

Pilot Study of Small-Scale Monitoring Methods of Herbicide Residues in Soil and Water

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ABSTRACT

Because of its concern for the environmental impact of roadside herbicide spraying, the Maine Department of Transportation initiated a preliminary study of small-scale monitoring methods of herbicide residues in soil and water. Samples were collected at certain time intervals after the application of herbicides to target plants. The herbicides were extracted in the department's Materials and Research Division chemistry lab, and the amount of the extracted herbicides was determined by high-performance liquid chromatograph (HPLC) in the Department of Food Science and Technology at the University of Maine, Orono. The phytotoxicity of Banvel 720 on brush was evident. One week after application, the plants started to show the effect of the herbicide, and by one month, all the foliage showed no signs of life. Herbicide residue was not detected in the water samples taken from the nearby streams. The results of soil analysis on the herbicide content were predictably erratic. The reasons for this could be attributed to many factors. For example, varying amounts of off-target spraying occurred; the sampling process was not totally systematic; and there was a long period of delay in analyzing all the samples stored in a freezer throughout the period. Viewing the individual test site separately, it is obvious that the level of herbicide suddenly diminished between 1 day and 1 week after application. In spite of the oversights and drawbacks of this project, it is encouraging that the methods of extraction and HPLC determination of the herbicide are adequate for future use. It is feasible to develop a low-budget monitoring program from local resources, the cost of which could be included in ongoing roadside spray operations.

Roadside vegetation management has long been an integral part of highway maintenance operations. Unwanted brush growth diminishes the driver's viewing range and increases pavement shading, which lowers surface temperatures thus causing ice to form in winter. Therefore public safety is a direct concern, in addition to the obvious aesthetic criteria for highway roadsides.

In order to achieve a safety clear zone between the edge of the pavement and the face of the woods, two methods are usually employed: (a) conventional mowing and hand cutting or the use of selective herbicide spray to control the unwanted brush chemically. The former is both time-consuming and costly. The latter, though effective, has aroused much public concern; the fear is that the residue may enter the groundwater or crops. The most suitable herbicide should be one that has a short, persistent period in the soil (but long enough to control the plant) and low environmental hazards.

Many factors influence the soil degradation of herbicides (1), among them: the chemical structure of the herbicide, soil surface mobility, vegetative ground cover, organic matter in the soil, soil pH, soil moisture and temperature, presence of other compounds or ions, clay content of the soil, herbicide formulation, and application methods. Therefore, the rate of degradation will vary from one location to another. The only way to know whether or not a certain herbicide has been degraded is to actually sample the soil near the target plants and test for that herbicide. If enough samples were taken in one area for one type of herbicide and soil conditions,

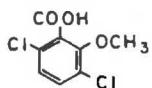
it is possible that eventually some correlation could be predicted.

The Maine Department of Transportation has been concerned about the environmental implication of roadside spray for a long time (2). Management strategies have centered on (a) chemical safety and effectiveness, (b) minimal tank-mix dilutions, (c) selective applications, (d) frequency of applications, (e) no-spray buffer zones, (f) personnel training, (g) monitoring, and (h) public information. Great strides have been made in all these areas.

In 1983 a proposal was developed to conduct a preliminary study of a method for monitoring the herbicide residues in soil and water. The main purpose of the study was to learn through experience. The study was a joint effort of the Maine Department of Transportation's Bureau of Maintenance and Operations and the Materials and Research (M&R) Division in spraying and sampling operations. The tests were performed in two parts. Part one, extraction, was carried out by the M&R chemistry lab, and part two, determination of the herbicides in the extracted samples, was accomplished by the Department of Food Science Technology under the supervision of R. Bushway.

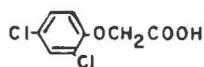
One of the herbicides used by the Maine Department of Transportation in 1983 was Banvel 720 (12.82 percent dicamba and 24.5 percent 2,4-D). The following is a summary of the chemistry of these two compounds.

1. Dicamba, 3,6 - dichloro-o-anisic acid (3)



This compound is a white crystalline solid. It is relatively mobile in the soil. Dicamba mobility in soil can be affected by leaching capillary movement or surface evaporation, or both. Metabolism by soil microorganisms is the major pathway of degradation under most conditions (3). The rate of biodegradation generally increases with increasing temperature and soil moisture, and tends to be faster when soil is slightly acidic (3). Study and experience have shown that dicamba can be leached out of the zone of activity in a humid region in a period of 3 to 12 weeks. The acute oral toxicity, LD₅₀, for rats is 2900 ± 800 mg/kg (3).

