PB86-228111

Report No. FHWA/RD-85/058

INVESTIGATIONS OF IMPACTS OF SELECTED HIGHWAY MAINTENANCE PRACTICES ON WATER QUALITY

Volume II

March, 1985
Final Report

Prepared for

FEDERAL HIGHWAY ADMINISTRATION
Office of Engineering and Highway Operation
Research and Development
Construction, Maintenance and
Environmental Design Division
Washington, D.C. 20590

Technical Report Documentation Page

1. Report No.
FHWA/RD-85/058

2. Government Accession No.

3. Recipient's Catalog No.
PB86-228111/AS

4. Title and Subtitle
Investigations of Impacts of Selected Highway Maintenance Practices on Water Quality -- Volume II

5. Report Date
March 1985

6. Performing Organization Code

7. Author(s)
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8. Performing Organization Report No.

9. Performing Organization Name and Address

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10. Work Unit No. (TRAIS)

11. Contract or Grant No.
DTFH61-82-C-00085

12. Sponsoring Agency Name and Address

Federal Highway Administration
Office of Research and Development
U. S. Department of Transportation
Washington, D. C. 20590

13. Type of Report and Period Covered
Final Report - Volume II
September 1982 - March 1985

14. Sponsoring Agency Code

15. Supplementary Notes

FHWA Contract Manager: Byron N. Lord, HNR-30

16. Abstract

This report, Volume II in a four-volume series of reports, describes a field research program to determine water quality impacts from two routine highway maintenance practices -- control of vegetation using herbicides and surface treatment (seal-coating) of asphaltic concrete pavements. It includes the details of monitoring site selection, precipitation and storm water runoff monitoring, performance of the above maintenance practices, and analysis of results. Two sites were monitored in the herbicide study; one was treated with 2,4-D, the other with picloram. For the surface treatment operation, an asphalt road was treated with a WS-90 asphalt emulsion followed by application of limestone gravel. Chemical analyses and bioassays conducted on runoff samples generally indicate these practices do not impact water quality.

The volumes in this series are:

Volume I - "Highway Maintenance Impacts to Water Quality - Executive Summary" (FHWA/RD-85/057)

Volume II - "Investigations of Impacts of Selected Highway Maintenance Practices on Water Quality" (FHWA/RD-85/058)

Volume III - "A Reference Manual for Assessing Water Quality Impacts from Highway Maintenance Practices" (FHWA/RD-85/059)

Volume IV - "Guidelines Manual for Minimizing Water Quality Impacts from Highway Maintenance Practices" (FHWA/RD-85/060)

17. Key Words

Water Quality
Highway Maintenance
Herbicide Application
2,4-D
Picloram
Surface Treatment (Seal Coating)
Polynuclear Aromatic Hydrocarbons

18. Distribution Statement

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161

19. Security Classif. (of this report)
Unclassified

20. Security Classif. (of this page)
Unclassified

21. No. of Pages
71

22. Price
$11.95

Form DOT F 1700.7 (8-72)

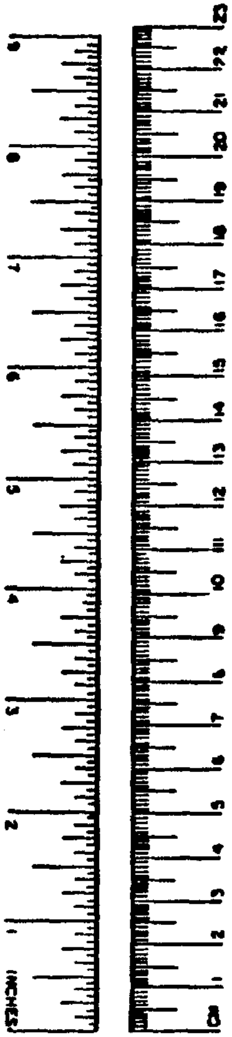
Reproduction of completed page authorized

NOTICE

METRIC CONVERSION FACTORS

APPROXIMATE CONVERSIONS FROM METRIC MEASURES

SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
	LENGTH			
in	inches	2.5	centimeters	cm
ft	feet	30	centimeters	cm
yd	yards	0.9	meters	m
mi	miles	1.6	kilometers	km
	AREA			
in²	square inches	6.5	square centimeters	cm²
ft²	square feet	0.09	square meters	m²
yd²	square yards	0.6	square meters	m²
mi²	square miles	2.6	square kilometers	km²
	acres	0.4	hectares	ha
	MASS (weight)			
oz	ounces	28	grams	g
lb	pounds	0.45	kilograms	kg
	short tons (2000 lb)	0.9	tonnes	t
	VOLUME			
tsp	teaspoons	5	milliliters	ml
tbsp	tablespoons	15	milliliters	ml
fl oz	fluid ounces	30	milliliters	ml
c	cups	0.24	liters	l
pt	pints	0.47	liters	l
qt	quarts	0.95	liters	l
gal	gallons	3.8	liters	l
ft³	cubic feet	0.03	cubic meters	m³
yd³	cubic yards	0.76	cubic meters	m³
	TEMPERATURE (exact)			
°F	Fahrenheit temprature	5/9 (after subtracting 32)	Celsius temperature	°C



APPROXIMATE CONVERSIONS FROM METRIC MEASURES

SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
	LENGTH			
mm	millimeters	0.04	inches	in
cm	centimeters	0.4	inches	in
m	meters	3.3	feet	ft
m	meters	1.1	yards	yd
km	kilometers	0.6	miles	mi
	AREA			
cm²	square centimeters	0.16	square inches	in²
m²	square meters	1.2	square yards	yd²
km²	square kilometers	0.4	square miles	mi²
ha	hectares (10,000 m²)	2.5	acres	
	MASS (weight)			
g	grams	0.035	ounces	oz
kg	kilograms	2.2	pounds	lb
t	tonnes (1000 kg)	1.1	short tons	
	VOLUME			
ml	milliliters	0.03	fluid ounces	fl oz
l	liters	2.1	pints	pt
l	liters	1.06	quarts	qt
l	liters	0.26	gallons	gal
m³	cubic meters	36	cubic feet	ft³
m³	cubic meters	1.3	cubic yards	yd³
	TEMPERATURE (exact)			
°C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature	°F

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INTRODUCTION

BACKGROUND

This report presents methods and results of a field research program established to determine water quality impacts from two highway maintenance practices, used nationwide:

- Control of vegetation on highway rights-of-way using herbicides
- Surface treatment (seal-coating) of asphaltic concrete pavements

This field research program is part of a project involving highway maintenance practices impacts to water quality. During initial background studies, routine highway maintenance practices were evaluated to determine their potential for impacting water quality. Each practice was compared to a set of criteria and classified by type: Type I - practices which can have a probable impact, Type II - practices which can have a possible impact, and Type III - practices which have no probable impact (see also Table 1). However, there is little evidence to directly support these classifications; rather, they are based on extrapolations from research findings on the impacts of similar activities in non-highway applications.

Thus, part of the project was to select two practices for intensive study to better define the magnitude and extent of impacts from specific practices. The above two practices were selected following a screening of the universe of practices listed on Table 1. Type III practices were not considered because they have no impact.

Of the Type I and II practices, chemical vegetation control and surface treatment operations were selected for study because each has the potential to impact water quality through the introduction of toxic substances. Several other maintenance practices were considered but not selected. In some cases, studies have already been conducted (e.g., bridge painting research by the California Department of Transportation); in other cases, the impacts are associated with erosion and sedimentation resulting from earthmoving, removal of vegetative cover, or in-stream work, and are adequately documented.

Table 1. Maintenance practices organized according to water quality impact types.

Maintenance practices which can have a probable impact (Type I)

- Repairing slopes, slips, and slides
- Cleaning ditches, channels, and drainage structures
- Repairing drainage structures
- Bridge painting
- Substructure repair
- Chemical vegetation control

Maintenance practices which can have a possible impact (Type II)

- Full depth repairs
- Surface treatments
- Blading and restoring unpaved berms and/or shoulders
- Repairing curbs, gutters, and paved ditches
- Bridge surface cleaning
- Bridge deck repairs
- Mowing
- Planting or care of shrubs, plants, and trees
- Seeding, sodding, and fertilizing
- Application of abrasives
- Care of rest areas
- Washing and cleaning maintenance equipment
- Bulk storage of motor fuels
- Disposal of used lubricating oils

Maintenance practices which have no probable impact (Type III)

- Blading unpaved surfaces
- Pothole patching
- Surface repairs
- Filling and sealing joints and cracks
- Pavement jacking
- Planing pavements - bituminous and concrete
- Bridge joint repair
- Superstructure repair
- Cleaning pavement
- Guardrail repair
- Snow plowing
- Crash attenuator repair
- Snow fence installation and removal
- Highway lighting
- Flat sheet, side-mounted, and overhead sign maintenance
- Pavement marking
- Bulk storage of nonfuel materials
- Controlling and disposal of roadside litter

RELATED DOCUMENTS

This document is part of a four-volume series of reports on water quality impacts of highway maintenance practices:

- Volume I: "Highway Maintenance Impacts to Water Quality -- Executive Summary" (Report No. FHWA/RD-85/057). This volume provides a concise summary of the major findings and conclusions of this project.
- Volume II: "Investigations of Impacts of Selected Highway Maintenance Practices on Water Quality" (Report No. FHWA/RD-85/058). This report presents the results of field research undertaken to improve the state of knowledge concerning impacts to water quality resulting from two highway maintenance practices, herbicide application and road surface treatment (seal-coating).
- Volume III: "A Reference Manual for Assessing Water Quality Impacts from Highway Maintenance Practices" (Report No. FHWA/RD-85/059). This manual provides full descriptions of the potential water quality impacts of most maintenance practices. Methods are detailed for determining if such impacts are likely to be significant for a specific maintenance project or program.
- Volume IV: "Guidelines Manual for Minimizing Water Quality Impacts from Highway Maintenance Practices" (Report No. FHWA/RD-85/060). This manual provides guidance for minimizing water quality impacts for any maintenance activity which may adversely affect water quality.

GENERAL APPROACH TO FIELD RESEARCH

The fundamental issue of this study is whether the two maintenance practices in question have sufficient potential for water quality impact that they should be items of future concern. The research designs were intended to give as clearcut an answer as reasonably possible to this question. The situations studied were selected to favor a finding of the hypothesized impact, without being extreme worst-case situations. The intent was to study the maintenance practices under typical or representative conditions but with bias towards an expectation of probable impact. Thus, a negative finding would provide a basis for not considering impacts from such activities in future projects.

RESEARCH DESIGNS AND METHODS

CONTROL OF VEGETATION USING HERBICIDES

Introduction

The use of herbicides to control weeds and brush on highway rights-of-way has been on the increase, as an alternative for more labor-intensive and costly practices such as mowing. Voorhees (1982) lists 36 herbicides in common use by State highway agencies. Comprehensive data on the amounts of herbicides used by highway agencies are not available, but it is evident from background research that most agencies use substantial amounts of herbicides. However, highway usage is minor when compared to agricultural, forestry, or even home usage.

Highway rights-of-way typically contain, or are near, water bodies. Herbicides are toxic to aquatic life, although typically less so than are insecticides. Available data on herbicide toxicity are given in Volumes III and IV in this series of reports, as are available data on the environmental persistence and aquatic fate of the 36 herbicides cited by Voorhees (1982). What had yet to be established was whether herbicides actually are found in runoff from highway rights-of-way in concentrations toxic to aquatic life following proper application.

Selection of Herbicides

A primary factor in selecting the herbicides for this study was the commonality of usage by State highway agencies. The more common the usage, the more germane the findings of this project to the management decisions of the agencies. Second, herbicides were considered based on potential for impacting water quality, taking into account recommended application rates, aquatic toxicity, and probable mobility in stormwater runoff. Herbicides which showed the greater potential for an impact were considered likely candidates for use.

Consideration was also given to the practical problems of being able to detect toxic concentrations in water. Analytical detection limits were compared with aquatic toxicity data. A related matter was a suitable bioassay for the herbicide, i.e., a bioassay test which is sensitive and accurate, yet simple, rapid, and not prohibitively expensive. Of the 36 herbicides examined, 2,4-D and picloram were found to best meet the above selection criteria.

Monitoring Site Selection

One of the first steps involved identifying appropriate criteria and selecting two study sites within the highway rights-of-way. Within each site, two relatively discrete drainage areas were selected, one to serve as a control, the other to be treated with herbicide based upon the following criteria:

- No herbicide application to the right-of-way in the previous 6-months.

- Adjacent land uses nonagricultural and not likely to be subject to herbicide applications.

- Suitable pair of drainage areas in the right-of-way, each about 0.5 to 5.0 acres (0.2 to 2.0 ha) in area and with well-defined drainage conveyance to a central discharge point for monitoring.

Numerous sites throughout northeastern Ohio were visited and evaluated against the above site selection criteria. Two sites were identified which satisfactorily met the above criteria.

I-71 Site -- This site is located in a rural environment approximately 35 miles (56 km) directly south of Cleveland, Ohio, at the interchange of I-71 and SR 3 in Medina Township. I-71 is a four-lane divided highway with an average daily traffic (ADT) of 32,100. Two grassed drainage areas were selected, one draining an area between the I-71 southbound lanes and the I-71 southbound exit-ramp (to serve as a control area) and a second draining a portion of the median strip (to serve as a treatment area). Figures 1 and 2 present typical photographic views of the two drainage areas. Figure 3 presents a schematic diagram of the entire I-71 site, showing drainage patterns of the control and treatment areas.

