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16. Abstract Mass balances conducted on soils adjacent to highways indicated low mobility of metals deposited on well-vegetated surfaces. Grass drainage channels were shown to effectively capture and retain metals (e.g. a 60 m channel removed 80 percent of the original Pb concentration). Mud or paved channels, however, demonstrated little or no ability to remove metals from runoff. Metal release studies suggested that acid precipitation could release metals bound in the soil, especially where low buffering capacity exists.					
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ABSTRACT

Mass balances conducted on soils adjacent to highways indicated low mobility of metals deposited on well-vegetated surfaces. Grassy drainage channels were shown to effectively capture and retain metals (e.g. a 60 m channel removed more than 80 percent of the original Pb concentration). Mud or paved channels, however, demonstrated little or no ability to remove metals from runoff. Metal release studies suggested that acidic runoff could release metals bound in the soil, especially where low buffering capacity exists.

TABLE OF CONTENTS

	<u>Page</u>
PREFACE	ii
LIST OF CHEMICAL SYMBOLS	vii
INTRODUCTION	1
EXPERIMENTAL METHODS	7
RESULTS AND DISCUSSION	12
Surface Soil Studies	12
Soil Core Studies	12
Channel Studies	16
Particle Size Fractionation Study	25
CONCLUSIONS	29
REFERENCES	31

PREFACE

The following pages list reports either completed or in process on the basis of the Highway Runoff Water Quality research results. Following the listing is an order blank to obtain a complementary copy of any report in the series.

Highway Runoff Water Quality Reports

Report No. 1. Horner, R.R. and E.B. Welch, "Effects of Velocity and Nutrient Alterations on Stream Primary Producers and Associated Organisms," November 1978.

Velocity and nutrient studies at 12 sites in Western Washington streams indicated that 50 cm/sec is the critical average current velocity where the productive base of the food web is impacted. Swiftly flowing streams rich in nutrients should not be slowed to this value, and slowly flowing streams should not be altered to have velocities greater than this value.

Report No. 2. Horner, R.R., S.J. Burges, J.F. Ferguson, B.W. Mar, and E.B. Welch, "Highway Runoff Monitoring: The Initial Year," January 1979.

This report covers the initial 15 months of effort to review the literature, select a prototype site, compare the performance of several automatic sampling devices, and install a prototype sampling site on I-5 north of Seattle.

Report No. 3. Clark, D.L. and B.W. Mar, "Composite Sampling of Highway Runoff: Year 2," January 1980.

A composite sampling device was developed that can be installed at less than ten percent of the cost of automatic sampling systems currently used in Federal highway runoff studies. This device was operated for one year, side-by-side the I-5 site, to demonstrate that the composite system provides identical results to the automated system.

Report No. 4. Vause, K.H., J.F. Ferguson, and B.W. Mar, "Water Quality Impacts Associated with Leachates from Highway Woodwastes Embankments," September 1980.

Laboratory and field studies of a woodchip fill on SR 302 demonstrated that the ultimate amounts of COD, TOC and BOD per ton of woodchips can be defined and that this material is leached exponentially by water. After a year the majority of the pollutant has been removed, suggesting that pre-treating of the woodchips prior to use in the fill can reduce the pollutant release from a fill. This chips should be protected from rainfall and groundwater intrusion to avoid the release of leachate. Release of leachate onto tidal lands can cause beach discoloration and an underground deep outfall may be required.

Report No. 5. Aye, R.C., "Criteria and Requirements for Statewide Highway Runoff Monitoring Sites," July 1979.

Criteria for selecting statewide monitoring sites for highway runoff are established to provide representative combinations of climate, traffic, highway, land use, geographic and topographic characteristics. Using these criteria, a minimum of six sites are recommended for use in this research.

Report No. 6. Asplund, R., J.F. Ferguson, and B.W. Mar, "Characterization of Highway Runoff in Washington State," December 1980.

A total of 241 storm events were sampled at ten sites during the first full year of statewide monitoring of highway runoff. Analyses of these data indicate that more than half of the observed solids in this runoff is traced to sanding operations. The total solids loading at each site was correlated with traffic during the storm. The ratio of other pollutants to solids was linear when there were sufficient traffic generated pollutants to saturate the available solids.

Report No. 7. Mar, B.W., J.F. Ferguson, and E.B. Welch, "Year 3 - Runoff Water Quality, August 1979 - August 1980," January 1981.

This report summarizes findings detailed in Report Nos. 4 and 6 plus the yet-to-be-published work of Karen Zawlocki on trace organics in highway runoff. Several hundred compounds tentatively identified by GC-MS were grouped into nine categories, which were not mutually exclusive, by Zawlocki. Major components of these categories were petroleum products used by vehicles and incompletely combusted hydrocarbons. The concentrations of these trace organics groups were low compared to criteria proposed for protection of aquatic life.

Report No. 8. Eagon, P.D., "Views of Risk and Highway Transportation of Hazardous Materials - A Case Study in Gasoline," November 1981.

While gasoline represents one-third of all hazardous materials transported in the country by trucks, the risk associated with gas transportation, as viewed by the private sector, is small. Public perceptions of risk are much greater due to lack of knowledge on probabilities and consequences of spills. Methods to improve knowledge available to the public on gasoline spills and methods to improve estimate of environmental damages from gasoline spills are presented. Generalization of methodologies to hazardous materials in general are discussed.

Report No. 9. Zawlocki, K.R., J.F. Ferguson, and B.W. Mar, "A Survey of Trace Organics in Highway Runoff in Seattle, Washington," November 1981.

Trace organics were surveyed using gas chromatography coupled to mass spectrometry for highway runoff samples from two Seattle sites. The characterization of the organics exhibited concentrations of aliphatic, aromatic and complex oxygenated compounds. Vehicles, including exhaust emissions, were concluded to be the source of many of the organics.

Report No. 10. Wang, T.S., D.E. Spyridakis, R.R. Horner, and B.W. Mar, "Transport, Deposition and Control of Heavy Metals in Highway Runoff," January 1982.

Mass balances conducted on soils adjacent to highways indicated low mobility of metals deposited on well-vegetated surfaces. Grassy drainage channels were shown to effectively capture and retain metals (e.g. a 40 m channel removed 80 percent of the original Pb concentration). Mud or paved channels, however, demonstrated little or no ability to remove metals from runoff. Metal release studies suggested that acid precipitation could release metals bound in the soil, especially where low buffering capacity exists.

Report No. 11. Portele, G.J., B.W. Mar, R.R. Horner, and E.B. Welch, "Effects of Seattle Area Highway Stormwater Runoff On Aquatic Biota," January 1982.

The impacts of stormwater runoff from Washington State freeways on aquatic ecosystems was investigated through a series of bioassays utilizing algae, zooplankton and fish. Algae and zooplankton were adversely affected by the soluble fraction of the runoff, while suspended solids caused high mortalities of rainbow trout fry. In addition, BOD₅ values similar to those reported in the stormwater literature were measured; however, there were indications that results were influenced by toxicity to microbial populations.

Report No. 12. Chui, T.W., B.W. Mar, and R.R. Horner, "Highway Runoff in Washington State: Model Validation and Statistical Analysis," November 1981.

Results of the second year of full-time operation of nine monitoring sites in the State of Washington produced 260 observations of highway storm runoff. A predictive model was developed based on the data from two years of observation for total suspended solid loads. A high correlation was demonstrated between total suspended solids and COD, metals and nutrients. The major factor controlling pollution loads from highways in Washington State is the number of vehicles passing during each storm, not those preceding storms.

Report No. 13. Mar, B.W., J.F. Ferguson, D.E. Spyridakis, E.B. Welch, and R.R. Horner, "Year 4 - Runoff Water Quality, August 1980 - August 1981."

This report summarizes findings presented in Report Nos. 10 - 12. Included are the results of studies aimed at improving and extending Asplund's solids loading model, increasing data on the ratios of various pollutants to TSS in the runoff, investigating the fate of heavy metals in drainage systems, and conducting bioassays on sensitive organisms exposed to highway runoff.

Report No. 14. Horner, R.R. and B.W. Mar, "Guide for Water Quality Impact Assessment of Highway Operations and Maintenance." (Draft issued Fall, 1981).