2. 2,4-D (2,4-dichlorophenoxy) acetic acid (3)



This compound is also a white crystalline solid, 2,4-D undergoes microbial breakdown in warm, moist soil (3). The average persistence in warm, moist soil is 1 to 4 weeks. The acute oral toxicity, LD₅₀, ranges from 300 to 1000 mg/kg for rats, guinea pigs, and rabbits (3).

Analysis of 2,4-D and dicamba has been the subject of numerous research publications. The extraction procedures also vary depending on the media analyzed. The Official Methods of Analysis of the Association of Official Analytical Chemists (4) included a method for formulation of the dimethylamine (DMA) salts of dicamba and 2,4-D, which are subsequently precipitated by hydrochloric acid, then extracted with acetone. The test methods include gas liquid chromatograph (GLC) (5), radioactive analysis (6), infrared spectroscopy (4), and high-pressure liquid chromatography (7).

EXPERIMENT

Selection of Application Sites

During project planning, a set of requirements were considered for the selection of an appropriate site. The site selected was close to Bangor, Maine, where the central laboratory is located. The study area included as many soil types as possible, and was to be at least 300 ft away from wells, ponds, lakes, or wetlands. The highway orientation was as close to east-west as possible; variations of slope gradient were also desirable. The population of the test area was to be sparse, and individual target plants had to be present.

Several sites were chosen and ultimately the site in Clifton on Route 9 just south of Peaked Mountain (Figure 1) was selected. The section starts at the Hancock County line running westward into Penobscot County to a point approximately 1,000 ft short of the roadside state picnic area. Target plants, both conifers and deciduous, were available on each side of this section of highway.

Before the spray operation, preliminary tests were carried out on control soil samples taken from these sites 2 days before spraying. Temperature, pH, and water content for each site are given in Table 1. The sieve analyses revealed that the soils at Sites 1 and 3 were silty sandy gravel, Sites 2 and 5 were pebbly silty sand, Site 4 was gravelly sand, and Site 6 was sandy clay silt.

Application of Herbicide

On July 27, 1983, a Maine Department of Transportation spray crew routinely sprayed the experimental section. The herbicide used was Banvel 720 (12.82