Drainage from the control area is relatively well defined and directed towards a central collection point (used as a monitoring location) before discharging to a perennial stream. Drainage from the treatment area flows southward to an inlet basin. Runoff is then carried eastward under I-71 through a 15 in (38 cm) culvert. The outlet end of the culvert is located on an embankment directly adjacent to the I-71 northbound lanes and served as the treatment area runoff monitoring location. The control and treatment drainage areas are delineated in Table 2.

Figure 1. Photographic view (looking south) of I-71 control drainage area, Medina Twp., OH.

Figure 2. Photographic view (looking north) of I-71 treatment drainage area, Medina Twp., OH.

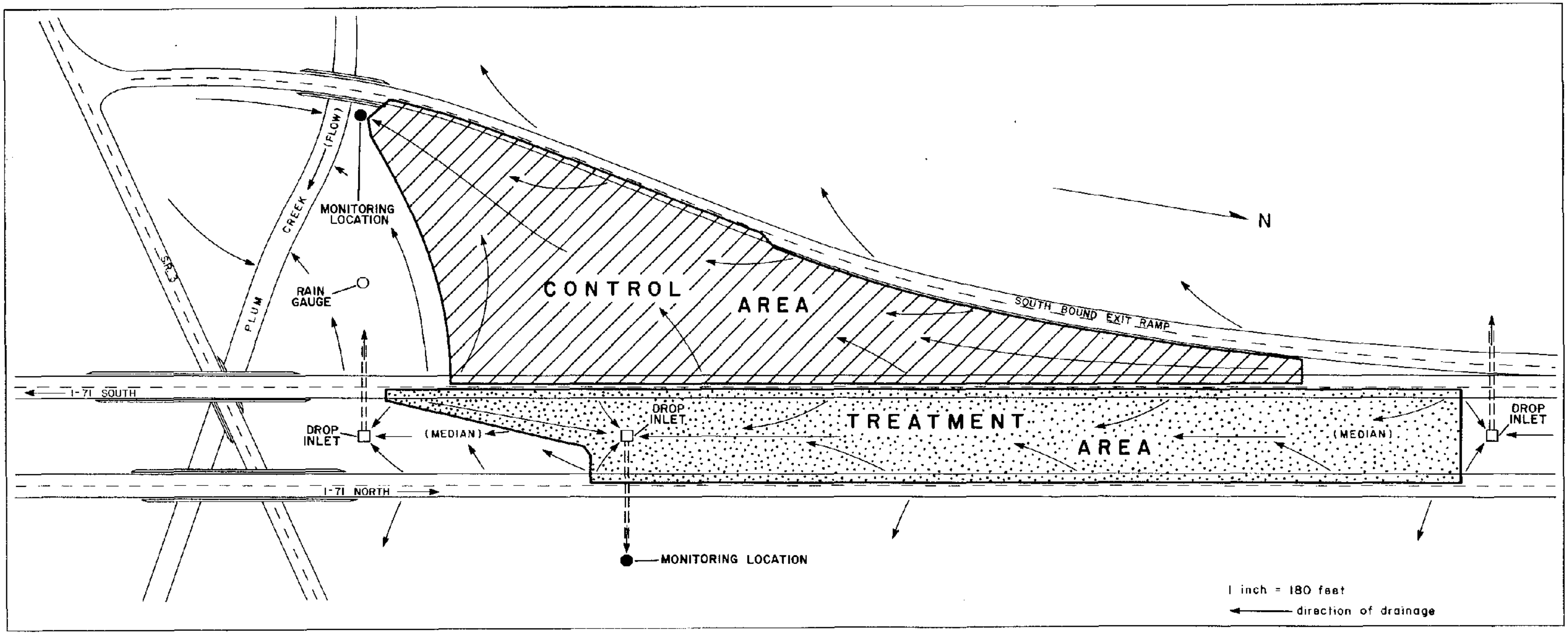

Figure 3. Schematic diagram of I-71 site, Medina Twp., OH.

Table 2. Control and treatment drainage areas of the I-71 study site.

	Total drainage area (acres)	Grassed drainage area (acres)	Total area grassed (%)
Control	3.41	2.68	79
Treatment	2.64	1.92	73

Metric Units: To convert acres to ha multiply by 0.405.

I-90 Site -- This site is located in a semirural environment approximately 45 mi (72 km) west of Cleveland at the interchange of I-90 and SR 57 in Elyria, Ohio. I-90 is a four-lane divided highway with an ADT of 22,560.

From the numerous drainage areas within the total area of the interchange, two were selected for use in this study. The control area drains an area adjacent to but northward of the I-90 west-bound exit-ramp (Figure 4). Drainage from this area flows generally eastward along a grassed channel which collects runoff at a central point. This was used as the monitoring location. The treatment area drains a basin-shaped area which lies between the westbound lanes of I-90 and the I-90 westbound exit-ramp (Figure 5). Overland drainage flows northward to a 21 in (53 cm) culvert which carries runoff under the I-90 westbound exit-ramp and discharges immediately downgrade of the control area. This discharge point served as the monitoring location for the treatment area. Figure 6 presents a schematic drainage plan of the I-90 site. The areas of the control and treatment drainage areas are summarized in Table 3.

Figure 4. Photographic view (looking west) of I-90 control drainage area, Elyria, OH.

Figure 5. Photographic view (looking east) of I-90 treatment drainage area, Elyria, OH.

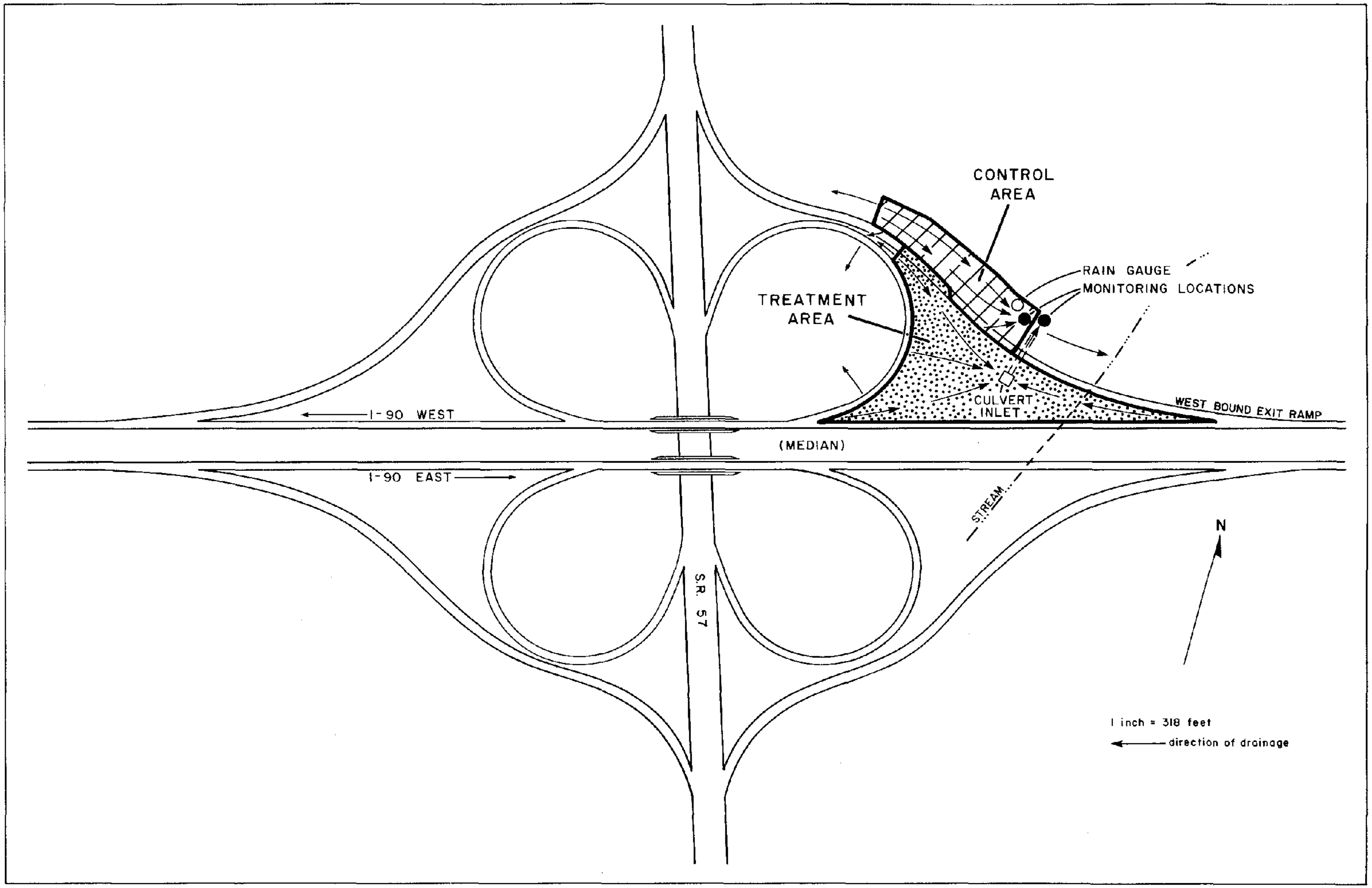

Figure 6. Schematic diagram of I-90 site, Elyria, OH.

Table 3. Control and treatment areas of the I-90 study site.

	Total drainage area (acres)	Grassed drainage area (acres)	Total area grassed (%)
Control	1.16	1.04	91
Treatment	5.08	4.53	89

Metric Units: To convert acres to ha multiply by 0.405.

Application of Herbicides

Application of herbicides to the I-71 and I-90 study sites was observed by research team personnel. The treatment area of the I-71 site was sprayed with 2,4-D on July 16, 1984. The I-90 treatment area was sprayed with picloram on August 23, 1984. Nalco-trol, an antidrift agent, was added to the picloram spray mixture. These areas were sprayed by the highway agency using a truck skid-mounted chemical sprayer (Figure 7). This unit consisted of a tank, pump, regulator, and manifold mounted on the bed of a truck, and a boom sprayer with seven nozzles attached to the front. These procedures and equipment are representative of those employed for herbicide application.

The application rate was based upon the manufacturer's recommendations. The application rate of the herbicides was verified by observing the dilution of the concentrate and by calibration of the sprayer equipment. Calibration was accomplished by spraying a known volume of water over a known area. This provided the delivery rate per unit area. By multiplying this number by the actual area to be sprayed, the total volume of mix to be sprayed was calculated. From this and the suggested application rates of the manufacturer and the highway agency, the exact amount of herbicide to be applied to the treatment area was established. In each case, a sample of the sprayed material was obtained for chemical and biological analysis. This sample also served to verify the type of herbicide used and as a check on the quantity applied. The specific details concerning these operations are presented in Table 4.

Figure 7. Highway agency sprayer unit used for applying herbicides in this study.

Table 4. Specifications of herbicide spraying operations.

Herbicide	Common name	Date applied	Site	Area sprayed (acres)	Sprayer swath width (ft)	Sprayer truck velocity (mph)	Application rate of mixed herbicide (gal/acre)	Application rate of active ingredient (lb/acre)
2,4-D, amine salt	Formula 40	7/16/84	I-71	1.92	7.5	10	62.5	4.3
Picloram, potassium salt	Tordon K	8/23/84	I-90	4.53	10.5	8	27.6	1.3

Metric Units: To convert acres to ha multiply by 0.4046.
To convert ft to m multiply by 0.3048.
To convert mph to km/h multiply by 1.609.
To convert gal/acre to L/ha multiply by 9.36.
To convert lb/acre to kg/ha multiply by 1.12.

The herbicide formulations were representative of those used by highway agencies with one exception: picloram (Tordon K) is rarely used alone, but rather mixed and sprayed in combination with 2,4-D (as Verton 2D or Esteron 99). It was used alone in this study in order to facilitate the investigation of its migration and toxicity, without regard to any synergistic effects which might be associated with its use with 2,4-D.

Monitoring Program

Precipitation and runoff monitoring equipment for both the I-71 and I-90 sites was installed and operative as of early July, 1984. Selected rainfall and runoff events were monitored from July 4 through August 18 at the I-71 site, and from July 4 through October 1 at the I-90 site.

Precipitation Measurement -- The duration, intensity, and total amount of precipitation were measured at each study site with an 8-day (192-hour) weighing type precipitation gauge (Belfort Instrument Company Model No. 5-780). One gauge was installed in each study site and calibrated in the field according to the manufacturer's recommendations.

Runoff Monitoring -- Runoff was sampled from both drainage areas of each site using flow-splitting composite samplers or "Mar" samplers (Clark et al., 1981). This device continuously removes a fixed fraction of the stormwater runoff proportional to the flow rate and automatically accumulates it in a collection vessel. This enables the collection of a composite sample which represents the average characteristics of the runoff.

The composite samplers used in this study consisted of a 10-ft long (3.1 m) by 25-in wide (63.5 cm) by 4 in high (10.2 cm) rectangular cross section open channel with vertical dividers placed near the outlet end, parallel to the direction of flow (Figures 8 and 9). The dividers diverted a flow proportional volume into a 1 ft by 1 ft by 2 ft (0.3 m by 0.3 m by 0.6 m), 12 gal (45.4 L) glass collection vessel just past the last divider. The device was completely covered, except for the last 2 ft (0.61 m) which were cut and hinged to provide easy access to the vertical dividers for maintenance. The base and top of the sampler was constructed of heavy plywood, and the sides were made of 2-in by 4-in (5.1 cm by 10.2 cm) boards. The vertical dividers were made of 1/8-in (0.3-cm-) thick flexible masonite fastened in grooves of 2-in by 4-in (5.1 cm by 10.2 cm) boards (Figure 10). The 12 gal (45.4-L) glass container was placed in a heavy plywood box which was then placed either wholly or partly in the ground at the outlet end of the splitter. The entire sampler and the box containing the glass container were coated with a fungicide-free, white latex paint.