Procedures particularly applicable to Washington State have been developed to assist the highway designer in evaluating and minimizing the impacts of highway runoff on receiving waters. The guide provides computation procedures to estimate pollutant concentrations and annual loadings for three levels of analysis which depend on the watershed, the discharge system and traffic. It further provides means to judge the potential impacts of the runoff on receiving waters.

Report No. 15. Horner, R.R. and E.B. Welch, "Impacts of Channel Reconstruction in the Pilchuck River." (To be issued Winter, 1982.)

Report No. 16. Report on dissertation project during Year 5. (To be issued Summer 1982).

Report No. 17. Final report. (To be issued Summer 1982).

Please send me copies of Report No. 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12,
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LIST OF CHEMICAL SYMBOLS

Cd	Cadmium
Co	Cobalt
Cr	Chromium
Cu	Copper
Fe	Iron
Mn	Manganese
Ni	Nickel
Pb	Lead
Zn	Zinc

INTRODUCTION

The Highway Runoff Water Quality project is a five-year effort initiated in 1977 by the Washington State Department of Transportation (WSDOT) to define the characteristics of stormwater runoff from Washington highways, define its impact on receiving waters and explore means of reducing that impact. In previous phases of this project, the emphasis was on the review of literature, selection of runoff sampling sites, the initial characterization of an urban site, the design and testing of a continuous sampling composite sampler, and the characterization of the pollutants found in highway stormwater runoff at nine sites in Washington State.

The major topics to be explored in this project report include:

1. An investigation of the transport of heavy metals released from automobiles.
2. Determination of the mobility of metals deposited onto the soils adjacent to the highway.
3. Comparison of pollutant retention and transport in various drainage channels.
4. Study of potential metal releases from soils.

Heavy metals in highway runoff originate from highway materials and various aspects of vehicle operations. Sources and the metals they contribute include gasoline and exhaust emissions (Pb, Ni), lubricating oils (Pb, Ni, Zn), grease (Zn, Pb), tire wear (Cd, Zn), concrete paving wear (various metals depending on aggregate source), asphalt paving wear (Ni, V), bearing wear (Cu, Pb), brake lining wear (Cu, Cr, Ni) and wear of moving engine parts (Fe, Mn, Cr, Co) (after Kerri et al., 1976; Hopke et al., 1980; Novotny and Chesters, 1981). In addition, metals deposited from surrounding lands on the highway are significant contributors to highway runoff contamination.

Among the toxic metals represented, Pb, Zn and Cu are most abundant in runoff and have received the most study.

Lead in automotive exhaust occurs in both a particulate fraction and an organic vapor phase (Brief, 1962). Most of the emitted lead is in the particulate inorganic form (Laxen and Harrison, 1977). It occurs in two distinct particle size ranges: $< 1 \mu\text{m}$ and $5 - 50 \mu\text{m}$ (Habibi, 1973; Ganley and Springer, 1974) with relatively little in the $0.5 - 5 \mu\text{m}$ range (Ter Haar et al., 1972).

Those particles in the larger range settle within a short distance. Habibi (1973) found in wind tunnel experiments that one-half to two-thirds of Pb particles greater than $9 \mu\text{m}$ are deposited within 7 m of the exhaust pipe.

Zimdhal (1972) discovered that lead concentrations at I-25 north of Denver were highest immediately adjacent to the roadway and rapidly diminished with depth in the profile and distance from the highway. The lead levels of soil samples obtained farther than 30 m from the roadway were indistinguishable from background levels. Values up to $1,300 \mu\text{g/g}$ were found in the top 1 cm of soil immediately adjacent to the highway.

Getz et al. (1975) measured Pb in surface soils along Illinois highways, finding that concentrations decreased to background within 50 m on the downwind side and within 20 m on the upwind side. Where average daily traffic volume (ADT) was under 2,000 vehicles, they found the decline to background to occur within 5 - 10 m. Scanlon (1977) found decreases to approximately background levels within 48 m of Virginia highways for Cd, Ni, Zn and Pb, except near heavily-trafficked I-95, where Pb remained well above background at 48 m. Gupta and Kobriqer (1980) discovered the same distribution trend for highway-generated metals in the surface soil adjacent

to I-94 in Milwaukee. The metal concentrations decreased rapidly within the first 9 m and reach background levels between 30 and 35 m from the paved surface. Laxen and Harrison (1977) summarized the clear evidence of the literature in this regard, stating that soil and vegetation Pb concentrations are generally indistinguishable from the local background within 30 m.

The large fraction of Pb emissions in the sub-micrometer particle size, however, can remain airborne for long periods of time. Several investigations, summarized by Laxen and Harrison (1977), have found close to half of all emitted Pb to be airborne at a substantial distance from a highway. As a result, the mass median equivalent diameter of Pb particles in urban atmospheres is in the respirable, aerosol range ($< 1 \mu\text{m}$).

A question of interest in research has been the mobility of deposited metals within the soil profile. Motto et al. (1970) measured Pb concentrations averaging 160 ppm in the upper six inches (15.2 cm) of soil at 25 ft. (7.62 m) from several New Jersey highways, decreasing to an average of less than 90 ppm at 75 ft. (22.9 m) or more from the traffic. In the soil layer 6 - 12 inches (15.2 - 30.5 cm) deep, Pb averaged 105 ppm at 25 ft. (7.62 m) and 47 ppm or less at 75 ft. (22.9 m) and greater distances. Getz et al. (1975) observed maximum Pb concentrations in the upper 10 cm of soil, with sharp declines below that point. Laxen and Harrison (1977) cited a number of studies to support their observation that Pb deposited on soil is generally effectively immobilized and confined to the top 15 cm.

Immobilization of Pb by soil was considered to be directly correlated with the soil cation exchange capacity (CEC) and inversely related to pH by Zimdhal (1972) and Hassett (1974). Hildebrand and Blum (1975) asserted that the organic content was the main factor in Pb soil fixation, with clay mineral adsorption being of less importance. The U.S. Environmental Protection

Agency (1980) has also taken the latter view and considers CEC to offer a first approximation but to not be the controlling factor in metal retention in soil assimilating wastewater or sludge.

The quantities of heavy metals in storm runoff and the forms they take depend on the physical and chemical behavior of the specific elements. Pb on the paved surface is nearly all insoluble (Pitt and Amy, 1973). Still, it has been observed that 5 - 50 percent of the Pb in runoff is dissolved (Sylvester and DeWalle, 1972; Shaheen, 1975; Getz et al., 1975). The apparent reason is that the soluble fraction can be carried by any size storm, whereas larger storms are required to suspend the solids which hold the large insoluble portion. There is evidence that dissolved Pb is present in highway runoff primarily as inorganic complexes (Laxen and Harrison, 1977). Getz et al. (1975) found that more than 90 percent of the particulate Pb in their samples was associated with particles of less than 2 mm diameter.

There is evidence that both sodium (Lagerwerff and Brower, 1973) and phosphates (Nriagu, 1974) effectively precipitate soluble Pb. Both quantities are present in highway runoff in significant amounts, with sodium particularly abundant during winter deicing.

Zn, Cu and Cd are all considerably more soluble than Pb. Shaheen (1975) observed that dissolved Zn was almost always higher than dissolved Pb in roadway runoff, despite the fact that Pb was approximately eight times more abundant in materials deposited on highways.

Chui (1981) found that ratios of Pb, Zn and Cu to total suspended solids (TSS) were all fairly constant from time-to-time at each of nine highway runoff sampling sites in Washington State. There was considerable variation of the ratio among sites, however, which could be explained satisfactorily ($R^2 \geq 0.82$) with linear regressions of metal mass loadings on ADT.

Although highway runoff is routinely drained through engineered channels, there is virtually no documentation of the effect that practice has on water quality. A common procedure is to keep such channels fairly clear of vegetation by scraping or herbicide application so as not impede flow. There is reason to believe, however, that maintaining vegetated channels would reduce contamination by advancing sedimentation and, possibly, creating conditions conducive to removal of dissolved quantities as well.

Applying treated municipal wastewater to land to achieve further water quality improvement has been well-studied and employed full-scale in a number of communities. The most common form of land treatment has been spray irrigation of cropped or wooded areas (U.S. Environmental Protection Agency, 1980), but overland flow treatment has also been employed (Hinrichs et al., 1980). Kao (1980) measured greater than 90 percent sediment trapping efficiencies in laboratory channels having artificial grass media, although efficiency tended to decrease over time.

