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HIGHWAY DEICING SALTS AND THE MOBILIZATION OF
SELECTED HEAVY METALS FROM STREAM SEDIMENTS

by

Harlie David Cole

A Dissertation
Submitted to the
Faculty of The Graduate College
in partial fulfillment of the
requirements for the
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Western Michigan University
Kalamazoo, Michigan
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HIGHWAY DEICING SALTS AND THE MOBILIZATION OF SELECTED HEAVY METALS FROM STREAM SEDIMENTS

Harlie David Cole, Ph.D.

Western Michigan University, 1990

This study was undertaken to: (a) determine the effect of sodium chloride concentration on mobilizing cadmium, copper, lead, nickel, and zinc from stream sediments; (b) determine if chloro-metal complexes may play a role in any such mobilization; and (c) determine the correlations between chloride ion and each of these metals in an urban stream during winter road-salting periods.

The drainage basin of the Red Run, an urban stream draining all or parts of several cities north of Detroit, Michigan, was chosen as a study site. Stream sediments containing the five heavy metals were stirred with sodium chloride or sodium nitrate solutions and heavy metal concentrations were determined in aliquots removed at specified time intervals. Cadmium concentration was found to have a high correlation ($r=.90$) and zinc a low correlation ($r=.49$) with chloride concentration. Cadmium was also found to be released into chloride solutions to a greater extent than into nitrate solutions. A similar but more subdued effect was found for zinc, but only for longer desorption periods. Copper was found to have a low, negative correlation ($r=-.38$) and nickel little, if any, negative correlation ($r=-.29$) with chloride concentration. Lead concentrations were below limits of detectability. These results indicate that the release of cadmium and, to a lesser extent, zinc, from stream sediments can be

facilitated by the formation of soluble chloro-metal complexes.

Winter stream studies revealed a moderate chloride-zinc correlation ($r=.57$) at one of three sampling stations. Otherwise, only low to little, if any, chloride-metal correlations could be detected for cadmium, copper, nickel or zinc at any location. Lead was again generally below limits of detectability.

Deicing salt was found to contain zinc, but only at levels calculated to contribute minimally to total zinc levels at each of the three sampling sites.

Changes in stream sediment heavy metal concentrations over an entire winter road-salting period, or over a single snow and road-salting event could not be unequivocally attributed to the use of highway deicing salts. Instead, differences in sediment heavy metal concentrations appeared to be more closely related to differences in the percent of sediment finer than 0.063 or 0.125 mm.

A general decline in both total and exchangeable sediment cadmium levels was observed throughout the study. This decline was most likely a response of Red Run sediments to controls placed on metal levels entering and being discharged from a wastewater treatment plant.

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metals from stream sediments**

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Western Michigan University, 1990

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Harlie David Cole

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CHAPTER I

INTRODUCTION AND LITERATURE REVIEW

Heavy Metals in the Environment

Beginning in antiquity, but mainly since the industrial revolution, man has been taking naturally occurring complexes of metals from the ground, refining and concentrating them, and using them for industrial, commercial, and domestic purposes. These metals are eventually released back into the environment where they have the potential to cause harm. The magnitude of the problem has been underscored by Nriagu and Pacyna (1988) in a quantitative assessment of worldwide contamination of air, water, and soils by trace metals. They point out that, although the 1984 atmospheric emission rates for copper, lead, and zinc were lower than those for 1975, "on average the anthropogenic emissions of As, Cd, Cu, Ni and Zn exceed the inputs of these elements from natural sources by two-fold or more; in the case of lead, the ratio of anthropogenic to natural emission rates is about 17" (p. 138). The inventories presented by Nriagu and Pacyna (1988) of trace metals mobilized by humans into the biosphere clearly show that mankind has become the dominant factor in the global cycling of these metals. These authors illustrate dramatically the magnitude of the human-induced mobilization of trace metals into the biosphere.

The annual total toxicity of all the metals mobilized, in fact, exceeds the combined total toxicity of all the radioactive and organic wastes generated each year, as measured by the quantity of water needed to dilute such wastes to drinking water standard. (p. 139)

In his opening address to the 1986 International Symposium on Metal Speciation, Separation & Recovery, Patterson (cited in Haggin, 1986) pointed to conservation of resources as another reason to be concerned with metals disposal. The limited reserves of many metals makes them particularly valuable. "Included among the more valuable metals are aluminum, cadmium, chromium, cobalt, copper, iron, lead, mercury, nickel, and zinc. The cumulative demand for [most of] these metals will exceed their known reserves before the end of the century" (Haggin, 1986, p. 42). Recovering them from wastes for reuse would thus contribute to alleviating both concerns with supply and concerns with pollution. Based on potential problems of a metal's toxicity in a landfill and on its strategic value, Patterson has prioritized a list of metals for which to develop recovery technology. The metals of highest priority are cadmium, lead, mercury, and zinc. Of medium priority are cobalt, copper, and nickel. Aluminum, chromium, and iron are in the lowest priority group.

Because the heavy metals¹ are not available or used to an equal extent, only a relative few give rise to widespread environmental concern. Even though approximately 59 elements may be considered "heavy" metals (specific gravity greater than 5.0), only 18 are

¹The terms "toxic metals," "heavy metals," "trace metals," and "trace elements" have come to be used synonymously in the literature and will be so used in this review.

considered both very toxic and potentially present in concentrations and in physico-chemical forms to be relatively available to biological systems (Table 1). In 1972, Hood and Kelley, using data from the early 1960s, estimated that eight of these 18 metals (Table 1) were being mobilized by man into the environment at rates greater than those occurring naturally. Their estimates compared only amounts of metals mined each year to estimated amounts delivered by rivers to the oceans and were crude at best. More recent atmospheric budgets (Nriagu & Pacyna, 1988; Pacyna, 1986) have indicated that of the 18 toxic and accessible metals, six have anthropogenic emissions greater than those from natural sources (Table 1).

Each of the rapidly mobilized metals can cause its own particular problems depending on its concentration, its form in the aquatic environment, the presence of other metals or toxic substances, the type and condition of organisms present, and the use which is made of the water. Some metals may have a positive biological role or may even be required by aquatic organisms at trace concentrations. Chapman (1978) has developed a general ranking of toxicity toward aquatic biota of nine trace metals (Table 2).

The biological and health effects of trace metals have been summarized in a number of sources (for example, DiFerrante, 1979; Luckey & Venugopal, 1977; National Research Council, 1977; Oehme, 1979; and U.S. Environmental Protection Agency [E.P.A.], 1976). Maximum concentration limits have been recommended for most of the common trace metals which may be found in water (Table 3). Most of the drinking water criteria are based on known deleterious health

Table 1
Toxic Metals of Particular Environmental Concern

Toxic and Relatively Accessible	Anthropogenic Mobilization Higher than Natural Rate	Anthropogenic Atmospheric Emissions Exceed those from Natural Sources
Co, Ni	Ni	Ni
Cu, Zn	Cu, Zn	Cu, Zn
Sn ^a , Se ^a	Sn	
As ^a , Te ^a		As
Pd ^a , Ag ^a	Ag	
Cd, Pt ^a		Cd
Au ^a , Hg ^a	Hg	
Tl ^a , Pb ^a	Pb	Pb
Bi, Sb	Sb	

Note. The data in column 1 are from "Metabolic Cycles for Toxic Elements in the Environment" (p. 52) by Wood et al., 1975. In International Conference on Heavy Metals in the Environment. Toronto, Ontario, Canada.

The data in column 2 are compiled from "Contamination and Coastal Pollution" (p. 154) by Hood and Kelley, 1972. In B. H. Ketchum (Ed.), The Water's Edge: Critical Problems of the Coastal Zone. Cambridge, Massachusetts: The MIT Press.

The data in column 3 are compiled from "Quantitative assessment of worldwide contamination of air, water and soils by trace metals." by J. O. Nriagu and J. M. Pacyna, 1988, Nature, 333, 134-139.

^aMetal alkyls stable in aqueous systems and reported to be biomethylated.

Table 2
General Ranking of Toxicity of Metals to Aquatic Biota

Metal	Toxic Level ^a
Ag, Cd, Hg	10^{-8}
Cu	10^{-7}
Ni, Pb, Zn	10^{-6}
Sb	10^{-5}
Sn	10^{-4}

Note. From "Toxicological considerations of heavy metals in the aquatic environment" (p. 70) by Chapman, G., 1978. In, Toxic Materials in the Aquatic Environment. Corvallis, Oregon: Oregon State University.

^aMolar concentration.

effects. For a few metals (copper, iron, manganese, zinc), however, the drinking water criteria are based primarily on aesthetic reasons such as taste or staining problems.

As a result of a 1978 court settlement between the United States Environmental Protection Agency (EPA) and a group of environmentally concerned plaintiffs, the EPA was required to publish a list of toxic pollutants for which industrial effluent limitations and guidelines would be required (Keith & Telliard, 1979). This settlement resulted in a list of 129 Priority Pollutants, 13 of which were metals. For each of the Priority Pollutants an average of 2617 industrial waste-water samples were obtained and analyzed. This was done in order to define which of the Priority Pollutants were in the

Table 3
Quality Criteria for Water

Metal	Drinking Water ^a Standards	Criteria for ^a Aquatic Life
As	50	0.04
Cd	10	0.4 - 1.2 ^b
Cr	50	100
Cu	1000	— ^c
Fe	300	1000
Pb	50	0.3 - 3 ^b
Mn	50	— ^c
Hg	2	.05
Ni	NR ^d	— ^c
Se	10	— ^c
Ag	50	— ^c
Zn	5000	— ^c

Note: Data compiled from Quality Criteria for Water, U.S. Environmental Protection Agency, 1976.

^aConcentration in ug/L. ^bexact criterion depends on hardness.
^cspecific criteria depend on species present. ^dNR = none recommended.

wastewaters of 28 (for metals) to 32 (for organics) industrial categories and subcategories. In this Screening Phase it was found that only 10 of the 129 pollutants were detected in at least 30 percent of the industrial wastewater samples for which they were analyzed. Out of this group of ten, six were metals, each of which was found in at

least 25 of the 28 industrial categories and subcategories. Thus, these six trace metals (cadmium, chromium, copper, lead, nickel, and zinc) were found in a disproportionate percentage of the samples for which the Priority Pollutants were analyzed.

Different regions of the United States may have their own unique trace metal problems. For example, PLUARG (Pollution from Land Use Activities Reference Group, 1978), in its study of the input of trace metals to the Great Lakes, ranked the following elements as present or potential hazards requiring close surveillance:

- I. Mercury, lead
- II. Arsenic, cadmium, selenium
- III. Copper, zinc, chromium, vanadium

Heavy metals as aquatic pollutants are particularly worrisome for three reasons. First, the heavy metals are conservative pollutants. That is, they are not degraded into other inert substances like most organic pollutants. They have, essentially, infinite lifetimes. Second, although most of the heavy metals quickly bind to clay particles or are precipitated out in neutral and alkaline receiving waters, acid discharges and acid precipitation can resolubilize them and convert them into forms more readily assimilated by living organisms (Capos, 1983; Haines, 1981). Even in the absence of an acidic environment, some metals may still bioaccumulate in aquatic organisms. Third, it appears that several of the heavy metals, even while bound up in bottom sediments, may be bio-methylated by bacteria and converted to especially toxic organometallic forms (Novotny & Chesters, 1981).

Cadmium

Cadmium and zinc are geochemically related and are reported to occur in most minerals and soils in cadmium to zinc ratios of 1:100 to 1:1000 (Thornton & Abrahams, 1984). Although cadmium is found in the rare mineral greenockite, cadmium sulfide, essentially all commercial cadmium is a by-product of zinc production. Cadmium can be separated from zinc by fractional distillation or selective electrolytic deposition. Since most commercial applications of zinc are unaffected by the small quantities of cadmium present, the extra effort and expense to remove it is not made. Thus, because the cadmium is not removed, pollution from zinc products also entails a lesser but concomitant cadmium pollution.

The first widely publicized case of poisoning attributed to cadmium pollution occurred along the Jintzu River, Toyama Prefecture, Japan in the late 1940s and 1950s. A zinc mine operated by the Makioko Company upstream of the affected area discharged its milling waste and flotation sludge directly into the river. Kobayashi found the average cadmium concentration of rice crops grown in areas irrigated by the contaminated Jintzu River to be over 10 times the average in rice from all other areas of Japan (cited in Forstner & Wittman, 1981). Many inhabitants of the area suffered kidney damage. The more severe cases of cadmium poisoning exhibited painful skeletal deformities which led to the condition being labeled "itai-itai" (meaning "ouch-ouch") disease (Friberg, 1971).

Concerning other sites of cadmium pollution, Forstner noted at

the International Symposium on Metal Speciation, Separation & Recovery held in 1986 that,

although the situation is less than catastrophic at present, there is potential danger in the Hudson River estuary because of pollution from a battery factory.... Similarly, effluents from an electronics plant present a danger in the Hitachi area near Tokyo. Other potentially dangerous areas include Palestine Lake, a village in Indiana, because of plating wastes; Solfjord, Norway, and Derwent, Tasmania, from smelter operations; and the Neckar River basin in West Germany from pigment wastes. None of these latter situations have yet resulted in pronounced effects among the human populations, but the potential is there. (Haggin, 1986, p. 38)

The major sources of cadmium entering the biosphere are non-ferrous metals smelters, with coal and oil combustion, refuse incineration, and urban refuse in general also making major contributions (Nriagu & Pacyna, 1988). Cadmium finds use in end-products such as batteries and tires, metal platings, low melting alloys, pigments, and the powders in fluorescent light bulbs. As these products wear out or are discarded, their cadmium content is released to the environment.

Cadmium pollution is not restricted to a technological, urban setting. In rural areas, cadmium can be introduced through the use of fertilizers. Western European countries have become concerned about the levels of cadmium that are accumulating in their agricultural soils (O'Sullivan, 1988). Cadmium is a natural component of rock phosphate used to make superphosphate for fertilizers. These phosphate fertilizers may contain 20-120 mg of cadmium per kg of phosphate content depending on the source of the raw materials used to make them. In the Federal Republic of Germany, 3.5 grams of cadmium per hectare per year are estimated to be introduced to the

soils from these fertilizers (Kloke, Sauerbeck, & Vetter, 1984). In Switzerland, heavy use of fertilizers and the practice of composting have increased the rate of accumulation of cadmium in soils.

Forstner estimated (cited in Haggin, 1986) that if these practices continue, the concentration of cadmium in composted soils will increase to the point that, by the year 2007, plants grown in the compost will be prohibited from consumption.

Cadmium was detected in 40 percent of the samples taken during a 1970 reconnaissance of selected minor elements in surface waters of the United States (Durum, Hem, & Heidel, 1970). Most concentrations of cadmium ranged from 1 to 10 ug/L², but about 4 percent of the river samples had concentrations in excess of 10 ug/L. The maximum concentration found was 130 ug/L. In an examination of water quality trends from 1974 to 1981 at more than 300 locations on major rivers in the United States, Smith, Alexander, and Wolman (1987) found widespread increases in the dissolved forms of cadmium. Increasing trends in cadmium concentration were found most frequently in streams of the northern Midwest. These increases were attributed primarily to increased atmospheric deposition of fossil-fuel combustion products.

A 1969 survey (McCabe, Symons, Lee, & Robeck, 1970) of 969

²Several concentration units are used interchangeably in the literature. The most common units and their use to describe water and sediment are:

	<u>water</u>	<u>sediment</u>
parts per million (ppm) =	mg/L = ug/mL	mg/kg = ug/g
parts per billion (ppb) =	ug/L	ug/kg

public water supply systems in the United States found only 3 systems yielding samples containing cadmium in excess of the existing 10 ug/L drinking water standard. One of these samples, however, had a cadmium concentration of 3940 ug/L.

Because of its known adverse effects on health, the United States Environmental Protection Agency (1985) has proposed lowering the maximum contaminant level standard for cadmium in drinking water from 10 to 5 ug/L.

Copper

Copper is widespread in the earth's crust and occurs at an average concentration of 50 ppm (National Research Council, 1977). Background levels of copper in natural surface waters are usually below 20 ug/L (U.S. E.P.A., 1985). Kopp and Kroner (cited in U.S. E.P.A., 1976) found copper in 74 percent of more than 1500 surface water samples in the United States. Concentrations ranged from 1 to 280 ug/L with a mean concentration of 15 ug/L.

Copper is considered to be an essential trace element in human and plant nutrition. A daily copper intake of 2 mg is considered adequate for human health (U.S. E.P.A., 1985). Both copper deficiency and toxicosis are rare in humans. Copper imparts an undesirable metallic taste to water in concentrations above approximately 1 mg/L. This taste threshold renders water unpalatable if it contains copper concentrations high enough to be dangerous to humans.

The United States Environmental Protection Agency (1988) has proposed a national primary drinking water regulation specifying a

maximum contaminant level of 1.3 mg/L for copper in water entering the distribution system. Concentrations above this level may be produced at the tap due to dissolution of copper in water pipe and plumbing fixtures. The 1969 survey of 969 water supply systems reported by McCabe et al. (1970) showed an average copper concentration of 0.134 mg/L. The highest concentration found was 8.35 mg/L. Eleven of the water systems contained copper in excess of the current drinking water standard of 1 mg/L.

The concentration at which copper is toxic to aquatic organisms is species specific and depends on the pH, alkalinity, and hardness of the water. The softer the water or the lower the pH, the lower the copper concentration necessary to produce toxic effects in aquatic organisms. It appears that concentrations of a few hundredths of a milligram per liter may be harmful for many aquatic species (Environmental Studies Board, 1972; U.S. E.P.A., 1976). The practice of adding copper sulfate to reservoirs, lakes, water towers, and powerplant condensers uses this effect to suppress undesirable growths of algae.

Lead

Humans have used lead and lead products since antiquity. English terms such as "plumbing" and "plumber" are derived from the Latin word for lead, "plumbum," and reflect an historic use of lead in water pipes and fixtures. The Romans were the first to use lead on a large scale. Lead was mainly used for piping and cisterns to supply water to towns and houses, but was also used for roofing,

cooking pots, plates, drinking cups, weights, and ship anchors. Bronze cooking pots were often lined with lead to prevent the taste of copper from contaminating the contents (Smith, 1986). The production of lead during the Roman period (50 B.C. - 500 A.D.) has been estimated to be about 540 grams per person per year. This compares to present-day industrial consumption in the United States of about 5500 grams per person per year (Thornton & Abrahams, 1984).

Today, lead finds its main use in the automotive industry-- principally lead storage batteries and, to a decreasing extent, as a fuel additive. Lead is also used in cable sheathing, specialty pipe applications, sheeting for building applications, bearings, ammunition, and stabilisers in plastics. A large proportion of lead fabricated into products is recovered and recycled.

Lead has no known beneficial or nutritional effects. It is a toxic metal that accumulates in bone and tissue and produces neurological dysfunction. Children exposed to elevated levels of environmental lead appear to be a particularly sensitive group. The Environmental Studies Board of the National Academy of Sciences (1972) states that there is a "narrow gap between the quantities of lead to which the general population is exposed through food and air in the course of everyday life, and the quantities that are potentially hazardous over long periods of time" (p. 70). The effects of lead toxicity in humans have been studied widely and summarized in a number of excellent reviews (Lansdown & Yule, 1986; Needleman, 1984; Singhal & Thomas, 1980; U.S. E.P.A., 1976, 1985, 1988).

Weiss, Whitten, and Leddy (1972) compared lead in human hair

dating from 1871 to 1923 to hair samples taken in 1971. Adult antique hair was found to contain 77-110 ug of lead per gram of hair compared to 5.4-7.7 ug/g for contemporary hair. Children's hair from these two time periods was found to contain 144-185 ug/g and 15-17 ug/g respectively. This study indicates that lead exposure among the general population in 1971 was less than it was 50 to 100 years earlier.

The inventories of global anthropogenic emissions of metals to the biosphere presented by Nriagu and Pacyna (1988) indicate that the non-ferrous metals industry and gasoline combustion account for the largest proportion of lead emitted to the atmosphere and aquatic ecosystems. Most of the lead entering natural waters comes from atmospheric deposition (Nriagu & Pacyna, 1988; Veron, Lambert, Isley, Linet, & Grousset, 1987). The International Joint Commission (cited in Hileman, 1988) estimates that approximately 21,305 metric tons of lead are emitted to the atmosphere over the United States each year. Gasoline combustion accounts for 72 percent of these emissions with municipal waste incineration and industrial processes contributing 13 percent and 11 percent respectively.

Because of its known detrimental effects on health, the United States Government and its agencies have taken the following steps to reduce environmental exposure to lead:

1. The maximum allowable content of lead in gasoline has been reduced.
2. The use of lead in pipe, solder, or flux has been prohibited in any system providing water for human consumption.

3. A national primary drinking water regulation has been proposed specifying a maximum contaminant level of 5 ug/L for lead in water entering the distribution system after treatment.

In 1982, a phase-down in the maximum content of lead in leaded gasoline was begun by lowering the allowed level from 2.5 grams of lead per gallon to 1.1 grams (Brown, 1987). This was reduced further in mid-1985 to 0.5 grams per gallon and again January 1, 1986, to 0.1 grams per gallon (Teel, 1985). A complete ban was considered for 1988. This plan was dropped, however, when studies showed that older engines, particularly those used on farm equipment, might be severely damaged if operated on lead-free fuel (Brown, 1987; "Take the Worry," 1988). An official ban on lead in gasoline may be unnecessary, however, since several major oil companies have stopped producing leaded gasoline (Brown, 1987).

Decreases in consumption of leaded gasoline have been reflected in declines in atmospheric lead and lead concentrations in rivers. Elsenreign, Metzger, and Urban (1986) found that annual volume-weighted mean lead concentrations in wet-only precipitation fell from 29 to 4.3 ug/L at an urban collection site in Minnesota and from 5.7 to 1.5 ug/L at a rural site from 1979 to 1983. During this same period, the total amount of lead used in gasoline decreased from 12.95×10^{10} grams to 5.66×10^{10} grams for the U.S. as a whole and from 3.17×10^9 grams to 1.4×10^9 grams for the state of Minnesota.