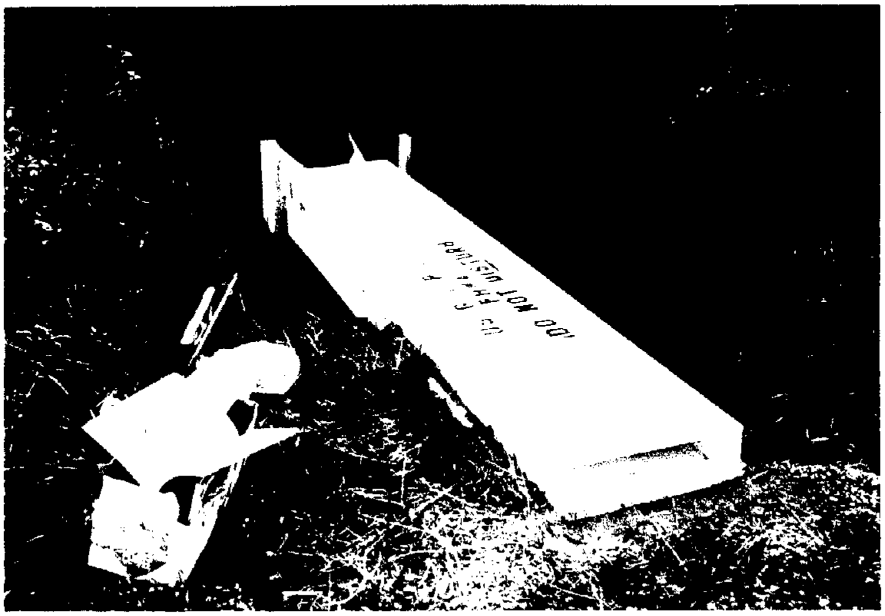

Figure 8. Flow-splitting composite sampler used during monitoring program.

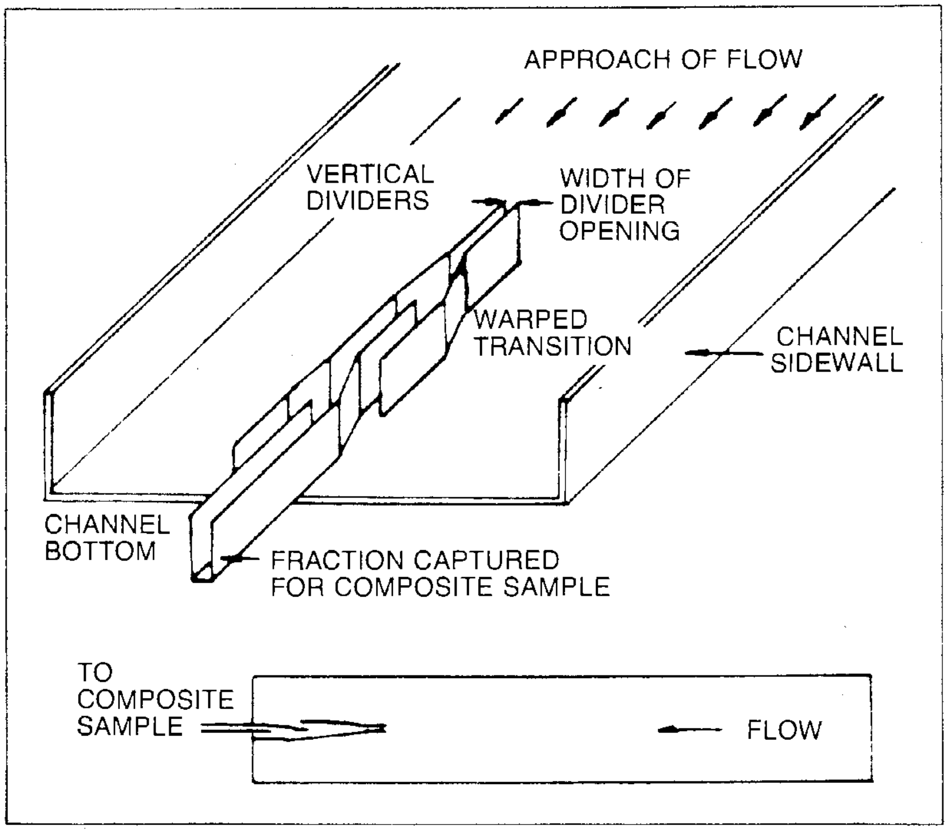

Figure 9. Schematic diagram of flow-splitting composite sampler.

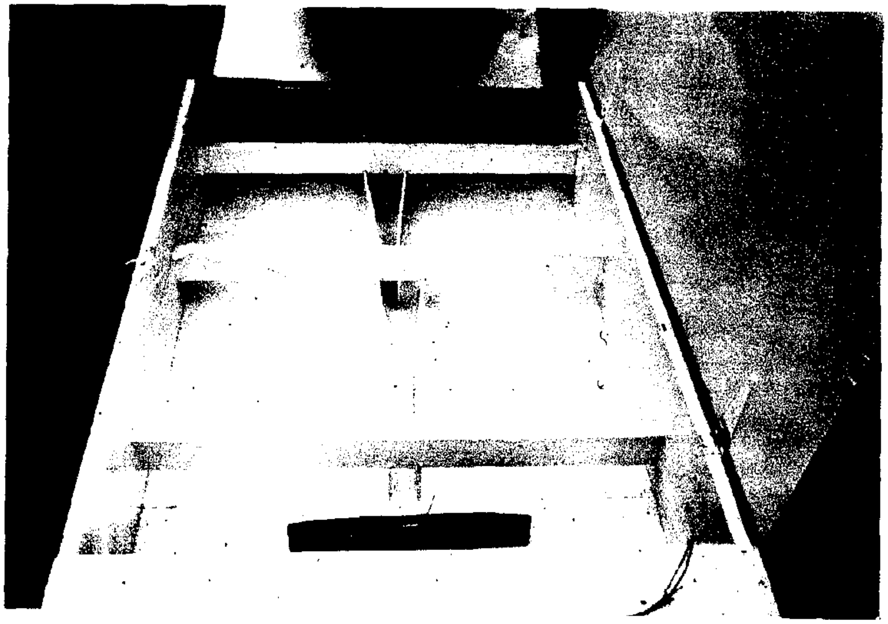

Figure 10. Closeup view of flow-splitting composite sampler showing vertical dividers. (Note carpenter's level in foreground.)

Drainage areas from 0.5 to 5 acres (0.2 to 2.0 ha) were considered during this study. Assuming a maximum runoff coefficient of 1.0, a 1-in (2.54 cm) rainstorm would produce about 1,815 ft^3 (51.4 m^3) for a 0.5-(0.2-ha) acre site and 18,150 ft^3 (514.0 m^3) for a 5 acre (2.0 ha) site. Because of design limitations, these samplers cannot reliably remove less than 1 percent of the total flow for a given runoff event. One percent of the possible flow from a 0.5- or 5-acre (0.2-to-2.0 ha) site means that the capacity of the collection vessels should be between 18.2 ft^3 (0.52 m^3) and 181.5 ft^3 (5.14 m^3), respectively.

Previous studies which have utilized this sampler for monitoring highway stormwater runoff have used plastic-lined collection vessels of up to 50 ft^3 (1.4 m^3) (Clark et al., 1981). However, herbicides are known to adsorb to plastic; and, therefore, any kind of plastic or plastic-lined collection vessel could not be used for this study. Instead, cornerless glass containers were used. The largest glass vessel available was 12 gal (45.4 L) or 1.6 ft^3 (0.05 m^3). Due to this limitation, there was a risk, throughout the study, that the collection vessels would overflow. To minimize this risk, the samplers were designed to collect 1 percent of the total flow. This was accomplished by using a 25-in (6.4-cm) wide channel and an initial divider opening of 1 in (2.5 cm), thereby isolating approximately one twenty-fifth of the runoff flow. The isolated flow was then split in half twice and the resultant one one-hundredth fraction of the total runoff directed into the glass collection vessel.

The 1 in (2.5 cm) initial divider width was chosen because it permits the majority of debris to pass through without clogging. An 8 ft (2.4 m) approach length to the dividers was used to dampen initial turbulence, so that the water reaches the dividers as a relatively uniform sheet. However, since some forceful flow and turbulence is necessary to prevent settling of solids along the approach and clogging of the dividers, the sampler was installed and maintained with a slope of at least 0.086 (Clark et al., 1981). All of the samplers used in the herbiciding portion of this study were built to the same specifications and maintained in excess of this slope.

Each sampler was calibrated to determine the actual percentage of flow removed. Each sampler was estimated to remove approximately 3 percent of the total flow.

The only notable difference among the samplers was in their monitoring location. At the I-71 site, the control area sampler was placed in an eroded gully at the end of the drainage conveyance, with the base of the inlet side of the samplers placed flush up against the edge of the drainage ditch at the grass-soil interface. The treatment area sampler was placed at the base of the culvert outlet which drained the treatment area. In both cases, the collection boxes were placed approximately halfway into the ground. At the I-90 site, the control area sampler was placed in the ground at the end of the drainage conveyance, with the base of the inlet side of the sampler flush against the grass soil-interface. The treatment area sampler was placed at the base of the culvert outlet which drained the treatment area. Both collection boxes were installed such that only the top 6 in (15.2 cm) of the boxes were aboveground.

Sampling at each site took place three times. The first runoff sample was collected from both drainage areas prior to any application of herbicide to the treatment area (preapplication sample). A second sample was collected during the next runoff event following application of herbicide (first postapplication sample). A third and final sample was collected at least two weeks after the second (second postapplication sample).

<u>Monitoring Operations</u> -- Monitoring operations were divided into two categories -- routine maintenance and precipitation events. Routine maintenance involved visiting each site at least once a week to change and reset the recording chart of the rain gauge, to ensure that the proper slope and level of each sampler was maintained, and to check on the general condition of the equipment and the site.

Precipitation events were tracked in the following manner. At each site, a local resident was enlisted to serve as a "weather-watcher" for that area with instructions to call the research team when a significant rainfall had taken place in that area. Generally, 0.1 in (0.25 cm) of precipitation was considered a significant rain event. In addition, the research team tracked local weather forecasts and initiated contact with the local weather watcher when appropriate. A trip to the site was made whenever a significant rainfall was confirmed or suspected.

The following routine was observed at each site following a precipitation event. First the rain gauge was examined, the amount of rainfall recorded and the glass collection vessels inspected for runoff samples. The volume of the sample was measured using a meter stick calibrated for volume. It had been previously determined that a sample of at least 1 qt (0.95 L) was required for accurate chemical and biological analysis. If less than 1 qt was measured, the sample was left in the container until the next runoff event. A situation was never encountered where, at a site, there was more than 1 quart in one vessel and less than 1 quart in the others. Therefore, the samples at each site were either collected or not collected together.

If more than 1 quart of runoff sample was collected, the sample was mixed well with a glass stirring rod in the glass vessel and collected in an amber bottle with a teflon-lined cap. A portion of each sample was isolated and temperature and dissolved oxygen measured electronically. The pH of a sample of rainfall from the precipitation gauge was also recorded.

To check on possible contamination of the collection system, a series of sample blanks were collected in the field using the following procedures. First, following installation of the collecting equipment, distilled water was poured through the flow splitter, collected in the previously cleaned glass vessel, and tested, except a bioassay was not performed. Following each runoff event when a runoff sample was collected, a sample blank was again collected after the glass vessel was analytically cleaned in the field using 50 percent hydrochloric acid

(HCl) and rinsed five times with distilled water. Distilled water was poured directly into the glass collection vessel rather than through the sample splitter to avoid contamination by particles which may have been deposited in the splitter during the runoff event.

Before leaving the site, the research team reset the precipitation gauge, verified the slope and level of each sampler, and placed the analytically cleaned glass vessels back in the collection vessel boxes. The samples and field blanks were transported back to the research laboratory in coolers and maintained near 39 °F (4 °C). At the research lab, a well-mixed portion of each sample was removed for use in bioassays. The remainder of each sample, along with the field blanks, were immediately sent to the analytical laboratory for chemical analysis of the herbicide in question.

Analytical Determinations

Chemical Analysis -- ASTM Method D3478-79 (ASTM, 1979) was used for the detection of 2,4-D and picloram. The analytic detection limit was 1 ug/L for 2,4-D and 0.5 ug/L for picloram.

It is important to determine whether the herbicide is dissolved in the runoff or bound to the sediment to establish its biological availability to aquatic organisms. Herbicides soluble in the water column are believed to have a greater impact on the environment than those bound to the sediment. The form in which the herbicide appeared was determined for each sample. Normally this is accomplished by filtering a portion of the total sample and analyzing the filter residue in addition to the total sample. However, the amount of sediment found in the runoff samples was insufficient to perform such an analysis. Instead, if the herbicide was found to be present in the total sample, a portion of the total sample was filtered through a 0.45 um filter and the analysis conducted on the filtrate and the total (unfiltered) sample. The amount of herbicide bound to the sediments was then inferred as the concentration difference between the total sample and the filtrate.

Quality Assurance/Quality Control (QA/QC) -- A significant amount of time and effort was expended to determine the quality of the data collected. In addition to the collection of the field blanks described earlier, a QA/QC program was conducted by the laboratory. All quality control work was done concurrently with sample analysis. The following types of sample analyses were performed by the analytic laboratory:

- Field blanks - to determine the level of contamination introduced by the sampling equipment and collection vessel.
- Field samples - at least three standards were analyzed to establish a standard calibration curve for quantifying sample results.
- Clean water method standard - to provide an indication of sample preparation and instrument performance through calculation of percent recovery of known amounts of herbicide which have been added to distilled water, extracted, and analyzed by GC.
- Total and filtrate matrix spike recoveries - to determine the effect of the runoff sample matrix on the measured quantities of the herbicide in the sample.

