



Project Summary

Collection and Treatment of Wastewater Generated by Pesticide Applicators

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A research project was conducted to develop a system for the control of pesticide-contaminated wastewaters generated by pesticide applicators. The problem was approached in three phases. First, the practices that are currently used to handle pesticide-contaminated wastewaters were evaluated, followed by the development of a system for collecting them. Finally, a treatment plant was developed to remove pesticides from the contaminated wastewaters and to produce high-quality effluents.

The treatment plant is well suited for treatment of pesticide formulations of varying concentrations. Much of the toxic material can be removed during the first coagulation stage, which is followed by activated carbon absorption to remove most of the remaining pesticides. This low-cost, low-technology system seems particularly appropriate for small-scale field operations.

This Project Summary was developed by EPA's Municipal Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The disposal of pesticide-contaminated wastewaters has attracted national attention during the past two

decades. Considerable environmental degradation has been caused by the improper disposal of pesticide-contaminated wastes. Current Federal regulations on the control and disposal of toxic wastes, along with existing pesticide certification programs, will have far-reaching impacts on how pesticide applicators dispose of wash water used to clean application equipment. In an effort to provide applicators with an alternative method for handling the wastewater, a low-cost collection and treatment system was developed.

The objectives of the research were:

1. To evaluate the practices used by pesticide applicators to control wastewater generated during the cleanup of application equipment
2. To construct a system to collect the wastewater generated by pesticide applicators.
3. To design, construct, and evaluate a wastewater treatment plant capable of removing pesticides from the wastewaters generated by pesticide applicators.

Wastewater Control Practices

Pesticide applicators have used numerous techniques to dispose of the wastewaters that are generated during cleanup of equipment. The triple rinse procedure for cleaning pesticide containers, which is recommended by the U.S. Environmental Protection Agency (EPA), is generally followed when cleaning a spray system. The 100 to 400

L of wastewater used each time a plane is cleaned is usually dumped in the cleanup area. A few applicators haul the dilute rinsewater back and spray it on the target area. As fuel costs increase, this practice is seldom followed. More common disposal practices involve dumping of wash water into a holding pond or gravel trench. Research is underway at Texas A&M and at Iowa State to provide applicators with evaporative disposal practices. The residue left after evaporation of the water usually accumulates in the evaporative disposal systems. The ultimate fate of the pesticide is unknown.

The cleanup practices used by aerial applicators vary, but several consistent practices were observed. The application equipment is thoroughly cleaned about once a week by most applicators. The spray system and hoppers are usually washed daily. Most applicators try to organize their daily operations so that insecticides and fungicides are applied first, and herbicide applications are made during the latter part of the day. After herbicides are applied, the equipment must be thoroughly cleaned to avoid any carryover to the next spray job. This management practice allows the applicator to minimize the amount of wastewater that is generated each day.

Wastewater Characteristics

Wastewater from an aerial applicator at Delray Beach, Florida, was obtained and analyzed for total suspended solids (TSS), suspended volatile solids (SVS), chemical oxygen demand (COD), and pH. Nineteen-liter buckets were used to collect the wastewater. Samples included the pesticide dumped out of the hopper, the wash water used to clean the spray boom, the wastewater used to clean the aircraft hopper, the wash water from the surface of the plane, and a composite sample of all the wash water and wasted pesticides that would be generated during the cleanup of the equipment. Results are presented in Table 1.

The highly variable concentration of pollutants represented a severe problem in developing a treatment system to handle the wastewater. The different types of pesticides (i.e., wettable powders, emulsifiable concentrates, granules, soluble salts, etc.) also challenged most treatment options.

Wastewater Collection

A simple wastewater collection system was installed at Monon, Indiana.