A 1970 nationwide reconnaissance (Durum et al., 1970) of selected trace metals in surface waters of the United States found lead occurring in 63 percent of the 720 samples in concentrations

most commonly ranging from 6 to 50 ug/L. Alexander and Smith (1988) examined water quality records from about 300 locations on major U.S. rivers for the period 1974 to 1985. Concentrations of dissolved lead declined during the study period at about one-third of the sampling locations whereas only 6 percent of the sites, clustered along the Texas-Gulf Coast and in the Lower Mississippi Basin, showed increases. Declines at nearly all stations occurred from 1979 to 1980. After 1980, dissolved lead concentrations at most locations remained at or near the detection limit of 2 ug/L. Alexander and Smith state that "gasoline-lead consumption in the United States declined approximately 75 percent from 1975 to 1985. More than one-half of this decline occurred from 1979 to 1980" (p. 562). This suggests that the observed declines in dissolved lead at most locations for 1979 to 1980 were most likely the result of the sharp decline in gasoline-lead consumption.

Most lead enters drinking water as a result of corrosion of plumbing (U.S. E.P.A., 1985, 1988). This is particularly a problem with soft, acidic waters that are allowed to stand in contact with lead pipe, lead fittings, or lead-containing solder for some length of time. Some water systems have frequently measured concentrations of lead in morning first draw samples as high as 1 to 2 mg/L. In order to decrease exposure to this source of lead, the Safe Drinking Water Act Amendments of 1986 prohibited the use of solder or flux containing more than 0.2 percent lead and pipe and pipe fittings containing more than 8 percent lead in all public water systems and residential and nonresidential plumbing providing water for human

consumption. In addition, the U.S. Environmental Protection Agency (1988) has proposed lowering the existing national primary drinking water regulation for lead specifying a maximum contaminant level of 50 ug/L to 5 ug/L. The lead concentration would be measured as it enters the distribution system, however, rather than at the tap.

Nickel

Metallic nickel has been known for about 200 years. Its use has increased to the point that, today, there are more than 3000 different alloys containing nickel (Duke, 1980). The production of stainless steel accounts for the largest single use of nickel. Canada is the largest producer of nickel, accounting for approximately one-third of the world's production. Cobalt is usually found with nickel in amounts ranging from a trace to as much as 1 part cobalt to 10 parts nickel (National Research Council, 1975).

The inventories presented by Nriagu and Pacyna (1988) indicate that combustion of oil and coal are the most important sources of airborne nickel. These sources contribute between 60 and 77 percent of the approximately 56,000 metric tons of nickel emitted to the atmosphere each year. Domestic wastewater accounts for almost 60 percent of the 113,000 metric tons of nickel discharged into the world's aquatic environment each year (Nriagu & Pacyna, 1988).

In a survey of major river basins of the United States, Kopp and Kroner (cited in National Research Council, 1975) reported that nickel was found in 16 percent of the samples at an average concentration of 19 ug/L. The highest concentration of nickel, 130 ug/L,

was found in Ohio's Cuyahoga River. A 1969 survey (McCabe et al., 1970) of 969 water supply systems in the United States found an average nickel concentration of 4.8 ug/L at the consumer's tap. A maximum concentration of 75 ug/L was found.

The National Research Council (1975) reported that humans ingest 300-600 ug of nickel per day. "Most of the ingested nickel is excreted in the feces, but a small proportion is absorbed and later excreted in the urine, bile, and sweat" (p. 192). On the basis of animal studies, it appears that nickel salts have a relatively low toxicity when administered orally. Nickel in water is considered to be relatively nontoxic. Consequently, no drinking water standards have been recommended for nickel. Nickel criteria have been recommended, however, for the protection of aquatic organisms. The International Joint Commission (cited in Birge & Black, 1980) has adopted a limit of 25 ug/L for the Great Lakes. The United States Environmental Protection Agency (1976) recommended a criterion of 0.01 times the 96 hour LC_{50} of the most sensitive important species in the locality.

Zinc

Zinc is ranked fourth in annual world consumption of metals, with only iron, aluminum, and copper being produced in greater quantities (Cammarota, 1980). Most zinc is produced from the mineral sphalerite (zinc sulfide). Zinc is widely used in alloys, as a protective coating on other metals, and in chemicals for use in rubber and paints.

Zinc occurs widely in surface waters of the United States. In a five-year survey (1962-1967) of trace metals in U.S. rivers and lakes, Kopp and Kroner (cited in U.S. E.P.A., 1976) found a mean soluble zinc concentration of 64 ug/L. A maximum concentration of 1,183 ug/L was observed in the Cuyahoga River at Cleveland, Ohio. The 1970 reconnaissance of U.S. surface waters by Durum et al. (1970) reported the concentration of zinc in most samples to be in the range of 10-50 ug/L. A few samples, however, exceeded 5000 ug/L. A study of water-quality trends at 288 stations on major U.S. rivers for the period 1974 to 1981 showed a 50th percentile station-mean zinc concentration of 15 ug/L (Smith et al., 1987).

Zinc is present in all body tissue and is required in human metabolism. It is an essential component of nearly one hundred different enzymes (Lehninger, 1932). The Food and Nutrition Board of the National Academy of Sciences-National Research Council (cited in Lehninger, 1982) has suggested a recommended daily allowance (RDA) of 10-15 mg of zinc. Unlike many of the heavy metals, zinc does not appear to accumulate in the human body. The National Research Council (1977) stated,

Zinc is considered an essential trace element in human and animal nutrition.... As far as human health in the general population is concerned, the major concern is not with toxicity, but rather with marginal or deficient zinc intake. The available data indicate that the contribution of drinking water to the daily nutritional requirement for zinc is negligible under most circumstances. (p. 299)

Because zinc does not appear to be potentially harmful at concentrations expected to be found in drinking water, the U.S. E.P.A. has not issued a primary drinking water regulation for it (U.S.

E.P.A., 1985). Zinc does, however, produce an undesirable taste in water in concentrations above about 5 mg/L. In high concentrations, zinc may also cause water to appear milky or appear to have a greasy scum upon boiling (Pettyjohn, 1972). For aesthetic reasons, therefore, a secondary drinking water standard of 5 mg/L has been established (U.S. E.P.A., 1976).

Zinc is highly toxic to fish and other aquatic animals. The level of toxicity is species dependent and varies with other properties of the water such as pH, temperature, and especially, hardness. The U.S. E.P.A. (1976) has established a criterion of 0.01 times the 96-hour LC_{50} of a sensitive resident species for the protection of aquatic life. For small rainbow trout in soft water, this criterion translates to 0.01 to 0.08 mg/L.

Urban Nonpoint Source Pollution

Water pollution abatement efforts have, until recently, focused on controlling municipal sewage and industrial discharges to water. These pollution sources were easy to identify and the effects they produced were, in most cases, obvious. Because secondary and even tertiary treatment of these point discharges has become widespread, the significance of nonpoint (or diffuse) sources of pollution has become more apparent. The possible magnitude of nonpoint pollution has only been recognized for the last 15 to 20 years. A nonprofit environmental research group study of the Hudson River found that "in the case of six hazardous substances--lead, cadmium, arsenic, mercury, PCBs, and oil--the estimates from nonpoint sources

'literally dwarf' those from point sources such as industrial discharge pipes and sewage treatment plants" (Hattangadi, 1987, p. 9). In the case of lead, urban and agricultural runoff accounted for approximately 182,300 lbs entering the Hudson, compared to 240 lbs from documented point sources. The magnitude of nonpoint pollution was legally acknowledged when the Federal Water Pollution Control Act Amendments of 1972 included the requirement that area pollution control planning should include both point and nonpoint sources.

Rural nonpoint pollution is related primarily to agricultural activities. Runoff from tilled lands may contain suspended sediments as well as pollutants derived from fertilizers and pesticides. Animal feedlot operations may contribute large quantities of sediment, phosphorus, nitrogen, biological oxygen demand, and fecal coliform to receiving waters. Strip mining activities may also result in the discharge of large quantities of sediment and acidity.

Urban stormwater runoff may have pollution levels rivaling that of raw sewage (Novotny & Chesters, 1981). In addition, urban runoff frequently contains elevated levels of pollutants such as heavy metals, asbestos, PCBs, and oil. In comparing total quantities of raw municipal wastes and urban runoff, Colston (1974) found that urban runoff contained 95 percent of the suspended solids and, depending upon the particular metal, between 57 and 94 percent of the heavy metals.

Trace Metals

On Street Surfaces

During a rainless period in an urban area, everything from dust and dirt to general litter, from oil to animal feces will gradually accumulate on city surfaces. When it rains, much of this material will make its way into surface waters by way of storm sewers.

In a statistical analysis of published data through 1972, Bradford (1977) summarized the concentrations of a number of potential water pollutants in dust and dirt on city streets as a function of several independent parameters. Of particular interest to this review is his summary of mean trace metal concentration as a function of land use (Table 4). He concluded that "using data available nationwide, generally, significant patterns in the relationship between land use and pollutants could not be shown" (p. 621).

In a widely cited study, Sartor and Boyd (1972) and Sartor, Boyd, and Agardy (1974) examined the water-pollution potential of material that commonly collects on city streets. They attributed the below average loading rates in commercial areas to the frequency with which these areas are swept. They also found that heavy metals accumulated on city streets at an average of 1.3 lbs per curb mile per day. These trace metals were not distributed evenly across all size ranges of street refuse but were concentrated in the "finer" fractions (51.3 percent of the trace metals were associated with particles smaller than 246 μm).

Cool, Marcoux, Paulin, and Mehra (1980) examined heavy metal

Table 4
Mean Metal Concentrations (ug/g) in
Street Surface Dust and Dirt

<u>Land Use</u>	<u>Cd</u>	<u>Cr</u>	<u>Cu</u>	<u>Fe</u>	<u>Pb</u>	<u>Mn</u>	<u>Ni</u>	<u>Zn</u>
Open Space	0.6	5	9	2,600	15		6	22
Residential	3.0	192	93	20,600	1430	392	28	350
Commercial	4.2	225	133	23,300	3440	397	48	520
Light Industry	4.0	288	128	21,800	2780	490	41	368
Heavy Industry	3.9	278	107	28,600	1160	570	37	317

Note. From "Urban stormwater pollutant loadings: a statistical summary through 1972" by W. L. Bradford, 1977, Journal of the Water Pollution Control Federation, 49, p. 618.

concentrations in soils adjacent to streets in a relatively nonindustrialized town in eastern Canada. The concentrations of cadmium, copper, lead, and zinc in the soils were found to decrease with increasing distance from the streets. The effect was most pronounced with lead, which dropped from a mean concentration of 0.407 mg/g soil at the street edge to a mean concentration of 0.122 mg/g at a distance of 7 m from the street.

Albasel and Cottenie (1984) likewise found decreases in the concentration of lead and zinc in soils and plants with increasing distance from highways in Belgium. They also found that the lead content of plants 10 to 20 m away from the roadside was still 3 to 10 times higher than the content of plants sampled at least 100 m from the roadside.

In Storm Drainage

As might be expected, increased urbanization brings about a concomitant increase in levels of some heavy metals delivered to adjacent aquatic systems. By examining the vertical profiles of heavy metals in dated sediment cores from a shallow estuary, Christensen and Scherfig (1978) were able to demonstrate clearly increased levels of lead and zinc beginning about the time urban development in the watershed began.

A number of studies conducted before the major decreases in gasoline lead content were mandated implicated automobile emissions as a source of urban lead pollution. Laxen and Harrison (1977) found that lead concentrations in highway runoff were 10^3 to 10^4 times background concentrations in surface waters. It seems reasonable to conclude, then, that runoff from an urban area with a high density of roads could provide a substantial load of lead to adjacent surface waters. This general conclusion was also reached in the following two studies.

Rimer, Nissen, and Reynolds (1978), in a study of nonpoint pollution in the Durham-Raleigh area of North Carolina, determined that peak lead concentrations in storm runoff increased with the percent imperviousness of the drainage area (Table 5). The only major exceptions were in the central business districts. The decreased levels of lead and suspended solids in these areas was attributed to less land disturbing activity and frequent street sweeping. The level of lead in stormwater runoff appeared to be

Table 5

Average Peak Concentrations of Pollutants in Stormwater Runoff

Land Cover Type	Percent Impervious Area	Suspended Solids ^a	Lead ^a
Low activity rural	2.7	284	0.1
High activity rural	5.1	416	0.1
Low activity commercial	12	575	0.2
Low activity residential	16	664	0.6
High activity residential	32	1199	2.1
High activity commercial	35	1082	1.7
Central business district	80	528	0.9

Note. Adapted from "Characterization and impact of stormwater runoff from various land cover types" by A. E. Rimer, J. A. Nissen, and D. E. Reynolds, 1978, Journal of the Water Pollution Control Federation, 50, p. 259.

^aConcentration in mg/L

closely correlated to the level of suspended solids. This implicated the transport of finely divided solids as the mechanism for the entry of lead into stormwater runoff.

The Northern Virginia Planning District Commission (cited in Klein, 1979), in its report on the Occoquan-Four Mile Run Nonpoint Source Correlation Study found that the loading rates of zinc and lead increased as the imperviousness of the watershed increased (Figure 1).

Although heavy metals were not specifically sampled in his study

of 27 small watersheds in the Piedmont province of Maryland, Klein (1979) concluded that "stream quality impairment can be prevented if watershed imperviousness does not exceed 15 percent" (p. 459). This conclusion was based on an examination of the diversity of the biota in each of the sampled streams.

Additional studies have examined the effect of land use on stormwater quality. In a general comparison of watersheds and land use, Ostry (1982) compared the Grand and Saugeen river basins in Canada under a Pollution from Land Use Activities Reference Group (PLUARG) study. The two rivers have adjacent headwater areas and are similar in geology, physiography, and climate. The Grand River basin, however, has an order of magnitude greater population (514,000 versus 57,000), approximately 85 percent of which is concentrated in urban areas. Only 50 percent of the 57,000 people in the Saugeen River basin are concentrated in urban areas and a greater proportion of the basin is wooded or idle area compared to the Grand River basin. As might be expected, the unit area loads of nearly all measured pollutants was greater in the Grand River. Specifically, the unit area load for lead was 1.2 times as high in the Grand River as in the Saugeen River. Predominantly homogeneous subwatersheds were also monitored to estimate unit area load ratios between the three major land use categories (Table 6). The urban areas contributed a much greater proportion of lead, zinc, and copper per unit area compared to the rural and wooded/idle areas.

In a more detailed comparison of runoff and land use, Helsel, Kim, Grizzard, Randall, and Hoehn (1979) sought to "characterize and

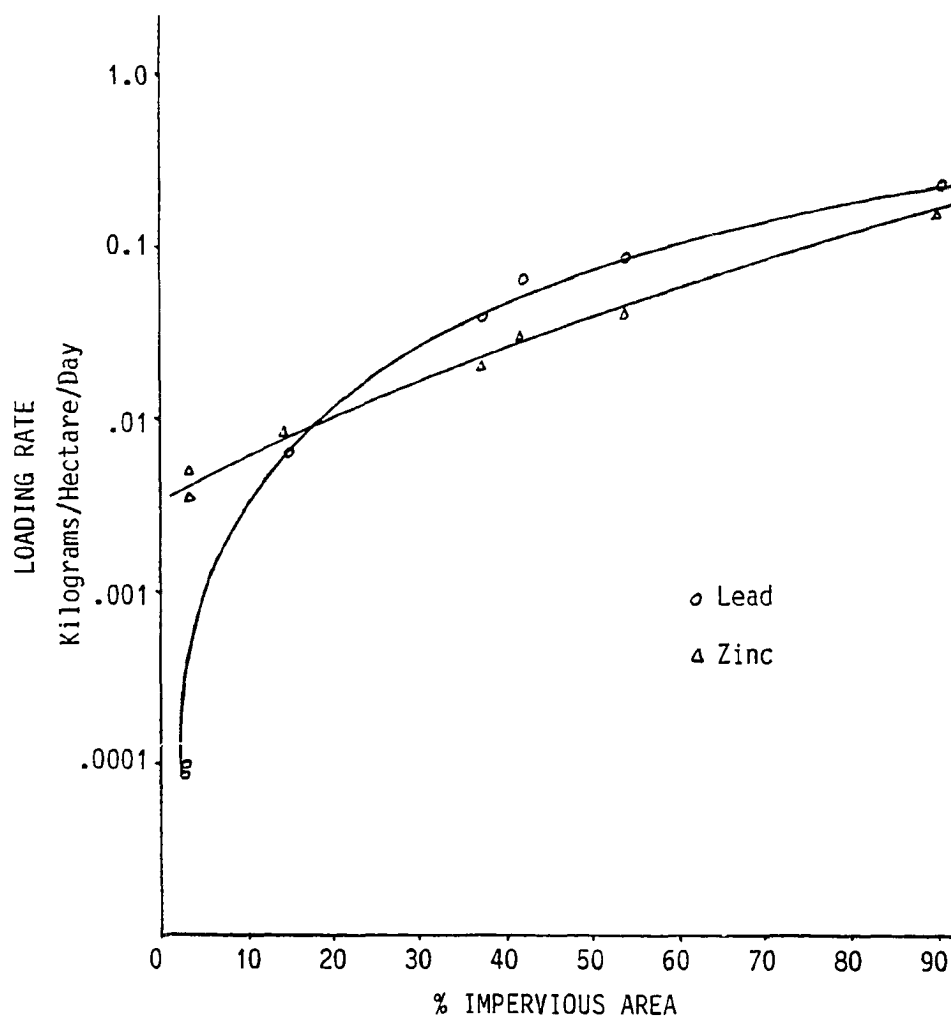


Figure 1. Total Extractable Metals Loadings versus Watershed Imperviousness.

Note: From "Urbanization and Stream Quality Impairment" by R. D. Klein, 1979, Water Resources Bulletin, 15, p. 957.

compare the surface runoff of seven metals from small basins of differing land-use types" (p. 709). Nineteen small subbasins, each composed entirely of a single land-use type, were selected for study

Table 6
Trace Metal Unit Area Load Ratios for the
Grand and Saugeen River Basins, Canada

Metal	Land Use Category		
	Urban	Rural	Wooded/Idle
Lead	40	: 2	: 1
Zinc	25	: 5	: 1
Copper	3	: 1	: 1

Note. From "Relationship of water quality and pollutant loads to Land uses in adjoining watersheds" by R. C. Ostry, 1982, Water Resources Bulletin, 18, p. 102.

from two watersheds in eastern Virginia. Individual storm events were automatically sampled at a number of times during passage of the flood wave and later analyzed for their content of zinc, lead, chromium, copper, cadmium, iron, and manganese. Cadmium was deleted from the analysis because a large percentage of the samples contained cadmium levels near or below the detection limit which precluded detecting significant differences between sampling stations. Seven subbasin land-uses were examined ranging from forested (taken as "background") to high-rise residential and commercial. None of the subbasins had industrial land-uses.

Only two types of significant differences were detected between the different land-use types. First, only agricultural areas yielded significantly higher average runoff levels of iron and manganese than the forested site. Second, all sampling stations containing

significantly higher levels of lead, zinc, and copper than the forested site were in urban locations.

Helsel et al. (1979) also found that, due to considerable inconsistencies among stations of the same land-use type, average metal values for a given land-use were poor predictors of metal loadings in individual subbasins. Rather, individual land-use characteristics gave better indications of stormwater quality. For example, lead, zinc, and copper gave good nonlinear correlations (Spearman correlation coefficient) with traffic and percent imperviousness. This implied that "motor vehicles are a major source of these metals, and that impervious surfaces deliver them efficiently to storm drainage systems" (p. 716).

Finally, this study demonstrated that a "first-flush" effect occurs more frequently with increased urbanization and that during rain events, storm water drainage in small urban subbasins can deliver several times the quantities of metals than the effluent from secondary wastewater treatment plants.

VanHassel, Ney, and Garling (1979) sought to relate total metal concentrations in stream sediments to adjacent highway traffic volume and season of the year. Sediment was collected from three sites on a stream during each of the four seasons and was analyzed for its total metal content. The farthest upstream site was away from all traffic contact and served as a reference. Highway traffic averaged 6,550 vehicles/day adjacent to the middle site and 15,000 vehicles/day at the downstream site. Sediment loads of lead, nickel, and zinc were found to be highly correlated with traffic volume. Concentrations of

lead and zinc were highest at each site in the spring and decreased through the summer, fall, and winter. Seasonal variations in the concentrations of nickel and cadmium were not detected--possibly because of detectability problems in the case of cadmium. The elevated levels of lead and zinc in the spring were attributed to "runoff of metal-laden snow from the roadsides and surrounding regions of particulate deposition, and subsequent adsorption to trapped sediments in the stream" (p. 594).

In a three-year study of a 4.6 mile stretch of the Saddle River in New Jersey, Wilber and Hunter (1977, 1979, 1979a) found significant enrichments of several heavy metals in river sediments downstream from the urban center of Lodi. Pollution in the study area was considered to originate from nonpoint or unrecorded wastes because industries and municipalities directed their wastewater by sewers to a treatment plant outside the area. The average enrichment in metals concentration downstream compared to upstream of the urban center was lead (670%), zinc (350%), copper (310%), nickel (280%), chromium (510%), cadmium (520%), manganese (120%), and iron (180%).

Since a large portion of sediment heavy metals are tightly bound to organic matter, iron and manganese hydroxides, and clay and silt, these authors also examined the availability of the metals. Only those metals which could be extracted from sediments with river water or which were ion-exchangable with 1.0 M ammonium acetate at pH 7 were considered "readily available" to the water column and biota. Generally, less than 20 percent of the total sediment heavy metals were determined to be "available." The enrichment of "available"

metals downstream compared to upstream of the urban center was determined to be lead (320%), zinc (610%), copper (420%), nickel (430%).