Bioassay Analysis -- Bioassays are tests which use the response of a living organism to determine the presence and/or concentration of a chemical in a sample. They are an analytic tool which indicates the biological activity of herbicides by testing the phytotoxic portion of the herbicide molecule (Santelmann, 1977). Bioassays function under the assumptions the bioassay species will show an effect in proportion to herbicide concentration, and the tests are reproducible. Bioassay species are chosen for their sensitivity to herbicides at very low concentrations.

The hypocotyl growth test was the bioassay used for both herbicides. Cucumber seeds were used for the 2,4-D bioassay (Kratky and Warren, 1971), and lettuce seeds for the picloram bioassay (Reid and Hurtt, 1969). Both bioassays were conducted as described below.

Dilutions of each runoff sample were made at 100, 10, 1 and 0 percent (control) concentrations. The diluent was distilled water. A Whatman No. 54 filter paper was placed in a 100 mm Petri dish and saturated with 2 mL of one of the test dilutions. The original research design required placing ten cucumber seeds (for 2,4-D) or ten lettuce seeds (for picloram) in each of five replicates for each dilution. The seeds adhere to the moist filter paper by surface tension. However, after the first 2,4-D bioassay was conducted, concerns about overcrowding of hypocotyls in the dishes prompted a modification of the bioassay procedure. Subsequent 2,4-D bioassays consisted of six replicates with six seeds in each. All picloram bioassays consisted of five replicates with six seeds in each. A positive control consisting of seeds exposed to a sample of the herbicide as applied was run with each bioassay.

To avoid desiccation, each Petri dish was sealed with Parafilm. Each test chamber was prepared similarly, differing only in the concentration of the runoff sample used. The dishes were incubated at room temperature, in the dark. Cucumber seeds were incubated for 96 hours and lettuce seeds for 72 hours. The dishes were incubated on edge so the geotrophic effect resulted in relatively straight hypocotyls, accurately measurable. Bioassays of samples collected on the same day were run together. Figure 11 illustrates this test procedure.

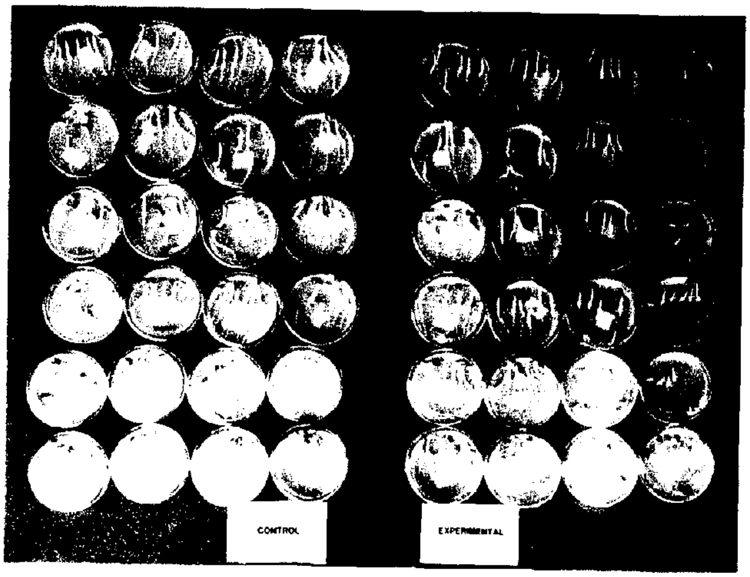

Figure 11. Example of hypocotyl growth test procedure.

At the end of the incubation period the number of germinated seeds in each dish were counted and the length of each hypocotyl was measured using vernier calipers. Percent germination and mean hypocotyl lengths for each runoff dilution were calculated.

ASPHALT-CONCRETE SURFACE TREATMENT WITH ASPHALT EMULSIONS

Introduction

The maintenance practice of using liquid asphalt for preserving bituminous asphalt concrete surfaces, more commonly known as seal coating or "chip and seal," is routinely performed by State highway agencies. Historically, highway agencies used asphalt materials that had been "diluted" or "cutback" with kerosene or naphtha. Use of cutbacks has become less common because of the high costs of petroleum-based solvents and potential for air pollution through evaporation of solvents.

At this time, the major types of materials used for surface treatments are asphalt emulsions made of a combination of liquid asphalt and an emulsifying agent. The mixture is then diluted with water to the desired consistency and expected curing rate. The exact composition of emulsifying agents is generally proprietary information, known only by the emulsion manufacturer. Generically, however, emulsifiers are often comprised of complex synthetic detergents or other detergent-like organic compounds, all of which are capable of solubilizing in both asphalt and water.

Asphalt potentially contains significant levels of polynuclear aromatic hydrocarbons (PAHs) (Trosett et al., 1977). Some representative PAHs found in asphalt at significant levels include pyrene, benzo(a)pyrene, phenanthrene, and chrysene. Although these compounds are relatively low in their toxicity to aquatic organisms, PAHs are suspected of causing cancer in mammals. Further, all of the above PAHs are included on U.S. Environmental Protection Agency's (EPA) toxic or "priority pollutants."

An additional water quality concern related to asphalt surface treatment practice and PAHs is the potential for contamination of sediments deposited in drainageways and streams. To date, research in this area has been aimed at determining the sorption capacity of PAHs to various substrates, primarily sediments. Means et al. (1980) demonstrated that PAHs sorption ability was strongly correlated with the organic carbon content of the soils and sediments tested. Data presented by Radding et al. (1976) show that PAHs are transported as adsorbed matter on suspended particles in water.

Asphalt emulsions are also of concern because of the chemical nature of the emulsifying agents. The toxicity to aquatic life of emulsifying agents in conjunction with asphalt is not well understood; yet, the very property of "detergentness" is toxic to many aquatic organisms. For this reason, a measurement of asphalt emulsion aquatic life toxicity using an appropriate and sensitive test organism on the stormwater runoff would be instrumental in determining the potential for water quality impacts.

Selection of Asphalt Emulsion Material

No special constraints were placed on the type of asphalt emulsion to be used other than that the material to be applied should be one commonly used by highway agencies.

Monitoring Site Selection

The following criteria were applied in the selection of a surface treatment site:

- A well-defined drainage system draining a specific paved area.
- Paved drainage conveyance so runoff does not pass over vegetated right-of-way prior to collection. This would provide a worst-case indication of PAHs in runoff, as removal by vegetation would not occur.
- Adjacent land area nonindustrial to reduce the possibility of elevated background levels of PAHs.
- Low traffic volumes to reduce the possibility of vehicle emissions as a source of PAHs.

The site selected for use in the surface treatment portion of the research program is located in Bloomingrove Township, Richland County, in rural northcentral Ohio. The site consists of a 0.24 mi (0.39-km) section of a two-lane road, named Snake Road (Figures 12 and 13). The total drainage area of the Snake Road site is 0.52 acres (0.21 ha), of which 0.49 acres (0.20 ha), or 94 percent of the total drainage area, are paved. The drainage area collects stormwater runoff from an area between two hills of the roadway. The road surface configuration is such that runoff tends to drain both lanes of the roadway towards one side of the road, so runoff is directed to a central collection point, used as the monitoring location, on the south side of the road at the base of the two hills (Figure 14).

Application of Asphalt Emulsion

Application of the asphalt emulsion or seal coat to Snake Road was observed by research team personnel on October 4, 1984. The day was sunny and calm and the ambient air temperature was 62 °F (17 °C). A WS-90 asphalt emulsion, composed of an asphalt compound, water, and detergent, was applied by the highway agency with a liquid asphalt distributor, i.e., a truck-mounted engine and pumping unit, with a boom with a series of nozzles attached to the rear. The distribution of the emulsion on the roadway was followed closely by a large dump truck which deposited a layer of coarse limestone gravel on the seal coat. This in turn was followed by a roller which imbedded the gravel into the asphalt.

Figure 12. Photographic view (looking southwest) of Snake Rd. site, Bloomingrove Twp., OH.

Figure 13. Photographic view (looking northeast) of Snake Rd. site, Bloomingrove Twp., OH.

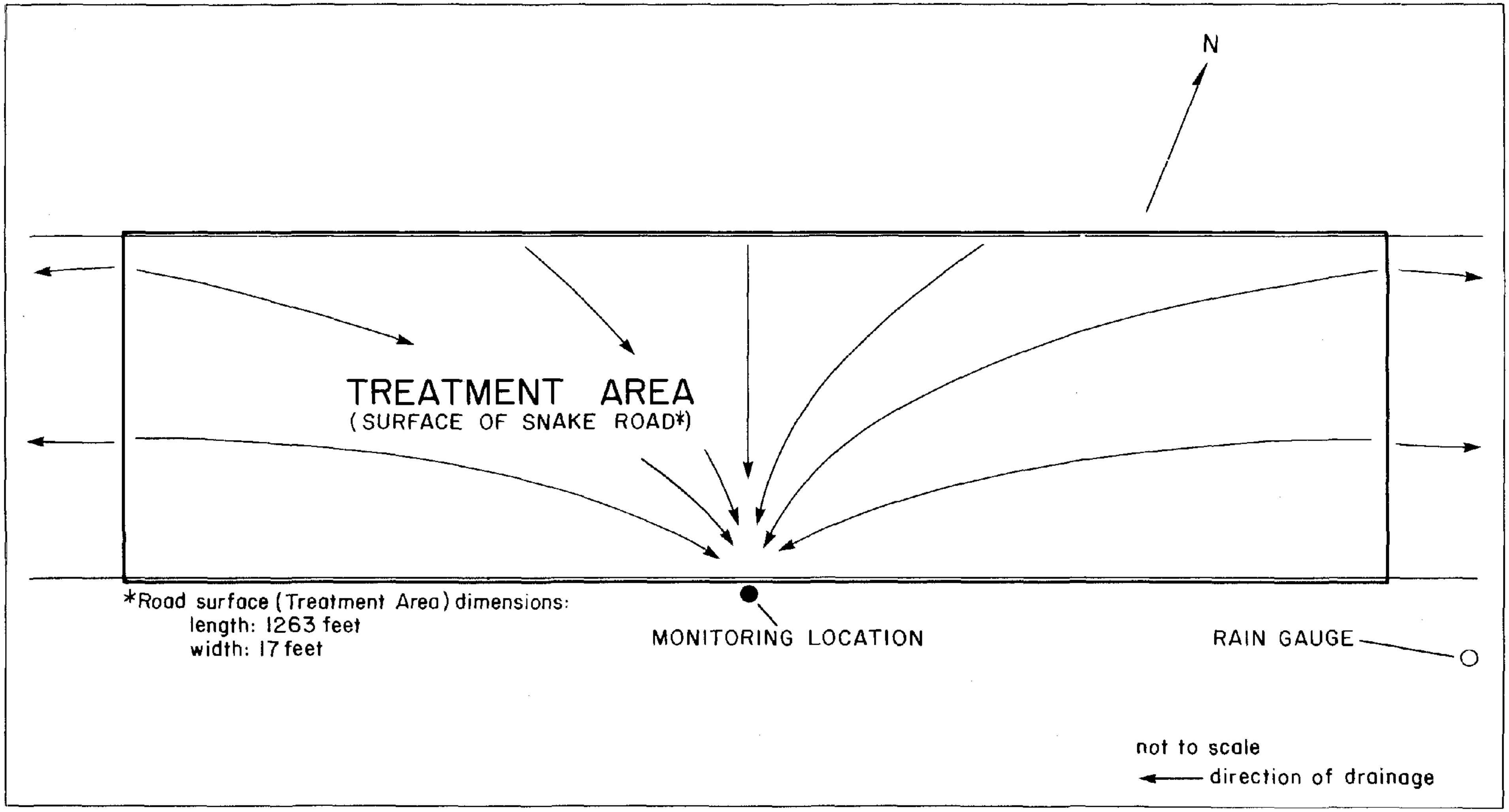

Figure 14. Schematic diagram of Snake Rd. site, Bloomingrove Twp., OH.

The emulsion application rate was estimated from a tachometer at the back of the truck which monitors engine speed. The engine speed controls the rate of flow. The tachometer is calibrated to the flow rate such that a known engine speed will produce a known application rate. The emulsion was applied at the rate of 0.4 gal/yd^2 (1.8 L/m^2). Based on this rate and the area of the Snake Road site (2,385 yd^2 or 1,995 m^2), the total amount of asphalt emulsion applied was 954 gal (3,591 L). The rate of application of the limestone gravel was estimated by highway personnel to be approximately 30 lb/yd^2 (16 kg/m^2). The total amount of gravel applied was approximately 71,600 lb (32,500 kg). A sample of the sprayed emulsion was collected in an amber bottle with a teflon-lined cap and shipped to the analytical laboratory in an iced cooler for chemical analysis of PAHs.

Monitoring Program

The necessary equipment for precipitation and runoff monitoring for the Snake Road site was installed and operative as of October 3, 1984. Rainfall and runoff events were monitored from this date until November 2, 1984.

Precipitation Measurement -- The duration, intensity, and total amount of precipitation was measured at the study site with an 8-day (192-hour) weighing type precipitation gauge (Belfort Instrument Company Model No. 5-780). This gauge was installed 0.5 mi (0.8 km) from the monitoring site and calibrated in the field according to the manufacturer's recommendations.

Runoff Monitoring -- Stormwater runoff was monitored from only one drainage area. Runoff was derived almost exclusively from the road surface. The original sampling plan for this practice required collecting one runoff sample prior to treating the area, followed by two posttreatment runoff samples. However, due to the scheduling of the highway agency and the lack of sufficient precipitation, a pretreatment runoff sample could not be collected. The sampling plan was modified to include the collection of three posttreatment runoff samples, collected consecutively.