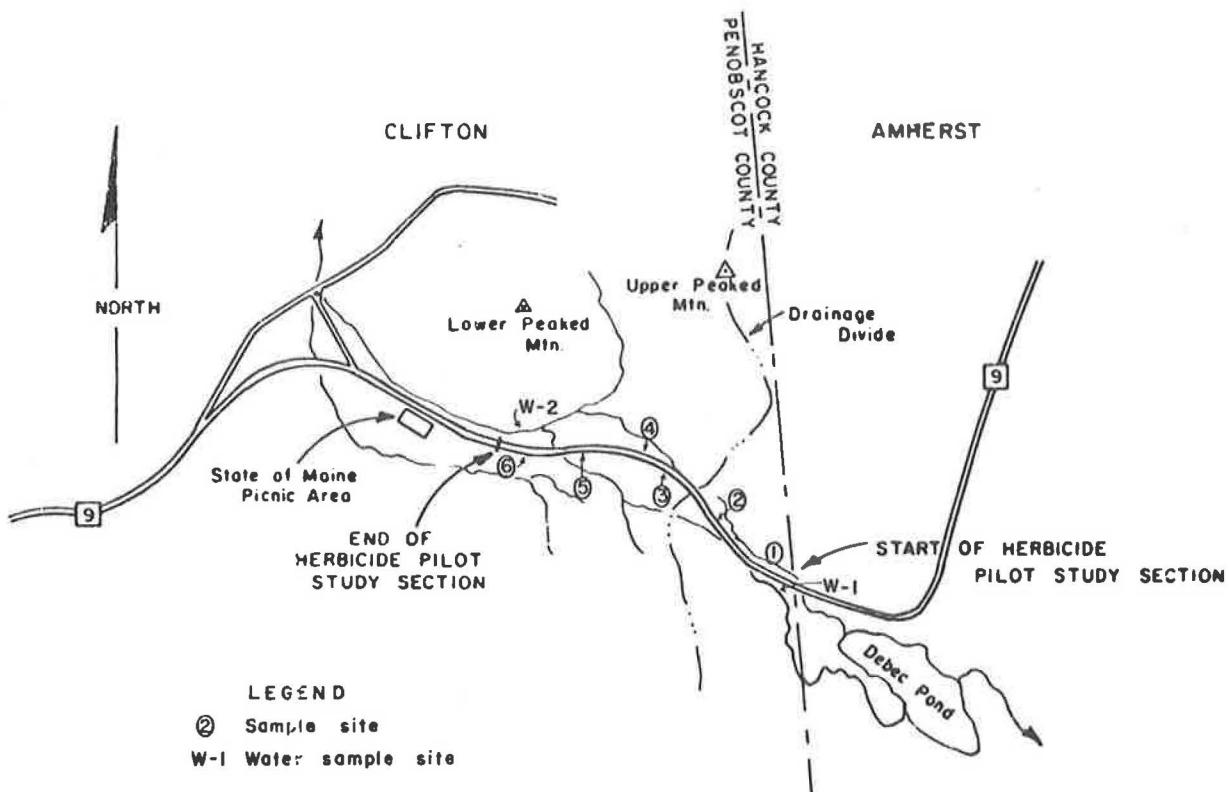


FIGURE 1 Drainage of herbicide pilot study location.

TABLE 1 pH and Temperature of the Soil at Various Spray Sites

Site	pH	Temperature (°F)	Water Content (%)
1	6.1	68	5.7
2	6.5	66	12.1
3	4.7	62	15.4
4	6.6	63	8.3
5	5.5	60	10.6
6	6.2	65	11.0

Note: Target plants are listed in Table 2.

percent dicamba, and 24.5 percent 2,4-D). The mixing rate was 3 qt/100 gal of water, or a 0.75 percent tank-mix solution.

The ambient temperature was 75°F at the time of application (daily high was 85°F, the low was 52°F) and the temperature of the soil was between 60° to 70°F, depending on the location. Sunshine was present throughout the day until around 5:00 p.m. when clouds began to form. By evening, light showers occurred for a short time.

Collection of Soil and Water Samples

Soil and water samples were collected at the following time intervals.

Control, 2 days before application	July 25, 1983
1 hr after application	July 17, 1983
8 hr after application	July 27, 1983
24 hr after application	July 28, 1983
1 week after application	August 3, 1983
1 month after application	August 26, 1983
2 months after application	September 23, 1983
3 months after application	October 25, 1983

The samples were taken with a soil sampler to within 12 in. Soils were immediately collected around the target plant at random distances. After the sample was collected, it was wrapped in a piece of heavy aluminum foil that was stored in a styrofoam ice cooler (with a piece of dry ice inside the cooler). After all the samples were collected, they were immediately transported to the chemistry lab of the M&R division and stored in a freezer. The water samples collected from nearby streams (Figure 1) were also stored in the freezer for eventual analysis by high-performance liquid chromatograph (HPLC) at the University of Maine, Orono. Direct injection was used in the HPLC procedure.

On each sampling trip the appearance of the target plants were investigated and photographic records were kept. A summary of the observation is given in Table 2.

Extraction of the Herbicide From the Soil Samples

The procedure for extracting herbicide from the soil samples was based on the procedure used by Olson et al. (5). The soil was first air-dried and then screened through a 40-mesh screen. One hundred grams of the sample was weighed into a 500 ml Erlenmeyer flask. Seventy-five milliliters of 1 N H₂SO₄ was added to the sample to make a slurry, after which 150 ml of ethyl ether was added and the mixture was shaken for 15 min on a platform shaker at a rate of 150 cpm. This solution was vacuum-filtered through a Buchner funnel, fitted with Whatman No. 1 filter paper, and washed with two portions of 5 ml water. The filtrate was transferred to a 250 ml separatory funnel, shaken for 1 min, and the aqueous layer was discarded. Fifty milliliters of 1 N NaOH were then added, shaken for 1 min, and the organic layer was evaporated. The aqueous solution was then mixed with 50 ml of methylene chloride (CH₂Cl₂) and subsequently the CH₂Cl₂ layer was discarded. The aqueous layer was acidified with 2 ml of concentrate H₂SO₄, after which 50 ml of ethyl ether was added, shaken for 1 min and the aqueous layer was discarded. The ether phase was transferred to a 500 ml suction flask and evaporated to dryness under vacuum at 50°C. The residue was then transported to the Department of Food Science Technology at the University of Maine, Orono for HPLC analysis.