Similar to the street-sweepings results of Sartor and Boyd (1972) and Sartor et al. (1974), Wilber and Hunter also found that the fine fractions of sediment had the highest concentrations of metals. Although the effect was most pronounced for particles smaller than 5.8 μm , the greatest total quantity occurred in the fraction larger than 125 μm simply because those fractions comprised most of the sediment.

Although agreement on their individual significances has not been established, a number of factors appears to affect the concentration of trace metals in urban runoff. The concentration of mercury in a number of combined sewer overflows in Rochester, New York, was measured by Murphy and Carleo (1978). Using regression analysis, they found that a high degree of correlation existed between the measured levels of mercury and the intensity of rainfall, the duration of a storm, and the number of dry days since the last storm.

One of the basic assumptions of the earlier versions of the EPA's Stormwater Management Model (SWMM) was that "the total pollution loading from urban runoff in a given storm varies with the length of time elapsed since the preceding rainfall" (Whipple, Hunter, and Yu, 1977, p. 2243). In a test of this assumption, however, Whipple et al. (1977) found that,

there seems to be a definite tendency for storm loadings of heavy metals to increase with total runoff during the storm. However, there does not appear to be any discernible tendency for storm loadings to vary with the number of days since the preceding rainfall. (p. 2245)

This conclusion was confirmed by Ellis, Harrop, and Revitt (1986). The delivery of sediment and its load of metals to a residential highway catchbasin in London, England, was examined in relation to five hydrological controls: (1) total rainfall volume, (2) maximum five minute duration rainfall intensity, (3) storm duration, (4) antecedent dry period length, and (5) total surface discharge. A linear regression analysis indicated that more than 90 percent of the variance in lead, cadmium, manganese, and sediment loadings and 79 percent of the variance in zinc loadings could be accounted for in terms of total rainfall, storm duration, and surface discharge. Antecedent dry period did not appear to be important in explaining variations in pollutant loadings.

Wilber and Hunter (1977) determined that the distribution of metals in precipitation is similar to that in stormwater runoff for the same area. Lead and zinc were dominant in both types of samples, but the calculated amounts of metals in rainfall were an insignificant proportion of the total amounts present in stormwater runoff.

Highway Deicing Salts

From 1940 to 1980 the use of highway deicing salts in the United States increased almost exponentially (Figure 2). The policy of highway departments in the snow belt to maintain bare pavement on major streets and roads during the winter virtually insures that the use of deicing salts will remain high. Salt use can be particularly heavy in urban areas where pavement is salted frequently. Local municipalities in southeast Michigan, for example, seasonally apply

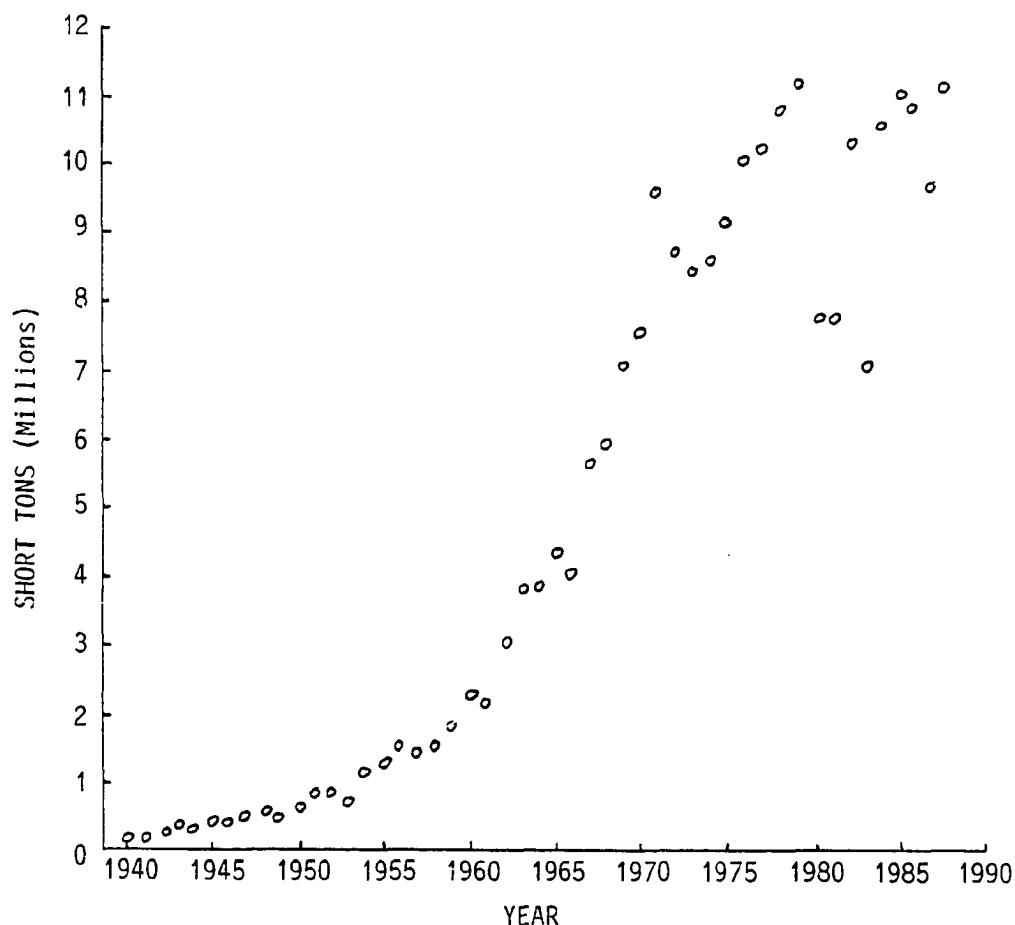


Figure 2. Use of Deicing Salts in the United States.

Note: Data for 1940 - 1970 are from "The Environmental Effects of Snow Dumping: A Literature Review" by W. S. Scott and N. P. Wylie, 1980, Journal of Environmental Management, 10, p.223. Data for 1971 - 1974 provided by B. Bertram of the Salt Institute. Data for 1975 - 1988 are averages of figures provided by B. Bertram of the Salt Institute and D. Kostick of the U. S. Bureau of Mines.

salt at rates ranging from about five tons of salt per mile of road to more than 100 tons per road mile (Southeast Michigan Council of Governments, 1978b).

The use of highway deicing salts can lead to a number of

environmental problems. The effect of salt on unprotected cars is renowned. A 1976 study by ABT Associates (cited in Southeast Michigan Council of Governments, 1978) indicated that 2 billion of the 2.9 billion dollars spent annually on all deicing salt activities were spent on repair or replacement of salt damaged vehicles. In addition, vegetation can be adversely affected (Roth & Wall, 1976; Wilcox, 1986; Williams, 1981), wells can become contaminated (Field, Struzeski, Masters, & Tafuri, 1974; Huling & Hollocher, 1972; Hutchinson, 1970; Jones, 1981), and small lakes, bays, and reservoirs receiving salt-laden runoff can acquire dense saline layers at their bottoms (Bubeck, Diment, Deck, Baldwin, & Lipton, 1971; Cherkauer & Ostenso, 1976; Hawkins & Judd, 1972; Hoffman, Goldman, Paulson, & Winters, 1981; Judd, 1970; Scott, 1979).

Increases in sodium and chloride ion concentrations in many of the nation's rivers have been attributed to the increased use of deicing salts. Peters and Turk (1981) compared the concentrations and annual yields of major ions (Na^+ , K^+ , Mg^{+2} , Ca^{+2} , Cl^- , SO_4^{+2} , HCO_3^-) in the Mohawk River, New York for the periods 1951-1953 and 1970-1974. All ions showed a general 20 percent increase in annual unit-area yields attributable to a 19 percent increase in mean stream discharge. The annual unit-area yields of sodium and chloride, however, increased by 72 percent and 145 percent respectively. An accounting of the sources of sodium and chloride indicated that salt used for road deicing was responsible for essentially all the increases in those ions over the two decade period. Although the mean concentration of chloride for the more recent period was

relatively low (13.5 mg/L), highway deicing salts were estimated to account for 41 percent of all chloride transported by the river.

Hoffman et al. (1981) examined the chloride levels in streams and small lakes in the Lake Tahoe, Truckee River, and Yuba River watersheds of California. Streams crossing salted highways showed dramatic increases in chloride levels during the winter and early spring. Chloride concentrations typically rose from about 1 mg/L in the summer and fall to about 70 mg/L during the winter and early spring. Stream chloride concentrations returned to normal levels within 10 to 30 days after deicing salt applications ceased in the spring. Streams with watersheds containing no major roads had low levels of chloride (mean of 1 mg/L) throughout the year with little seasonal differences.

Monthly sampling of selected river mouths in Southeast Michigan was conducted from August 1976 to February 1977 by the Southeast Michigan Council of Governments (1978) to gather data to determine mean pollutant loadings to the lower Great Lakes system. A general increase in chloride concentration was observed in the winter months for the four major rivers (discharge greater than 100 cubic feet per second) sampled. The increase was most pronounced for the Clinton River, whose chloride concentration rose from about 10 mg/L in August to 230 mg/L in December.

Smith et al. (1987) examined water-quality records from more than 300 locations on major U.S. rivers for the period 1974 to 1981 and found widespread increases, averaging 30 percent, in salinity. Their analysis of concurrent changes in basin conditions indicated

that:

1. Chloride trends were moderately correlated with basin population changes, reflecting the fact that human wastes are a major source of chloride in many populated basins.
2. Increasing sodium and chloride concentrations were significantly associated with high rates of highway salt use and with large increases in its use (especially in the Ohio, Tennessee, lower Missouri, and Arkansas-Red basins).
3. Although irrigated agriculture has a large influence on the salinity of certain western rivers, chloride trends were not significantly correlated with changes in irrigated acreage nationally.
4. Increases in sulfate were especially frequent in the Missouri, Arkansas, and Tennessee basins and were highly correlated with changes in surface coal production from 1974 to 1981. (p. 1613)

Unusually high levels of chloride ion have been reported in some streams carrying deicing salts. Limited sampling of the Kinnickinnic, Milwaukee, and Menomonee Rivers in Milwaukee, Wisconsin in 1969 showed chloride levels as high as 2005, 2680, and 2730 mg/L respectively (The Salt Institute cited in Field et al., 1974). Chloride levels of 700 to 4000 mg/L were found in a single winter sampling of ten small streams and storm sewers discharging into Irondequoit Bay in Rochester, New York (Bubeck et al., 1971). Meadow Brook in Syracuse, New York, was frequently found to contain chloride concentrations in excess of a few thousand milligrams per liter. One sample taken in 1969 contained about 11,000 mg/L of chloride (American Public Works Association cited in Field et al., 1974).

Chloride levels have also risen in Lakes Erie and Ontario from about 5 mg/L in the early 1900s to about 20 and 28 mg/L, respectively, today (Jones, 1981; Sonzogni, Richardson, Rodgers, & Monteith,

1983). Although industrial sources are considered the most significant contributors of chloride to the Great Lakes, road salt still contributes an important fraction (about 1/3) of the total. For Lake Ontario, road salt contributes an estimated 11 percent of the total chloride loadings (Jones, 1981).

Chloride Complexation of Heavy Metals

Essentially all of the trace metals will form complexes with one or more ligands commonly present in natural waters. Consequently, a particular trace metal will rarely exist as a single species in solution. Instead, the metal will exist as a mixture of the free ion and a variety of complexes. The concentrations of the species present will be interrelated through a series of interconnected equilibria. Calculating the simultaneous concentrations of each of these species or the proportion of each to the total is a difficult task requiring the knowledge of a large number of physical and chemical parameters. More than 50 computer programs have been written to handle the laborious calculations involved. Many of these programs have been reviewed by Nordstrom and Ball (1984).

The effect of a single ligand can often be examined when it is present in large quantities relative to other components of the system or when its concentration varies as the concentration of the other components remain constant. A number of studies have indicated that the chloride ion can form relatively stable complexes with many of the heavy metals and, thereby, affect the mobilization of those metals from sediments and soils.

Published values of complex formation constants and solubility products were used by Hahne and Kroontje (1973) to calculate the ionic and molecular species distribution of Hg^{2+} , Cd^{2+} , Pb^{2+} , and Zn^{2+} as a function of hydroxyl and chloride ion concentration. Results indicated that "both the hydroxy and chloride complexes may contribute to the mobilization of these heavy metals in the environment" (p. 444). Chlorides, for example, complex with Hg^{2+} at chloride concentrations above 10^{-9} M (35×10^{-6} ppm) but above about 10^{-3} M (35 ppm) for Zn^{2+} , Cd^{2+} , and Pb^{2+} . Whether hydroxy or chloro species predominate depends on the simultaneous concentrations of hydroxide and chloride ions. For example, at a pH of 8.5 and a chloride concentration between 350 and 60,000 ppm, Hg^{2+} and Cd^{2+} are mainly complexed as chlorides, whereas Zn^{2+} and Pb^{2+} are present mainly as hydroxy complexes.

Zirino and Yamamoto (1972) developed a model to calculate the extent of complexation of Cd^{2+} , Cu^{2+} , Pb^{2+} , and Zn^{2+} with OH^- , Cl^- , SO_4^{2-} , HCO_3^- , and CO_3^{2-} in seawater as a function of pH. Complexes with coordination numbers greater than 4, polynuclear, and mixed-ligand species were not included in the model. Their calculations showed that all four metals are complexed to a considerable extent in seawater (Table 7). Further,

in seawater, copper interacts primarily with hydroxide and carbonate ions, zinc with hydroxide and chloride ions and lead with carbonate and chloride ions. On the other hand, cadmium interacts primarily only with chloride ion. Consequently, the distributions of the chemical species of copper, zinc, and lead vary considerably with pH, while those of cadmium species do not. (p. 667)

Table 7
Speciation of Heavy Metals in Seawater

Metal	Species Present ^a (Percent)	
Cd	CdCl_2^0 (51)	CdCl^+ (39)
	CdCl_3^- (6)	Cd^{2+} (2.5)
Cu	Cu(OH)_2^0 (90)	CuCO_3^0 (8)
	Cu^{2+} (1)	Cu(OH)^+ (1)
Pb	PbCO_3^0 (80)	PbCl^+ (10)
	PbCl_2^0 (4)	Pb^{2+} (1.8)
	PbCl_3^- (1.7)	
Zn	Zn(OH)_2^0 (62)	Zn^{2+} (17)
	ZnCl^+ (6.4)	ZnCO_3^0 (5.8)
	ZnSO_4^0 (4)	ZnCl_2^0 (4)

Note: Compiled from "A pH dependent model for the chemical speciation of copper, zinc, cadmium, and lead in seawater" by A. Zirino and S. Yamamoto, 1972, Limnology and Oceanography, 17, p. 661-671.

^aAt the average seawater pH of 8.1.

Brown, Sutherland, and Leharne (1987) examined the effect of pH and chloride ion concentration on the mobilities of cadmium, cobalt, copper, lead, nickel, and zinc through soil by the use of soil thin layer chromatography (TLC). TLC plates were prepared from a finely ground silt loam soil, spotted with 0.1 M solutions of the metal ions, and then developed in closed tanks. The developing solution was prepared from deionized water using nitric acid to adjust the pH or sodium chloride to produce the chloride solutions. Their results

(Table 8) show that all the metal ions except lead were considerably more mobile in the more acidic solution. The increased mobility at lower pH was attributed to increased competition between hydrogen ions and metal ions for exchange sites on clay and humus materials. The relative immobility of lead was hypothesized as being due to the formation of insoluble lead/humic acid complexes. Cadmium was apparently the only metal for which the effect of chloride ion concentration on mobility was examined. They found that as the chloride

Table 8
Effect of pH on Cation Mobility

Cation	P - value	
	pH = 7	pH = 4.7
Cd^{2+}	0.25	0.37
Co^{2+}	0.09	0.43
Ni^{2+}	0.08	0.15
Cu^{2+}	0.07	0.35
Pb^{2+}	0.04	0.08
Zn^{2+}	0.03	0.25

Note: From "The Effect of pH and Chloride Ion Concentration on the Mobilities of Various Cations in Soil" by M. Brown, M Sutherland, and S. Leharne, 1987, Journal of Chemical Education, 64, p. 448.

ion concentration increased, cadmium became progressively more mobile (Table 9). The increased solubility of cadmium ions as a result of the formation of stable chloro-complexes was postulated as causing

Table 9
Effect of Chloride Ion Concentration on Cd^{2+} Mobility

Concentration (M)	R_f
0.00	0.25
0.06	0.30
0.08	0.38
0.10	0.47

Note: From "The Effect of pH and Chloride Ion Concentration on the Mobilities of Various Cations in Soil" by M. Brown, M Sutherland, and S. Leharne, 1987, Journal of Chemical Education, 64, p. 449.

the increase in R_f values.

Doner (1978) sought to determine the effect of chloride ion on the mobility of nickel, copper, and cadmium ions through soil. Sandy loam soil columns were leached with 0.1 to 0.5 M sodium chloride or sodium perchlorate solutions containing 10 mg/L Ni(II), Cu(II), or Cd(II). The perchlorate solutions were used for comparison because the perchlorate ion is not considered to form complexes with the metals. Leachate metal concentrations were monitored relative to the number of pore volumes passing through the column. The mobility of the metals was found to be 1.1 to 4 times greater in chloride solution than in perchlorate solution. The increase in mobility was comparable for nickel and copper and greatest for cadmium. The greater increase in mobility of cadmium was explained in terms of its greater tendency to form chlorocomplexes. Copper was found to be held more strongly to the soil than either nickel or cadmium.

Doner, Pukite, and Yang (1982) sought to determine the mobility of cadmium, copper, lead, and zinc ions in geothermal brine water through agricultural soils. Columns of soil were leached with geothermal brine water containing chloride ion at a concentration of 3.43 molal (about 122,000 ppm) and having a pH of 3.6. The concentrations of the heavy metals were monitored in the effluent and compared with their original concentrations to determine whether retention or leaching of the metals took place and to what extent. The soils were found to retain small amounts of lead and zinc initially, but, negligible amounts after the passage of 10 pore volumes of the geothermal brine water. Copper was not adsorbed from the water whereas there was a net removal of cadmium from the soil. Calculations using the computer program GEOCHEM indicated that 50 to 100 percent of all the heavy metals were complexed with chloride.

Feick, Horne, and Yeaple (1972), in a widely cited study, compared the release of mercury into water and into NaCl and CaCl₂ solutions from sandy and organic sediments contaminated with mercury. They found the addition of about 21,000 ppm NaCl or 105,000 ppm CaCl₂ to increase the amount of mercury in solution in equilibrium with the sediments by two to five or more orders of magnitude. Examination of their data, however, revealed that the effect of lower pH was confounded with the effect of NaCl and CaCl₂ in most of their data. The pH in their desorption trials ranged from 6.7 to 3.6--nearly a 1300-fold difference in hydrogen ion concentration. Sediments are known to release heavy metals at low pH.

Ramamoorthy and Rust (1978) loaded sediment samples (fine sands

and silty sands) from the Ottawa River, Canada with mercury, lead, and cadmium by stirring the sediments with 2 ppm solutions of the metal nitrate salts. The samples were then washed with distilled water to remove the nonsorbed ions and then leached by shaking with 10^{-4} M NaCl (3.5 ppm Cl^-) for four days. Subsequent analysis revealed that approximately 75 percent of the mercury, 50 percent of the cadmium, and 7 to 21 percent of the lead had desorbed into solution, even at this low concentration of NaCl.

Seawater has been shown to release heavy metals from particulates in partially treated wastewater effluent. Rohatgi and Chen (1975) mixed samples of the primary effluent, digested sludge, and mixtures of the primary and secondary effluents from a wastewater treatment plant with seawater at various dilution ratios and measured the release of heavy metals from the suspended particulates as a function of time. The same type of studies were also done with suspended solids from the Los Angeles River. In most cases, cadmium, copper, lead, nickel, and zinc were released from the suspended particulates to a greater extent than iron, chromium, and manganese (Table 10). Iron was not released under any of the experimental conditions. Only in the case of the digested sludge were chromium and manganese released, and then only to an extent of 2 percent and 35 percent respectively. In general, a greater percentage of the particulate heavy metals was released at higher seawater to effluent ratios. The release of heavy metals occurred in two stages: a rapid initial release, followed by a slower, long-term release. The particulate concentrations of lead and cadmium were found to decrease

Table 10
Percentage of Trace Metals Released at Equilibrium
to Seawater from Suspended Particulates

	Digested Sludge	Primary Effluent	Mixture of Primary and Secondary Effluent	Dry Weather Flow from L. A. River
Seawater: Effluent	100:1	5:1	5:1	2:1
Cd	95.0	94.7	92.8	---
Cu	5.6	67.0	69.4	65.9
Cr	2.0	0	0	0
Fe	0	0	0	0
Mn	34.7	0	0	0
Ni	58.0	57.0	62.8	72.2
Pb	35.4	52.9	58.4	16.7
Zn	24.4	43.9	38.1	60.0

Note: From "Transport of trace metals by suspended particulates on mixing with seawater" by N. Rohatgi and K. Y. Chen, 1975, Journal of the Water Pollution Control Federation, 47, pp. 2300 & 2301.

in the initial phase to a much greater extent than copper, nickel, and zinc.

Several studies have investigated the role of seawater in mobilizing trace metals from sediments in estuaries. Lentsch, Kneip, Wrenn, Howells, and Eisenbud (1971) found that manganese was leached from bottom sediments of the Hudson River Estuary during periods when seawater intruded into normally freshwater regions. As a result, the

concentration of dissolved manganese was found to vary by almost three orders of magnitude over the course of a year.