Table 1. Volume and Characteristics of Wastewater Generated by Aerial Pesticide Applicators

Source	Volume (L)	Characteristics				
		COD Total (mg/L)	COD Soluble (mg/L)	pH	TSS (mg/L)	SVS (mg/L)
Pesticide formulation in hopper	5-20	60,000	—	—	—	—
Rinse water used to clean spray boom	40-100	13,000	9,600	6.5	11,600	8,900
Wash water used to clean hopper	20-40	88,500	5,000	7.0	18,000	14,000
Wash water used to clean aircraft	75-200	1,200	500	7.5	600	350
Composite wastewater samples	150-360	1,200	900	6.9	1,100	950

The existing concrete pad was modified to divert all wastewater to one corner of the pad, where a sump was installed (Figure 1). Wastewater was pumped from the sump to a steel storage tank.

At 1980 prices, a collection system would cost an applicator about \$1,600 for a 15- x 15-m concrete slab with a sump, \$150 for a chemically resistant sump pump, and \$500 for a 2,000-L above-ground storage tank. All wastewater is stored in one composite tank with this type of collection system. Rain water is also collected unless provision can be made to divert the runoff. With this simple collection system, a treatment system is required that can handle the wide variety of pesticides used by aerial applicators.

Treatment System

Based on the results for several treatment options analyzed in the laboratory, a pilot treatment system was developed consisting of coagulation/flocculation/sedimentation, filtration, oil coalescence, and activated carbon absorption (Figure 2). After initial tests, the filters and oil coalescers were removed, and the pilot plant was mounted on a small trailer. The filtration step was discontinued because the fabric filter and diatomaceous earth filters did not significantly improve effluent quality, and the oil coalescer plugged too quickly to be practical.

Coagulation Studies

The coagulation/flocculation/sedimentation process was expected to reduce the pesticide concentration to its water solubility level or below. Two-liter



Figure 1. Sump installed in one corner of a concrete pad to collect all wastewater.

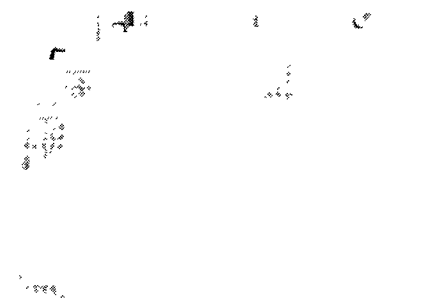


Figure 2. Pilot plant treatment system for wastewater from pesticide application equipment.

jar tests were conducted on synthetic wastewater solutions containing (1) carbaryl (Sevin),* a widely used N-alkyl carbamate insecticide, (2) malathion (cythion), a commonly used phosphorodithioate insecticide, and (3) metribuzir (Sencor), a triazine herbicide.

*Mention of trade names or commercial products does not constitute endorsement or recommendation for use

Even though alum was chosen as the coagulant for this study, it should be noted that in preliminary studies, equivalent doses of ferric chloride were equally effective. When aluminum or iron salt coagulants are used, sufficient alkalinity must be present in the solution to allow a complete reaction. Approximately 0.85 mg/L of alkalinity as CaCO₃ must be present for each mg/L of alum reacted. Sufficient alkalinity was maintained by adding NaOH to the solution. Effective alum coagulation is limited to the pH range of 6.5 to 8.0. Only one of the collected samples was outside this pH range, and this was easily adjusted to the proper level by adding NaOH.

After a series of 2-L jar tests was conducted, pilot-scale studies were begun. The pilot plant (Figure 3) consisted of a 380-L tank, 0.7 m in diameter and 1.1 m high. Three taps were located on the tank: two on the side (approximately 0.5 and 0.7 m below the top of the tank) and one at the bottom of the tank. The side taps were used to draw off supernatant after settling. A variable-speed mixer was mounted above the tank with a 10- x 30-mm paddle blade mixer inserted into the tank to a depth of approximately 0.7 m. Flocculation of the suspended solids (SS) was achieved by adding alum, alkalinity, and an anionic polymer to 350-L batches of wastewater and mixing at full speed (about 250 rpm) for 2 min. The variable-speed mixer was slowed to 30 rpm for 30 min to build the large flocs that would settle rapidly (in less than 1 hr) when the mixer was stopped (see Table 2). After 1 hr, the solids settled 0.5 m, and a transparent supernatant was obtained. Little additional settling was observed after 1 hr.