Hinrichs et al. (1980) documented the results of operating municipal wastewater overland flow treatment systems at eight locations, representing the following ranges of experimental variables:

Slope	2 - 10 Percent
Slope length	30 - 75 m
Hydraulic loading rate	5 - 44 cm/wk
Organic loading rate	2.2 - 166 Kg BOD/ha/day

Average removal percentages ranged as follows: BOD -- 55 - 99; TSS -- 48 - 99; nitrogen -- 25 - 94; phosphorus -- 30 - 89. Nitrogen and phosphorus removals were all greater than or equal to 64 percent and 45 percent, respectively, except at the cold weather test location during winter.

It was the objective of the research reported here to investigate in

one coordinated study the questions of metal deposition with respect to distance from the highway, mobility in soils, and removal during transport through channels for several metals of concern in highway runoff.

EXPERIMENTAL METHODS

In order to study the transport and fate of metals originating in highway runoff, samples of soils and channel sediments, stormwater and bulk precipitation were collected adjacent to Seattle, Washington area freeways at several sites. Table 1 lists site characteristics, and Figure 1 shows their locations.

Soil and channel sediment cores were collected using heavy duty plastic tubing of tenite butyrate having 38.48 cm² or 9.62 cm² internal cross-sectional area. Cores to 13 cm in length were successfully retrieved. Upon return to the laboratory, the top organic layer was removed and stored separately; and the remaining soil was carefully extruded in 1 - 2 cm thick sections. Individual soil sections were weighed, dried at 70° C for 36 hours, and reweighed. Following drying, the samples were comminuted and homogenized with a mortar and pestle and stored in plastic polyethylene bags.

In order to study pollutant transport in relation to particle size, a size fractionation study was performed with solids swept from the highway shoulder at the I-5/N.E. 158th Street site. The size separation was accomplished according to the procedure outlined by Jackson (1969).

The soil and channel sediment samples and size-fractionated highway solids (100 mg quantities) were digested in 10 ml teflon crucibles using HNO₃-HF-HClO₄-HNO₃ (Bortleson and Lee, 1972). Filtered digestrates were then analyzed for Pb, Zn, Cu, Ca, Cd, Co, Fe, Mg and Mn by emission spectroscopy using a Jarrel-Ash (Atomcomp) Inductively Coupled Plasma (ICP) spectrophotometer. In addition, some Pb and Zn samples were analyzed with an Instrumentation Laboratory IL-353 atomic absorption spectrophotometer for comparison. The methods offer roughly equal precision. ICP, however, exhibits better detection limits, fewer chemical interferences and more linear standard curves than atomic absorption spectrophotometry. Table 2 compares the detection limits of the two instruments. The comparative analyses

Table 1: Sampling Site Characteristics

Site Location	Site Description	Highway Description	Traffic Volume (ADT)	Surrounding Land Use	Type of Sample
1. I-5 @ 158 I-5 & NE 158th Northbound Right-of-way	A well-vegetated area with a combined mud-grassy channel, & with some flat area before channel	4-12' concrete lanes, 10'-DL-asphalt-curb, 10'-ML-asphalt-NJ	53,000	Urban Residential	Surface soil Soil core Grassy channel Mud Channel
2. I-5 @ 159 I-5 & NE 159th Northbound Right-of-way	A site north and adjacent to I-5 @ 158 site, well-vegetated with a grassy channel, collects street runoff	"	"	"	Grassy channel
3. I-5* I-5 & NE 157th Northbound Right-of-way	A site south and adjacent to I-5 @ 158 site, well-vegetated with a grassy channel which drains highway runoff of new site at I-5	"	"	"	Grassy channel
4. I-5 @ Northgate I-5 & Northgate Northbound Right-of-way	A site with a steep downslope, generally well-vegetated	"	63,000	Urban	Surface soil
5. I-5 @ 165 I-5 & NE 165th Northbound Right-of-way	A site with a steep upslope, generally with some soil erosion	"	53,000	Residential	Surface soil
6. I-5 @ 188 I-3 & SW 188th Lynnwood Median	A site with several north to south paved channels in median	3-12' concrete lanes, 10'-DL-asphalt-curb, 8'-ML-asphalt	45,000	Urban	Paved channel
7. I-405 @ 132 I-405 & NE 132nd Kirkland Southbound Right-of-way	A site with grassy median which drains runoff into a pipe and to a paved channel, and a grassy channel	"	45,000	Urban	Grassy channel Paved channel
8. SR 509 @ 188 SR 509 & S 188th Southbound Right-of-way	A new highway site with 2 yrs of use	2-12' asphalt lanes, 8'-DL-asphalt-curb, 6'-ML-asphalt-NJ	17,000	Urban	Soil core

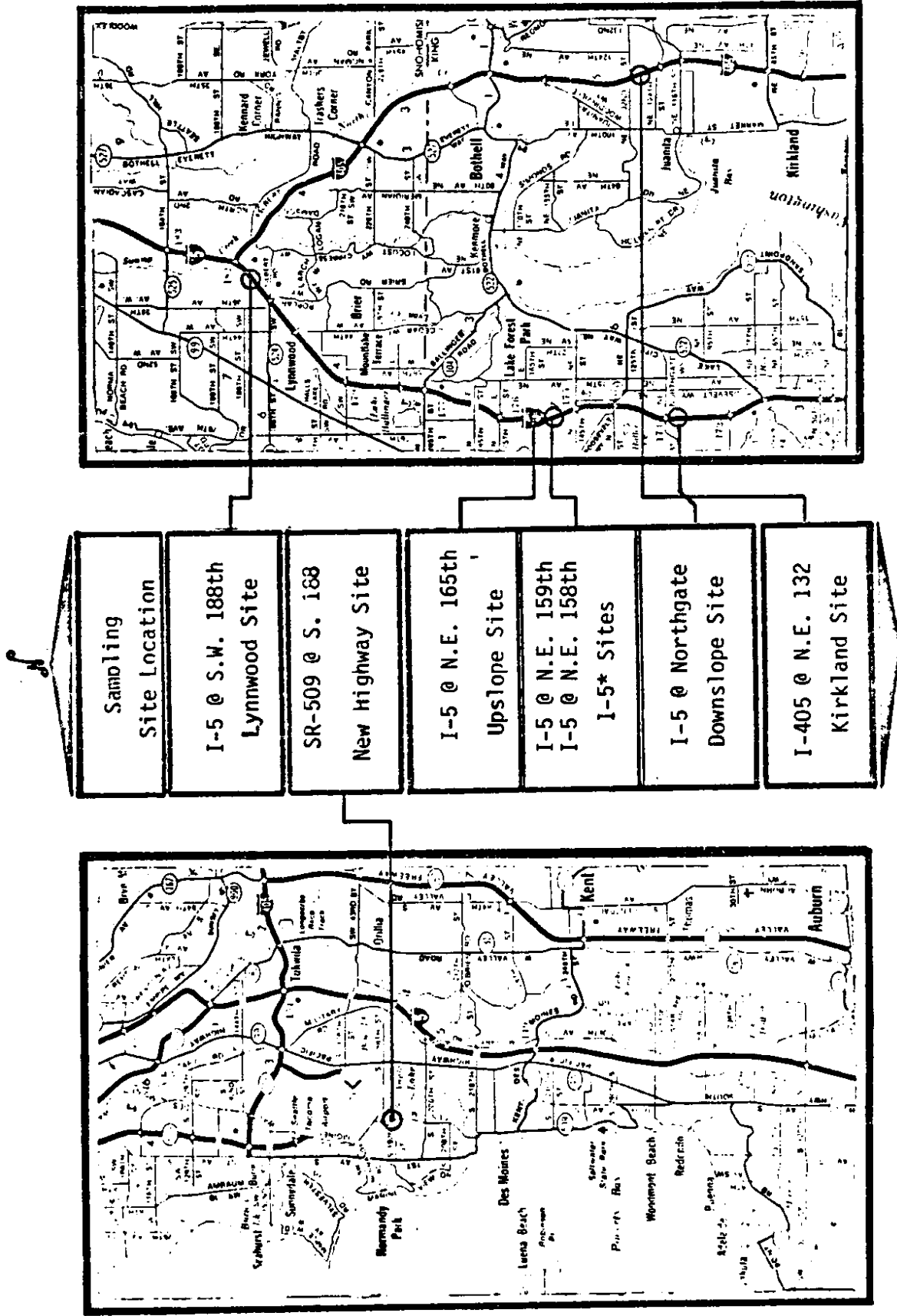


Figure 1: Sampling Site Locations

indicated that ICP produced results 11 - 12 percent higher than those obtained by atomic absorption spectrophotometry.