Three studies attempted to model the behavior of metal-laden sediments in an estuary by measuring concentrations of metals desorbed from sediments agitated in mixtures of freshwater and seawater or in solutions representing salinity concentrations that may be found in an estuary. Frenet-Robin and Ottmann (1978) determined the proportion of mercury desorbed after four hours when different clays were stirred in "freshwater" or salt water (Table 11). Mercury

Table 11

Percentage of Mercury Desorbed from Clays after Four Hours Agitation

Clay Mineral	Freshwater ^a	Salt Water ^b
Calcic Montmorillonite	6.8	5.4
Sodic Montmorillonite	3.5	4.2
Illite	10.6	14.6
Kaolinite	4.1	19.6

Note: From "Comparative study of the fixation of inorganic mercury on the principal clay minerals and the sediments of the Loire Estuary" (p. 433) by M. Frenet-Robin and F. Ottman, 1978, Estuarine and Coastal Marine Science, 7, p. 433.

^aThe exact meaning of "freshwater" was not defined.

^bsalinity = 20 o/oo.

was found to desorb most readily from kaolinite in saltwater and least readily from the montmorillonites. Dissolved mercury concentrations were also determined at flood tide, slack tide, and ebb tide

in four zones moving upstream from the Loire Estuary in France. In each zone, the concentration of mercury was highest during flood tide--corresponding to the tide with the highest salinity.

The desorption of heavy metals from suspended matter taken from the Rhine River was studied as a function of pH and salinity by van der Weijden, Arnoldus, and Meurs (1977). These authors resuspended material taken from the Rhine River in distilled water, in diluted artificial sea water (1:1), in artificial sea water, and in "nitrate sea water" (chloride and sulfate replaced by nitrate), respectively, at pHs of 7.5 and 8.0. The concentrations of nine heavy metals desorbed into each of these solutions was then determined after nine days of agitation. When heavy metal concentrations in the desorption solutions themselves were accounted for, adsorption rather than net desorption was found to occur for iron and lead. For the remaining metals (Table 12), the following observations were made:

1. desorption at pH 7.5 exceeds desorption at pH 8.0,
2. desorption increases with ionic strength, and
3. desorption in artificial sea water exceeds desorption in "nitrate sea water." (van der Weijden et al., 1977, p. 134)

Because the nitrate ion is known to be a weak ligand, van der Weijden et al. (1977) noted that the second and third observations are consistent with a high degree of complex formation between metal ion and ligands--particular chloride ion. They further noted that the order of decreasing desorption of metals in diluted sea water and in sea water was:



Comparison of this order of desorption with calculated percentages of

Table 12

Desorption of Heavy Metals from Rhine River Suspended Sediment

Desorption Medium	pH	Percent Desorbed						
		Cr	Mn	Co	Ni	Cu	Zn	Cd
double distilled water	7.5	0.2	0.2	<0.3	5	1	5	4
	8.0	0.2	0.4	0.3	4	1	3	3
1:1 diluted sea water	7.5	0.2	17	5	11	3	20	56
	8.0	0.2	11	5	7	3	12	45
sea water	7.5	0.2	17	8	14	5	21	80
	8.0	0.3	12	6	7	5	9	58
"nitrate sea water"	7.5	0.2	17	3	7	0.2	17	17
	8.0	0.2	9	3	3	0.4	9	12

Note: From "Desorption of metals from suspended material in the Rhine Estuary" (p.134) by C. H. van der Weijden, M. J. H. L. Arnoldus, and C. J. Meurs, 1977, Netherlands Journal of Sea Research, 11, p. 134.

free ions and complex ion species present in seawater indicated that, except for zinc, the order corresponds to the decrease of chloride plus sulfate complexing for these metals.

van der Weijden et al. (1977) also determined heavy metal concentrations in suspended matter and in solution for samples collected at a tidal station in the Rhine Estuary and in the Waal River, a branch of the Rhine upstream of the region of estuarine mixing. Except for manganese, all the metals examined were present in much lower concentrations in the estuarine suspended matter than in the Waal suspended matter. The higher ionic strength of the seawater and the ability of chloride and sulfate to form complexes with the

adsorbed heavy metals might be used to explain these observations. The predicted increase in dissolved metal ion concentrations, however, was not observed. In fact, except for nickel and lead, the dissolved metal concentrations in the estuary samples were significantly lower than those in the freshwater samples. The authors admitted difficulty in explaining the field observations. They postulated flocculation and sedimentation of the suspended material at an early stage of estuarine mixing (that is, at low salinities) which largely trapped the metals in the sediments. The desorption of heavy metals would not be important at such low salinities and the remaining solution would barely be enriched in heavy metals before mixing with seawater and marine suspended material became important. Sampling and analysis after significant mixing with seawater and its suspended matter would, therefore, show decreased metal concentrations in both the suspended material and in solution. A similar explanation was offered by Hart and Davies (1981) to account for a decrease in the total and filterable cadmium concentrations in going from fresh to estuarine conditions on the Yarra River in Australia.

Elbaz-Poulichet, Martin, Huang, and Zhu (1987) examined the concentration of dissolved cadmium as a function of chlorinity in the estuaries of the Gironde and Rhone rivers in France and of the Yellow and Yangtze rivers in China. In contrast to the preceding studies, however, they found a variable but systematic increase in dissolved cadmium with chlorinity. This was accounted for by the formation of stable, soluble chlorocomplexes. They postulated that desorption occurred first, followed by complex formation with chloride ion. The

fact that the cadmium concentration maximum occurred at different chlorinities in the four estuaries was attributed to the dependence of desorption on varying water conditions. They suggested that differences in calcium and magnesium ion concentrations competing with cadmium for adsorption onto particles, as well as differences in pH, redox potential, microbiological activity, organic matter degradation, and residence time of particles in the mixing zone play an important role in cadmium desorption. The authors further indicated that the mobilization of cadmium from particulate matter into the water column appears to be a general trend in estuaries and suggested a re-evaluation of dissolved cadmium inputs to the oceans by a factor of 2-30.

Comans and van Dijk (1988) investigated the reversibility of cadmium sorption on suspended particles in fresh-water and the desorption of pre-adsorbed cadmium in more saline water. Suspended matter used in the investigation was taken from the Rhine River and exchangeable metals were removed by dialysis. The rate and quantity of adsorption of radioactive cadmium onto this material was determined by resuspension in dilute electrolyte solutions (ionic strength = 0.003 M) containing between 1 and 20 ug Cd(II)/L at pH 7.85. Small aliquots were removed at intervals for analysis. After equilibration for 12 days, the suspended material with adsorbed cadmium was separated and resuspended in the same dilute electrolyte solution without the added cadmium and in various combinations of the electrolyte and filtered Atlantic surface water. These latter solutions had salinities of 2.0 o/oo, 5.9 o/oo, and 35.5 o/oo. The desorption of

cadmium in these solutions was studied in the same manner as the adsorption trials.

Comans and van Dijk (1988) determined that the sorption of cadmium to Rhine River suspended particles was completely reversible. Their results, in conjunction with equilibrium speciation calculations (Table 13), further indicated that cadmium adsorbed to the Rhine suspended material in proportion to the Cd^{2+} activity and desorbed in proportion to its complexation in solution.

Table 13
Cadmium Speciation at Different Salinities

Species ^c	Calculated Speciation Percent of Total Dissolved Cd(II) ^{a,b}			
	A	B	C	D
	0 o/oo	2.0 o/oo	5.9 o/oo	35.5 o/oo
Cd^{2+}	76.8	17.7	6.9	0.9
CdCl^+	--	45.7	48.5	31.7
CdCl_2	--	4.7	13.7	44.7
CdCl_3^-	--	--	0.6	10.0
CdCl_4^{2-}	--	--	--	0.7
CdSO_4	--	3.1	2.3	0.6
CdCO_3	0.8	0.3	1.1	--
Cd(OH)^+	0.3	0.1	0.4	--

Note: Adapted from "Role of complexation processes in cadmium mobilization during estuarine mixing" by R. N. J. Coumans and C. P. J. van Dijk, 1988, *Nature*, **336**, p. 152.

^a% species = activity species/total dissolved Cd(II) concentration.
^bA = 0 o/oo salinity, pH 7.69; B = 2.0 o/oo salinity, pH 7.88; C = 5.9 o/oo salinity, pH 7.86; D = 35.5 o/oo salinity, pH 8.24. ^cThe following species were also included in the calculations but contributed negligibly to the total: Cd(OH)_2 , Cd(OH)_3^- , Cd(OH)_4^{2-} , CdF^+ , CdF_2 , $\text{Cd(SO}_4)_2^{2-}$, $\text{Cd(SO}_4)_3^{4-}$, $\text{Cd(SO}_4)_4^{6-}$, $\text{CdCO}_3(\text{s})$, $\text{Cd(OH)}_2(\text{s})$.

Statement of the Problem

In view of the large quantities of highway deicing salts used in many parts of the country, and in view of the limited knowledge of the effect of road salting on mobilizing heavy metals from stream sediments, this study was undertaken to: (a) determine the effect of NaCl concentration on mobilizing cadmium, copper, lead, nickel, and zinc from stream sediments; (b) determine if complexing by chloride ion may play a role in releasing cadmium, copper, lead, nickel, and zinc from stream sediments; and (c) determine the correlations between chloride ion concentrations and cadmium, copper, lead, nickel, and zinc concentrations in an urban stream during a period when the stream is receiving runoff containing deicing salts.

CHAPTER II

DESIGN AND METHODOLOGY

The Study Area

The Red Run drainage basin (Figures 3 and 4) is located in southwestern Macomb and southeastern Oakland counties directly north of the city of Detroit, Michigan. The watershed is more than 75% developed with more than 45% of total land use being residential in nature, 17% devoted to commercial and industrial uses, and 11% classified as public lands. The area is projected to be nearly 100% developed by the year 2000 (U.S. Army Corps of Engineers, 1979, cited in Michigan Department of Natural Resources, 1988). Most or all of the cities of Warren, Sterling Heights, Troy, Centerline, and Madison Heights (Figure 3) transport much of their surface runoff by storm sewers directly to the Red Run. A population in excess of 300,000 lives within the 127 square miles of the watershed.

Most of the Red Run drains an area of glacial lake beds and has a slope near 2 ft/mile. The soils in the watershed are predominantly poorly drained clays (Southeast Michigan Council of Governments, (1978a). The area has a mean annual temperature of 48.7°F and receives a mean of 40 inches of snowfall and 31 inches of total precipitation per year (Sillars & Betzold, 1984).

The Red Run drains into the Clinton River 16.7 miles above the

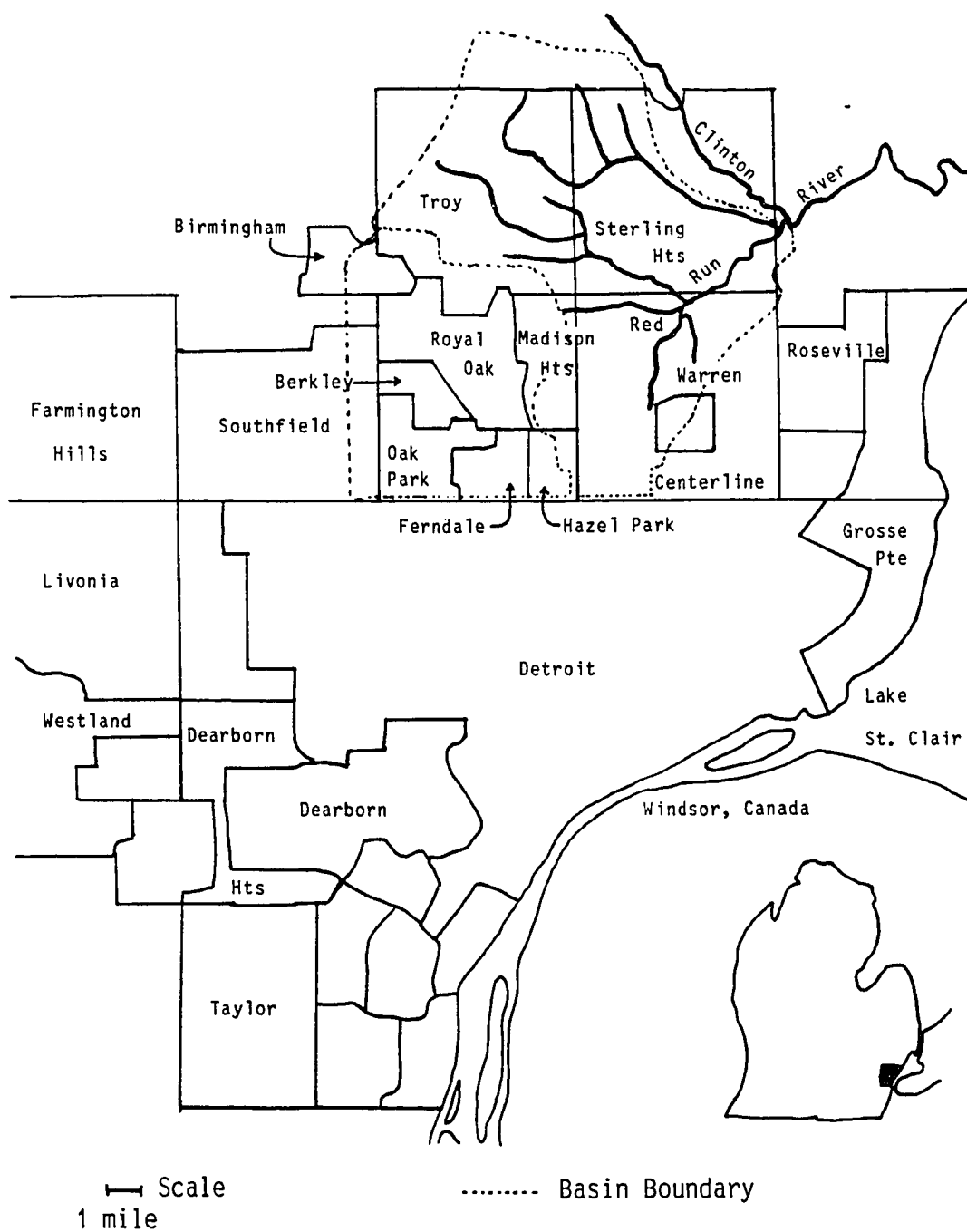


Figure 3. Red Run Drainage Basin Location Map.

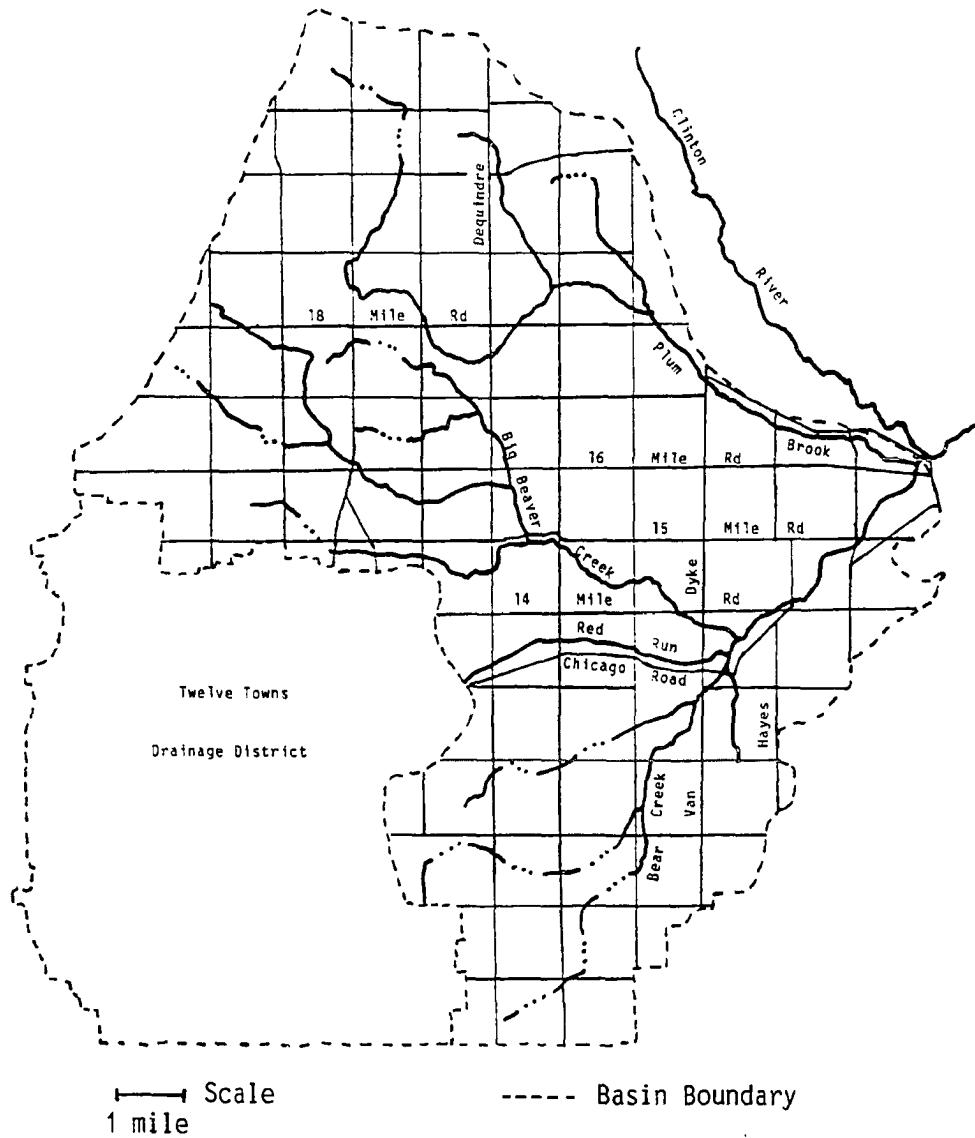


Figure 4. Red Run Drainage Basin.

natural tributary which received storm and sanitary wastes from several suburbs just north of the Detroit City limits. Increased runoff resulting from urban development exceeded the natural capacity of the Red Run and led to large-scale flooding during major rain events. In 1954, the U.S. Army Corps of Engineers completed a widening and straightening project on all of the now exposed length of the Red Run. This project increased bottom widths to 40 feet upstream of Bear Creek, 80 feet below Bear Creek, 100 feet below Beaver Creek, and 125 feet below Plum Brook (U.S. Army Corps of Engineers, 1976 cited in MDNR, 1988). The top of the channel varies from 90 to 200 feet in width. The channel capacity of the Red Run at its confluence with the Clinton River is $227 \text{ m}^3/\text{s}$ ($8000 \text{ ft}^3/\text{s}$).

Further urbanization of the area led to the construction of the Twelve Towns Drainage System in 1965. Many of the natural and previously existing drains were enclosed and their volume increased. The 38-square-mile system drains all or parts of Hazel Park, Madison Heights, Troy, Ferndale, Royal Oak, Clawson, Berkley, Huntington Woods, Oak Park, Pleasant Ridge, Beverly Hills, Royal Oak Township, Southfield, and Birmingham (McKinnen, 1987, cited in MDNR, 1988). Normal flow from this system was directed to the Detroit Wastewater Treatment Plant. Volumes in excess of its capacity of 32.5 million gallons overflowed into an open portion of the Red Run. Overflows from this combined sewer system severely degraded the entire Red Run and several miles downstream on the Clinton River (MDNR, 1988).

In 1973 the Southeastern Oakland County Sewage Disposal System/

Pollution Control Facility was built "for greater storage capacity, to reduce the number and amount of overflows to Red Run, to provide primary treatment and to route its daily discharge to the Detroit wastewater treatment plant..." (MDNR, 1988, p. 225 & 229). Approximately 3.4 kilometers (2.1 miles) of the Red Run adjacent to the Twelve-Towns Drainage System was enclosed providing a storage capacity of more than 235,000 m³ (62.2 million gallons). The facility discharges 170,000 - 198,000 m³ per day (44 - 52 million gallons/day) to the Detroit wastewater treatment plant during dry weather and up to 595,000 m³ (157 million gallons) per day during wet weather. When the facility is full, the excess is chlorinated and discharged to the Red Run. Overflows from this system averaged 12 per year between 1973 and 1987 with an annual average overflow of 7,435,000 m³ (1.96 billion gallons).

Approximately 3.5 miles downstream from the outlet of the Twelve Towns Pollution Control Facility is located the Warren Wastewater Treatment Plant. This facility is a tertiary wastewater treatment system with a design capacity of 60 million gallons/day, and an average flow of 31 million gallons/day. The annual flow from the Warren wastewater treatment plant is about six times that of the combined annual overflows from the Twelve Towns Pollution Control Facility; yet, the overflows contribute more than twice the annual BOD₅ load and nearly 17 times the annual suspended solids load (MDNR, 1988). About 25 percent of the treatment plant's inflow comes from nearly 2400 business and industrial facilities. Many of these non-domestic users discharge metals to the treatment plant. Ten

continuous and two intermittent industrial dischargers also hold National Pollution Discharge Elimination System (NPDES) permits to release primarily non-contact cooling water, cooling tower blowdown, and/or stormwater directly to the Red Run.

In spite of the number of industrial and municipal dischargers to the Red Run, nonpoint pollution, specifically urban stormwater, remains the major source of pollution. Although quantitative stormwater characterizations have not been made, the Southeast Michigan Council of Governments (1978a cited in MDNR, 1988) estimated that an annual load of 18,223 metric tons of suspended solids, 620 metric tons of BOD₅, 78 metric tons of nitrogen, and 34 metric tons of phosphorus is discharged to the Red Run. These quantities are in excess of those from other sources (Table 14).

Although the Warren Wastewater Treatment Plant monitors its effluent for a number of water quality parameters, no consistent effort has been made to regularly assess the water quality of the Red Run. Instead, a number of sporadic studies by several agencies have provided a general picture of its water quality (Table 15). None of the studies appear to have been conducted during winter months.