Since the coagulation/flocculation/sedimentation treatment system produced a sludge after each treatment, studies were conducted to determine the effect of this buildup of sludge solids on the treatment of subsequent batches. To conduct this test, wastewater was added to the settled sludge. The solids concentration of the mixture ranged from an initial 2,000 to 20,000 mg/L TSS after 10 batches of wastewater were treated. At the higher solids concentration, settling took longer (up to 90 min), but the solids concentrations of the supernatant was less than 40 mg/L TSS. Above 15,000 mg/L TSS, alum addition was unnecessary. Large floc formed and settled with only the addition of 1 mg/L anionic polymer. The

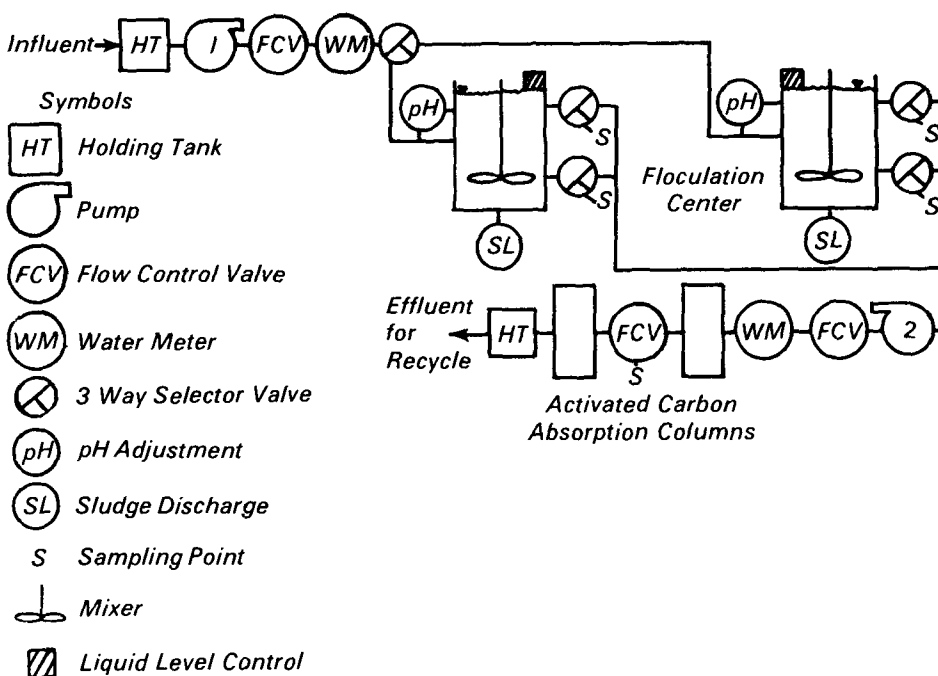


Figure 3. Schematic diagram of the pesticide treatment plant.

samples tested in this experiment contained the wettable powder formulation of carbaryl.

After the successful removal of wettable powder formulations such as carbaryl, the next phase was to analyze emulsion removal. Initial jar tests were performed on tap water solutions of malathion at a concentration of 200 mg/L (water solubility, 145 ppm). Alum doses of 100 mg/L or greater (with anionic polymer) gave excellent supernatant quality. The effects of varying the malathion dose at a constant alum dose (100 mg/L) and 1 mg/L anionic polymer are illustrated as follows:

Initial Malathion Concentration (mg/L)	Final Malathion Concentration (mg/L)
10	9-14
30	9-11
75	11-13
150	15-18
300	20-25

Based on these results, full-scale tests were conducted using field samples of wastewater mixed with previously settled alum sludge and sufficient malathion formulation to give 180 to 200 mg/L of the pesticide. With an SS concentration of 24,000 mg/L, it took 60 to 90 min for the solids layer to settle 0.7 m. The supernatant malathion concentration was 35 mg/L. Studies of tap

Table 2. Settling Rate of Waste-Treated with Alum

Settling Time (min)	Sample Tap*	SS (mg/L)
30	Top	205
	Bottom	225
45	Top	25
	Bottom	52
60	Top	16
	Bottom	42