Runoff was collected using a flow-splitting composite sampler, as described in the previous discussion of herbicide application. The sampler was calibrated to determine the actual percentage of flow removed. The sampler was estimated to remove approximately 3 percent of the total flow.

Runoff from the roadway had eroded a small depression on the side of the road and the runoff sampler was installed in this depression perpendicular to the road. Due to the rather sharp drop-off from the side of the road, the collection box was installed completely aboveground.

Monitoring Operations -- Monitoring operations were conducted in a routine identical to that described in the previous section on herbicide applications.

Analytical Determinations

Chemical Analysis -- Samples and field blanks were analyzed for polynuclear aromatic hydrocarbons (PAHs) using EPA Method 625 for Base/Neutral Compounds (Longbottom and Lichtenberg, 1982). The specific PAHs analyzed for are presented in Table 5.

Table 5. Specific polynuclear aromatic hydrocarbons (PAHs) analyzed.

Acenapthene
Acenapthylene
Anthracene
Benzo(a)anthracene
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(a)pyrene
Benzo(ghi)perylene
2-Chloronapthalene
Chrysene
Dibenzo(a,h)anthracene
Fluoranthene
Fluorene
Indeno(1,2,3-cd)pyrene
Napthalene
Phenanthrene
Pyrene

PAHs may be adsorbed to sediments. Thus, an analytic protocol was established whereby when PAHs were found in total samples, a portion of each total sample was to be filtered through a 0.45 um filter and the analysis performed on the filtrate and the total (unfiltered) sample. The amount of PAHs bound to the sediments could then be inferred as the concentration difference between the whole sample and the filtrate.

Quality Assurance/Quality Control (QA/QC) -- A QA/QC program was performed by the laboratory throughout the study to determine the quality of the data collected. This program was identical to that described in the previous discussion of herbicide applications.

Bioassay Analysis -- Unfiltered runoff samples were analyzed for toxicity to *Daphnia magna* using a 48-hour static bioassay test following the Standard Methods bioassay procedure for *Daphnia* (APHA, 1981).

The total (unfiltered) runoff sample was thoroughly mixed to test containers prepared with the following dilutions of sample: 100, 10, 1, 0.1, and 0 percent (control). The diluent was distilled water. Each test dilution was run in triplicate. Ten neonate *Daphnia magna* were introduced into each test vessel and observations were made for non-motile neonates after 1, 2, 4, 8, 16, 24, and 48 hours.

RESULTS AND DISCUSSION

CONTROL OF VEGETATION USING HERBICIDES

Rainfall and Runoff Data for the I-71 Study Site

The amount of runoff which flows from any given drainage area is a function of a number of interrelated factors including drainage area size, vegetative cover, evaporation rate, topography, antecedent soil moisture content, soil type and permeability, and amount, duration, and intensity of precipitation (Wauchope et al., 1977). Within this context, each runoff occurrence may be considered a unique event.

During the 6-week monitoring period at the I-71 site, 11 storm events were recorded (Table 6). Following the sampling design, runoff samples from three of these events were collected, one before and two after the application of 2,4-D. These were derived from storms which produced at least 1 qt (0.95 L) of runoff sample, the minimum required for collection and analysis. The first significant storm of 0.95 in (2.45 cm) occurred on July 4 and resulted in the collection of composite samples of 1.8 L from the control area and 5.7 L from the treat- ment area. Although a storm event of 0.70 in (1.8 cm) occurred on July 6, no further runoff sample collection was attempted until after July 16, which was the date of 2,4-D application to the treatment area. Storms on July 18 and 23 produced insufficient amounts of runoff sample to retrieve for analysis. A storm on July 26 to 27 of 1.13 in (2.87 cm) of rain caused collection vessels in the control and treatment areas to overflow. Thus, the samples collected were not truly composite, but rather flow-proportional, extended-duration grab samples.

In order to determine the persistence of the herbicide, collection of the third runoff sample did not occur until 2 weeks after the first postapplication runoff event. During this intervening period, five storms produced a total of 1.63 in (4.14 cm) of rainfall, including a 1-in (2.54-cm) storm on August 7. For the third runoff sample, a storm on August 18 produced 0.65 in (1.7 cm) of rain and also caused both control and treatment area collection vessels to overflow. Again, these samples are not true composites, but flow-proportional, extended-duration grab samples.

Table 6. Precipitation data and runoff quantities collected at the I-71 study site.

Storm event no.	Date(s) of storm event[a] (1984)	Total precipitation per event (in)	Storm duration (hr)	Average intensity (in/hr)	Number of dry days between storms[g]	Cumulative precipitation (in)	Date of sample collection	Quantity of runoff collected (L)	
								Control area	Treatment area
1	7/4	0.95	3	0.32	---	0.95	7/5	1.8[c]	5.7[c]
2	7/6	0.70	2	0.35	1.5	1.65	NA	[f]	[f]
3	7/18	0.15	0.5	0.30	11.5	1.80	NA	0.50[b]	0.20[b]
4	7/23	0.05	1	0.05	5.5	1.85	NA	0.10[b]	0.10[b]
5	7/26 - 7/27	1.13	16	0.07	3.0	2.98	7/27	>45.4[c,d]	>45.4[c,d]
6	8/2	0.08	2	0.04	6.5	3.05	NA	[e]	[e]
7	8/3	0.40	1	0.40	0.5	3.45	NA	[e]	[e]
8	8/7	0.05	0.5	0.10	4.0	3.50	NA	[e]	[e]
9	8/7	1.00	1	1.00	4.5	4.50	NA	[e]	[e]
10	8/9	0.10	1	0.1	2.0	4.60	NA	[e]	[e]
11	8/18	0.65	2	0.33	9.5	5.25	8/20	>45.4[c,d]	>45.4[c,d]

NA = Not applicable.

[a] 2,4-D applied to treatment area on 7/16/84.

[b] Quantity of runoff collected insufficient for analysis.

[c] Runoff sample retrieved for analysis.

[d] Quantity of runoff collected greater than capacity of collection vessel.

[e] No sample collected for at least two weeks after second sample was collected.

[f] No sample collected because this storm occurred between collection of the pre-application sample and the application of the herbicide.

[g] Rounded to the nearest half-day.

Metric Units: To convert in to cm multiply by 2.54.

Chemical Analysis of I-71 Runoff Samples

The concentration of 2,4-D in the mix applied to the treatment area was 8.3 x 10^6 ug/L. Concentrations of 6.2 and 25 ug/L were detected in runoff from this area 11 and 35 days, respectively, after treatment (Table 7). The proportion of herbicide found soluble in the water column in comparison to the total sample was 35 percent for the first postapplication sample collected on July 27, and 36 percent for the second postapplication sample collected on August 20. This indicates that most of the herbicide in these samples (65 and 64 percent, respectively) was adsorbed to sediments of >0.45 um. 2,4-D was not detected in the preapplication runoff from the treatment area nor in any of the control area samples.

The validity of these results is verified by an analysis of the quality control data presented in Appendix A. Each sample was analyzed twice, once alone and then a second time following the addition of a known concentration which served as a matrix spike. For example, 6.2 ug/L of 2,4-D was detected in the first postapplication treatment area runoff sample. A concentration of 1.608 ug/L 2,4-D was then added to a separate aliquot of the same sample and the analysis performed again, this time resulting in 7.3 ug/L, or a 72 percent recovery of the spiked concentration. A similar analysis conducted on the sample filtrate resulted in an 87 percent recovery. The same analysis conducted on the second postapplication treatment area sample produced similar results, i.e., 2,4-D concentrations in the unspiked total, and filtrate samples were close to the spiked samples. The same procedure was performed on the first and second post-application control area samples. 2,4-D was not detected in unspiked aliquots of these samples.

Temperature, dissolved oxygen, and pH of the runoff samples were recorded to provide a general indication of sample integrity. Each parameter was relatively consistent among sampling events and between control and treatment areas (Table 8). Generally, these results indicate that all samples collected were in a relatively undegraded condition.

The mobility of some herbicides can be increased by acidic rainfall and soil conditions (Harrison, 1984). However, in this case, the relatively neutral pH of the precipitation does not appear to be a determining factor of herbicide mobility.

These results differ from those of studies described in the literature, in three ways. First, the concentrations detected in the runoff are significantly lower than

Table 7. Concentrations (ug/L) of 2,4-D detected in runoff samples collected from the I-71 study site.

Date (1984)	Area	Total sample	Filtrate	Difference[a]
7/5	Control	ND[c]	b	NA
	Treatment	ND[c]	b	NA
7/27	Control	ND[c]	b	NA
	Treatment	6.2	2.2	4.0
8/20	Control	ND[c]	b	NA
	Treatment	25	9.0	16.0

NA = Not applicable.

[a] Difference equals total sample concentration minus filtrate concentration and assumed to be sediment-attached.

[b] Unfiltered (total) sample was not found positive; therefore, filtered sample was not analyzed.

[c] Non-detectable. Detection limit equals 0.5 ug/L.

Table 8. Summary of temperature, dissolved oxygen, and pH at the I-71 study site.

	Stormwater runoff sample				Precipitation sample
Date (1984)	Area	Temp.(°C)	Dissolved oxygen (mg/L)	pH	pH
7/5	Control	16.9	[a]	7.45	[a]
7/5	Treatment	19.9	6.2	7.16	[a]
7/27	Control	21.5	4.9	7.54	7.39
7/27	Treatment	20.4	5.4	7.75	[b]
8/20	Control	19.8	5.5	7.36	7.23
8/20	Treatment	20.0	4.0	7.58	[b]

[a] Not obtainable due to instrument malfunction.

[b] Precipitation of pH was determined on rainfall collected in the rain gauge located in the control area. Because of the proximity of the control and treatment areas, the pH of rain falling on both areas is assumed to be equivalent.

those found in studies which have used comparable herbicide application rates. Secondly, the highest concentration of herbicide is usually expected in the first runoff event following herbicide application and decreases with subsequent storm events. The opposite was observed at I-71. Finally, 2,4-D is considered to have a low capacity for sorption to sediments, but most of the herbicide detected was sediment-attached. These findings are further discussed below.

The concentration of herbicide in runoff will be affected by antecedent site conditions, storm intensity, and properties of the herbicide itself including degradation rate in the soil, adsorption to and desorption from sediments, water solubility, and method and rate of application (Wauchope et al., 1977). 2,4-D is considered to be a nonpersistent herbicide with most studies indicating that the majority of 2,4-D is degraded microbially after four weeks in the soil (White et al., 1976; Harrison Biotech, 1984). Due to its high solubility in water, it is also considered to be relatively mobile in soils, and has often been found in runoff and streams with drainage from treated areas. Several researchers have detected higher 2,4-D concentrations in runoff at lower application rates than that used at I-71. Harrison Biotech (1984) reports that Wilson and Cheng (1976) applied 1 lb/acre (1.1 kg/ha) of 2,4-D to 16 to 17 percent slopes and detected 2,000 ug/L in the runoff, Evans and Duseja (1973) (cited in White et al., 1976) used an application rate of 4 lb/acre or 4.48 kg/ha (similar to that used at the I-71 site) and detected 4,200 ug/L in the runoff. White et al. (1976) applied a much lower rate (0.5 lb/acre or 0.56 kg/ha) each spring for 3 years and detected maximum runoff concentrations between 2.5 and 8.1 ug/L, comparable to those at I-71.

Site characteristics and precipitation data may explain the relatively low concentrations of 2,4-D in I-71 runoff. Factors which encourage overland flow and herbicide runoff include long slopes with steep gradients and high intensity rainfall. The treated area of I-71 is relatively flat. Three storm events of low to moderate intensity occurred between the application of the herbicide on July 16 and the collection of the first postapplication sample on July 27 (Table 6). These factors tend to promote subsurface vertical migration of soluble herbicides through the soil than surface migration in runoff. Subsurface migration of 2,4-D has been reported to be up to three times greater than surface migration via runoff (White et al., 1976).

The movement of very soluble herbicides like 2,4-D in runoff is most likely when the first rainfall after application is of sufficient intensity to exceed the infiltration capacity of the soil (Harrison Biotech, 1984). Generally, runoff concentrations are expected to be high immediately following herbicide application, and decrease with subsequent storm events. However, reported cases where concentrations of herbicides have been higher in subsequent runoff events (Mayeux et al., 1984) have been attributed to the fact that the earlier event was the result of a storm which produced a much larger volume of runoff than subsequent storms. The lower earlier concentration was probably the result of a greater dilution volume. Such may be the case at the I-71 site where a lower concentration of 2,4-D was reported in the first postapplication treatment area runoff than in the second. These runoff events were the result of storms of 1.13 in (2.87 cm) and 0.65 in (1.1 cm), respectively. The lower concentration of the earlier sample may be attributed to the greater amount of water available for dilution from the larger storm. Another explanation is that most of the herbicide in both postapplication treatment area samples was bound to the sediment. The affinity of 2,4-D for sorption to soils is not considered to be high, although reports cited by Harrison Biotech (1984) indicate that high organic content soils tend to be more adsorptive. Sediment-bound herbicides are most likely to be transported in runoff during high-intensity storms which produce high rates of runoff. The intensity of the second postapplication storm was almost five times greater than the first and it is possible that this may have led to a higher concentration in the second postapplication runoff.

As noted, because the sample collection vessels overflowed, what was collected was not a true composite sample. These concentrations are probably representative of early and peak runoff. Generally, runoff of 2,4-D is greatest early in storm events and decreases with storm duration (White et al., 1976). The samples collected at I-71 are probably representative of the greater portion of 2,4-D that ran off the treated area. If these samples are more representative of early and peak runoff concentrations than later runoff concentrations, the average concentration of the entire runoff event may actually have been lower.