Water samples were collected upstream of and within vegetated channels in 250 ml acid-washed plastic bottles. An aliquot of the well-mixed sample was transferred into 60 ml acid-washed plastic bottles and acidified with high purity HNO₃ to pH less than 2. Prior to metals analysis, the acidified samples were filtered through pre-washed 0.45 µm Millipore filters. The metal concentrations were determined with the same instrumentation used for soil and sediment samples. For one storm event, total and volatile suspended solids (TSS and VSS) and chemical oxygen demand (COD) were also measured according to the procedures in Standard Methods (American Public Health Association, 1975).

Dustfall/rainfall samples were collected in 0.1 m² mouth rigid-form polyethylene jars. Two jars were placed 10 m from the edge of highway I-5 at N.E. 158th Street in July 1980. Three collections were made, each four months in length.

Table 2: Detection Limits in $\mu\text{g/l}$ (ppb) for Inductively Coupled Plasma Atomic Emission Spectrophotometers (Ward,1976), and Atomic Absorption Spectrophotometers (Kahn, et al., 1979). Values in parentheses are from this study.

<u>Element</u>	<u>ICP</u>	<u>Flame AA</u>	<u>Furnace AA</u>
Al	10	20	0.004
As	15	100	0.06
B	2	1000	---
Ca	(0.2)		
Cd	1 (0.2)	1	0.008
Co	2 (8)	5	0.03
Cr	2	3	0.005
Cu	2 (0.6)	2	0.008
Fe	1 (2)	5	0.003
Mg	(10.3)		
Mn	0.5 (0.3)	3	0.004
Mo	5	10	0.06
Ni	5	8	0.02
P	30	10 ⁵	3.0
Pb	15 (30)	10 (50)	0.03
Pt	20	50	0.45
Se	15	100	0.10
Si	10	60	0.10
Ti	1	50	0.30
U	75	7000	--
V	2	20	0.15
Zn	1 (20)	0.6 (5)	0.0007

RESULTS AND DISCUSSION

Surface Soil Studies

The concentration of metals as a function of distance from the highway was measured at three sites. The N.E. 158th site on I-5 was selected as representative of a flat site, the Northgate I-5 site representative of a downsloping site and the N.E. 165th I-5 location as representative of an upsloping site. Tables 3 - 5 summarize the results of surface soil metal analyses. The variations in the various metal concentrations as a function of distance from the highway are similar at each site and suggest that there is little movement of metals once they are deposited on the ground. Decrease to relatively low concentrations, seemingly representative of the background, occurred within approximately 15 m at each site. This trend generally follows that reported in the literature but occurs within a shorter distance than cited in some studies.

When vegetation is sparse, as within the first several meters at each site, soil erosion apparently occurs; and increased metal concentration at the boundary between vegetated and unvegetated areas is noticeable. Generally higher concentrations of metals at the upsloping site is likely the result of interception of wind-transported particles by the upslope area.

Soil Core Studies

Three sites representing high traffic volumes, lower traffic volumes, and new highway operating conditions were the subject of core sample studies. Six cores were taken from the I-5/N.E. 158th (approximate 100,000 ADT) site, two cores were taken from the SR-509 site (approximately 35,000 ADT) and two cores were taken from a marsh adjacent to the SR-509 (new highway) site. Cores at I-5 and SR-509 were collected at a point 10 m from the pavement, while the marsh core was taken approximately 100 m from the highway.

Table 3: Surface Soil (Upper 1 cm) Metal Concentrations versus Distance from Edge of Pavement at I-5 at N.E. 158th Flat Site.

<u>Distance</u> <u>(m)</u>	<u>Cd</u> <u>($\mu\text{g/g}$)</u>	<u>Cu</u> <u>($\mu\text{g/g}$)</u>	<u>Fe</u> <u>($\mu\text{g/g}$)</u>
0	34.1	120	42,300
1	33.5	63.9	44,300
1	70.5	115	60,200
2	61.2	80.8	18,500
3	72.6	90.5	34,400
4	27.6	43.8	25,000
5	25.3	35.8	24,000
6	26.7	35.4	26,500
8	15.9	36.4	21,400
10	18.6	27.0	21,300
12	24.1	25.7	23,000
13	24.9	29.2	24,600
18	23.1	30.2	23,400
21	30.4	34.5	27,400
24	16.9	25.0	21,500

<u>Mn</u> <u>($\mu\text{g/g}$)</u>	<u>Pb</u> <u>($\mu\text{g/g}$)</u>	<u>Zn</u> <u>($\mu\text{g/g}$)</u>
700	3,640	522
849	3,930	610
1,050	4,460	526
788	1,680	251
809	1,360	265
635	646	226
615	645	225
614	617	201
526	486	145
576	313	141
630	288	180
674	354	135
625	201	178
671	181	142
558	176	145

Table 4: Surface Soil (Upper 1 cm) Metal Concentrations versus Distance from Edge of Pavement at I-5 at Northgate Downslope Site.

<u>Distance (m)</u>	<u>Cd ($\mu\text{g/g}$)</u>	<u>Cu ($\mu\text{g/g}$)</u>	<u>Fe ($\mu\text{g/g}$)</u>
0	28.8	62.1	33,900
1	30.5	86.2	39,200
1	36.3	109	43,800
2	30.2	77.9	39,600
2	30.2	77.4	30,200
3	27.5	45.6	25,700
4	24.3	41.8	25,000
6	25.0	63.5	24,500
9	23.0	31.0	22,700
12	24.5	29.3	24,300
15	24.3	25.9	23,800

<u>Mn ($\mu\text{g/g}$)</u>	<u>Pb ($\mu\text{g/g}$)</u>	<u>Zn ($\mu\text{g/g}$)</u>
642	1,100	356
683	4,030	774
763	3,420	1,470
634	2,260	707
592	1,680	583
596	970	632
572	711	202
605	726	147
528	450	162
593	381	245
587	279	254

Table 5: Surface Soil (Upper 1 cm) Metal Concentrations versus Distance from Edge of Pavement at I-5 at N.E. 165th Upslope Site.

<u>Distance (m)</u>	<u>Cd ($\mu\text{g/g}$)</u>	<u>Cu ($\mu\text{g/g}$)</u>	<u>Fe ($\mu\text{g/g}$)</u>
0	27.0	74.1	28,900
0	22.4	76.6	25,400
1	23.6	37.4	22,800
2	23.8	36.9	25,600
3	22.3	29.6	24,300
4	24.2	32.6	25,800
6	22.6	34.5	21,200
8	20.6	29.6	19,900
10	19.7	25.4	22,400
12	24.3	23.1	25,100
15	20.7	37.0	21,300

<u>Mn ($\mu\text{g/g}$)</u>	<u>Pb ($\mu\text{g/g}$)</u>	<u>Zn ($\mu\text{g/g}$)</u>
559	2,420	603
535	2,980	635
664	1,260	357
651	993	208
598	642	193
678	591	133
642	1,220	324
548	752	120
684	633	136
665	291	121
702	476	231

Table 6 lists metals concentrations as functions of depth for one of the cores taken near I-5. The results demonstrate a sharp decrease in Cu, Pb and Zn within 3 - 5 cm depth and little movement beyond that point. Other metals, which are important in the natural soil make-up, do not follow this trend.

Table 7 summarizes an analysis of metal areal concentrations at the I-5 site. Deposition in the top layer was compared to concentrations in the layer at 4 - 12 cm depth, assumed to represent the background. Average annual deposition rates over the 20 year period of highway service were then estimated. The estimated rates were 0.01, 0.48 and 0.24 $\mu\text{g}/\text{m}^2/\text{yr}$ for Cu, Pb and Zn, respectively.

Pb concentrations in the soil profiles of the three sampling sites are compared in Table 8. SR-509 had been in use for only two years at the time of sampling. Whereas surface Pb concentration was an order of magnitude larger at I-5, it declined to just twice that at SR-509 at 3 cm depth and to an approximately equal concentration 11 cm deep in the profile.