The drought flow of the Clinton River above the mouth of the Red Run is 54.0 cubic feet per second (cfs). The Red Run adds 76.5 cfs made up of 0.4 cfs tributary flow, 55.7 cfs wastewater treatment plant flow, and 20.4 cfs industrial flow. Thus, essentially 100% of the Red Run's drought flow is treated wastewater and industrial noncontact cooling water. Further, this effluent makes up more than 50% of the total drought flow of the Clinton River measured at its

Table 14
Estimated Annual Pollutant Loadings to the Red Run^a

Source	Suspended Solids	BOD ₅	Nitrogen	Phosphorus
Point Source	139.2 (0.7%)	49.8 (5.6%)	3.9 (2.5%)	14.9 (21.4%)
Urban Stormwater	18223 (95.3%)	620 (69.7%)	78 (50.0%)	34 (48.9%)
Runoff from Grassland	87.0 (0.5%)	27 (3.0%)	13.5 (8.7%)	1.2 (1.7%)
Active Crop-land Runoff	38.0 (0.2%)	23 (2.6%)	11.5 (7.4%)	1.0 (1.5%)
Combined Sewer Overflow	636 (3.3%)	170 (19.1%)	49.0 (31.4%)	18.4 (26.5%)
Total	19123.2	809.8	155.9	69.5

Note: From Remedial Action Plan for Clinton River Area of Concern by Michigan Department of Natural Resources, 1988, p. 194.

^aIn metric tons per year and percent of total loading.

mouth.

The identification, risk assessment, and priority evaluation of environmental contamination sites in the state of Michigan is provided for by the Michigan Environmental Resource Act (Public Act 307). Each year the Environmental Response Division of the Michigan Department of Natural Resources develops two lists of environmental contamination sites. One list identifies sites requiring further "evaluation and interim response activities." The other list identifies sites where "response activities" are to be undertaken (MDNR,

Table 15

General Water Quality in Red Run and Bear Creek^a

Location	Year	Temp C	Conduct. (umhos/cm)	D.O.	pH	BOD	Fec Coli #/100 mL	Total Diss. Solids	Susp. Solids	Cl	Total PO ₄	NH ₃ & NH ₄	NO ₂ & NO ₃
RR-16 Mi Rd	1976	21.0		8.3	8.0	4.0	122.8 G	588.6	26.8		0.82	0.90	7.83
	1977	18.0		8.2	7.4	5.6	186.0 G	750.4	48.4		0.79	1.10	5.66
	1978	19.5		5.4	7.1	7.9	99.5 G	546.4	131.2		0.67	0.92	5.46
	1979	17.0		6.8	7.4	2.5	-	712.5	23.0		0.58	0.73	7.57
	1981	22.2	750.0										
RR-15 Mi Rd	1976	20.2		7.1	7.3	2.0	1086.0	428.0	24.7	87.0	0.85	0.26	5.51
	1981	28.3	807.5	7.5	-	-	-	-	-	-	-	-	-
	1987	22.0		4.7	-	-	-	-	-	-	-	-	-
RR-14 Mi Rd	1976	22.5		8.8	7.6	3.6	16.7 G	579.0	10.8		0.92	0.77	6.59
	1977	20.0		8.8	7.4	4.3	27.1 G	710.3	42.8		0.97	1.13	5.90
	1978	20.5		5.5	7.2	7.3	102.9 G	660.8	34.8		0.62	0.60	5.60
	1979	18.2		7.8	7.6	1.4	-	683.5	13.0		0.60	0.61	6.45
	1987	22.0		8.0									
Bear Creek	1976	18.5		4.2	7.4	5.9	6809.0	355.0	21.5	84.0	0.30	0.25	0.86
Michigan Water Quality Standards				5.0	6.5-9.0		200	500		125	1.0		

Note. Adapted from Remedial Action Plan for Clinton River Area of Concern by Michigan Department of Natural Resources, 1988, p. 63, 351-358.

^aYearly averages of available data. Results are in mg/L, unless otherwise noted. G = value calculated is geometric mean instead of arithmetic mean.

1986a cited in MDNR, 1988). In 1985, a three-mile stretch of the Red Run was included on the Act 307 list requiring evaluation and interim response activities. Several landfills (Figure 5) that received municipal, industrial, and household wastes in the 1950s and 1960s are located in this reach of the Red Run (E. C. Jordan, 1986 cited in MDNR, 1988). Leachate samples collected from these sites contained organics such as toluene and benzene as well as the heavy metals lead, nickel, and chromium.

Thus, because the channel of the Red Run has been extensively modified to alleviate regional flooding; because it is used as a drain to receive urban stormwater runoff, industrial and municipal discharges, and combined sewer overflows; and because it may be suffering further degradation from old landfills, it is obvious that the drainage basin has been heavily impacted by human activities.

Design

This study was conducted in two separate phases: (1) a series of sediment desorption studies, and (2) a series of stream studies.

Desorption Studies

Weighed subsamples of dried bottom sediments collected from the Red Run at 16 Mile Road were paired and subjected to desorption studies. One member of each pair was stirred with a sodium chloride (NaCl) solution of known concentration prepared by adding NaCl to water collected from the same Red Run site. The other member was stirred with the same concentration of sodium nitrate (NaNO_3)

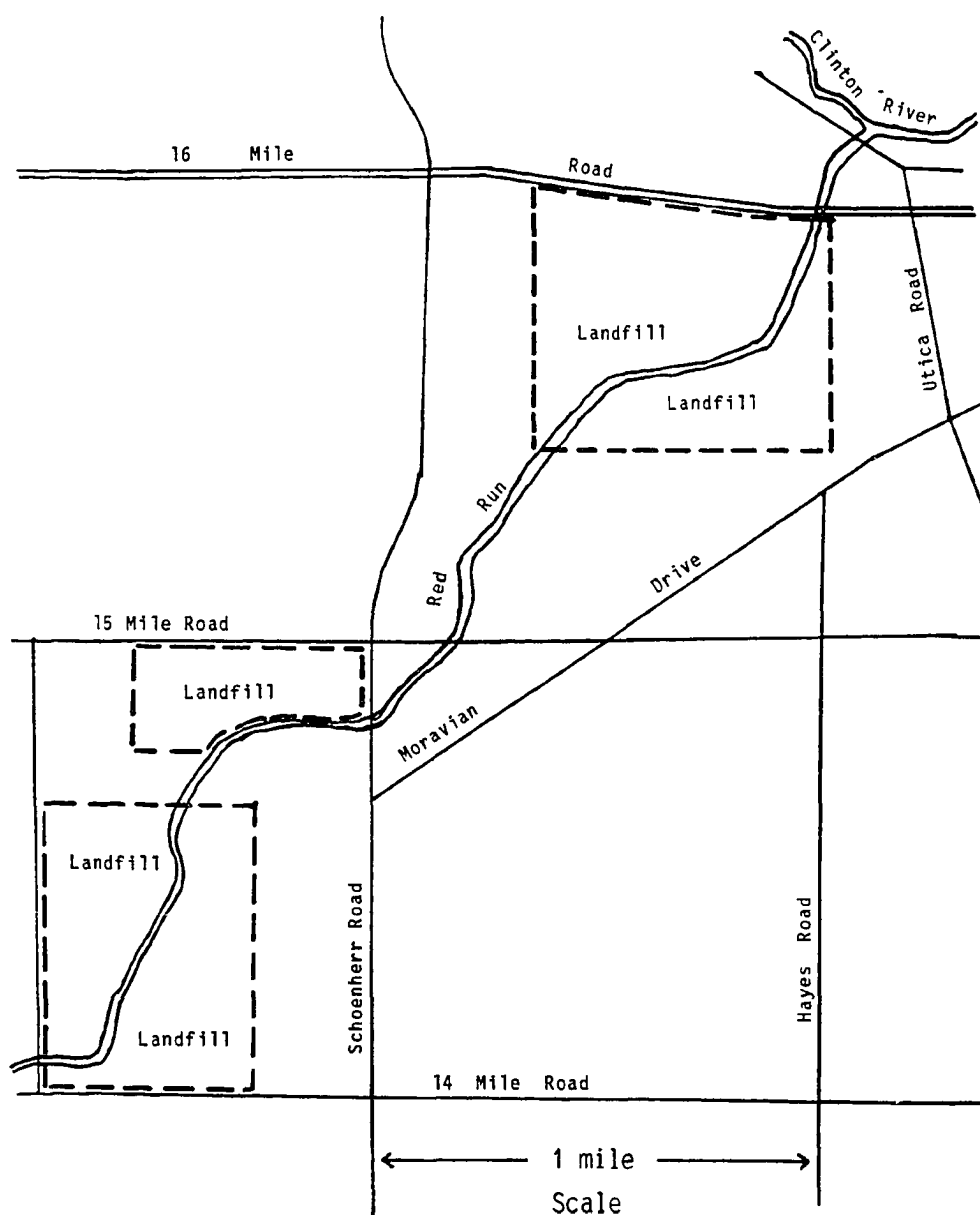


Figure 5. General Site Location of Red Run Landfills.

Note: From E. C. Jordon Co., 1986. In Michigan Department of Natural Resources. (1988). Remedial Action Plan for Clinton River Area of Concern. Lansing, MI: author, p. 240.

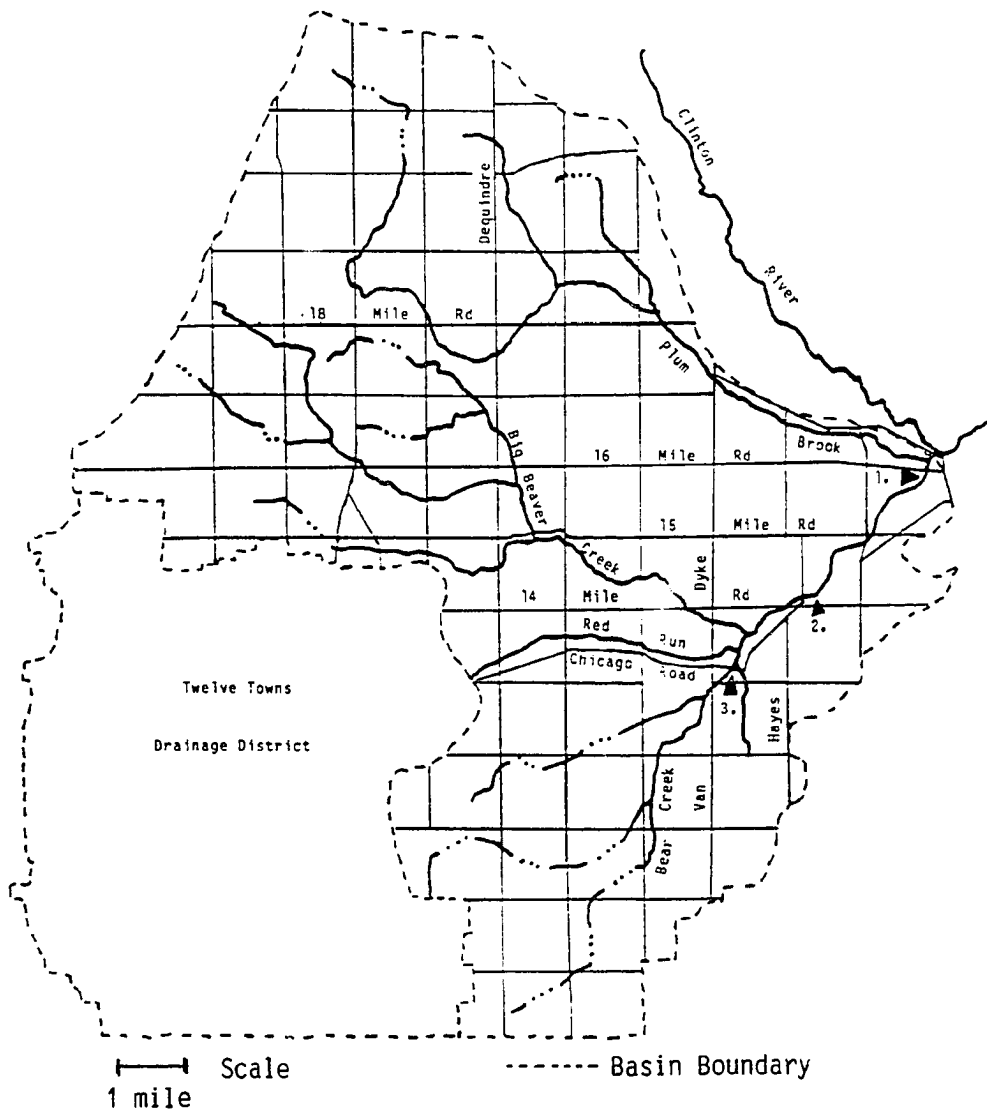
prepared in the same manner. Solution concentrations of cadmium, copper, lead, nickel, and zinc were determined in aliquots removed from each solution at specified time intervals. The desorption trials were repeated at different NaCl and NaNO₃ concentrations. Although many heavy metals are known to form complexes with chloride ion, complexes with nitrate ion are considered to occur to a negligible extent. Thus, any release of heavy metals into the NaNO₃ solutions was considered primarily due to ion exchange and any additional release into the NaCl solutions was considered to be primarily a result of complexing with chloride ion.

Stream Studies

The main focus of the stream studies was an examination of the relationship between chloride ion concentration and the concentration of cadmium, copper, lead, nickel and zinc during periods when the Red Run was receiving runoff containing deicing salts. The concentration of those same metals in Red Run bottom sediments was also briefly examined.

Metals in Red Run Water

Three sites (Figure 6) were selected from which to collect water samples for analysis: (1) the upstream side of the 16 Mile Road bridge across the Red Run about 1300 feet upstream from its confluence with the Clinton River; (2) the mouth of Schoenherr Drain, a major storm sewer discharging directly into the Red Run; and (3) the upstream side of the Chicago Road bridge across Bear Creek, a



1. Red Run at 16 Mile Road
2. Schoenherr Drain Mouth
3. Bear Creek at Chicago Road

Figure 6. Sampling Sites in Red Run Drainage Basin.

major upstream tributary to the Red Run receiving runoff from a heavily urbanized area. These stations sample drainage areas of 54.7, 8.45, and 16 square miles, respectively (Nowlin, 1973; U.S. Army Corps of Engineers, 1982). When the Pollution Control Facility of the Southeastern Oakland County Sewage Disposal System overflows, part of the drainage from an additional 38.6 square miles flows through the Red Run.

Water samples were collected from the three sampling sites before, during, and after several winter snow storms when the surrounding streets received applications of road salt. These samples were then analyzed for their concentrations of dissolved cadmium, copper, lead, nickel, and zinc as well as chloride ion in order to determine any chloride ion concentration-heavy metal concentration relationship. These samples were compared to water samples similarly collected and analyzed for a summer rain event.

Metals in Red Run Bottom Sediments

Bottom sediment samples were collected from the 16 Mile Road site in the late fall and early spring and analyzed for their heavy metals content in an attempt to detect any changes occurring over the entire snow/road-salting season. Bottom sediment samples were also collected before and after a single road-salting period and before and after a summer rain event.

Methodology

General Laboratory Procedures

Every reasonable attempt was made to prevent or minimize contamination of samples with heavy metals. Accepted methods (APHA, AWWA, WPCF, 1981) were followed for cleaning glassware and other surfaces coming in contact with samples to be used for trace metal analysis.

Sample Collection

Water for the desorption studies was collected November 12, 1987, from the Red Run-16 Mile Road site using an all plastic horizontal Alpha bottle (also known as a Nance water sampler). The water was taken from a point approximately 1-2 feet below the surface, immediately transferred to clean polyethylene carboys, and refrigerated at 1-4°C until use.

Water samples used for analysis in the stream studies were also collected using a horizontal Alpha bottle. Part of the collected water was transferred directly to a glass or polyethylene bottle and reserved for analysis of its chloride ion content. Another 25-50 mL of the stream water was filtered through a 0.45 μ m membrane filter, used to rinse the filtration flask, and then discarded. An additional 200-250 mL of water was then passed through the same filter and transferred to a clean polyethylene sample bottle to which about 1.5 mL of concentrated nitric acid had been added. These samples were reserved for analysis of their heavy metals content and were

refrigerated at 1-4°C.

Bottom sediments were collected using an Ekman bottom dredge, emptied into a clean plastic pan, and transferred to a polyethylene sample bag using a plastic spoon. The collected sediments were transferred to clean porcelain evaporating dishes that had been rinsed with 35% nitric acid and dried at 100-110°C for 12-24 hours. The dried sediments were ground in a clean, acid-rinsed mortar and pestle, passed through a 2 mm sieve to remove larger particles, and stored in polyethylene sample bags. A sample splitter was used to divide the sediments into subsamples for metals analysis or desorption studies. One subsample was wet-sieved (Krumbein & Pettijohn, 1938) to determine its particle size distribution.

In order to determine the concentrations of trace metals in salt applied to roads in the study area, two samples of salt were collected from widely separated points in each of the covered salt piles maintained by the Sterling Heights Department of Public Works, the Warren Department of Public Works, and the Macomb County Road Commission. Each sample of approximately 220 g was collected in a glass bottle from a point about two to three inches below the surface of the pile. The salt samples were then dried in the glass bottles at 110°C for several hours and then tightly capped. The heavy metal content of each sample was determined by atomic absorption spectrometry on a solution containing 10,000 ppm Cl^- .

Desorption Studies

Weighed subsamples of sediment were subjected to desorption trials using either NaCl or NaNO₃ solutions. Water for the desorption solutions was collected from the Red Run-16 Mile Road site and filtered through a 0.45 μ m membrane filter. Reagent grade NaCl or NaNO₃ was added to the filtered water to produce solutions of the desired concentrations (Table 16). The solutions were then gently aerated with an aquarium bubbler for 3-4 hours to ensure that the desorption trials began with comparable levels of dissolved oxygen.

To a 50.0 g subsample of sediment in a clean 2 L polypropylene flask was added 1500 mL of a desorption solution and a large, teflon-coated magnetic stirring bar. The sediment and solution were mixed well and the flask placed on a foam rubber or styrofoam insulating pad on top of a magnetic stirrer. A pH electrode was placed in the solution and an attempt was made to control the pH at 7.6 ± 0.1 throughout the experiment by judicious dropwise addition of 1 M HNO₃ or 2 M NaOH. At specified time intervals (Table 16) a 140-150 mL aliquot was removed by pipet and filtered through a 0.45 μ m membrane filter which had been rinsed with 10 mL of 7.9 M HNO₃ and 20 mL of double distilled water. The receiving flask contained 0.5-1 mL concentrated HNO₃ as a preservative. The filtered, acidified aliquot was then transferred to a clean polyethylene bottle and refrigerated until analysis.

Table 16
Desorption Study Parameters

Solution Concentration of added Chloride or Nitrate ^a (ppm)	Sampling Times
10,000	20 min
5,000	1 hr
2,500	3 hr
1,000	24 hr
500	3 days
250	7 days
0	15 days

^aAs NaCl or NaNO₃. The Red Run water used to prepare the desorption solutions contained an additional 122 ppm chloride. General water quality analyses dating back to 1973 (Table 15 and MDNR, 1988) suggest the initial Red Run water contained less than 10 ppm nitrate.

Total Metals in Sediments

A strong acid digestion procedure (Cool et al., 1980) was used to measure the "total" metals in the sediment. A weighed subsample of sediment (mean 15 g) was heated with either 50 or 100 mL of 1:1 1 M HNO₃:1 M HCl at 75°C for about 3 hours in an acid-washed pyrex flask with frequent swirling of the flask contents. The flask was then allowed to cool to room temperature and the sediment allowed to stand in contact with the acid mixture for an additional 24 hours with occasional swirling. The clear supernatant was removed by pipet and filtered through an acid-rinsed 0.45 µm membrane filter. The

sediment was rinsed several times with fresh portions of the acid mixture and filtered as before. The combined filtrate was made up to a total volume of 250 mL with the same $\text{HNO}_3\text{:HCl}$ mixture and analyzed according to standard techniques (APHA, AWWA, WPCF, 1981) using acetylene-air flame atomic absorption spectrometry. Standards used for preparation of the calibration curves were prepared in the same $\text{HNO}_3\text{:HCl}$ acid mixture.

Exchangeable Metals in Sediments

Metals considered to be "exchangeable" or "readily available" in the sediments were determined by extraction with 1 M ammonium acetate, NH_4OAc (Gibson & Farmer, 1984; Lau & Wong, 1983). A weighed sub-sample of sediment was mixed with sufficient 1 M NH_4OAc to give a sediment:solution ratio of 1:5 and the mixture stirred intermittently for 3 days at room temperature. The clear supernatant was then removed by pipet and filtered through a 0.45 μm membrane filter which had been rinsed with 7.9 M HNO_3 followed by double-distilled water. The remaining sediment was rinsed several times with fresh 1 M NH_4OAc , filtered as before, and the combined filtrate made up to a total volume of 250 mL with 1 M NH_4OAc . Metals were again determined using flame atomic absorption spectrometry. Standards were prepared in double-distilled water to which 1.5 mL concentrated HNO_3 per liter had been added. A blank of 1 M NH_4OAc was used to check and correct for any trace metals in the extracting solution.

Heavy Metals Analysis

Metal concentrations were determined by flame atomic absorption spectrometry using either a Varian Dial Atom III or a Buck 200A atomic absorption spectrometer. These instruments integrate absorbance readings for either 4 or 7 seconds before displaying a single value. The average of several of integrated readings was used as the absorbance measurement for each standard or sample. For each set of analyses, a fresh set of seven standard solutions was prepared from commercial stock solutions. The exact range of concentrations prepared depended upon the metal being analyzed and whether the direct aspiration or chelation-extraction method was to be used. A fresh blank was also prepared at the same time. Analytical standards and solutions were prepared from distilled water which had been distilled a second time through an all glass apparatus.