The fact that most of the 2,4-D in the runoff was apparently bound to the sediments is unusual. The previous discussion on precipitation and site characteristics may provide an explanation. Due to low rainfall intensity and negligible slope, conditions were favorable for subsurface vertical migration of the herbicide. What actually appears in the runoff may be from the small amount of 2,4-D which remained near the surface bound to the sediments. The more mobile soluble fraction may have percolated into the soil. However, these conditions are highly representative of roadsides where herbicides are applied and conditions under which herbicides are applied.

Bioassay Analysis of I-71 Runoff Samples

The two plant responses investigated in this analysis were the percentage of seeds which germinated after exposure to the test solution, and the effect of the test solution on hypocotyl growth length. (2,4-D is known to inhibit hypocotyl growth of newly germinated seedlings [Kratky and Warren, 1971; Santelmann, 1977].) As Table 9 shows, runoff samples did not have a significant effect on seed germination, as all test solutions showed germination of 96 percent or better. Positive controls consisting of seeds exposed to the herbicide as applied also resulted in almost 100 percent germination, although hypocotyls were too small to measure.

Analysis of variance of the bioassays run on the control and treatment area preapplication runoff samples (July 5) indicated hypocotyl lengths were significantly longer for seeds grown in the runoff than in distilled water ($p<0.05$). This increase in hypocotyl length is most directly attributable to the availability of plant nutrients which were undoubtedly present in higher concentrations in the runoff than in the distilled water. 2,4-D was not detected analytically in either sample from this date.

Bioassays using control area runoff from July 27 (first postapplication sample) showed that hypocotyls from seeds grown in test solutions of undiluted runoff were slightly longer than those grown in distilled water, but the difference was not statistically significant ($p>0.05$). Again, 2,4-D was not detected chemically in the sample and an inhibition of growth was not observed. Bioassays run on the treatment area runoff for this date reveal that hypocotyl lengths were significantly shorter for seeds grown in the runoff than in distilled water ($p<0.05$). The inhibitory effect was related directly to the concentration of runoff, as the difference among the four concentrations (0, 1, 10, and 100 percent) was significant. The 100 and 10 percent runoff dilutions were also significantly different from the control area for this date, and from the control and treatment areas from July 5. A concentration of 6.2 ug/L of 2,4-D was detected in whole samples of this runoff.

Hypocotyls of seeds grown in the second postapplication runoff samples (August 20) from both the control and treatment areas were significantly longer than those grown in distilled water ($p<0.05$). Hypocotyl lengths of seeds grown in treatment area dilutions of 100, 10, and 1 percent were not significantly different from hypocotyl lengths of seeds grown in corresponding dilutions of control area runoff. Therefore, although 25

Table 9. Percent germination, mean length (mm) and standard deviation (SD) of cucumber seed hypocotyls for 2,4-D bioassay for samples collected from the I-71 study site.[a]

Date (1984)	Area	Concentration dilution[b] 0	1	10	100
7/5	Control				
	% Germination	100	100	100	96
	Mean length	38.78	49.38	51.02	57.11
	SD	6.21	11.60	4.87	7.16
7/5	Treatment				
	% Germination	100	100	98	100
	Mean length	38.78	44.62	52.22	59.09
	SD	6.21	6.43	9.79	8.69
7/27	Control				
	% Germination	100	100	100	100
	Mean length	58.08	46.67	57.51	63.02
	SD	8.96	7.49	3.93	4.70
7/27	Treatment				
	% Germination	100	100	100	100
	Mean length	58.08	50.10	22.62	11.19
	SD	8.96	4.37	1.40	0.57
8/20	Control				
	% Germination	100	100	100	100
	Mean length	47.72	55.81	56.98	56.32
	SD	5.89	2.85	4.19	4.63
8/20	Treatment				
	% Germination	100	100	100	100
	Mean length	47.72	56.62	53.58	56.35
	SD	5.89	7.28	4.18	3.35

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[a] Values represent the mean and standard deviation of five replicates with ten seeds in each (for 7/5), and six replicates with six seeds in each (for 7/27 and 8/20).

[b] Dilutions based on percentage of runoff in test samples.

ug/L of 2,4-D was detected in the runoff from the treatment site for this sample, no inhibition of hypocotyls was detected.

The higher concentration of 2,4-D in the second postapplication sample is, as explained above, a function of the amount of dilution water, storm intensity, and the amount of herbicide bound to sediments. The inhibition of hypocotyl growth at 6.2 ug/L, and not at 25 ug/L, is not readily explainable. Possibly, the herbicide in the second postapplication sample was either not biologically active or not in a biologically available form. The more plausible explanation of the two is that the herbicide degraded to a biologically inactive form. 2,4-D is a nonpersistent herbicide of moderate mobility, the majority of which degrades after four weeks in the soil. The second postapplication sample was collected 35 days after the herbicide was applied. Given this, it appears unlikely that the 2,4-D present in the runoff from this date is biologically active. Rather, what was chemically measured was probably one or more of the many noninhibitory metabolites of 2,4-D (Aizawa, 1982; Harrison Biotech, 1984).

The alternative reason for the benign hypocotyl results from the second runoff sample, i.e., the possibility that the herbicide was in a biologically unavailable form, was also investigated. Herbicides bound to sediments are generally considered to be less available to the biota than those fractions which are not bound. Although the relative percentages of bound to unbound herbicides in the two samples are very close (35 and 36 percent, respectively), the concentration of both fractions was higher in the second postapplication event, indicating the biological availability of 2,4-D due to sorption on the sediments had not changed significantly.

Rainfall and Runoff Data for the I-90 Study Site

During the 12-week monitoring period at the I-90 site, 20 storm events were recorded (Table 10). Composite samples were collected from three of these events--one before and two after application of picloram. A preapplication storm on July 26-27 produced 0.90 in (2.3 cm) of rain and resulted in the collection of composite samples of 1.0 L from the control area and 0.95 L from the treatment area. Five storm events produced 3.50 in (8.89 cm) of rain over the next three weeks, although further runoff sample collection was not attempted until after August 23, the date picloram was applied to the treatment area.

A storm on September 11 produced 0.10 in (0.25 cm) of rain in 1 hour and resulted in the collection of composite samples of 15.1 L and 1.0 L from the control and

Table 10. Precipitation data and runoff quantities collected at the I-90 study site.

Storm event no.	Date(s) of storm event[a] (1984)	Total precipitation per event (in)	Storm duration (hr)	Average intensity (in/hr)	Number of dry days between storms[g]	Cumulative precipitation (in)	Date of sample collection	Quantity of runoff collected (L)	
								Control area	Treatment area
1	7/4	0.10	1	0.10	---	0.10	NA	0.05[b]	0.10[b]
2	7/26-7/27	0.90	10	0.09	2	1.00	7/27	1.0[c]	0.95[c]
3	8/3	0.40	2	0.20	7.5	1.40	NA	f	f
4	8/4	2.40	11	0.22	0.5	3.80	NA	f	f
5	8/9	0.10	1	0.10	5	3.90	NA	f	f
6	8/13	0.45	11	0.04	4	4.35	NA	f	f
7	8/18	0.15	1	0.15	5.5	4.50	NA	f	f
8	8/29	0.10	1	0.10	11	4.60	NA	0	0
9	8/30	0.45	6	0.08	1	5.05	NA	0.05[b]	0.05[b]
10	9/3	0.20	17	0.01	3.5	5.25	NA	0.10[b]	0.10[b]
11	9/5	0.10	1	0.10	2.5	5.35	NA	0	0
12	9/10	0.50	6	0.08	5	5.85	NA	0	0
13	9/11	0.10	1	0.10	1.5	5.95	9/12	15.1[c]	1.0[c]
14	9/13-9/14	0.25	8	0.03	2	6.20	NA	d	d
15	9/19	0.10	1	0.10	5.5	6.30	NA	d	d
16	9/23	0.20	4	0.05	4	6.50	NA	d	d
17	9/25	0.30	1	0.30	2	6.80	NA	d	d
18	9/26	0.30	3	0.10	0.5	7.10	NA	d	d
19	9/29	0.15	4	0.04	3	7.25	NA	0	0
20	10/1	0.35	16	0.02	1.5	7.60	10/2	>45.4[c,d]	2.5[c]

NA = Not applicable.

[a] 2,4-D applied to treatment area on 8/23/84.

[b] Quantity of runoff collected insufficient for analysis.

[c] Runoff sample retrieved for analysis.

[d] Quantity of runoff collected greater than capacity of collection vessel.

[e] No sample collected for at least two weeks after second runoff sample was collected.

[f] No sample collected because this storm occurred between collection of the pre-application sample and the application of the herbicide.

[g] Rounded to the nearest half-day.

Metric Units: To convert inches to cm multiply by 2.54.

treatment areas, respectively. In order to provide an indication of the persistence of the herbicide, collection of the third runoff sample (second postapplication) was delayed until two weeks after the first postapplication runoff sample had been collected. During the intervening period, six storms produced 1.30 in (3.30 cm) of rainfall. A storm on October 1 produced 0.35 in (0.89 cm) of rainfall and resulted in the collection of a composite sample of 2.5 L from the treatment area, however, the control area collection vessel overflowed.

Chemical Analysis of I-90 Runoff Samples

The concentration of picloram in the mix applied to the treatment area of I-90 was 5.4 x 10^6 ug/L. Picloram was detected in the second postapplication treatment area sample at a concentration of 0.92 ug/L (Table 11). It was not detected in the filtrate and is therefore presumed to be entirely sediment-attached. Picloram was not detected in any other runoff sample collected. The integrity of the runoff samples, as indicated by temperature, dissolved oxygen, and pH, did not vary significantly among sampling events or between control and treatment areas (Table 12). The analytic quality control results for these analyses are presented in Appendix A.

As with 2,4-D, these results differ from those described in the literature in three ways. First, the runoff concentration was much lower than other studies have detected using comparable application rates. Secondly, picloram was not detected at all in the first postapplication runoff event. Finally, most of the herbicide detected was sediment-attached.

The relatively high mobility of picloram in most soils is attributed to its solubility in water, its low initial adsorption to soil colloids, and to its relative persistence (Harrison Biotech, 1984). Picloram concentrations in runoff from grassed areas are normally less than 1,000 ug/L. Studies which have used comparable application rates (1 lb/acre or 1.1 kg/ha active ingredient) have detected maximum concentrations of 48 and 250 ug/L in initial runoff events with concentrations generally decreasing with each successive storm event (Mayeux et al., 1984). This was not the trend observed at the I-90 site.

Precipitation and runoff data may explain why picloram was not detected in the first postapplication treatment area runoff sample. Mobility of picloram is closely correlated with the amount of water flowing through the soil (Harrison Biotech, 1984), with high concentrations most likely when large rainstorms immediately follow herbicide application. Application of the herbicide occurred on

Table 11. Concentrations (ug/L) of picloram detected in runoff samples collected from the I-90 study site.

Date (1984)	Area	Total sample	Filtrate	Difference[a]
7/27	Control	ND[c] - 1.0	[b]	NA
	Treatment	ND - 0.50	[b]	NA
9/12	Control	ND - 1.0	[b]	NA
	Treatment	ND - 1.0	[b]	NA
10/2	Control	ND - 0.50	[b]	NA
	Treatment	0.92	ND - 0.10	0.92

NA - Not applicable.

[a] Difference equals total sample concentration minus filtrate concentration and assumed to be sediment-attached.

[b] Unfiltered (total) sample was not found positive; therefore, filtered sample was not analyzed.

[c] Non-detectable. Detection limits are shown next to ND notations.

Table 12. Summary of temperature, dissolved oxygen, and pH at the I-90 study site.

Date (1984)	Stormwater runoff sample Area	Temp.(°C)	Dissolved oxygen (mg/L)	pH	Precipitation sample pH
7/27	Control	22.0	6.8	7.85	6.96
7/27	Treatment	22.8	5.8	8.03	[b]
9/12	Control	19.5	5.6	7.9	7.29
9/12	Treatment	23.0	4.4	7.86	[b]
10/2	Control	18.3	6.6	[a]	[a]
10/2	Treatment	19.9	6.2	[a]	[b]

[a] Not obtainable due to instrument malfunction.

[b] Precipitation pH was determined on rainfall collected in the rain gauge located in the control area. Because of the proximity of the control and treatment areas, the pH of rain falling on both areas is assumed to be equivalent.

August 23. The first postapplication samples were collected 19 days later on September 11. During the period from August 23 to September 10, five storms produced a total of 1.35 in (3.43 cm) of rainfall. None of these storms produced enough surface runoff to cause a sufficient amount of sample to be collected for analysis. This suggests that much of the rainfall was percolating through the soil. Picloram usually remains in the upper 8 to 12 in (20 to 30 cm) of soil, but studies cited by Harrison Biotech (1984) have reported that its high solubility and low sorption properties have resulted in downward migrations of up to 47 in (120 cm).

The rainfall and subsequent negligible surface runoff which occurred from August 23 to September 10 would appear to be more conducive to subsurface migration of picloram than surface migration via runoff. The topography of the treatment area, with its slopes leading to a large flat expanse before draining to a culvert, would also tend to encourage vertical rather than horizontal migration of soluble herbicides. Other researchers have reported that herbicides lost through subsurface runoff can be up to three times greater than through surface runoff (White et al., 1976). Therefore, it is likely that these storm events caused a downward migration of picloram such that surface runoff was not the major mechanism of transport.

