimadzu 14-A gas chromatograph equipped with a nickel 63 Electron Capture Detector (ECD) and an RTX-35 30m x 0.53mm, 0.53 μ m df capillary column was used to detect the varying levels of chemicals found in the sample matrices. In appendices A, there is a column labeled "peak height" which represents the y value of the chromatographic peak as identified by comparison to the known standard. The peak indicates both the chemical present and the amount. The actual concentration is calculated using the calibration curve and adjusted for initial sample weight and final sample volume. The calibration curve consisted of four different concentrations for each of the seven chemicals tested labeled as μ g/mL. Comparing the unknown peak to the calibration curve determined the concentration of the extracted sample.

Discussion and Conclusion: It is apparent from data collected in this study that the VTX catalytic process is effective in oxidizing the selected acid herbicides. The efficacy of the technique, however, varied between the test herbicides (Table 2). Three of the herbicides were not reduced to a point lower than the legal limit after a single treatment. All of the chemicals were reduced, 4 of which, were reduced greatly. It is likely that a higher dosage of catalyst and peroxide would have increased the destructive efficiency.

The chemicals showing the greatest reductions were dicamba, 2,4-D, bentazon and picloram. Again, using a greater amount of VTX process components, the process would probably yield more reduction. Picloram, which reduced to the greatest efficiency, might require less of the VTX components.

It would be important in the future to determine the amount of VTX catalyst and peroxide required, by using alternate amounts of the catalyst and noting reductions accordingly. It would also be beneficial to test the VTX process on multiple sample matrices such as water, plant tissue and animal tissue. Finally, mass spectroscopy could be used to determine if breakdown products of the various pesticides are present in the sample after treatment. The gas chromatographic techniques used, however, did not indicate that breakdown products existed as identifiable within the constraints of the techniques used.

Overall the effectiveness of the process for the reduction of phenoxy herbicides is promising.

It can be concluded that treatment by the VTX catalytic process is effective at reducing phenoxy acids. Further testing is needed to determine the relative concentration of catalyst components for optimal reduction of each of the phenoxy acids.

This treatment process could be advantageous to the environmental industry. It was estimated that the cost of treatment using this process for soil would be under \$80/ton, which is well below the market

pricing for treating soil contaminants of this nature. For example, rotary kiln costs were found to range from \$250 to \$400 per ton of soil treated. Landfilling of low level pesticide contaminated soil, where possible, are typically in the \$120 per ton range plus transportation fees. The VTX process is accomplished on site and appears to be a cleaner and less expensive way to treat acid herbicides than competitive approaches.

Table 1. EPA MRL Tolerance

Herbicide	MRL ppm
Dicamba	0.5 ppm
2,4-D	0.5 ppm
Silvex	0.5 ppm
Triclopyr	0.5 ppm
2,4,5-T	0.5 ppm
Bentazon	0.3 ppm
Picloram	0.5 ppm

Table 2. Comparison of Untreated and Treated Samples

Untreated groups, average concentration (three sample repetitions)

Herbicide	ppm before VTX
Dicamba	0.9730
2,4-D	2.9934
Silvex	2.5450
Triclopyr	0.9549
2,4,5-T	1.4861
Bentazon	0.6512
Picloram	1.5225

Treated groups, average concentration (three sample repetitions)

Herbicide	ppm after VTX	Average Percentage Reduction
Dicamba	0.4772	51%
2,4-D	0.1629	84%
Silvex	0.6986	73%
Triclopyr	0.7564	21%
2,4,5-T	0.8178	45%
Bentazon	0.1616	75%
Picloram	0.0350	98%

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