Because the concentrations of most metals in the stream water samples, the desorption samples, and the solutions prepared from the road salt samples were below or near the detection limit of the atomic absorption spectrometer in the direct aspiration mode, the chelation-extraction method was used (APHA, AWWA, WPCF, 1981). In this method, the trace metals are complexed with ammonium pyrrolidine dithiocarbamate (APDC) and extracted into methyl isobutyl ketone (MIBK) before atomic-absorption analysis. Compared to the direct aspiration method, the chelation-extraction method permits the determination of lower concentrations of metals. The concentration of metals that can be detected depend; in large measure, on the

concentration factor used in the extraction step. The method also has the advantage of permitting the determination of trace metals in solutions of high salt concentration--solutions that can often produce troublesome interference effects in direct aspiration techniques (Brooks, Presley, & Kaplan, 1967). Unfortunately, the chelation-extraction method also has some significant practical disadvantages:

1. It severely reduces the volume of sample available for analysis. In this study, the concentrations of five metals in each sample were typically determined in 20 to 40 mL of MIBK extract.
2. The laboratory work required to prepare each sample for analysis introduces additional potential sources of error.
3. It approximately triples the total time required for analysis.

Because the complexes may not be stable for more than several hours, the MIBK extracts were immediately frozen with dry ice. Immediately prior to analysis, all the MIBK extracts from standard solutions and sample solutions were thawed together and the droplets of water which had formed at the bottoms of the containers were removed.

Atomic Absorption Sensitivity and Precision

One measure of the ability of an atomic absorption instrument to detect small concentrations of metal is the sensitivity. "The sensitivity of flame atomic absorption spectrometry is defined as the metal concentration that produces an absorption of 1% (an absorbance of approximately 0.0044)" (APHA, 1985, p. 153). The sensitivity

varies with the instrument, the metal determined, and the technique used. The detection limit for a particular metal is approximately one fourth to one tenth the sensitivity depending on the metal. The sensitivity for each metal was determined from the appropriate calibration curves (Table 17).

The precision of the atomic absorption determinations was calculated from the calibration curves as described by Kolthoff, Sandell, Meehan, and Bruckenstein (1969).

Table 17
Mean Atomic Absorption Sensitivities^a (mg/L)

Method	Cd	Cu	Pb	Ni	Zn
Direct Aspiration of Aqueous Solutions	.02	.05	.2	.11	.02
Chelation-Extraction	.002	.006	.014	.012	.001

^aConcentration that produces an absorbance of 0.0044.

Analysis for Chloride Ion

The chloride ion (Cl^-) concentration in each of the stream samples was determined by duplicate Mohr titrations (APHA, AWWA, WPCF, 1981; Ayres, 1958; Fischer & Peters, 1968).

Statistical Analyses

All statistical computations were carried out using SPSS-X Release 3.1 on a VAX 3600 computer.

CHAPTER III

RESULTS AND DISCUSSION

Desorption Studies

Desorption solutions were prepared from water collected from the Red Run-16 Mile Road station November 12, 1987. This water contained 122 ± 1 mg/L chloride. The metals content of this water was determined (Table 18) and subtracted from the corresponding concentrations of metals measured in the desorption trials. The sediment used for the desorption trials was collected from the Red Run-16 Mile Road station October 31, 1985 and its total and exchangeable metals content determined (Table 19). Although an attempt was made to control the pH of each desorption experiment at 7.6 ± 0.1 , the actual pH usually ranged from 7.6 - 7.8. On a few occasions the pH briefly ranged as high as 8.0 before being corrected back to 7.6.

Aliquots were removed from each of the sodium chloride or sodium nitrate desorption solutions at specified time intervals and analyzed for their heavy metals content (Tables 20, 21, 22, & 23). Lead was generally below detection limits and was, therefore, deleted from further analysis. The data for each metal and sampling time were subjected to a multiple regression analysis using a "dummy" variable technique (Kleinbaum & Kupper, 1978). The dummy variable served to categorize the chloride data and the nitrate data. Doing so permit-

Table 18

Metal Concentrations (ug/L) in Water Used for Desorption Trials

Metal	Cd	Cu	Pb	Ni	Zn
Concentration	1 _± .6	4 _± .5	nd ^a	16 _± 2	54 _± 4

^and = none detected.

Table 19

Metals Content (mg/kg dry wt) in Sediments
Used for Desorption Trials

Metal	Cd	Cu	Pb	Ni	Zn
Total	5.2 _± .3	46 _± 1.1	119 _± 1.1	36 _± 1.4	277 _± 3
Exchangeable	1.2 _± .1	3.0 _± .1	2.0 _± .2	1.8 _± .1	28.9 _± .8

ted both the incorporation of a regression of metal concentration on chloride concentration and a regression of metal concentration on nitrate concentration into a single model. For example, if the dummy variable $Z = 0$ is assigned to the chloride data and $Z = 1$ to the nitrate data, both sets of data can be fitted to an equation of the form:

$$Y = B_0 + B_1X + B_2Z + B_3XZ + E \quad (1)$$

where Y = the concentration of the metal of interest and X = the anion concentration, either chloride or nitrate. Thus, for the chloride data, when $Z = 0$, the equation becomes:

$$Y = B_0 + B_1X + E \quad (2)$$

where B_0 and B_1 are the intercept and the slope, respectively, of the

Table 20
Cadmium Concentration (ug/L) in Desorption Solutions^a

Time	Added Anion	Concentration of Added Anion (mg/L)							Test for Parallelism	Test for Coincidence
		0	250	500	1000 ^b	2500 ^b	5000	10,000	F(df)	F(df)
20 min	Cl ⁻	nd ^c	nd	1	1	2	4	7	57.76(1,10)**	46.86(2,10)**
	NO ₃ ⁻		1	nd	1	nd	1	2		
60 min	Cl ⁻	nd	nd	1	nd	2	5	9	37.27(1,10)**	25.89(2,10)**
	NO ₃ ⁻		1	nd	nd	2	2	4		
3 hr	Cl ⁻	nd	1	1	nd	2	-- ^d	9	19.07(1,9)*	13.21(2,9)*
	NO ₃ ⁻		1	nd	1	1	3	5		
24 hr	Cl ⁻	1	2	1	1	3	6	9	23.81(1,10)**	18.74(2,10)**
	NO ₃ ⁻		2	nd	2	2	2	4		
3 days	Cl ⁻	nd	2	2	1	3	7	12	59.75(1,10)**	43.20(2,10)**
	NO ₃ ⁻		2	1	2	2	2	3		
7 days	Cl ⁻	1	3	3	--	5	8	13	73.06(1,9)**	84.66(2,9)**
	NO ₃ ⁻		2	1	1	1	3	3		
15 days	Cl ⁻	2	2	3	2	5	11	15	63.69(1,10)**	50.22(2,10)**
	NO ₃ ⁻		3	1	3	1	3	2		
Precision										
Cl ⁻ data			+0.3	+0.3	+1	+1	+1	+1		
NO ₃ ⁻ data		+0.1	+0.6	+0.1	+1	+1	+0.6	+0.6		

^aCorrected for cadmium in water used for desorption solutions and for cadmium in added NaCl and NaNO₃. ^bThe 1000 and 2500 ppm NO₃⁻ samples were analyzed together. A small change in instrument conditions during the analysis necessitated using the calibration curve determined at the beginning of the analysis for the first five samples and the calibration curve determined at the end of the analysis for the last nine samples.

nd = none detected. -- = not determined.

* $p < 0.005$

** $p < 0.001$

Table 21
Zinc Concentration (ug/L) in Desorption Solutions^a

Time	Added Anion	Concentration of Added Anion (mg/L)							Test for Parallelism	Test for Coincidence
		0	250	500	1000	2500	5000 ^b	10,000 ^b	F(df)	F(df)
20 min	Cl ⁻	31	23	26	24	24	32	27	7.08(1,10)*	3.54(2,10)ns ^c
	NO ₃ ⁻		27	40	32	25	16	17		
60 min	Cl ⁻	26	24	34	16	23	41	38	2.29(1,10)ns	1.28(2,10)ns
	NO ₃ ⁻		25	37	22	27	23	29		
3 hr	Cl ⁻	30	18	35	16	20	-- ^d	36	2.31(1,9)ns	1.17(2,9)ns
	NO ₃ ⁻		27	51	25	21	10	23		
24 hr	Cl ⁻	29	26	38	11	15	46	34	3.37(1,10)ns	3.02(2,10)ns
	NO ₃ ⁻		20	33	17	18	9	11		
3 days	Cl ⁻	29 ^e	7	7	7	19	42	34	10.12(1,10)**	5.17(2,10)*
	NO ₃ ⁻		19	21	32	15	6	6		
7 days	Cl ⁻	22 ^e	6	40	21	16	50	44	9.20(1,10)*	5.07(2,10)*
	NO ₃ ⁻		39	28	20	25	23	2		
15 days	Cl ⁻	21 ^e	20	35	18	36	76	46	4.96(1,10)*	6.66(2,10)*
	NO ₃ ⁻		19	12	36	22	4	2		
Precision										
Cl ⁻ data			+3	+3	+5	+5	+3	+3		
NO ₃ ⁻ data		+6	+4	+6	+4	+4	+7	+7		

^aCorrected for zinc in water used for desorption solutions and for zinc in added NaCl and NaNO₃. ^bThe calibration curve for the nitrate data showed some curvature. Estimated error +3 ug/L. ns = not significant. -- = not determined. ^cEstimated from corrections to data, necessitated by electrical failure during analysis.

* $p < 0.05$ ** $p < 0.01$

Table 22
Copper Concentration (ug/L) in Desorption Solutions^a

Time	Added Anion	Concentration of Added Anion (mg/L)							Test for Parallelism	Test for Coincidence
		0	250	500	1000	2500	5000	10,000	F(df)	F(df)
20 min	Cl ⁻	20	27	29	11	14	11	12	0.11(1,10)ns ^b	0.06(2,10)ns
	NO ₃ ⁻		20	31	10	15	14	13		
60 min	Cl ⁻	23	36	34	12	16	13	18	0.32(1,10)ns	0.35(2,10)ns
	NO ₃ ⁻		19	32	10	16	12	20		
3 hr	Cl ⁻	28	38	33	13	16	-- ^c	19	0.04(1,9)ns	0.02(2,9)ns
	NO ₃ ⁻		24	47	18	16	12	19		
24 hr	Cl ⁻	33	42	41	17	20	20	25	0.06(1,10)ns	0.38(2,10)ns
	NO ₃ ⁻		24	35	20	19	18	22		
3 days	Cl ⁻	26	30	23	--	20	18	25	0.03(1,9)ns	1.49(2,9)ns
	NO ₃ ⁻		16	26	17	15	14	19		
7 days	Cl ⁻	28	29	35	26	10	13	19	0.06(1,10)ns	1.26(2,10)ns
	NO ₃ ⁻		12	30	7	9	9	12		
15 days	Cl ⁻	24	20	20	13	12	24	18	0.64(1,10)ns	0.58(2,10)ns
	NO ₃ ⁻		20	29	7	7	12	13		
Precision										
Cl ⁻ data			<u>+2</u>	<u>+4</u>	<u>+4</u>	<u>+2</u>	<u>+2</u>	<u>+2</u>	<u>+2</u>	
NO ₃ ⁻ data				<u>+3</u>	<u>+2</u>	<u>+2</u>	<u>+2</u>	<u>+1</u>	<u>+1</u>	

^aCorrected for copper in water used for desorption solutions and for copper in added NaCl and NaNO₃. ^bns = not significant. ^c-- = not determined.

Table 23
Nickel Concentration (ug/L) in Desorption Solutions^a

Time	Added Anion	Concentration of Added Anion (mg/L)							Test for Parallelism	Test for Coincidence
		0	250	500	1000	2500	5000	10,000	F(df)	F(df)
20 min	Cl ⁻		35	34	6	6	15	12	1.19(1,9)ns ^b	0.64(2,9)ns
	NO ₃ ⁻	24	-- ^c	28	9	18	18	25		
60 min	Cl ⁻		38	32	6	9	11	18	0.75(1,9)ns	0.46(2,9)ns
	NO ₃ ⁻	26	--	22	1	18	12	24		
3 hr	Cl ⁻		37	30	6	12	--	14	0.13(1,8)ns	0.07(2,8)ns
	NO ₃ ⁻	28	--	40	12	11	11	24		
24 hr	Cl ⁻		42	35	7	9	13	19	0.21(1,9)ns	0.21(2,9)ns
	NO ₃ ⁻	28	--	28	10	14	9	21		
3 days	Cl ⁻		26	18	1	13	10	15	0.02(1,9)ns	0.48(2,9)ns
	NO ₃ ⁻	17	--	13	8	5	5	13		
7 days	Cl ⁻		19	19	13	nd ^d	4	8	0.31(1,9)ns	1.48(2,9)ns
	NO ₃ ⁻	11	--	13	-7 ^e	-1	-3	6		
15 days	Cl ⁻		8	4	1	nd	3	7	0.00(1,9)ns	0.78(2,9)ns
	NO ₃ ⁻	8	--	7	-11	-5	-2	4		
Precision										
	Cl ⁻ data		+13	+13	+3	+3	+4	+4		
	NO ₃ ⁻ data	+6		+6	+5	+5	+3	+3		

^aCorrected for nickel in water used for desorption solutions and for nickel in added NaCl and NaNO₃. ^bns = not significant. ^c-- = not determined. ^dnd = none detected. ^enegative sign indicates a net adsorption of nickel.

chloride regression line. For the nitrate data, when $Z = 1$, the equation becomes:

$$Y = (B_0 + B_2) + (B_1 + B_3)X + E \quad (3)$$

where $(B_0 + B_2)$ and $(B_1 + B_3)$ are the intercept and slope, respectively, of the nitrate regression line.

The following two hypotheses were then tested for Equation 1:

1. The two regression lines are parallel ($H_0: B_3 = 0$).

If $B_3 = 0$, the slope of both the chloride and the nitrate regression lines is B_1 , meaning the lines are parallel. The hypothesis is tested using an F test calculated from:

$$F = \frac{SS \text{ regression } (X, Z, XZ) - SS \text{ regression } (X, Z)}{MS \text{ residual } (X, Z, XZ)} \quad (4)$$

A significant F allows the hypothesis to be rejected and indicates the slopes of the two regression lines are not equal. If the slope of the chloride regression line is greater than the slope of the nitrate regression line, a significant F further implies that increasing chloride ion concentrations produce a greater release of the metal in question from the sediments than does the corresponding increase in nitrate ion concentrations.

2. The two regression lines are coincident ($H_0: B_2 = B_3 = 0$).

If both B_2 and B_3 are zero, the nitrate regression line (Equation 3) reduces to the chloride regression line (Equation 2), meaning the two lines are coincident. The hypothesis is tested using an F test calculated from:

$$F = \frac{[SS \text{ regression } (X, Z, XZ) - SS \text{ regression } (X)]/2}{MS \text{ residual } (X, Z, XZ)} \quad (5)$$

A significant F allows the hypothesis to be rejected and indicates the two regression lines are not coincident. Thus, if corresponding increases in chloride or nitrate concentration produce the same increase in metal concentration (the slopes of the two lines are equal), one anion could still produce an overall greater release of metal compared to the other. The test for coincidence allows one to test for this possibility. The test for parallelism and the test for coincidence, taken together, permit a statement of the efficacy of chloride versus nitrate in releasing heavy metals from sediments.

Results of these statistical tests (Tables 20, 21, 22, & 23) indicate that cadmium is released from sediments to a greater extent under the influence of chloride ion than under the influence of nitrate ion. Not only are overall levels of cadmium released greater with chloride ion, but the amounts released increased to a greater extent with increasing chloride concentration than with increasing nitrate concentration. Because the nitrate ion is a weak ligand at best and forms relatively few stable complexes (van der Weijden et al., 1977; Masterton & Slowinski, 1977), these results are supportive of a desorption model in which nitrate solutions increase cadmium solubility primarily through ion-exchange at sediment adsorption sites, whereas chloride ion additionally forms complexes with cadmium and increases its mobilization from sediments.

A similar, but more subdued effect was observed for zinc. The F tests for parallelism and coincidence were simultaneously significant ($p < .05$) for only the three longest desorption periods. These tests demonstrate that the chloride and nitrate regression lines for each

desorption period were not coincident and had different slopes. Along with the observed concentrations, this implies that zinc desorbs to a greater extent under the influence of chloride ion than under the influence of nitrate ion at the longer desorption periods. These results suggest that the formation of chloro-zinc complexes in the chloride solutions increase the solubility of zinc compared to that in the nitrate solutions where such complexes cannot occur to an appreciable extent. Further, the more pronounced results for cadmium compared to zinc suggest that the formation of soluble chloro-metal complexes are more important in the desorption of cadmium than they are for zinc. These are the results one might expect if zinc desorbs from sediments more slowly and to a lesser extent than does cadmium.

A number of other studies have pointed to the fact that chloride ion concentration influences the desorption or adsorption of cadmium to a greater extent than zinc. van der Weijden et al. (1977) compared the percent metal desorbed from Rhine River suspended sediment in sea water versus "nitrate sea water" at pH 7.5 and obtained results analogous to those of this study. Cadmium was found to desorb to a much greater extent in sea water compared to "nitrate sea water" (80% versus 17%, Table 12). For zinc, the effect was much less pronounced (21% versus 17%). Tyler and McBride (1982) found the order of mobility of metals in organic and mineral soil columns leached with 0.01 M CaCl_2 to be: $\text{Cd} \geq \text{Ni} \geq \text{Zn} \gg \text{Cu}$. Salomons (1980) determined the influence of chlorinity on the adsorption of cadmium and zinc onto Rhine River suspended sediment to be smaller

for zinc than for cadmium. For example, an increase in chloride concentration from 0 to 19,000 ppm at pH 8.5 decreased the percentage of cadmium adsorbed from 60% to 5%. For zinc the change was from 75% to 57%.

In their study of the effect of calcium magnesium acetate on the mobility of heavy metals in a silt loam soil, Elliott and Linn (1987) failed to detect differences in the extent of zinc desorption between 0.01 M calcium magnesium acetate or the corresponding chloride or nitrate salts at pHs between 4 and 6.5.

The multiple regression analyses did not reveal any significant differences for either copper or nickel in levels of metal desorbed from sediments with chloride solutions versus nitrate solutions (Tables 22 & 23). Analogous results were obtained by Doner (1978) in his investigation of the mobilities of nickel, copper, and cadmium ions through soil. Little difference was found in the concentration of copper or nickel in the effluent from sandy loam columns with 0.1 M NaCl (3550 ppm Cl) versus 0.1 M NaClO₄. Cadmium concentrations, however, were up to 10 times greater in the NaCl effluent than in the NaClO₄ effluent--the exact value depending upon the number of pore volumes of solution that had passed through the column.

In this study, an overall Pearson correlation coefficient was calculated for each metal for chloride ion concentration versus metal concentration (Table 24). A correlation coefficient for nitrate ion concentration versus metal concentration was also calculated for comparison. Of the four metals, cadmium was found to correlate most strongly with chloride ($r=.90$). Thus, higher concentrations of

Table 24
Anion-Metal Correlations^a in Desorption Trials

Metal	Chloride Correlation (<u>r</u>)	Nitrate Correlation (<u>r</u>)
Cadmium	.90 (very high positive) ^b	.68 (moderate positive)
Copper	-.38 (low negative)	-.35 (low negative)
Nickel	-.29 (little if any)	-.03 (little if any)
Zinc	.49 (low positive)	-.58 (moderate negative)

^aPearson correlation coefficients. ^bTerms describing the degree of correlation are from: Hinkle, D. E., Wiersma, W., & Jurs, S. G. (1979). Applied statistics for the behavioral sciences. Boston: Houghton Mifflin.

dissolved cadmium were associated with higher concentrations of chloride ion with 81% of the variance in cadmium levels being associated with the variance in chloride levels. Cadmium was also observed to have a moderate correlation (r=.68) with nitrate ion concentration. The "moderate" cadmium-nitrate correlation is what would be expected if increased solution ionic strength increased cadmium solubility through ion exchange at sediment adsorption sites. The "very high" cadmium-chloride correlation is what would be expected if chloride ion additionally formed strong chloro-cadmium complexes which dominated the cadmium species in solution. High chloride levels would then favor the additional release of cadmium from sediments compared to the same levels of nitrate ion.

For zinc, a positive but somewhat lower correlation of metal and chloride levels (r=.49) was observed. The variance in zinc

concentration was associated with only 24% of the variance in chloride concentration. A less pronounced correlation of zinc and chloride levels would be expected if chloro-zinc complexes were in competition with other major zinc species (for example, Zn^{2+} , $\text{Zn}(\text{OH})_2^0$, and ZnCO_3^0) in solution.

Li, Burkhardt, and Teraoka (1984) attempted to model the behavior of trace metals during estuarine mixing. They added radio-tracer spikes to mixtures of seawater and Hudson and Mississippi riverwaters and determined distribution coefficients between suspended sediments and water as a function of time and salinity. Similar to the results of this study, they found that cadmium and zinc along with cobalt, manganese, cesium, and barium were desorbed from river suspended particles at higher salinities. Significant fractions of dissolved iron, tin, bismuth, cerium, and mercury, however, were coagulated and removed from solution. After one day of equilibration, the distribution coefficients reached nearly constant values. They further found that an increase of 0.2 pH units produced virtually no change in the distribution coefficients for cadmium for salinities of 0 o/oo, 6 o/oo, and 29 o/oo. The same increase in pH caused a small increase in adsorption for zinc with the effect most noticeable at a salinity of 0 o/oo. Other studies (Salomons, 1980; van der Weijden et al., 1977) have confirmed the almost negligible change in cadmium desorption or adsorption with a change in pH of 0.5 pH units. Those same studies, however, have demonstrated a rather strong dependence of zinc desorption or adsorption on pH. The implication for this study is that small variations in pH during the

desorption trials probably had a negligible effect on the measured concentrations of cadmium but may have made some contribution to the variability observed in the zinc data.

Copper and nickel were found to have low ($r = -.38$) to little, if any ($r = -.29$), negative correlations, respectively, with chloride ion concentration in the desorption trials of this study. If copper and nickel do not form soluble chloro-species even at elevated chloride concentrations, one might expect the corresponding metal-chloride correlations to be very small, but positive, due to ion-exchange with the sediment. On the other hand, elevated concentrations of salt are known to promote flocculation of organic substances and their consequent removal from solution (Forstner & Wittmann, 1981). Metals that are strongly associated with such organic matter would, as a result, also be removed from solution. The solution concentration of these organically bound metals would, therefore, be expected to show a negative correlation with chloride concentration.