Arthur D. Little, Inc. (1979) (as cited by Harrison Biotech, 1984) reported that because of its persistence, picloram has been found in runoff and in soils over one year after application at levels of 1 to 4 ug/L (Harrison Biotech, 1984). A trace of picloram (0.92 ug/L) was detected in runoff from the treatment area 40 days after application. The detection limit for this sample was 0.5 ug/L (Table 11). Unknown compounds present in the runoff from the first postapplication runoff event caused interference in the analytic procedure and resulted in a higher detection limit of 1.0 ug/L. It is therefore possible that the runoff concentration from the first post-application runoff event was similar to the second, but was not detected due to the higher detection limit.

Several studies indicate that adsorption of picloram to sediments increases with acidity and is minimal in alkaline or neutral soils (Harrison Biotech, 1984). At this site, soil conditions were not acidic and significant adsorption of picloram would not be expected (Table 11). However, the picloram found in the runoff was apparently sediment-attached. This may be due to unknown characteristics of the soil (e.g., organic content) which may have increased its sorption capacity, especially at such low concentrations.

Bioassay Analysis of I-90 Runoff Samples

The percentage of lettuce seeds which germinated after exposure to the test solutions, and the effect of the test solutions on hypocotyl growth length, were investigated in the bioassay analysis of the I-90 runoff samples. Picloram is known to inhibit hypocotyl growth of newly germinated lettuce seedlings at levels from 0.0072 to 7.2 ug, the upper limit approaching complete inhibition of growth (Reid and Hurtt, 1969). Growth stimulation occurs from 0.00072 to 0.0072 ug.

Analysis of variance of preapplication runoff sample bioassay results (July 27) showed that there was no significant difference in hypocotyl length among dilutions, or between the control and treatment area samples ($p>0.05$) (Table 13). Seeds exposed to 100 percent runoff from the treatment area exhibited a slight decrease in percent germination, although no picloram was detected analytically. This may have been due to the random selection of some infertile seeds. It is also possible that an undetected inhibitory compound was present in the treatment area runoff. However, percent germination did not appear to be dependent on concentration as this effect was not observed at 10 or 1 percent dilutions of this sample.

Bioassays run on the control area runoff for September 12 (first postapplication sample) showed that seeds grown in a 1 percent dilution were significantly longer than those grown in the other dilutions from this sample. Seeds grown in runoff from the treatment area for this date exhibited a slight but significant growth ($p<0.05$). Picloram was not detected in either of these samples. However, since picloram is known to stimulate hypocotyl growth at very low levels, it is possible that an undetected trace was present which caused stimulation of growth in the 100 percent treatment area bioassay. In general, all dilutions (including 0 percent) of the control and treatment area bioassays for this date exhibited significantly shorter hypocotyl lengths than seeds grown in the preapplication samples ($p<0.05$). The pre- and postapplication bioassays were run on different days and the fact that the 0 percent bioassay dilutions also exhibited significantly different hypocotyl lengths indicates that undetectable changes in humidity or temperature probably had a general inhibitory effect on hypocotyl growth in all dilutions in the second set of bioassays. Comparisons among dilutions and between areas are probably most relevant for those bioassays which were run at the same time. On this basis, there were no significant differences by dilution between the control and treatment areas for the first postapplication bioassays ($p>0.05$).

Table 13. Percent germination, mean length (mm) and standard deviation (SD) of lettuce seed hypocotyls for picloram bioassay for samples collected from the I-90 study site[a].

Date (1984)	Area	Concentration dilution[b] 0	1	10	100
7/27	Control				
	% Germination	97	100	97	92
	Mean length	18.28	20.36	18.67	20.2
	SD	3.44	3.21	3.94	4.47
	Treatment				
	% Germination	89	94	100	64
	Mean length	18.28	20.36	21.48	19.76
	SD	3.44	1.36	2.45	3.85
9/12	Control				
	% Germination	100	92	92	86
	Mean length	12.39	16.33	13.15	13.35
	SD	2.18	1.03	1.90	1.94
	Treatment				
	% Germination	100	89	97	94
	Mean length	12.39	14.75	14.19	15.22
	SD	2.18	2.21	0.65	1.59
10/2	Control				
	% Germination	90	93	97	87
	Mean length	23.28	25.00	25.31	19.25
	SD	3.24	3.97	4.23	2.91
	Treatment				
	% Germination	90	90	97	73
	Mean length	23.28	20.74	23.77	21.17
	SD	3.24	4.98	2.69	5.37

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[a] Values represent the mean and standard deviation of five replicates with six seeds in each.

[b] Dilutions based on percentage of runoff in test samples.

Hypocotyls of seeds grown in samples from the second postapplication runoff generally exhibited no significant difference among dilutions or between control and treatment area samples ($p>0.05$). The only significant difference was between seeds grown in 10 and 100 percent of control area runoff. The trace of picloram (0.92 ug/L) detected in the treatment area runoff theoretically should have resulted in some growth inhibition in the 100 percent sample. However, because significant growth inhibition was not observed, either the picloram detected was unavailable for plant uptake (possibly because it was sediment-attached), or it was a metabolite in a biologically inactive form. Some inhibition of seed germination was observed in the undiluted runoff from both the control and treatment areas but this was apparently not dependent on concentration and probably is more indicative of general seed viability.

ASPHALT-CONCRETE SURFACE TREATMENT WITH ASPHALT EMULSION

Rainfall and Runoff Data for the Snake Road Study Site

A total of seven storm events were recorded during the 4-week monitoring period following surface treatment of the Snake Road study site (Table 14). A storm on October 7 and 8 produced 0.25 in (0.64 cm) of precipitation, from which a 1.04 L composite runoff sample was collected. This was followed by three storm events which collectively yielded 0.50 in (1.27 cm) of rainfall, but which did not result in sufficient quantities of runoff samples for analysis. The second runoff sample of 2.37 L was collected on October 29 following a 0.80 in (2.03 cm) storm on October 28. The third and final runoff sample was collected on November 2 following a storm on November 1 which produced 0.80 in (2.03 cm) of precipitation. The three runoff samples were thus collected 5, 25, and 29 days following treatment of the road surface.

Chemical Analysis of Snake Road Runoff Samples

Analysis of the three runoff samples (total fraction) showed that PAHs were not present at or above a detection limit of 3 ug/L nor were they detectable in the asphalt emulsion as applied at a detection limit of 4 mg/kg. Runoff samples generally did not show any signs of deterioration, as indicated by sample temperature, dissolved oxygen, and pH results (Table 15). Appendix A contains the quality control (QC) results for PAH analyses.

Although Wallcave et al. (1971) showed average concentrations of specific PAHs in eight different asphalt samples ranged from 0.08 to 39 mg/kg, the above results indicate that PAHs were not present in the WS-90 asphalt emulsion used in this study. This suggests that it may be

Table 14. Precipitation data and runoff quantities collected at the Snake Road study site.

Storm event no.	Date(s) of storm event (1984)	Total precipitation per event (in)	Storm duration (hr)	Average intensity (in/hr)	Number of dry days between storms[c]	Cumulative precipitation (in)	Date of sample collection	Quantity of runoff collected from treatment area (L)
1	10/7	0.20	4	0.05	---	0.20	NA	[a,d]
2	10/7 - 10/8	0.25	8	0.03	0.5	0.45	10/9	1.04[b]
3	10/16	0.05	0.5	0.10	8.0	0.50	NA	0.10[a]
4	10/20 - 10/21	0.25	11	0.02	5.0	0.75	NA	d
5	10/22	0.20	4	0.05	0.5	0.95	NA	0.50[a]
6	10/28	0.80	5	0.16	6.0	1.75	10/29	2.37[b]
7	11/1	0.80	9	0.09	4.0	2.55	11/2	4.73[b]

NA = Not applicable.

[a] Quantity of runoff collected insufficient for analysis.

[b] Runoff sample retrieved for analysis.

[c] Rounded to the nearest half-day.

[d] Quantity of runoff collected during this storm event unknown.

Metric Units: To convert in to cm multiply by 2.54.

Table 15. Summary of temperature, dissolved oxygen, and pH at the Snake Road study site.

Date (1984)	Stormwater runoff sample Temp. (°C)	Dissolved oxygen (mg/L)	pH
10/9	18.5	3.8	7.25
10/29	16.4	5.5	7.34
11/2	9.8	6.8	7.81

composed of other hydrocarbons, such as oils, typically found in petroleum-based materials. However, it should be noted that the complex nature of the asphalt emulsion resulted in a relatively high detection limit. Therefore, it is uncertain if PAHs were positively absent from this material.

Furthermore, PAHs were not detected in runoff samples at comparatively lower detection limits of 3 ug/L, suggesting that degradation may be occurring even if they were present in the applied material. A likely degradation mechanism is photolysis, in this case, probably from direct sunlight on the road surface (Radding et al., 1976). Finally, it should be noted that Kobriger et al. (1982) found PAHs ranging from 0.2 to 12.0 ug/L in a composite runoff sample from an asphalt paved highway in Milwaukee, Wisconsin. However, the Milwaukee site is located in an urban area and has an ADT of over 100,000, suggesting that PAHs found in runoff are originating from vehicle exhaust or industrial sources. Thus, relative to other sources, surface treatment with asphalt emulsion does not appear to be a significant source of PAHs.

Bioassay Analysis of Snake Road Runoff Samples

Table 16 shows the results of static bioassays performed on runoff samples using *Daphnia magna* as the test organism. The results were subjected to logarithmic probability analysis (log-probit) to calculate a median lethal concentration (i.e., LC_{50}) for each runoff sample. However, because none of the tests showed more than 37 percent mortality, LC_{50} values could not be calculated. Further, the probit analysis showed no pattern or relationship between the mortality and dilution of runoff tested. These results indicate the runoff from this site was relatively nontoxic.

Table 16. Percent mortality of *Daphnia magna* in runoff samples from the Snake Road study site.[a]

Date (1984)	Exposure time	Concentration dilution[b]				
		0.01	0.1	1.0	10	100
10/9	24 hr	0	27	10	0	3
	48 hr	0	37	13	10	33
	Dissolved oxygen	6.0	5.9	6.1	5.2	5.0
	pH	7.09	7.26	7.24	7.14	7.36
10/29	24 hr	13	0	0	0	0
	48 hr	17	0	0	0	0
	Dissolved oxygen	6.0	5.8	5.5	4.6	4.1
	pH	6.90	7.14	7.22	7.24	7.34
11/2	24 hr	7	30	3	0	10
	48 hr	13	30	3	20	17
	Dissolved oxygen	5.5	5.5	5.57	5.4	5.2
	pH	7.05	6.94	6.91	7.00	6.78

[a] Percentages represent the mean of three replicates with ten *Daphnia magna* in each, corrected for control mortality. Dissolved oxygen and pH values of the test dilutions represent the mean of the three replicates, recorded after 48 hours exposure time.

[b] Dilutions based on percentage of runoff in test sample.

POTENTIAL FOR WATER QUALITY IMPACTS

The potential for water quality impacts presented by the common highway practices investigated in this report is assessed below.

Herbicide Application

The impact of a herbicide on an aquatic environment is dependent upon several factors including timing, rate and method of application, and toxicity, mobility, persistence, and bioaccumulation characteristics of the herbicide. The timing, rate, and method of application of both herbicides in this study were representative of those used by highway personnel and are within the manufacturers' specifications.

The fact that 2,4-D is nonpersistent and does not bioaccumulate in a variety of aquatic and terrestrial organisms tested reduces the probability of water quality impacts. However, its high solubility in water, relative mobility in stormwater runoff, and longer persistence time in water increases the probability of impacts. In general, 2,4-D appears to be moderately toxic in acute and subchronic tests. However, the amine salt form used in this study is considered less toxic than the ester forms.

The relatively high mobility of picloram, its moderate to high persistence in the soil, and its toxicity to some fish increases the probability of water quality impacts. Factors which reduce probable impacts include its shorter persistence time in water, its very low toxicity to lower aquatic organisms, and the fact that it does not bioaccumulate in aquatic food chains and webs (Harrison Biotech, 1984).

Acute toxicity to aquatic organisms is usually expressed as a measure of the concentration that is lethal to 50 percent of the test organisms, referred to as an LC_{50}, over a specified time period (e.g., 24, 48, or 96 hours). LC_{50}s provide a general measure of toxicity within a taxon (i.e., fish), although it may vary from species to species. The lowest reported LC_{50} values give a worst-case indication of toxicity for the tested toxicant. The lowest reported LC_{50} for warmwater fish for the formulation of 2,4-D used in this study (amine salt) is 58.1 mg/L or 58,100 ug/L (Schneider, 1979). The concentrations of 2,4-D found in the runoff samples from the treated area following herbicide application were several orders of magnitude lower than this (6.2 and 25 ug/L). The 96-hour LC_{50} for warmwater fish for the potassium salt of picloram is 1.4 mg/L or 1,400 ug/L (Johnson and Finley, 1980). The concentration detected in the posttreatment area runoff from the I-90 site was 0.92 ug/L.

Short-term or acute toxicity tests are not necessarily indicative of harmless concentrations of a toxicant under conditions of long-term exposure. The U.S. Environmental Protection Agency (1972) states that the concentration in the receiving waters of nonpersistent, noncumulative toxicants (i.e., 2,4-D) should not exceed 10 percent of the lowest reported 96-hour LC_{50}. For cumulative or persistent toxicants (i.e., picloram), the receiving water concentration should not exceed 5 percent of the lowest reported 96-hour LC_{50}.

Using this approach, the highest acceptable concentration for the amine salt form of 2,4-D in a receiving stream is 5.81 mg/L or 5,810 ug/L; for the potassium salt form of picloram, 0.07 mg/L or 70 ug/L. The highest acceptable concentrations in the runoff would be one to several orders of magnitude higher than the accepted safe in-stream concentrations, and would be determined by the discharge volume of the stream at that time. The concentrations of both herbicides in the runoff from their respective sites were well below these levels.