*The sample taps were located 0.5 and 0.7 m below the surface of the tanks, which were 1.1 m deep.

water with malathion added were less successful, yielding a supernatant concentration of 55 mg/L. Later tests on a solution with lower SS concentrations showed a malathion reduction from 400 to 41 mg/L after 1 hr of settling. Increasing alum dosages up to 500 mg/L did not improve performance. As the SS increased to near 50,000 mg/L in the sample, so did the malathion concentration of the supernatant, reaching as high as 81 mg/L in one case. This solution of wastewater was diluted to 12,000 to 15,000 mg/L SS; 200 mg/L of malathion was then added along with alum and anionic polymer. Settling after coagulation reduced malathion concentration to 27 mg/L. No change in malathion concentration was observed after 18 hr of settling.

Subsequent coagulation studies on solutions of widely differing SS concentrations showed that the 12,000 to 15,000 mg/L concentration range was the maximum that could be effectively treated with our system. Higher concentrations did not settle below the bottom tap after 45 to 60 min of settling.

Later attempts to use the standard alum coagulation procedure on a mixture of wetttable powders and emulsions collected at the Purdue University farm were completely unsuccessful, even at greatly increased coagulant doses, with and without polymers. Several alternative techniques, including acid cracking of the emulsion, were likewise unsuccessful. The difficulties seemed to arise from the presence of a wetting agent added to the mixture. Addition of calcium salts (approximate calcium to wetting agent molar ratio of 2:1) destabilized the emulsion and made it amenable to alum coagulation. Another field sample collected sometime later also required the addition of calcium salts. In this case, 0.5 to 1 mg/L of Ca (introduced as CaCl₂) successfully destabilized the emulsion.

In the next series of tests, metribuzin, a soluble herbicide, was added to wastewater and mixed with resuspended alum sludge. Some dissolved metribuzin was removed by coagulation. This removal is especially apparent in the three lowest concentrations shown in Table 3. One possible explanation is that previously settled emulsified material, when resuspended, may have contributed to a partial extraction and hence removed some of the dissolved organic compounds from solution. This explanation is consistent with the low malathion concentrations observed after coagulation. Since the sludge contains some emulsifying chemicals, resuspending the sludge allows them to extract some of the dissolved pesticides. This conclusion was corroborated with full-scale testing in which metribuzin concentrations of 200 and 264 mg/L reduced solids levels of 12,000 to 15,000 mg/L to 115 and 140 mg/L, respectively — well below the water solubility concentration of 1,200 mg/L.

Based on our observations, jar testing of solutions should be used to determine proper coagulant dose and subsequent settleability. This method should provide enough information to indicate when solids wasting is necessary or when additions of calcium salts are required.

Table 3. Effect of 200- and 500-mg/L Alum Doses on Metribuzin Removal by Flocculation/Sedimentation

Alum Dosage (mg/L)	Initial Concentration of Metribuzin (mg/L)	Final Concentration of Metribuzin (mg/L)
200	100	81
500	100	90
200	500	330
500	500	315
200	750	585
500	750	585
200	1,250	1,050
500	1,250	1,125
200	2,000	996
500	2,000	982
200	3,000	920
500	3,000	1,000

Carbon Absorption Studies

The original field-collected carbaryl solution had a concentration of 450 to 480 mg/L after coagulation and sedimentation, and the main hydrolysis product (naphthol) had a concentration of 225 mg/L. The high carbaryl concentration indicated that a good deal of suspended material was left in the supernatant, but these tests were conducted early in the study before the coagulation procedure had been optimized. By passing the solution through the carbon columns at 3.8 L/min (90 L/min per m²) with a contact time of 8 min, the concentrations of both carbaryl and naphthol were reduced to less than 1 mg/L.