Analysis of Herbicides in the Extracted Samples

For each of the extracted samples, 10 ml of HPLC grade acetonitrile CH₃CN was added, sonicated for 3 to 5 min, and transferred to a scintillation vial that was then frozen until ready to inject on HPLC. The HPLC conditions were as follows:

Solvent: 67 percent 30 mM phosphoric acid, pH = 28
 33 percent CH₃CN
 Flow rate: 2.9 ml/min
 0.04 absorbance unit full scale (AUFS)
 $\lambda = 230 \text{ nm}$
 Column = μ Bondapak C₁₈
 psi = 1900
 50 μ l volume injected

The stock solution contained 20 mg dicamba (99.9 percent pure) and 23.9 mg 2,4-D (99 percent pure) in a 25-ml volumetric flask and diluted to the mark with HPLC CH₃CN. The standard solutions were prepared by diluting 1/2, 1, and 2 ml of preceding stock solution to 100 ml with HPLC CH₃CN.

The standard solutions, as well as the sample solutions, were injected to Waters High Performance Liquids Chromatograph, Model ALC-220. The amount of sample in each solution was then determined by peak height using the standard curve. If there appeared to be interferences at or around the expected retention time, the sample was then spiked 50:50 with the

TABLE 2 Target Plants and Their Appearance After Certain Time Interval

Site	Name of Plant	Time Period After Application				
		1 Day	1 Week	1 Month	2 Months	3 Months
1	White pine	Healthy	1/5 needles brown	95 percent brown	All dark brown	10 percent needles gone
2	Gray birch	Healthy	1/3 leaves brown	All brown	All dark brown	Most leaves gone
3	Silver maple	Healthy	1/2 leaves brown	All brown	Most leaves gone	Leaves all gone
4	Staghorn summac	Healthy	2/3 leaves brown	Most leaves gone	Leaves all gone	Leaves all gone
5	Black spruce	Healthy	5 percent brown	95 percent brown	Needles gone	Needles gone
6	Gray birch	Healthy	1/5 leaves brown	All brown	75 percent leaves gone	Most leaves gone

most concentrated standard solution. If the peak was increased, it would be confirmed as the desired compound. If two separate peaks appeared, the presence of the herbicide in that sample would be ruled out.

RESULTS AND DISCUSSION

The phytotoxicity of Banvel 720 was evident from the results given in Table 2. One week after application, the plants began to show the effect of the herbicide, and by 1 month, all of the target foliage were without signs of life.

The water samples collected from the nearby streams were analyzed by direct injection to the HPLC. Analysis of the water samples showed that the herbicide levels were all under the detectable value.

Known amounts of herbicides were added to the control soil samples collected before the spray operation. These mixtures were extracted and analyzed for both dicamba and 2,4-D. The results are given in Table 3. It is apparent that the extraction process did not result in total recovery at the levels of 1 or 0.1 ppm. However, it can be inferred that none of these types of herbicides existed in the control soil samples.

TABLE 3 Herbicide Contents in Control Soil Samples

Sample No.	Dicamba Added (ppm)	Dicamba Found (ppm)	2,4-D Added (ppm)	2,4-D Found (ppm)
1A	1	0.42	1	0.46
2A	1	0.53	1	0.44
3A	1	0.40	1	0.50
4A	1	0.13	1	0.27
5A	1	0.62	1	0.74
6A	1	0.62	1	0.60
2B	0.1	Not detected	0.1	0.08
3B	0.1	0.08	0.1	0.13
4B	0.1	0.07	0.1	0.12

Note: Known amount of herbicide was added.

The results of soil analysis on the herbicide content given in Table 4 are erratic. The reasons for this could be attributed to many factors, for example, the spray mix coverage on targeted foliage canopies was not easily controlled, and the distances between the spray gun on top of the spray truck and the target plants varied from 10 to 30 ft. Depending

on the shape and size of the plant, different volumes of herbicide mix were sprayed in order to properly control plant growth. Moreover, the soil samples, taken at different time periods after application, were collected from around the plants, which varied geometrically at each location.