A number of extraction and leaching studies have shown that some metals have particular affinities for the organic phase in soils and sediments. Hamilton, Revitt, and Warren (1984) determined the association of cadmium, copper, lead, and zinc in five physical and chemical fractions of road dust and found copper to be distributed predominately (70%) in the organic phase. The organic associations of the remaining metals ranged from 13% for zinc to 24% for cadmium. A similar study by Harrison, Laxen, and Wilson (1981) of street dusts and roadside soils likewise found a disproportionate percentage of copper (48-58%) in the organic fraction compared to cadmium (8%),

lead (8-12%), and zinc (8-9%). Nriagu and Coker (1980) examined Lake Ontario sediments and found that copper and nickel were enriched in the humic acid fraction compared to the associated sediment fraction by mean factors of 29.9 and 2.1 respectively. For cadmium and zinc, the factors were 0.60 and 0.57 respectively. Tyler and McBride (1982) added cadmium, copper, nickel, and zinc to two mineral soils and one organic soil and compared their relative extractability with 0.1 M HCl. Whereas nearly 100% of all four metals were extractable from one mineral soil and 55-63% were extractable from another, only 32% of the copper and 44% of the nickel were extractable from the organic soil. Zinc and cadmium were extractable to an extent of 54% and 60% respectively.

Tyler and McBride also examined the relative mobility of cadmium, copper, and nickel through a mineral soil column and an organic soil column upon elution with 0.01 M CaCl_2 . They found that both cadmium and nickel eluted later and in much smaller quantities from the organic soil than from the mineral soil. Copper did not elute at all from the organic soil.

These studies indicate that copper and, to a lesser extent, nickel are more strongly bound to organic material in road dusts and soils than cadmium and zinc. As it applies to this study, the negative correlations of copper and nickel with chloride concentration in the desorption studies may be a reflection of the lower solubility of organically bound copper and nickel in solutions of higher ionic strength.

Stream Studies

Heavy Metals in Water

Water samples were collected from the three sampling stations immediately before, during, and after several snowfall-road salting events (Tables 25, 26, & 27). A set of samples was similarly collected for a summer rain event and single samples were collected immediately after a major snow-melt and rain (January 19, 1986) and at the beginning of the spring season (March 29, 1986). All the snow event samples exhibited elevated chloride concentrations reflecting increased loads of deicing salts from street runoff. Chloride levels were generally highest at the Bear Creek site, slightly lower in Schoenherr Drain, and lowest at the 16 Mile Road site. This ranking of chloride concentrations indicates the amount of dilution of street runoff with water from other sources. The peak chloride concentration at each station was recorded during the same snow event (February 17 & 18, 1986). These maxima were: Bear Creek, 5425 ppm; Schoenherr Drain, 4571 ppm; and Red Run, 1830 ppm. These chloride concentrations are 38, 27, and 16 times higher than their respective summer means. Thus, deicing salts produce large changes in chloride levels at these sampling stations.

At each station, zinc was found in the highest concentrations, generally followed by nickel and copper, with cadmium being detected at the lowest levels. Lead was below the limits of detectability in nearly all the samples and was, therefore, eliminated from further consideration. In general, Bear Creek had the highest concentrations

Table 25
Dissolved Metal Concentrations (ug/L) in Red Run at 16 Mile Road^a

Date	Time	Precip- itation ^b	Snow- fall ^c	Sample Number	ppm Cl	Cd	Cu	Ni	Zn
12-02-85	7:45 am	31	1.2	1	99	2	12	26	47
12-22-85	3:00 pm	20	1.9	6	270	1	8	29	45
12-22-85	8:40 pm			9	303	3	7	37	34
12-23-85	11:05 pm			12	333	1	8	40	40
12-23-85	9:15 pm			15	830	1	5	28	25
12-24-85	7:50 am			18	1157	nd ^d	5	38	62
1-04-86	10:50 pm	20	2.5	22	883	1	2	27	77
1-04-86	11:00 pm			21E	836	1	5	27	56
1-05-86	6:55 am			25	501	1	1	23	66
1-05-86	2:45 pm			28	540	1	4	23	52
1-05-86	11:20 pm			32	896	nd	3	24	49
1-06-86	1:35 pm			35	818	1	7	24	44
1-19-86	4:15 pm	38		38	250	3	9	--	20
2-08-86	1:05 am	31	5.8	39	564	1	2	18	61
2-08-86	2:10 pm			42	531	1	4	21	58
2-17-86	12:30 am	37	5.1	45	503	1	1	33	52
2-17-86	9:50 am			48	647	nd	2	38	58
2-17-86	10:10 am			49E	651	nd	3	41	46
2-17-86	4:10 pm			52	818	1	1	34	53
2-17-86	10:35 pm			55	1016	1	1	26	75
2-18-86	12:30 pm			58	1830	2	7	26	101
2-18-86	7:45 pm			61	1505	2	9	21	113
3-29-86	1:10 pm	0		62	249	3	3	18	48
1-02-87	1:45 am	19	2.8	64	135	2	--	37	94
1-02-87	2:00 am			63E	134	1	--	36	44
1-02-87	11:59 am			67	157	nd	--	33	43
1-02-87	8:00 pm			70	592	1	--	45	12
1-03-87	1:00 pm			73	894	1	--	42	79
1-03-87	9:10 pm			76	430	3	--	35	47
Pearson r (metal:chloride)						-0.18	-0.09	-0.18	0.57
Probability						0.17	0.33	0.18	0.001
8-27-88	8:45 pm	17		77	111	1	1	17	52
8-27-88	11:45 pm			80	100	nd	1	13	47
8-28-88	1:40 am			83	104	1	1	14	41
8-28-88	7:00 am			86	120	nd	--	--	58
8-28-88	10:15 am			89	131	1	2	14	37
Mean Precision					+1	+1	+2	+4	+7

^aWinter samples: temp. 4 - 14.5°C, mean pH = 7.6. Summer: temp. 20 - 23°C, mean pH = 7.3.

^bin hundredths of an inch water equivalent. Entries are totals for each precipitation event and are averages of data from six rain gauges located in and around the study area. From: Nurnberger, R. V., & Ordiway, A. R. (1985-1988). [SEMOG precipitation, annual summaries]. Unpublished raw data. ^cin inches. Data courtesy of William McNeil, Weather Station Chief, Selfridge Air National Guard, Mt. Clemens, MI. ^dnd = none detected.

Table 26
Dissolved Metal Concentrations (ug/L) in Schoenherr Drain Mouth^a

Date	Time	Precip- itation ^b	Snow- fall ^c	Sample Number	ppm Cl	Cd	Cu	Ni	Zn
12-02-85	8:30 am	31	1.2	2	126	3	21	24	86
12-02-85	4:30 pm			4	266	3	9	14	32
12-22-85	4:00 pm	20	1.9	7	537	1	2	12	49
12-22-85	9:10 pm			10	1047	2	6	14	57
12-23-85	12:15 pm			13	2643	3	6	12	46
12-23-85	9:45 pm			16	2654	2	8	9	78
12-24-85	8:25 am			19	2217	3	5	7	70
1-04-86	11:30 pm	20	2.5	23	1273	nd ^d	4	17	67
1-05-86	7:25 am			26	1461	nd	9	13	87
1-05-86	3:20 pm			29	1721	nd	4	14	55
1-05-86	3:30 pm			30L	1206	nd	2	13	60
1-05-86	11:45 pm			33	2289	2	3	8	63
1-06-86	2:00 pm			36	3101	1	5	5	95
2-08-86	1:25 am	31	5.8	40	656	1	2	11	44
2-08-86	3:55 pm			43	1375	3	3	9	71
2-17-86	1:05 am	37	5.1	46	1833	2	13	7	72
2-17-86	10:45 am			50	3921	3	14	15	91
2-17-86	4:40 pm			53	3987	3	12	7	136
2-17-86	11:00 pm			56	4571	5	19	16	144
2-18-86	1:35 pm			59	2860	1	14	13	167
1-02-87	2:30 am	19	2.8	65	262	1	--	10	158
1-02-87	12:25 pm			68	1208	nd	--	25	95
1-02-87	8:25 pm			71	2402	1	--	14	113
1-03-87	1:30 pm			74	858	2	--	15	135
Pearson r (metal:chloride)						0.42	0.36	-0.07	0.38
Probability						0.02	0.06	0.37	0.03
8-27-88	9:25 pm	17		78	190	1	1	8	67
8-28-88	12:15 am			81	216	nd	2	nd	72
8-28-88	2:10 am			84	203	nd	3	2	34
8-28-88	7:20 am			87	108	nd	3	--	71
8-28-88	10:45 am			90	114	1	2	14	29
Mean Precision					+1	+ .8	+2	+2	+6

^aWinter samples: temp. 5 - 9°C, mean pH = 7.7. Summer: temp. 19 - 21°C, mean pH = 7.3.

^bin hundredths of an inch water equivalent. Entries are totals for each precipitation event and are averages of data from six rain gauges located in and around the study area. From: Nurnberger, R. V., & Ordiway, A. R. (1985-1988). [SEMOG precipitation, annual summaries]. Unpublished raw data. ^cin inches. Data courtesy of William McNeil, Weather Station Chief, Selfridge Air National Guard, Mt. Clemens, MI. nd = none detected.

Table 27
Dissolved Metal Concentrations (ug/L) in Bear Creek^a

Date	Time	Precip- itation ^b	Snow- fall ^c	Sample Number	ppm Cl	Cd	Cu	Ni	Zn
12-02-85	9:00 am	31	1.2	3	149	4	15	24	121
12-02-85	5:10 pm			5	544	1	9	16	329
12-22-85	4:30 pm	20	1.9	8	590	nd ^d	7	19	33
12-22-85	9:40 pm			11	705	1	6	18	24
12-23-85	1:00 pm			14	2337	2	--	13	63
12-23-85	10:15 pm			17	2951	nd	6	18	105
12-24-85	8:50 am			20	3442	2	10	28	177
1-04-86	11:59 pm	20	2.5	24	1420	nd	4	15	78
1-05-86	7:50 am			27	1578	1	3	12	81
1-05-86	3:50 pm			31	2359	2	8	16	57
1-06-86	12:10 am			34	3516	1	18	36	70
1-06-86	2:20 pm			37	3414	1	10	29	75
2-08-86	1:55 am	31	5.8	41	2862	2	9	13	84
2-08-86	4:20 pm			44	4593	2	15	18	79
2-17-86	1:35 am	37	5.1	47	3385	2	12	48	90
2-17-86	11:10 am			51	2935	1	4	22	93
2-17-86	5:20 pm			54	5425	4	27	36	167
2-17-86	11:20 pm			57	4328	4	91	24	157
2-18-86	1:55 pm			60	3058	2	43	34	288
1-02-87	3:00 am	19	2.8	66	355	nd	--	22	53
1-02-87	12:55 pm			69	2162	1	--	16	74
1-02-87	9:00 pm			72	1992	1	--	28	70
1-03-87	1:50 pm			75	726	nd	--	33	76
Pearson r (chloride:metal)						0.49	0.45	0.37	0.15
Probability						0.01	0.03	0.04	0.24
8-27-88	9:50 pm	17		79	163	1	2	5	31
8-28-88	12:30 am			82	195	1	3	3	27
8-28-88	2:25 am			85	172	nd	4	--	66
8-28-88	7:45 am			88	101	1	3	--	44
8-28-88	11:10 am			91	87	1	3	7	24
Mean Precision					<u>+1</u>	<u>+1.9</u>	<u>+2</u>	<u>+3</u>	<u>+8</u>

^aWinter samples: temp. 1 - 8°C, mean pH = 7.7. Summer: temp. 20 - 22°C, mean pH = 7.4.

^bin hundredths of an inch water equivalent. Entries are totals for each precipitation event and are averages of data from six rain gauges located in and around the study area. From: Nurnberger, R. V., & Ordway, A. R. (1985-1988). [SEMCOG precipitation, annual summaries]. Unpublished raw data. ^cin inches. Data courtesy of William McNeil, Weather Station Chief, Selfridge Air National Guard, Mt. Clemens, MI. ^dnd = none detected.

of zinc and copper, Red Run the highest nickel, and Bear Creek and Schoenherr Drain approximately comparable levels of cadmium.

The metals content of Red Run water has been analyzed on an intermittent basis since 1971. Most sampling took place in the 1970s. Only four water samples have been analyzed for metals in the 1980s. In 1980, one sample from the 16 Mile Road station was analyzed only for zinc, and only one of three samples collected in 1987 was taken from a location permitting reasonable comparison to the data from this study (Table 28). This 1987 sample, from the Red Run at 15 Mile Road, had levels of cadmium, copper, nickel, and zinc that were comparable to those found in this study at the 16 Mile Road location. The decline in concentration for nickel and zinc from the late 1970s to the levels found in 1987 and in this study are most dramatic. Levels of copper were found to decline by smaller amounts.

Using the data from the winter samples at each sampling location, Pearson correlation coefficients were determined between the chloride ion concentration and each of the heavy metals in question (Tables 25, 26, & 27). A moderate correlation ($r=.57$) with zinc was found in Red Run. Low correlations were found with cadmium and with copper in Schoenherr Drain and Bear Creek, with zinc in Schoenherr Drain, and with nickel in Bear Creek.

The significant, positive correlations between chloride and cadmium in Schoenherr Drain and Bear Creek and between chloride and zinc in Red Run and Schoenherr Drain are what would be expected if chloride ion from highway deicing salts forms complexes with these metals and increases their solubility. Even with the strongest

Table 28

Selected Metals in Red Run Water, 1976 - 1987

Location	Year	Total Cadmium	Total Chromium	Total Copper	Total Iron	Total Lead	Total Nickel	Total Zinc
RR-16 Mi Rd	1976		30.0	24.0	480.0		117.0	218.0
	1978		18.0	15.5	1445.0		1260.0	295.5
	1979		22.5	10.5	1210.0		146.0	150.0
RR-14 Mi Rd	1976		13.0	22.0	470.0		466.0	304.0
	1978		24.0	13.0	435.0		1330.0	636.5
	1979		16.5	11.5	840.0		131.5	187.0
RR-15 Mi Rd	1987	0.4	10.0 ^a	13.1		10.0 ^a	19.0	58.3
WWWTP Effluent ^b	1986	0.6	4.2	5.7	60.0	1.5	26.1	52.0
Michigan Water Quality Standard ^c		0.8	111.0	49.0		13.0	181.0	213.0

Note: Yearly averages of available data in ug/L. Adapted from Remedial Action Plan for Clinton River Area of Concern by Michigan Department of Natural Resources, 1988, p. 84.

^aActual concentration is less than the value shown. ^bCalculated from Warren Wastewater Treatment data presented in reference above, p. 219. ^cLong term safe criteria for aquatic life. Exact criterion depends on hardness. Values listed are for a hardness level of 250 mg/L. From reference above, p. 383.

correlation detected in this study (zinc in Red Run, $r=.57$, $p=.001$), however, the variance in chloride concentration can explain only 32 percent of the variance in metal concentration. Thus, other variables not included in this study (for example pH, stream discharge, suspended sediment, organic matter, dissolved oxygen, etc.) also play a role in determining the concentration of heavy metals in winter runoff.

Cadmium levels in Red Run samples were consistently low and more homogeneous than cadmium levels in Schoenherr Drain and Bear Creek. Red Run chloride concentrations averaged between one-third and one-fourth those found in Schoenherr Drain and Bear Creek. Red Run chloride concentrations also varied by only one-third to one-fourth those of Schoenherr Drain and Bear Creek as measured by the standard deviation of the mean. Hinkle, Wiersma, and Jurs (1979) note that the magnitude of the correlation coefficient decreases as the homogeneity of either or both variables increases. The combination of these factors may be responsible for the inability to detect a significant cadmium-chloride ion correlation at the Red Run-16 Mile Road site.

Even though concentrations of zinc and chloride ion were highest at the Bear Creek station, there was little, if any, correlation between the two.

The low, but significant, positive correlations of chloride ion with copper in Schoenherr Drain and Bear Creek were not expected. Calculations by Zirino and Yamamoto (1972) of copper speciation in seawater as a function of pH from 7.0 to 9.0 indicated that, at most,

copper-chloride species make up only few percent of the total copper in solution. Similar calculations by van der Weijden et al. (1977) with seawater and 1:1 diluted seawater at pH 7.5 and pH 8.0 gave analogous results. In addition, their study of the desorption of heavy metals from suspended sediments into seawater and 1:1 diluted seawater also showed that only 5 percent and 3 percent, respectively, of sediment copper desorbed into solution. Thus, if copper desorbed only minimally from sediments under the influence of nearly 10,000 to 20,000 ppm chloride, it would not be reasonable to predict the same or a greater level of desorption with 1500 to 5400 ppm chloride. The pH of Bear Creek samples taken February 18, 1986 and January 2 and 3, 1987 ranged from 7.6 to 8.1 and averaged 7.7. Assuming these values represent a normal range of pHs, the release of copper from sediments due to increases in acidity, which would also have to correlate with increases in chloride ion, seems unlikely.

In a comparison of the surface runoff of seven heavy metals from different land use types, Helsel et. al. (1979) found good, nonlinear correlations between extractable lead, zinc, and copper versus traffic volume and percent impervious cover. This implied that, "motor vehicles are a major source of these metals, and that impervious surfaces deliver them efficiently to storm drainage systems" (p. 716). Wilber and Hunter (cited in Whipple and Hunter, 1977) monitored total heavy metals in streams draining two heavily urbanized watersheds at Lodi, New Jersey and found lead, zinc, and copper to be present in the highest concentrations. They also found that most of the lead and zinc were in the form of particulates. If a

similar behavior is assumed for runoff into Bear Creek, the observed low correlation of copper with chloride may be the result of each correlating with runoff from a nearby, major seven lane thoroughfare. This highway slopes toward Bear Creek and crosses it less than 2000 feet upstream from the sampling station.

Heavy Metals in Deicing Salt

An analysis for heavy metals in deicing salt applied to streets showed that only zinc could be detected consistently (Table 29). A mean 0.69 mg Zn/kg NaCl was detected in the six samples from the three separate salt storage areas. If this salt were used to make a solution containing 5000 ppm chloride, the solution would also contain approximately 5.7 ug Zn/L as well. The contribution of zinc from dissolved deicing salt to the total concentration of zinc found at each of the three sampling stations is, therefore, minimal. If zinc contributed by deicing salt is subtracted from the zinc concentrations found in water samples collected from each of the three sampling stations, the effect on the zinc versus chloride correlation is, likewise, minimal (Table 30). Cadmium was detected in only one sample at a level barely above the detection limit of the atomic absorption instrument.

Heavy Metals in Red Run Bottom Sediments

Comparisons with Road Salting Periods

If highway deicing salts promote the mobilization of heavy

metals from stream sediments, one might predict that stream sediments collected after a road-salting period should contain lower levels of

Table 29
Metals in Road Salt (mg/kg NaCl)^a

Metal	Salt Source			Mean
	Sterling Heights DPW	Warren DPW	Macomb County Road Commission	
Cd	nd ^b	nd	nd	0.01
	0.06	nd	nd	
Cu	nd	nd	nd	nd
	nd	nd	nd	
Ni	nd	nd	nd	nd
	nd	nd	nd	
Zn	0.49	0.55	0.85	0.69±.2
	0.49	0.85	0.91	

^aCalculated from analysis of 10,000 mg/L chloride solutions prepared from highway deicing salt. ^bnd = none detected.

those metals compared to sediments collected before road-salting. With this simplistic approach, grab samples of sediment were collected from the Red Run-16 Mile Road site and analyzed for their total and exchangeable heavy metals content (Table 31). The October 31, 1985 samples were taken before the beginning of the 1985 - 1986 winter snow season and the March 29, 1986 samples were taken at the end of the snow season after all the snow had melted and the

Table 30
Corrected and Uncorrected
Zinc versus Chloride Correlations^a

Sampling Location	Without Zn in Salt Correction	With Zn in Salt Correction
Red Run-16 Mile Rd	0.57 ($\underline{p} < .001$)	0.56 ($\underline{p} < .001$)
Schoenherr Drain	0.38 ($\underline{p} < .03$)	0.35 ($\underline{p} < .05$)
Bear Creek	0.15 ($\underline{p} < .24$)	0.13 ($\underline{p} < .27$)

^aPearson correlation.

likelihood of an additional major snowfall was remote. With the exception of lead and zinc at station 2, the total sediment concentration of each of the metals was found to decrease between the two dates. The observed decrease was greatest for cadmium which decreased an average of 49 percent. Copper, lead, nickel, and zinc decreased 33, 18, 29, and 12 percent respectively, averaged over both sets of samples.

With the exception of copper, nickel, and zinc at station 2, the sediment concentration of the exchangeable heavy metals also decreased from the beginning to the end of the road-salting period. As with the total metals concentration, cadmium decreased most, an average of 44 percent. Lead levels decreased 28 percent averaged over both sets of samples, whereas copper and nickel levels fell an average of 5 and

Table 31

Metals in Red Run Sediments (mg/kg dry wt.)