The capacity of activated carbon to absorb pesticides varies with the pesticide. Exhaustion tests were conducted on malathion and metribuzin to determine this capacity. Small glass columns that held 25 g carbon were used for this test. Figure 4 shows the breakthrough curve for malathion. The carbon had absorbed 0.17 g malathion/g carbon by the time the effluent malathion concentration reached 3 mg/L. The carbon was exhausted (that is, the effluent malathion concentration reached the influent concentration) after 0.28 g malathion/g carbon had been absorbed. The activated carbon can absorb more metribuzin. In similar studies, the exhaustion point for metribuzin was found to be 0.43 g metribuzin/g carbon.

By using 2 carbon columns in series, it is possible to saturate the first column with pesticide before the pesticide concentration leaving the second column reaches the detection limit.

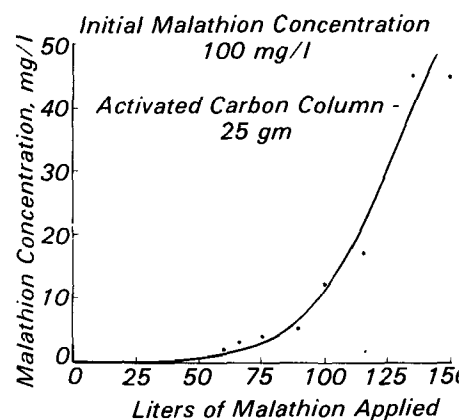


Figure 4. Breakthrough curve for malathion applied to activated carbon.

The ability of activated carbon to absorb a variety of pesticides was tested in additional samples in which malathion, carbaryl, and metribuzin were added to wastewater samples that had been collected in the field. Although these initial tests demonstrated that the pilot plant carbon columns would absorb the pesticide to below the detection limits, no attempt was made to determine the exhaustion point of pilot plant columns. Additional studies determined the exhaustion points for mixed groups of pesticides and herbicides.

The carbon columns on the pilot plant were not exhausted in the field test because each column held about 20 kg of carbon. To exhaust them, about 40,000 L of typical wastewater would have to be treated. During our test, only 20,000 L of wastewater could be collected.

Conclusions

The pesticide treatment plant described here appears to be well suited for treatment of pesticide formulations of varying concentrations. A large percentage of these toxic materials can be successfully removed during the first coagulation stage. The phase separation process is followed by activated carbon, an adsorbent well known for removing many types of organic compounds from aqueous solution. This low-cost, low-technology system seems particularly appropriate for small-scale field operation, an area in which acceptable treatment alternatives are notably lacking. One possible advantage of the system (over and above the obvious benefits of protecting wildlife, crops, and water supplies) might be the reuse of the treated water for mixing new formulations or for washing the application equipment. Such an option would achieve the goal of zero discharge.

The following conclusions are based on the test conducted to evaluate the two-step process to remove pesticides from contaminated wastewater:

1. All pesticide-contaminated wastewater that is generated during the cleanup of application equipment can be combined in one collection and storage system. The widely varying concentrations, types of formulations, and variety of pesticides can be treated by the two-stage process.
2. Alum can be used as a flocculant to reduce the concentration of pesticide in the contaminated wastewater to below the water solubility of the compound. An anionic polymer enhances the sedimentation.
3. Activated carbon can remove most other pesticides in the supernatant of the first stage sedimentation process. The capacity of the carbon to absorb the contaminant depends on the chemical structure and characteristics of the pesticide.
4. Particle size filtration and oil coalescence are not effective in removing pesticides from wastewater.

Recommendations

The disposal of the sludge and spent activated carbon must be considered. These problems appear to be manageable, though more study is needed. Approximately 20,000 L of wastewater was treated in this study, with an accumulation of less than 200 L of

sludge. Several techniques to encapsulate or fix the sludge in a concrete mixture were also evaluated with some success. The carbon can be thermally destroyed or regenerated by commercial firms. Other techniques for disposal of the waste sludge and carbon must also be found. Currently the sludge and carbon would be considered a hazardous waste and would require disposal in an approved landfill.

The detection of pesticide breakthrough during carbon absorption must also be further evaluated to ensure that the effluent is free of trace quantities of pesticides.

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The complete report, entitled "Collection and Treatment of Wastewater Generated by Pesticide Applicators," (Order No. PB 82-255 365; Cost: \$12.00, subject to change) will be available only from:

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