Pb was more concentrated in the marsh soils than nearer the highway. Concentrations in deeper layers indicate that the background Pb is higher at the marsh location, possibly as a result of more effective retention of metals by the more highly organic soils. There may be some enrichment of the surface layer by Pb transported from the highway, but that material has not penetrated to the adjacent layer.

Channel Studies

The channel studies were concerned with comparing heavy metals transported by stormwater runoff draining through a paved channel, a mud-bottomed ditch and channels vegetated with grasses. A total of eight storm events were monitored at three sites having asphalt-paved, V-shaped channels.

Table 6: Metal Concentrations in Dry Soil Samples versus Soil Depth from Soil Core S-4-1 (I-5 at N.E. 158th site).

Depth (cm)	Cd ($\mu\text{g/g}$)	Cu ($\mu\text{g/g}$)	Fe ($\mu\text{g/g}$)
0	16.0	50.0	17,000
1	26.0	36.4	21,800
3	22.3	33.9	21,400
5	25.5	25.3	24,300
7	25.0	22.2	24,900
9	23.0	21.2	23,800
11	28.5	36.3	27,500

Mn ($\mu\text{g/g}$)	Pb ($\mu\text{g/g}$)	Zn ($\mu\text{g/g}$)
429	1,630	201
598	607	295
621	128	69.5
644	185	67.5
636	139	38.2
541	168	26.9
606	66.8	25.7

Table 7: Comparison of Lead Concentration Versus Soil Depth for Dry Soil Core Samples from I-5, SR-509 and a Marsh.

Depth (cm)	Pb Concentration ($\mu\text{g/g}$)		
	I-5	SR-509	Marsh
0.	1628.48	120.900	252.078
1.	606.97	79.525	171.000
3.	128.03	60.150	172.975
5.	184.60	67.080	233.325
7.	139.34	61.000	231.450
9.	168.05	63.750	177.000
11.	66.76	71.000	151.600

Table 8: Comparison of Lead Concentration in Dry Soil Core Samples Taken Near I-5 and SR-509 and From a Marsh Area.

Depth (cm)	Pb Concentration ($\mu\text{g/g}$)		
	I-5	SR-509	Marsh
0	1,628.48	120.900	252.078
1	606.97	79.525	171.000
3	128.03	60.150	172.975
5	184.60	67.080	233.325
7	139.34	61.000	231.450
9	168.05	63.750	177.000
11	66.76	71.000	151.600

Although few mud-bottomed channels exist in the Washington State highway system, the initial portion of the ditch at the I-5 sampling site is unvegetated. Flow in this portion of the channel was sampled simultaneously with that in the succeeding grass section. Nine sets of water samples were collected at four grass channel locations.

Figure 2 illustrates Pb and Zn concentrations versus distance traveled in the paved channel. The concentrations did not exhibit a steady decline with distance. It may thus be surmised that particles largely remained in suspension in the relatively high velocities prevalent in the paved channels.

Figure 3 presents a typical pattern for heavy metal variation in the I-5 mud/grass channel. A small decrease in Pb concentration occurred in the initial mud portion, followed by a rapid decline to a very low level in the vegetated section.

Table 9 summarizes metal removal efficiencies observed at the grass channel sampling sites. While a considerable amount of unevenness exists in the data, several trends are clear. First, 60 - 80 m of grass channel transport removed the majority of all metals in all cases. Channels at the I-405 and I-5* sites achieved high removal efficiencies in a shorter distance than occurred at the other two sites. Pb was more effectively and consistently removed than the other metals, apparently because of its relatively low solubility and strong association with particulate matter.

The Pb results were further investigated statistically through the derivation of second order polynomial regression equations best fitting the data for each case. These nine equations were employed to predict the effectiveness in reducing Pb of grass channels 20, 40 and 60 m in length. Means and 95 percent confidence limits for the predicted values were then established. Table 10 presents the results.

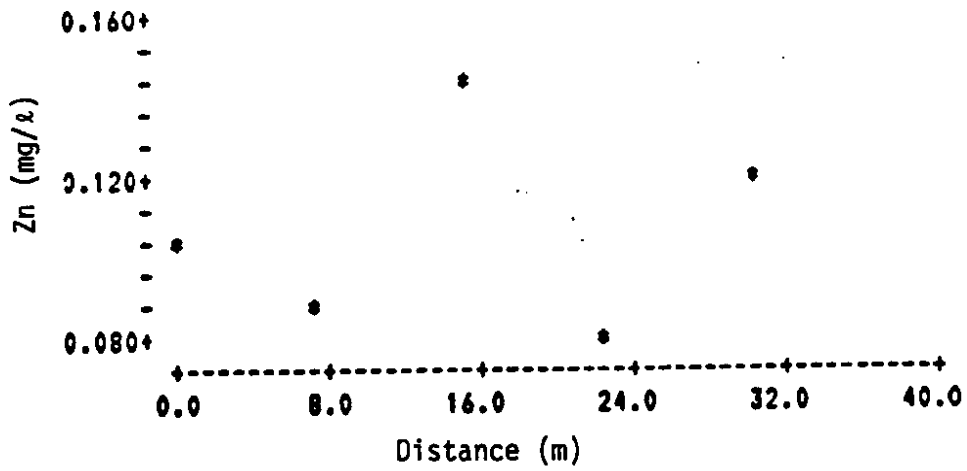
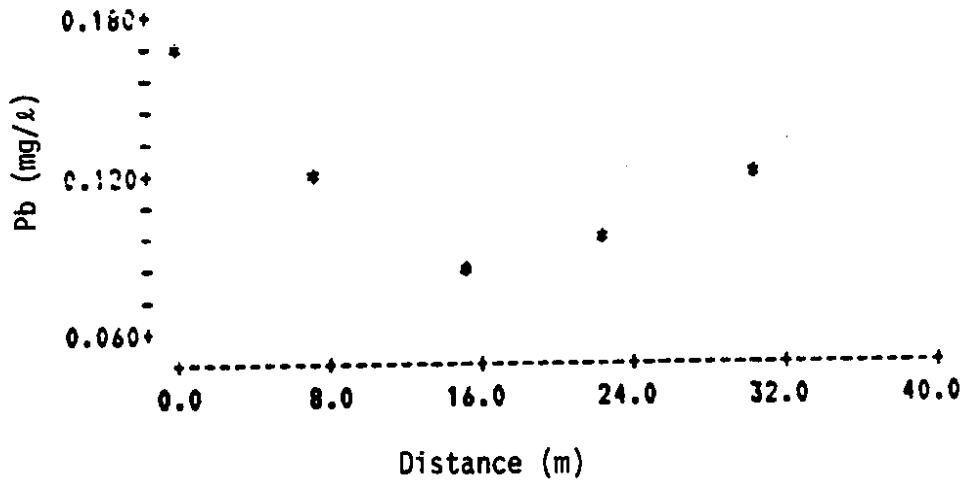


Figure 2: Pb and Zn Concentrations Versus Distance Traveled in Paved Channel.