Location	Sample Number	Date	Cadmium		Copper		Lead		Nickel	
			Total	Exchangeable	Total	Exchangeable	Total	Exchangeable	Total	Exchangeable
Clinton River below Red Run		1970	36.2		390					
RR-15 Mi Rd		9-09-76	8.6		88		270		120	
RR-16 Mi Rd ^a Station 1	1	10-31-85 ^b	5.2	1.2	46.6	3.0	118.5	2.0	36.1	1.8
	2	1-19-86	3.4	1.0	26.4	2.5	73.8	1.0	28.1	1.7
	3	3-29-86	2.7	0.8	22.7	2.4	56.9	1.2	21.6	1.6
	4	1-02-87	2.5	0.6	20.6	1.1	68.3	2.3	31.7	1.4
	5	1-03-87	2.1	0.5	16.3	1.2	57.0	2.0	25.5	1.3
RR-16 Mi Rd ^c Station 2	6	10-31-85	6.9	2.7	32.6	3.0	64.0	3.1	27.0	1.3
	7	1-19-86	5.0	1.7	42.4	3.8	101.6	2.2	29.6	1.8
	8	3-29-86	3.5	1.2	28.0	3.3	74.7	2.4	22.2	1.3
	9	1-02-87	1.9	0.7	18.6	2.3	59.8	2.2	21.4	1.7
	10	1-03-87	2.5	0.8	26.7	2.5	76.6	2.7	26.0	1.7
	11	8-27-88	1.8	0.5	18.1	1.1	56.4	2.3	21.4	1.5
	12	8-28-88	2.2	0.5	26.8	1.6	73.3	2.5	26.7	1.2
Mean Precision			±.1	±.1	±.5	±.1	±1.4	±.3	±1.2	±.1

Note: Data in first row is from Heavy metals in surface waters, sediments and fish in Michigan by J. Hesse & E. F. Resources Commission, 1972, p. 26. Data in second row is from A sediment survey of the Clinton River, Pontiac to 1976 by J. Grant, Michigan Department of Natural Resources, 1976, p. 4.

^a This study, sediment collected about 25 feet from east bank. ^b Sample used for desorption studies. ^c This study, sediment collected about 25 feet from west bank.

Table 31

als in Red Run Sediments (mg/kg dry wt.)

um	Copper		Lead		Nickel		Zinc	
angeable	Total	Exchangeable	Total	Exchangeable	Total	Exchangeable	Total	Exchangeable
	390						948	
	88		270		120		440	
1.2	46.6	3.0	118.5	2.0	36.1	1.8	276.6	28.9
1.0	26.4	2.5	73.8	1.0	28.1	1.7	192.5	22.5
0.8	22.7	2.4	56.9	1.2	21.6	1.6	151.6	19.5
0.6	20.6	1.1	68.3	2.3	31.7	1.4	133.8	7.9
0.5	16.3	1.2	57.0	2.0	25.5	1.3	104.6	9.6
2.7	32.6	3.0	64.0	3.1	27.0	1.3	160.8	15.9
1.7	42.4	3.8	101.6	2.2	29.6	1.8	290.4	33.1
1.2	28.0	3.3	74.7	2.4	22.2	1.3	195.3	26.4
0.7	18.6	2.3	59.8	2.2	21.4	1.7	126.7	26.2
0.8	26.7	2.5	76.6	2.7	26.0	1.7	165.8	31.3
0.5	18.1	1.1	56.4	2.3	21.4	1.5	115.9	26.2
0.5	26.8	1.6	73.3	2.5	26.7	1.2	155.6	15.7
+1.1	+1.5	+1.1	+1.4	+1.3	+1.2	+1.1	+3.6	+1.6

s in surface waters, sediments and fish in Michigan by J. Hesse & E. Evans, Michigan Water
 second row is from A sediment survey of the Clinton River, Pontiac to mouth, September 9,
 ural Resources, 1976, p. 4.

t from east bank. ^b Sample used for desorption studies. ^c This study, sediment collected

6 percent respectively. Exchangeable zinc levels fell 33 percent at station 1 but rose 66 percent at station 2, giving an average rise of 17 percent.

Thus, except for exchangeable levels of zinc, the average total and exchangeable levels of the five metals decreased between October 31, 1985 and March 29, 1986. From this data one might be tempted to infer that the decrease in sediment heavy metals may be correlated with the use of highway deicing salts during the snow season. Deicing salt use, however, is only one variable that could explain the observed average decline in metals between the two dates. Several studies have shown, for example, that heavy metals tend to be concentrated in the finer fractions of sediment (Forstner & Wittmann, 1981; Mudroch, 1985; Sartor & Boyd, 1972; Sartor et al., 1974). Following their three-year study of the concentration and distribution of heavy metals in a section of the Saddle River in New Jersey, Wilber and Hunter (1979b) noted that

concentrations of [total] heavy metals in Saddle River sediments were found to be quite variable. ...Of the factors studied which contribute to the variation in metals concentration..., particle size seems to play the largest and most significant role.
(p. 797 & 799)

A sieve analysis of the Red Run sediment samples (Table 32) revealed that the percent of sediment finer than 0.063 mm showed an average relative decline of 27.4 percent between October 31, 1985 and March 29, 1986. Thus, the decline in the finest sediment fractions may explain the decline in most of the sediment heavy metals. Cadmium levels appear to have declined more than can be explained by changes in grain size distribution between these two dates.

Table 32

Sieve Analysis of Red Run-16 Mile Road
Sediments (percent finer by weight)^a

Location	Sample		Sieve Opening (mm)					
	Number	Date	<0.063	0.125	0.250	0.420	1.00	2.00
Station 1 ^b	1	10-31-85	36.6	46.9	67.0	87.5	95.1	98.6
	2	1-19-86	18.3	27.0	58.5	87.7	96.3	99.4
	3	3-29-86	25.6	33.2	61.1	89.0	96.7	99.5
	4	1-02-87	17.8	21.3	45.6	77.6	92.1	98.8
	5	1-03-87	17.8	21.2	42.5	77.1	93.6	100.0
Station 2 ^c	6	10-31-85	36.7	49.8	85.9	95.3	97.8	98.7
	7	1-19-86	39.7	52.8	89.2	96.5	98.4	99.0
	8	3-29-86	27.6	44.1	90.9	97.8	99.4	99.7
	9	1-02-87	12.7	20.4	88.5	98.6	99.3	99.5
	10	1-03-87	17.3	23.1	89.0	98.4	98.9	98.9
	11	8-27-88	13.5	22.6	75.9	95.8	98.1	99.4
	12	8-28-88	40.3	53.6	88.3	97.1	98.8	99.2

^aSediment samples previously sieved to remove particles larger than 2.00 mm. ^bCollected about 25 feet from east bank. ^cCollected about 25 feet from west bank.

To further examine the relationship between grain size and heavy metal concentration, Pearson correlation coefficients were calculated (Table 33) between percent grain size and heavy metal concentration for the two finest fractions of sediment. At station 1, high, significant ($p < .05$) correlations were found with cadmium, copper, lead, and zinc and the percent of each of the sediment fractions. Significant, high correlations with exchangeable levels of cadmium, copper, nickel, and zinc were found with only the <0.125 mm grain size

Table 33
Correlations Between Percent Grain Size and
Sediment Heavy Metal Concentrations^a

Metal	<0.063 mm		<0.125 mm	
	Station 1 ^b	Station 2 ^c	Station 1	Station 2
Total				
Cd	.86 [*]	.64	.90 [*]	.63
Cu	.90 [*]	.80 [*]	.93 [*]	.73 [*]
Pb	.82 [*]	.59	.82 [*]	.51
Ni	.47	.79 [*]	.44	.67 [*]
Zn	.84 [*]	.62	.90 [*]	.57
Exchangeable				
Cd	.76	.54	.86 [*]	.53
Cu	.76	.45	.87 [*]	.43
Pb	.08	.29	-.09	.30
Ni	.72	-.40	.84 [*]	-.53
Zn	.79	-.40	.89 [*]	-.45

^aPearson correlation coefficient. ^bRed Run-16 Mile Road, about 25 feet from east bank. ^cRed Run-16 Mile Road, about 25 feet from west bank.

*
p < .05

fraction. High, but nonsignificant ($p > .05$) correlations were calculated for the same metals with the <0.063 mm fraction.

At station 2, significant, moderate to high correlations were observed for total levels of copper and nickel and each of the sediment fractions. Significant correlations were not detected with

exchangeable concentrations of metals and percent grain size at station 2.

The sediment samples collected January 19, 1986 were collected immediately after a 3 - 4 inch snow cover had melted with a 0.31 inch rainfall. With the exception of exchangeable lead, sediment concentrations of both total and exchangeable metals at station 1 were intermediate between the October 31, 1985 levels and the March 29, 1986 levels. At station 2, higher levels of both total and exchangeable metals, except cadmium and exchangeable lead, were found in the January 19, 1986 sample compared to either the October 31, 1985 or the March 29, 1986 samples.

The January 2, 1987 samples were collected as a 2.8 inch snowfall (0.2 inch water equivalent) was beginning. The January 3, 1987 samples were collected 44 hours later--more than 24 hours after the snowfall ended. During the intervening period, the condition of area streets changed from snow-covered to salted to clear and dry. Chloride levels at the sample site rose from 134 ppm to a high of 894 ppm and then declined to 430 ppm. Total sediment heavy metal concentrations at station 1 decreased an average of 19 percent during this period while exchangeable metal levels, except for zinc, changed very little. Exchangeable zinc increased by nearly 22 percent. The two station 1 sediment samples were identical in their percent grain size distribution in the finest fraction. In contrast, total sediment heavy metal concentrations at station 2 increased an average of 31 percent at the same time exchangeable metals increased an average of 8 percent. Some of this increase could be due to the 36 percent

relative increase in the finest ($<.063$ mm) sediments in the January 3 sample compared to the January 2 sample at station 2.

The August 27 sediment sample was collected at the beginning of a 3 hour, 0.2 inch rainfall. The August 28 sample was collected approximately 13 hours later--about 9 hours after rainfall ceased. The Red Run was at a low flow stage throughout the sampling period. Total heavy metals increased an average of 32 percent between these two samples. If a comparison is made between the January 2 and 3, 1987 and the August 27 and 28, 1988 sediment samples at station 2, a striking similarity is noticed. Except for exchangeable copper and exchangeable zinc in the August samples, both the absolute levels of heavy metals found and their direction and magnitude of change are closely matched. This suggests that for similar amounts of light precipitation, rainfall runoff and salt-induced snowmelt runoff produce similar changes in sediment heavy metal concentrations. This initial conclusion, however, should be tempered by the observation that the August 28 sediment sample contains two to three times more of the finest sediment fraction ($<.063$ mm) than either of the January samples or the August 27 sample.

In general, the concentrations of heavy metals in Red Run bottom sediments were found to be somewhat variable. Clearly accounting for this variability in terms of either short-term or long-term road-salting periods is impossible with the limited data available. In addition to the possible effect of dissolved highway deicing salts, other variables that can also play a role in determining sediment heavy metal concentrations include:

1. Sediment grain size distribution. Because heavy metals are usually more concentrated in the finer fractions of sediment, it is difficult to make comparisons between sediments that have different grain size distributions. Forstner and Wittman (1981) noted that:

grain size exercises a determining influence on the metal concentrations.... This fact must be taken into consideration particularly with respect to studies of river sediments where variations in grain size are usually large. One can even go as far as to state that without a correction for grain-size effects, a mutual comparison of metal data in fluvial deposits would be impossible. (p. 124)

2. Percent organic matter. Some metals appear to be preferentially bound by organic material in sediments (Hamilton et al., 1984; Harrison et al., 1981; Tyler & McBride, 1982). Differences in sediment metal concentrations may be a reflection of differences in organic matter content. As it relates to this study, the concentration of organic material and its heavy metal content in overflows from the Southeast Oakland County Sewage Disposal System/Pollution Control Facility on sediment heavy metals is unknown. This facility overflows an average of 11 times per year and contributes an annual average of 1.6 million lbs of suspended solids and 250,000 lbs of BOD-5 loadings to the Red Run (MDNR, 1988). Overflows occurring within one month of sampling times were recorded in October 1985 (1 day, 230 million gallons), November 1985 (2 days, 303 million gallons) and March 1986 (2 days, 110 million gallons). Overflow data were unavailable for 1987 and 1988.

3. Flow rates in the stream. Differences in flow rates between sample dates can affect the type of sediment sample obtained. High flow rates tend to favor resuspension of the finest sediments,

whereas low flow rates tend to favor their deposition. Sediment collected during a high flow period would be expected to contain a lower percentage of the finest fractions whereas sediment collected under low flow conditions would be expected to contain a higher percentage of the finest fractions. Resuspension of bottom sediments also promotes their chemical interaction with dissolved metals or other solutes in the water column.

4. Source of sediments and time of residence in the stream. Sediments comprising a particular sample may be made up of material that had just recently entered the stream as well as material that had been in the stream for an extended period of time. Sediments with such histories may differ considerably in their heavy metals content. As a result, the potential variation in sediment heavy metals content would be expected to be greatest when comparing samples from a low flow period to samples collected either during or shortly after a high flow period.

5. Dissolved metal concentrations. Under normal conditions, stream sediments tend to adsorb and concentrate heavy metals from the water column. Changes in sediment heavy metal concentrations occur more slowly than changes in dissolved metal levels. Consequently, if long intervals of time elapse between samples, changes in sediment heavy metal concentrations may reflect long-term changes that have occurred in solution.

Historical Comparisons

An examination of the changes in sediment heavy metal concentra-

tions occurring over the duration of this study reveals a fairly consistent decline in both total and available cadmium. Coincident with the beginning of this study, the City of Warren implemented an industrial wastewater pretreatment program to reduce the burden to the Warren Wastewater Treatment Plant (MDNR, 1988; W. Hare, personal communication, November 21, 1989). The effect on the total cadmium concentration in water discharged from the treatment plant to the Red Run was dramatic. Total cadmium concentrations had increased from an average of 3.3 ug/L in 1982 to an average of 8.39 ug/L in 1985. The industrial pretreatment program was implemented in November 1985 and reduced the 1986 average cadmium concentration to 0.59 ug/L. Thus, the overall decline in both total and exchangeable sediment cadmium discovered in this study is probably a reflection of the sediment's response to decreased cadmium discharges. The nearly three-year period covered by these sediment samples is also an indication of the long time periods required for a relatively mobile metal like cadmium to begin to clear from sediments.

In April and May of 1970 the Michigan Water Resources Commission conducted a survey of heavy metals in stream sediments from 46 industrial and municipal locations throughout the state of Michigan (Hesse & Evans, 1972). These sampling stations were then assigned a priority ranking based on the concentrations of heavy metals found. Two stations on the Clinton River were included in those samples. Out of the 46 locations, sediment from a station located just below Red Run (Table 34) had the second highest concentration of cadmium (36.2 ppm) and was ranked eighth in total metals concentration. A 1976 survey

by the Michigan Department of Natural Resources (Grant, 1976) found that sediment cadmium levels at this same location had fallen to 4.4 ppm. This same survey found sediment cadmium at 8.6 ppm in the Red Run at 15 Mile Road (Table 34). This station was located approximately one mile upstream from the 16 Mile Road site of this study.

Table 34

Metals in Red Run and Clinton River Sediments (mg/kg dry wt.)

Location	Date	Cadmium	Copper	Lead	Nickel	Zinc
Clinton River ^a below Red Run	1970	36.2	390			948
Clinton River ^b below Red Run	1976	4.4	68	130	110	300
RR-15 Mile Rd ^b	1976	8.6	88	270	120	440
RR-16 Mile Rd ^c	1987-88	2.2	21.2	65.2	25.5	133.7
Percent change in Red Run metals, 1976 - 1988		-74	-76	-76	-79	-70

^aFrom Heavy metals in surface waters, sediments and fish in Michigan by J. Hesse & E. Evans, Michigan Water Resources Commission, 1972, p. 26. ^bFrom A sediment survey of the Clinton River, Pontiac to mouth, September 9, 1976 by J. Grant, Michigan Department of Natural Resources, 1976, p. 4. ^cThis study, mean of six samples.

The documentation of long-term trends in sediment heavy metals was not a prime focus of this study. It does appear, however, that sediment heavy metal concentrations have undergone significant long-term declines. The five heavy metals examined in this study were found to be present in sediment at concentrations well below those

found in the 1970 and 1976 surveys in the same area. If the sediment data for each metal in this study are averaged for 1987 and 1988 and then compared to the 1976 survey, each metal is found to have declined substantially, and by about the same percentage (Table 34). Although these comparisons are based on data from stations only one mile apart, and such comparisons of different stations may not be entirely valid, they are probably indicative of long-term trends for the Red Run.

CHAPTER IV

CONCLUSIONS AND RECOMMENDATIONS

The purposes of this study were to: (a) determine the effect of sodium chloride concentration on mobilizing cadmium, copper, lead, nickel, and zinc from stream sediments; (b) determine if chloro-metal complexes may play a role in any such mobilization; and (c) determine the correlations between chloride ion and each metal in an urban stream during periods when the stream was receiving runoff containing highway deicing salts.

Stream sediments found to contain these five heavy metals were stirred with sodium chloride or sodium nitrate solutions of known concentration. Aliquots were removed at specified time intervals and concentrations of dissolved metals were determined by flame atomic absorption spectrometry. A regression analysis was used to compare levels of metals desorbed into the chloride solutions versus the nitrate solutions.

The drainage basin of the Red Run, an urban stream draining all or parts of several cities north of Detroit, Michigan, was chosen as a study site. Chloride and metal concentrations were measured in water samples taken from the Red Run itself, Schoenherr Drain, and Bear Creek during periods when street runoff contained elevated levels of deicing salt. Metal concentrations were also determined in Red Run sediment before and after a single snow and road-salting

event and before and after an entire winter season. The following conclusions and recommendations are a result of this study.

Conclusions

1. In laboratory desorption trials with Red Run bottom sediments, the concentration of cadmium in solution was found to have a high correlation ($r=.90$) with chloride ion concentration. Cadmium was also desorbed from Red Run sediments by chloride solutions to a greater extent than by nitrate solutions of the same concentration (in mg/L). This is thought to agree with a desorption model in which nitrate solutions increase cadmium solubility primarily through ion-exchange at sediment adsorption sites, whereas chloride ions additionally form stable chloro-complexes with cadmium, thereby favoring its increased release into the water column.

2. In laboratory sediment desorption trials, zinc concentration was found to have a low correlation ($r=.49$) with chloride ion concentration. Zinc was desorbed from Red Run sediments by chloride solutions to a slightly greater extent than by nitrate solutions of the same concentration, but only at longer desorption periods. This may indicate that only a moderate percentage of total zinc species in solution are in the form of chloro-complexes and that these are in competitive equilibrium with other major zinc species.

3. In laboratory desorption studies, copper and nickel concentrations were found to have low negative ($r=-.38$) and little if any ($r=-.29$) negative correlations, respectively, with chloride ion. Significant differences were not detected between the concentrations

of copper or nickel in chloride solutions versus nitrate solutions of the same concentration. These observations were found to be consistent with other studies which indicate that copper and nickel have particularly strong affinities for organic matter that becomes less soluble as the solution ionic strength is increased. Lead concentrations were generally below limits of detectability of the instrumentation used.

4. Chloride ion concentrations in stream samples collected during the summer were found to vary by, at most, a factor of two. Compared to the respective summer means, maximum winter chloride ion concentrations were found to be higher by factors of 16, 27, and 38 for Red Run, Schoenherr Drain, and Bear Creek respectively.

5. A moderate chloride versus zinc correlation was found for winter water samples from Red Run. Otherwise, only low to little, if any, chloride-metal correlations could be detected for cadmium, copper, nickel, or zinc at any location. Lead was generally below limits of detectability.

6. Only zinc could be consistently detected in salt from municipal and county salt piles used for highway deicing purposes. The contribution of zinc from deicing salt to total zinc levels found at each of the sampling sites was found to be minimal and to have a minimal effect on overall chloride versus zinc correlations.

7. Changes in stream sediment heavy metal concentrations over an entire winter road-salting period, or over a single snow and road-salting event could not be unequivocally attributed to the use of highway deicing salts. Instead, differences in sediment heavy metal

concentrations appeared to be more closely related to differences in the percent of sediment finer than 0.063 or 0.125 mm. In general, total heavy metal levels showed moderate to high correlations with the percent fine sediments. Exchangeable levels of cadmium, copper, nickel, and zinc showed high correlations with the percent fine sediments at only one of two sampling sites. Little, if any, correlation was found with exchangeable lead concentrations and percent fine sediments.

8. When the results of this study were compared with the results of previous Red Run and Clinton River studies, levels of sediment heavy metals were found to show a substantial long-term decline. This decline represents a response of the stream to controls placed in the 1970s on point source metal discharges. The decline observed for cadmium for the duration of this study was most likely a response of the Red Run to controls placed in November, 1985 on metal levels entering and being discharged from the Warren Wastewater Treatment Plant.

Recommendations

1. Measurements of the speciation of each metal in stream samples containing different concentrations of deicing salts would permit more definitive statements regarding the role of chloro-metal complexes in mobilizing heavy metals from sediments. Such speciation studies are necessary to verify species distributions obtained by calculation and might also provide insights into the role that soluble organic complexes may play in competing with chloro complexes.

2. Attempts to model the movement of heavy metals in streams usually do not consider the possibility that elevated chloride ion concentrations may increase their mobility. Measurements of the heavy metal partition coefficients between sediments and the solution phase with different chloride ion concentrations could provide valuable refinements to those models. This would be expected to be most significant in models of streams that have high sediment concentrations of metals that interact strongly with chloride and that carry elevated levels of deicing salts during snow periods.

3. Heavy metals are generally believed to be more concentrated in the finer fractions of sediment. An examination of heavy metals in suspended sediment during winter road-salting periods could provide more direct evidence of the significance of chloride ion in heavy metal desorption than that obtained in this study.

4. Temperature is known to have an effect on the kinetics and position of equilibrium in chemical reactions. Yet the effect of temperature on metal sorption or desorption is conspicuously absent in studies reported in the literature. An examination of such temperature effects may provide additional insights into the movement of heavy metals between sediments and the water column in colder climates.

5. Overflows from the Southeastern Oakland County Sewage Disposal System Pollution Control Facility have an unknown effect on metal concentrations in Red Run water and sediments. Measurements of metal concentrations in these overflows could reveal the relative significance of this source to the total input of metals to the Red

Run.

6. Leachate samples from landfills located along the Red Run have been found to contain toxic organics as well as lead, nickel, and chromium. A study to determine the extent to which leachate from these landfills enters the Red Run could reveal their current and potential impact on Red Run and Clinton River water quality.

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