Viewing the individual test sites separately, it is obvious that the level of herbicide suddenly diminished between 1 day and 1 week after application. The explanation for this phenomenon can only be speculative. One factor involved was the storage period of the sample. There was a long period of delay in analyzing all the samples. The samples from the early collections were analyzed after 10 to 11 months storage in the freezer and the samples from later dates were analyzed after 12 to 14 months.

Another variation was the location of sampling at different time periods. Because the spray application was not uniform, concentration of the herbicide in the vicinity of the plant would not be uniform. Instead of sampling at random as was done during this project, the sample should be collected at one particular station.

Weather conditions also greatly influence herbicide degradation. A summary of the temperature and precipitation records for Bangor and vicinity for the months of July to October 1983 is given in Table 5. Closer examination of the daily temperature between July 27 and August 3, 1983, showed high temperature readings of 85, 90, 83, 88, 82, 72, 84, and 86°F, consecutively. Moderate rainfall occurred during that period. Traces of rainfall occurred on July 27, July 29, August 1, and August 3; 0.37 in. occurred on August 30, and 0.36 in. occurred on August 2. Therefore it is conceivable that the herbicide degraded at a seasonably faster-than-normal rate.

It has been reported that the persistent period of 2,4-D is 1 month and that of dicamba is 2 months (8,9). The rate of degradation depends on the content of organic matter in the soil, pH, clay content, and water content. At this stage of the study, it is difficult to pinpoint the reason (or reasons) for the quick disappearance of the herbicide.

It is unfortunate that samples were not collected between 1 day and 1 week, thus the exact trend during this period was not detected. Improvement of this aspect of the experimental design to include sampling between 1 and 8 hr, 8 and 24 hr, 1 and 7 days, and 1 week to 1 month would reveal more of a trend on the degradation pattern.

Further research should also (a) quantitatively control the spray operation, (b) define clearly the

TABLE 4 Herbicide Contents in Soil Samples at Various Time Periods After Application

Sample No.	1 Hour	8 Hours	24 Hours	1 Week	1 Month	2 Months	3 Months
Dicamba (ppm)							
1	8.61	2.55	8.64	ND	ND	ND	ND
2	0.47	ND	0.81	ND	ND	ND	ND
3	4.62	15.7	15.3	ND	ND	ND	ND
4	5.44	3.49	10.1	ND	ND	ND	ND
5	2.75	5.95	5.98	ND	ND	ND	ND
6	1.61	1.98	3.50	ND	ND	ND	ND
2,4-D (ppm)							
1	13.9	3.74	14.3	ND	ND	ND	ND
2	0.69	ND	1.56	ND	ND	ND	ND
3	6.28	20.5	22.8	ND	ND	ND	ND
4	9.10	4.63	15.9	ND	ND	ND	ND
5	4.04	8.02	8.89	ND	ND	ND	ND
6	2.56	3.23	5.38	ND	ND	ND	ND

Note: ND = none detected at a detection level of 40 ppb.

TABLE 5 Climatological Data for July-October 1983,
Bangor and Vicinity

Month	Temperature (°F)			Total Precipitation (in.)
	Average Maximum	Average Minimum	Average	
July	81	60	71	7.25
August	78	58	68	2.65
September	75	50	63	1.57
October	58	38	48	2.13

sampling location, (c) shorten the storage period between sampling and test, and (d) quantitatively determine the efficiency of the extraction procedure.

In spite of the oversights and drawbacks of this project, it is encouraging that, with better experimental design, the methods of extraction and HPLC determination of the herbicide are adequate for future use. Because this was a pilot study, the goal of learning through practice was accomplished.

CONCLUSION

An in-house method of extracting the herbicide Banvel 720 (12.82 percent dicamba and 24.5 percent 2,4-D) was developed. The extracted material was analyzed for dicamba and 2,4-D by means of high-performance liquid chromatograph. The result showed a sudden disappearance of the herbicide between 1 day and 1 week. At present the reasons for this phenomenon are only speculative.

It appears routinely possible to monitor herbicides in soil and water on a small scale suited for maintenance spray program management. Data collected over time may provide a sound statistical base for major management decisions.

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