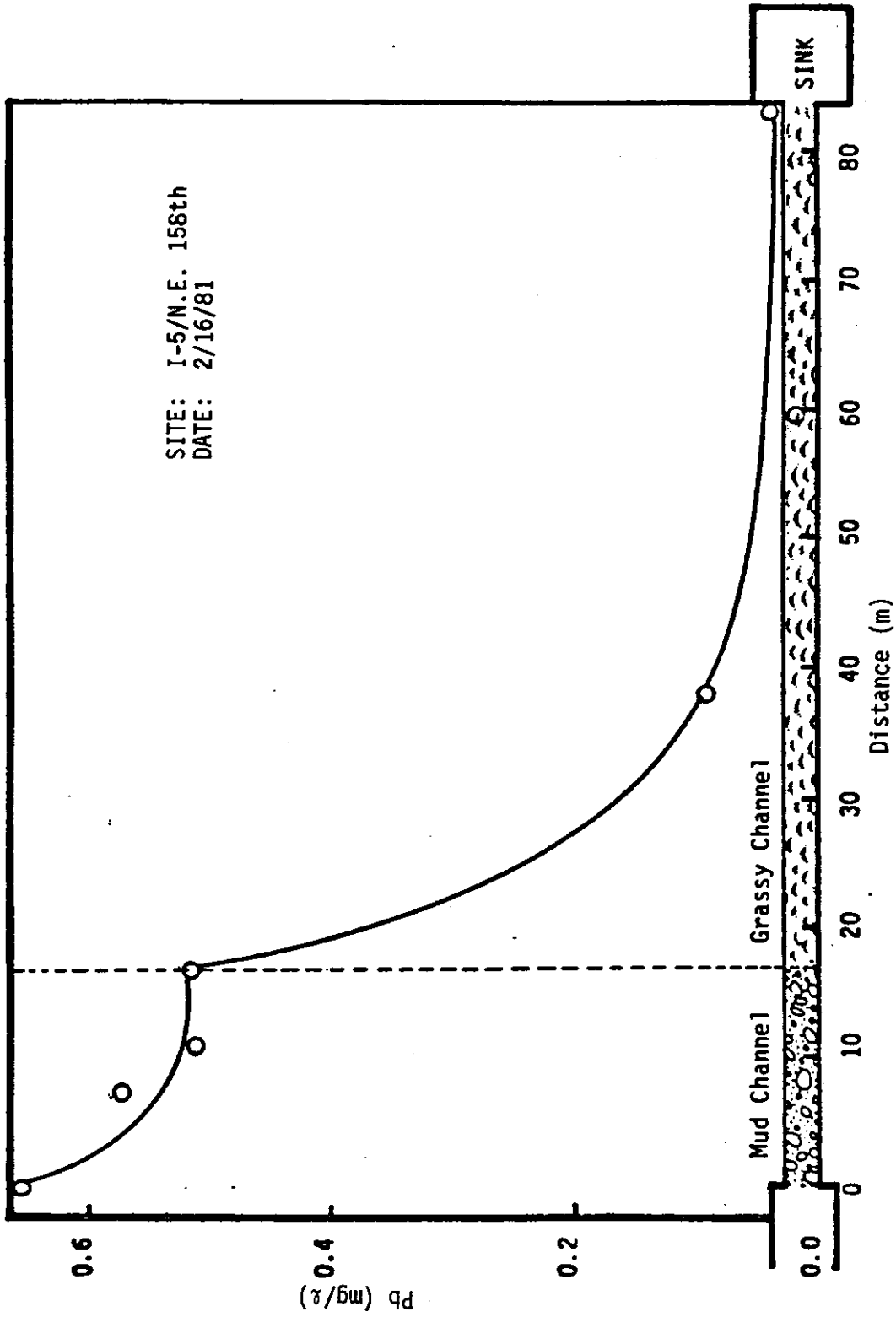


Figure 3: Typical Pattern of Reduction in Runoff Lead Concentration with Distance Traveled in Mud and Grassy Channel.

Table 9. Grass Channel Metal Removal Efficiencies (Note 1) (Note 2)

Site	Distance (m)	No. Samples	Removal Efficiency (%)					
			Cd	Cu	Fe	Mn	Pb	Zn
I-5 @ N.E. 158th	15-21	6	51.4 (46.0)	24.6 (24.3)	53.8 (31.2)	40.5 (25.2)	59.3 (18.8)	35.5 (16.1)
	31	1	60.0	53.5	53.1	50.6	70.4	31.4
	40-50	6	80.0 (44.7)	39.2 (22.6)	73.4 (12.6)	61.2 (32.3)	72.0 (15.0)	69.7 (10.4)
	67	6	100 (0)	63.1 (24.0)	76.7 (9.2)	54.3 (43.2)	83.8 (11.7)	69.7 (10.4)
I-5 @ N.E. 159th	15-20	2	100 (Note 3)	40.1 (37.8)	39.7 (11.4)	59.4 (1.4)	37.5 (0.1)	23.6 (14.6)
	30-40	2	100 (Note 3)	51.1 (19.2)	35.1 (17.6)	62.0 (0.6)	54.1 (5.0)	50.8 (9.8)
	50-60	2	34.8 (Note 3)	20.3 (19.7)	54.0 (2.1)	75.0 (7.8)	66.9 (20)	64.2 (1.3)
	67	1	(Note 3)	43.4	62.0	93.3	90.2	65.4
	77	2	(Note 3)	57.5 (7.4)	70.5 (33.9)	91.8 (6.5)	80.6 (15.3)	72.1 (14.6)
I-405 @ Kirkland	2.5	1	(Note 3)	< 0	3.6	1.2	2.9	2.1
	10.0	1	(Note 3)	29.3	39.8	49.2	58.6	16.6
	15.0	1	(Note 3)	51.9	54.9	83.6	68.1	19.4
	20.0	1	(Note 3)	63.7	49.9	81.9	77.3	45.9
	25.0	1	(Note 3)	70.7	63.3	83.4	86.7	57.1
I-5*	2.5	1	< 0	< 0	8.1	19.3	2.1	12.9
	5.0	1	45.8	34.4	68.0	72.9	72.4	60.2
	15.0	1	100	68.1	80.4	84.7	78.5	93.2
	25.0	1	100	53.3	76.0	78.1	82.4	94.0

Note: (1) Distance runoff flowed in channel from beginning of vegetated area.
 (2) Mean (standard deviation) given for multiple samples.
 (3) One or more values were below detectable limit.

Table 10: Statistics for Predictions of Lead Removal Efficiencies by Grass Channels of Various Lengths

Channel Length (m)	Predicted Removal Efficiency (Percentage)	
	Mean	95 Percent Confidence Interval
20	59.4	40.9 - 77.9
40	80.5	68.4 - 92.7
60	90.3	82.0 - 98.6

Table 11: Grass Channel TSS, VSS and COD Removal Efficiencies

Channel Length (m)	Removal Efficiency (Percentage)		
	TSS	VSS	COD
21	90.4	90.9	81.5
43	93.2	86.4	81.5
67	94.5	100	88.3

A conservative interpretation of the experimental measurements and the statistical analysis of the data indicates that a 60 m grass channel of small slope can be relied upon to reduce highway runoff Pb concentrations by 80 percent or more. Removal efficiencies for more soluble metals are less but should be approximately 60 percent for Cu and 70 percent for Zn in a 60 m channel. Results from the I-405 and I-5 sites suggest that effective metal reductions may be obtained with considerably shorter grass ditches. Additional work is required to document fully the conditions consistent with high removal efficiencies and establish and validate predictive expressions.

During one storm event at the I-5 at N.E. 158th Street site, TSS, VSS and COD concentrations were measured in addition to the various metals. Table 11 summarizes the removal efficiencies observed. Reduction of these pollutants was quite complete within the first 20 m of grass channel transport, apparently due to the rapid loss of large particulates. A minority of the COD was seemingly dissolved and, like the dissolved metals, persisted through the channel.

An important question posed by the use of grass channels to treat stormwater runoff concerns pollutant accumulation in the channel soils and the probability of eventual release. To provide some insight in this area, Pb concentrations were measured in the top 1 cm of the soils in the channel at I-5 and N.E. 158th Street. Figure 4 illustrates the variation along the mud and grass portions of the ditch. The initial bare section exhibited poor Pb retention. In the grass portion, concentrations followed a skewed Gaussian distribution, with a maximum about 30 m from the beginning of the grass cover. It is hypothesized that the maximum represents the point of dynamic chemical equilibrium between the liquid and solid phases. It is expected that contaminant break-through would not occur unless this point shifted to the end of the channel. Further research is required to test