To summarize, 2,4-D was detected at low levels in both postapplication runoff samples from the treatment area of I-71; in the first postapplication runoff, it was biologically active and inhibited hypocotyl growth of cucumber seeds. The higher concentration detected in the second postapplication runoff may have been biologically inactive. The trace of picloram detected in the second postapplication runoff event from the treatment area of I-90 was either biologically inactive or in a form unavailable for uptake.

On the basis of these analyses, it is improbable that any significant water quality impacts can be expected from the use of the amine salt form of 2,4-D or the potassium salt of picloram when used under conditions and rates which are typical of those used by highway personnel. However, each runoff occurrence is a unique event and other applications may result in significantly more or less herbicide runoff, dependent upon site-specific conditions including drainage area size, vegetative cover, evaporation rate, topography, antecedent soil moisture content, soil type and permeability, and especially amount, duration, and intensity of precipitation. Site-specific conditions during this study were more conducive to subsurface vertical migration of these soluble herbicides than to surface migration via runoff. Sites with steeper slopes and significant rainfall immediately after application will probably result in greater runoff concentrations. However, even the higher concentrations reported in the runoff from other studies which used lower or similar application rates are normally below the safe in-stream concentrations, and, therefore, unlikely to impact water quality.

Surface Treatment

The results of this study suggest that water quality impacts are not likely from surface treatment operations such as those conducted at the Snake Road site. Although the complex nature of runoff samples resulted in analytic detection limits above the World Health Organization (1970) recommended drinking water limit of 200 parts per trillion (ppt), the lack of significant levels of PAHs in these samples stormwater runoff suggests that this operation poses a minimal threat to mammals from exposure to PAHs, especially when evaluated relative to other sources. Finally, stormwater runoff from the treated area does not appear to be toxic to aquatic life based on static bioassays with the freshwater microcrustacean *Daphnia magna*.

SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

CONTROL OF VEGETATION USING HERBICIDES

Grassed drainage areas within two stretches of highway right-of-way were each treated with a herbicide under conditions and rates representative of those used by highway agencies in the routine control of vegetation. One drainage area was sprayed with the amine salt of 2,4-D, the other with the potassium salt of picloram. Adjacent untreated drainage areas within each site served as controls. Three stormwater runoff samples were collected from each area, one before and two after herbicide application. Chemical analyses and bioassays using hypocotyl growth tests were performed on samples. The overall results were as follows:

- Concentrations of 6.2 and 25 ug/L of 2,4-D were measured in runoff samples 11 and 35 days, respectively, following treatment. Over half of the 2,4-D was sediment-attached.
- Picloram was detected only once in runoff following treatment at a concentration of 0.92 ug/L, all of which was sediment-attached.
- 2,4-D detected in runoff 11 days after treatment showed significant inhibition of hypocotyl growth. 2,4-D detected 35 days after treatment was not inhibitory and, therefore, was considered to be biologically inactive. Picloram detected in runoff did not inhibit hypocotyl growth and may have been biologically inactive or unavailable.

The following conclusions may be drawn from these results:

- Rainfall-runoff and site-specific characteristics of the treatment areas appear to have promoted vertical subsurface migration of herbicides and may explain the relatively low runoff concentrations.
- Comparisons of runoff concentrations with estimated safe concentrations for aquatic life indicate that significant short-term impacts are not likely. Dilution of runoff concentrations with receiving stream waters would further reduce the probability of significant water quality impacts.

- Runoff samples from these study sites generally showed no significant effects on hypocotyl growth in bioassays, further indicating that impacts are not likely.

Recommended areas of future research into water quality impacts from the use of herbicides include:

- Monitoring herbicide runoff from highway areas having a variety of soil types, slopes, and climatic conditions.
- Examination of potential groundwater contamination from the use of herbicides in highway rights-of-way.
- Evaluation of the potential for water quality impacts from these and other commonly used herbicides applied in combination to assess potential synergistic or additive effects.
- Evaluation of the potential chronic or sublethal effects on aquatic life from long-term exposure to low levels of herbicides.

ASPHALT-CONCRETE SURFACE TREATMENT WITH ASPHALT EMULSION

An asphalt concrete roadway located in a rural environment was treated with a WS-90 asphalt emulsion and limestone gravel. Three stormwater runoff samples were collected following treatment and analyzed for polynuclear aromatic hydrocarbons (PAHs) and toxicity using Daphnia magna in static bioassays. The following results were obtained:

- PAHs were not found in the asphalt emulsion at a detection limit of 4 mg/kg, nor in runoff samples at a detection limit of 3 ug/L.
- Runoff samples were relatively nontoxic as demonstrated by the low mortality of Daphnia magna in static bioassays.

The following conclusions may be made regarding surface treatment using asphalt emulsions:

- The absence of PAHs in runoff samples above the 3 ug/L detection limit suggests that this maintenance practice poses a minimal threat to mammals from exposure to PAHs.
- Stormwater runoff from areas treated with asphalt emulsions generally do not appear to be toxic to aquatic life.

An area of recommended future research is the further chemical characterization of asphaltic materials commonly used in highway maintenance and an assessment of their potential for impacting water quality.

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APPENDIX A - ANALYTIC QUALITY CONTROL RESULTS

In this section, Appendix A, analytic quality control results are summarized for the 2,4-D (I-71 site) and picloram (I-90 site) analyses. Analytic quality control percent recoveries of selected PAHs (Snake Road site) are also given (Tables 17 through 19).

Table 17. Summary of analytic quality control results of 2,4-D analysis for the I-71 study site.

Area	Event description	Sample description	Spike concentration (ug/L)	Sample result (ug/L)	Background[a] (ug/L)	Background corrected (ug/L)	Percent recovery
Control	Field blank no. 1	Total	---	ND - 0.10	---	---	---
Treatment	Field blank no. 1	Total	---	ND - 0.10	---	---	---
Treatment	Field blank no. 1	Total matrix spike	1.60	1.08	0.04[b]	1.04	65
Control	Pretreatment runoff sample	Total	---	ND - 0.50	---	---	---
Control	Pretreatment runoff sample	Filtrate	---	[c]	---	---	---
Treatment	Pretreatment runoff sample	Total	---	ND - 0.50	---	---	---
Treatment	Pretreatment runoff sample	Total matrix spike	1.60	1.04	ND - 0.50	1.04	65
Treatment	Pretreatment runoff sample	Total matrix Spike duplicate	1.60	1.16	ND - 0.50	1.16	72
Treatment	Pretreatment runoff sample	Filtrate	---	[c]	---	---	---
---	---	Clean water method standard for pre-treatment samples	1.60	1.21	ND - 0.50	1.21	76
Control	Field blank no. 2	Total	---	ND - 0.50	---	---	---
Treatment	Field blank no. 2	Total	---	ND - 0.50	---	---	---
Treatment	Field blank no. 2	Total matrix spike	1.61	1.09	ND - 0.50	1.09	68
Control	First post-treatment runoff sample	Total	---	ND - 0.50	---	---	---
Control	First post-treatment runoff sample	Filtrate	---	[c]	---	---	---
Treatment	First post-treatment runoff sample	Total	---	6.2	---	---	---
Treatment	First post-treatment runoff sample	Total matrix spike	1.61	7.3	6.2	1.16	72
Treatment	First post-treatment runoff sample	Filtrate	---	2.2	---	---	---
Treatment	First post-treatment runoff sample	Filtrate matrix spike	2.68	4.53	2.2	2.33	87
---	---	Clean water method standard for first post-application samples	1.61	1.03	ND - 0.50	1.03	64

Table 17. Summary of analytic quality control results of 2,4-D analysis for the I-71 study site. (Continued)

Area	Event description	Sample description	Spike concentration (ug/L)	Sample result (ug/L)	Background[a] (ug/L)	Background corrected (ug/L)	Percent recovery
Control	Field blank no. 3	Total	---	ND - 0.50	---	---	---
Treatment	Field blank no. 3	Total	---	ND - 0.50	---	---	---
Treatment	Field blank no. 3	Total Matrix Spike	1.61	1.05	0.39[b]	0.66	41
Control	Second post-application runoff sample	Total	---	ND - 0.50	---	---	---
Control	Second post-application runoff sample	Filtrate	---	[c]	---	---	---
Treatment	Second post-application runoff sample	Total	---	25	---	---	---
Treatment	Second post-application runoff sample	Total matrix spike	1.61	24.98	25	0	[d]
Treatment	Second post-application runoff sample	Filtrate	---	9.0	---	---	---
Treatment	Second post-application runoff sample	Filtrate matrix spike	2.68	10.5	9.0	1.50	56
---	---	Clean water method standard for second post-application samples	1.61	1.19	ND - 0.50	1.19	74
---	---	Herbicide as applied	---	8,300,000	---	---	---

ND = Not detectable. Detection limits are shown next to ND notations.

[a] Background represents concentration in field blank or runoff sample, except as noted.

[b] Value represents instrumentation baseline drift.

[c] Total sample was not found to be positive; therefore, filtered sample was not analyzed.

[d] Percent recovery not calculated because background concentration was greater than spiked concentration.

Table 18. Summary of analytic quality control results of picloram analysis for the I-90 study site.

Area	Event description	Sample description	Spike concentration (ug/L)	Sample result (ug/L)	Background[a] (ug/L)	Background corrected (ug/L)	Percent recovery
Control	Field blank no. 1	Total	---	ND - 0.10	---	---	---
Treatment	Field blank no. 1	Total	---	1.3	---	---	---
Treatment	Field blank no. 1	Total matrix spike	66.7	2.5	1.3	23.7	36
Control	Pretreatment runoff sample	Total	---	ND - 1.0	---	---	---
Control	Pretreatment runoff sample	Filtrate	---	b	---	---	---
Treatment	Pretreatment runoff sample	Total	---	ND - 0.50	---	---	---
Treatment	Pretreatment runoff sample	Total matrix spike	50.0	18.6	ND - 0.50	18.6	37
Treatment	Pretreatment runoff sample	Total matrix spike duplicate	50.0	39.6	ND - 0.50	39.6	79
Treatment	Pretreatment runoff sample	Filtrate	---	b	---	---	---
---	---	Clean water method standard for pretreatment samples	25	17.0	ND - 1.0	17	68
Control	Field blank no. 2	Total	---	1.6	---	---	---
Treatment	Field blank no. 2	Total	---	1.8	---	---	---
Treatment	Field blank no. 2	Total duplicate analysis	---	1.2	---	---	---
Control	First post-treatment runoff sample	Total	---	ND - 1.0	---	---	---
Control	First post-treatment runoff sample	Filtrate	---	b	---	---	---
Treatment	First post-treatment runoff sample	Total	---	ND - 1.0	---	---	---
Treatment	First post-treatment runoff sample	Total matrix spike	25.0	34.0	0.80[c]	33.2	130
Treatment	First post-treatment runoff sample	Filtrate	---	b	---	---	---
---	---	Clean water method standard for first post-application samples	25.0	44.0	ND - 1.0	44.0	180

Table 18. Summary of analytic quality control results of picloram analysis for the I-90 study site. (Continued)

Area	Event description	Sample description	Spike concentration (ug/L)	Sample result (ug/L)	Background[a] (ug/L)	Background corrected (ug/L)	Percent recovery
Control	Field blank no. 3	Total	---	ND - 0.5	---	---	---
Treatment	Field blank no. 3	Total	---	ND - 0.5	---	---	---
Treatment	Field blank no. 3	Total matrix spike	33.3	41.5	0.30[c]	41.2	120
Control	Second post-application runoff sample	Total	---	ND - 0.5	---	---	---
Control	Second post-application runoff sample	Filtrate	---	[b]	---	---	---
Treatment	Second post-application runoff sample	Total	---	0.92	---	---	---
Treatment	Second post-application runoff sample	Total matrix spike	25.0	13.1	0.92	12.2	49
Treatment	Second post-application runoff sample	Filtrate	---	ND - 0.1	---	---	---
Treatment	Second post-application runoff sample	Filtrate matrix spike	25.0	13.0	ND - 0.1	13.0	52
---	---	Clean water method standard for second post-application samples	25.0	27.0	ND - 0.50	27.0	108
---	---	Herbicide as applied	---	5,400,000	---	---	---

ND = Not detectable. Detection limits are shown next to ND notations.

[a] Background represents concentration in field blank or runoff sample, except as noted.

[b] Total sample was not found to be positive; therefore, filtered sample was not analyzed.

[c] Value represents instrumentation baseline drift.

Table 19. Summary of analytic quality control percent recoveries of selected polycyclic aromatic hydrocarbons (PAHs) for the Snake Road study site.

Compound	Field blank no. 1 total matrix spike	First postapplication runoff sample total matrix spike	First postapplication runoff sample total matrix spike duplicate	Clean water method standard for first post application runoff sample	Field blank no. 2 total matrix spike	Second postapplication runoff sample total matrix spike	Field blank no. 3 total matrix spike	Third postapplication runoff sample total matrix spike
Acenapthene	80	127	127	83	107	140	146	63
Acenapthylene	92	93	93	58	86	86	109	57
Anthracene	98	68	70	53	106	94	107	255
Benzo(a)anthracene	130	117	137	65	103	148	135	75
Benzo(b)fluoranthene	118	117	121	158	133	126	260	50
Benzo(k)fluoranthene	96	NA	NA	NA	NA	NA	NA	NA
2-Chloronapthalene	38	116	137	67	85	130	137	61
Chrysene	84	67	84	48	70	77	84	97
Fluorene	104	113	112	68	88	105	112	80
Napthalene	NA	126	158	72	150	127	158	10
Phenanthrene	NA	91	84	57	93	87	84	92
Pyrene	NA	115	117	67	113	135	117	71

NA - Not analyzed