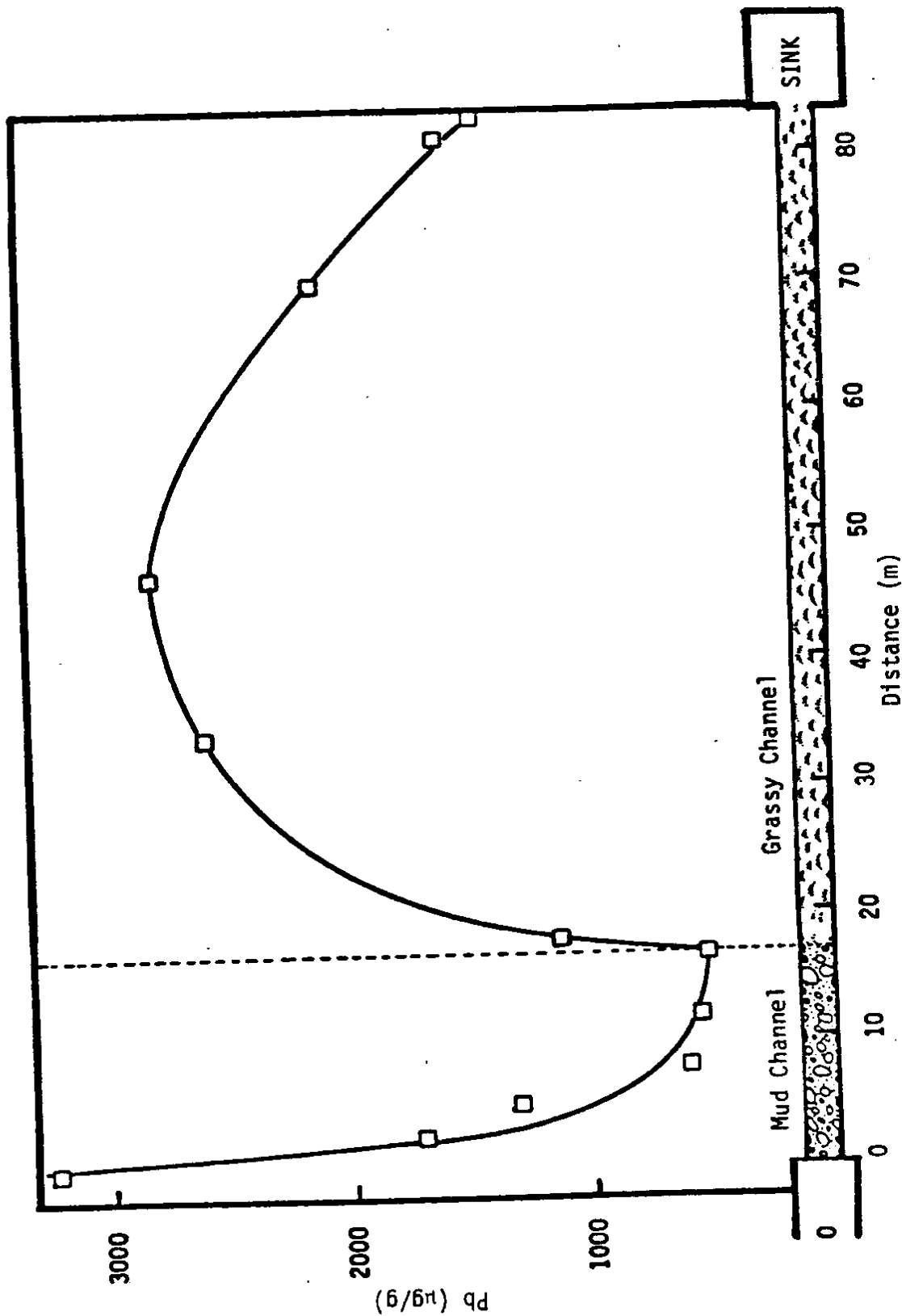


Figure 4: Pb Concentration in Upper 1 cm of Dry Sediment from Mud and Grass Sections of Channel at I-5/N.E. 158th Site.

these hypotheses. If they are true, periodic soil core sampling could be performed to evaluate the condition of grass runoff treatment channels and schedule ditch maintenance when needed.

The question of metals release was further evaluated by exposing roadside soils to solutions of different pH. Table 12 presents the experimental results. In all cases metal release increased as pH decreased. Among the metals, Pb and Zn were most sensitive to pH change. Interpolation using the Pb and Zn release versus pH plots, Figure 5, indicates pH 4 would cause the release of approximately 30 percent of the adsorbed Pb and Zn. Therefore, significant quantities of metals retained in highway runoff transport channels could be released by waters acidified by sulfates and nitrates in precipitation or accidentally spilled chemicals. Additional tests demonstrated that adsorbed metals were released within one hour after first contact with a low pH solution.

Particle Size Fractionation Study

The transport of solid phase pollutants is a function of particle size distribution. A larger particle, with its associated pollutant load, will settle closer to the source than a smaller particle. In order to determine the potential for Pb removal while runoff flows in a channel, solids swept from the I-5/N.E. 158th Street shoulder were size-fractionated and analyzed for Pb.

Table 13 summarizes the results of this study. The smaller size fractions contained more Pb per unit weight than the larger fractions. The largest particles, however, held most of the total lead mass. The consequences of this distribution may be seen in the pattern illustrated in Figure 4. Large particles, containing relatively large quantities of Pb settled sooner, while smaller particles, holding small Pb masses, were carried

Table 12: Metal Concentrations Released from Roadside Soil Sample at Various pH Values.

<u>pH</u>	<u>Cd</u> <u>($\mu\text{g/g}$)</u>	<u>Cu</u> <u>($\mu\text{g/g}$)</u>	<u>Fe</u> <u>($\mu\text{g/g}$)</u>
0.0	6.04	101	34,400
1.1	3.61	75.0	5,000
2.0	3.50	42.4	2,430
2.3	2.56	60.0	1,600
3.7	2.18	20.3	38.0
5.1	0.95	2.2	4.1

<u>Mn</u> <u>($\mu\text{g/g}$)</u>	<u>Pb</u> <u>($\mu\text{g/g}$)</u>	<u>Zn</u> <u>($\mu\text{g/g}$)</u>
257	7,420	1,050
138	7,280	966
71.4	6,630	824
117	5,200	810
21.7	2,230	588
6.28	25.2	136

CONCLUSIONS

The results of the research demonstrate that draining highway runoff directly to receiving waters via pipes or paved or bare channels should be avoided. Flow through grass channels substantially reduces heavy metal contaminants and, on the basis of a few data, organic components as well. The objective of maintenance operations should then be to nurture vegetation in drainage conduits, rather than to remove it in order to increase velocities. Maintenance would then concentrate on preventing succession from grasses to larger growth. Periodically, should tests indicate that channel sediment concentrations are maximum near the end of the channel, threatening pollutant break-through, it may be necessary to remove the sediments and replant grasses.

Intending to operate runoff channels in grass would, in general, necessitate different designs than employed where the operating mode would be bare surface. Hydraulically, the channel must be capable of transporting water from the highway, such that ponding is prevented, at the reduced velocity caused by friction with vegetation. Water pollutant removal considerations must also be incorporated in the design to employ channels as effective treatment devices.

Relationships between treatment performance and channel geometry, slope and velocity are not yet sufficiently well-established to offer reliable design guidelines. The most that can be concluded from the results reported is that a slightly sloped channel of hydraulically sufficient cross-sectional area and 60 m in length is capable of removing 60-80 percent of the Pb, Zn and Cu in highway runoff. It may be surmised, but has not been proven, that greater contaminant reduction would accrue from greater length. There are indications that comparable treatment can occur in considerably shorter

channels. More extensive and focused research is required to pinpoint conditions favorable to treatment and formulate design bases.

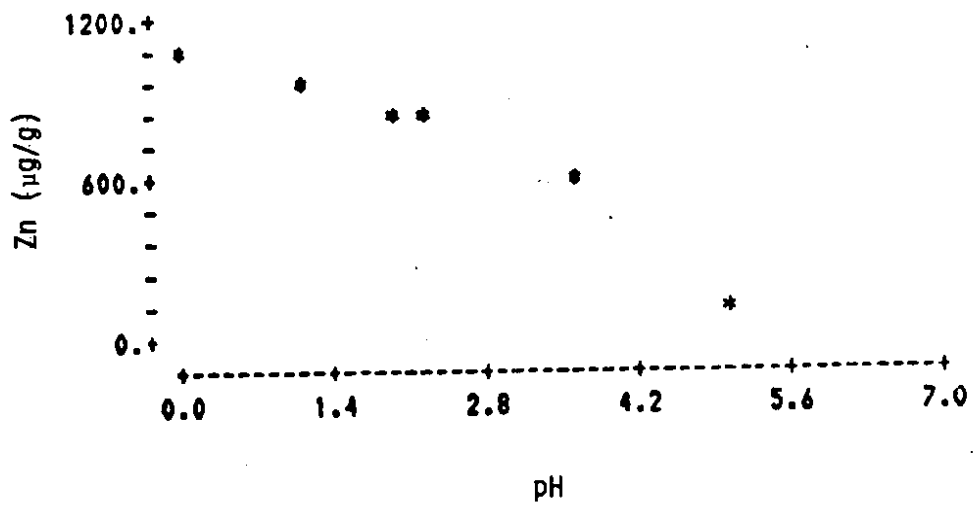
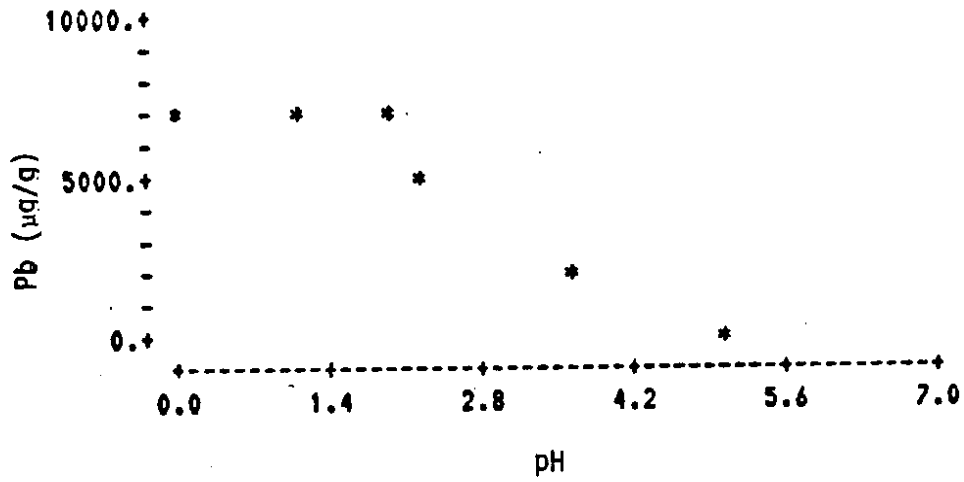


Figure 5: Pb and Zn Release from Roadside Soil Samples Versus pH.

farther. Thus, the channel sediment concentration pattern is skewed toward the beginning of the channel.

Table 13. Lead Content of Highway Particle Size Fractions.

Particle Size (μm)	Weight %	Pb Concentration of Fraction (mg/g)	% Total Pb Associated With Fraction
< 0.2	2.44	(1)	0.14 ⁽¹⁾
0.2-5	0.41	24.83	0.96
5-10	0.89	19.46	1.66
10-20	3.93	14.83	5.59
> 20	92.34	10.37	91.67
Total	100	10.45	100

Note: (1) % total Pb includes quantity in solution, as well as that associated with the solids.

REFERENCES

- American Public Health Association, Standard Methods for the Examination of Water and Wastewater. American Public Health Association, Washington, D.C. (1975).
- Bortleson, G.C. and G.F. Lee, "Recent Sedimentary History of Lake Mendota, Wisconsin." Environ. Sci. Technol., 6, 799 (1977).
- Brief, R.S., "Air Lead Concentrations from Automobile Engines." Arch. Environ. Health, 5, 527 (1962).
- Chui, T.W., "Highway Runoff in Washington State: Model Validation and Statistical Analysis," M.S.E. Thesis, University of Washington, Seattle (1981).
- Ganley, J.T. and G.S. Springer, "Physical and Chemical Characteristics of Particulates in Spark Ignition Engine Exhausts." Environ. Sci. Technol., 8, 340 (1974).
- Getz, L.L., A.W. Haney, R.W. Larimore, J.W. McNurney, H.V. Leland, P.W. Price, G.L. Rolfe, R.L. Wortman, J.L. Hudson, R.L. Solomon, and K.A. Reinhold, "Transport and Distribution in a Watershed Ecosystem," in Lead in the Environment, R. Boggess, Ed., National Science Foundation, Washington, D.C., pp. 105 - 134 (1975).
- Gupta, M.K. and N.P. Kobriger, "Sources and Migration of Highway Runoff Pollutants," Envirex, Inc., Milwaukee (1980).
- Habibi, K., "Characterization of Particulate Lead in Vehicle Exhaust-Experimental Techniques." Environ. Sci. Technol., 4, 239 (1973).
- Hassett, J.J., "Capacity of Selected Illinois Soils to Remove Lead from Aqueous Solution." Communications in Soil Science and Plant Analysis, 5, 499 (1974).
- Hildebrand, E.E. and W.E. Blum, "Fixation of Emitted Lead by Soils." Z. Pfl Ernähr. Düng. Bodenk., 3, 279 (1975).
- Hinrichs, D.J., J.A. Faisst, D.A. Pivetti, and E.D. Schroeder, "Assessment of Current Information on Overland Flow Treatment of Municipal Wastewater," U.S. Environmental Protection Agency, Washington, D.C., EPA-430/9-80-002 (1980).
- Hopke, P.K., R.E. Lamb, and D.F.S. Natusch, "Multielemental Characterization of Urban Roadway Dust." Environ. Sci. Technol., 14, 164 (1980).
- Jackson, M.L., Soil Chemical Analysis -- Advanced Course, 2nd ed., University of Wisconsin, Madison (1969).
- Kahn, H.L., S.B. Smith, Jr., and R.G. Schleicher, "Plasma Emission Spectroscopy - The Present Status," Instrumentation Laboratory, Inc., Wilmington, MA (1979).

- Kao, D.T., "Determination of Sediment Filtration Efficiency of Grass Media, Vol. 1, Sediment Filtration Efficiency of Continuous Grass Media." Water Resources Research Institute, University of Kentucky, Lexington, Research Report No. 124 (1980).
- Kerri, K.D., M. Baad, E.C. Shirley, R.B. Howell, E. Torguson, and G. Winters, "Water Quality Manual, Vol. V: Chemical, Bacteriological, and Ecosystem Analysis of Water from Highway Sources for Environmental Impact Assessments," Federal Highway Administration, Washington, D.C. (1976).
- Lagerwerff, J.V. and D.L. Brower, "Exchange Adsorption or Precipitation of Lead in Soils Treated with Chlorides of Aluminum, Calcium and Sodium." Proc. Soil Sci. Soc. Amer., 37, 11 (1973).
- Laxen, D.P.H. and R.M. Harrison, "The Highway as a Source of Water Pollution: An Appraisal with the Heavy Metal Lead." Water Res., 11, 1 (1977).
- Motto, H.L., R.H. Daines, D.M. Chilko, and C.K. Motto, "Lead in Soils and Plants: Its Relationship to Traffic Volume and Proximity to Highways." Environ. Sci. Technol., 4, 231 (1970).
- Novotny, V. and G. Chesters, Handbook of Nonpoint Pollution, Sources and Management. Van Nostrand Reinhold Company, New York, p. 322 (1981).
- Nriagu, J.O., "Lead Orthophosphates - IV: Formation and Stability in the Environment." Geochim. Cosmochim. Acta, 38, 887 (1974).
- Pitt, R.E. and G. Amy, "Toxic Materials Analysis of Street Surface Contaminants," U.S. Environmental Protection Agency, Washington, D.C., EPA-R2-73-283 (1973).
- Scanlon, P.F., "A Study of Lead, Cadmium, Nickel and Zinc levels in Soil, Vegetation, Invertebrates and Mammals Associated with Highways of Different Traffic Densities," Report to U.S. Department of Transportation by Department of Fisheries and Wildlife Sciences, Virginia Polytechnic Institute and State University, Blacksburg (1977).
- Shaheen, D.G., "Contributions of Urban Roadway Usage to Water Pollution," Biospherics, Inc., Rockville, MD, EPA-600/2-75-004, NTIS Pb-245-854 (1975).
- Sylvester, R.O. and F.B. DeWalle, "Character and Significance of Highway Waters: A Preliminary Appraisal," Report to Washington State Highway Commission by Department of Civil Engineering, University of Washington, Seattle (1972).
- Ter Haar, G.L., D.L. Lenane, J.N. Hu, and M. Brandt, "Composition, Size and Control of Automotive Exhaust Particulates." J. Air Poll. Control Assoc., 22, 39 (1972).

U.S. Environmental Protection Agency, "Innovative and Alternative Technology Assessment Manual," U.S. Environmental Protection Agency, Washington, D.C., EPA-430/9-78-009 (1980).

Ward, A.F., "Inductively Coupled Argon Plasma Spectroscopy." Amer. Lab., 10, 79 (1978).

Zimdahl, R.L., "Impact on Man of Environmental Contamination Caused by Lead," In Interim Report, National Science Foundation Grant GI-4, H.W. Edwards, Ed., Colorado State University, Fort Collins, p. 98 (1972).