

***STORM AND GROUND WATER QUALITY
IMPACTS OF CHEMICAL DEICER USAGE
IN MISSOULA, MONTANA***

***Prepared
by***

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1.0 INTRODUCTION

This report summarizes work completed by the Missoula Valley Water Quality District to evaluate the water quality impacts of using liquid deicer in Missoula as a replacement for sand and salt. The study was jointly funded by the Missoula Valley Water Quality District (District) and the Montana Department of Health and Environmental Sciences (DHES), now the Montana Department of Environmental Quality (DEQ). Funding from DEQ was obtained under DHES Contract number 240109. The project was based on a study proposal drafted by the Missoula Valley Water Quality District, entitled *Preliminary Study Proposal for Evaluation of the Impacts of Chemical Deicers on the Missoula Valley Aquifer*.

The general approach for the study was to evaluate the impacts of the liquid deicers and sanding materials on storm and ground water quality, and then evaluate the potential impacts of storm water on surface water. The study area boundary established was the Air Quality Management Zone designated in the Montana State Implementation Plan (SIP). This area, shown in Figure 1, covers 44 square miles.

2.0 BACKGROUND

The Missoula urban area was designated as non-attainment for particulate matter less than ten microns (PM-10) by the U.S. Environmental Protection Agency (EPA) on November 15, 1990 due to exceedances of the National Ambient Air Quality Standards (Bennitt, 1993). Air quality impacts from road dust created by sanding materials are a documented problem in Missoula. A recent report completed for Missoula indicates that road dust accounted for half of the PM-10 particulate during the winter (TRC, 1996). The substitution of liquid deicers for the sanding materials was initiated to improve air quality by reducing particulate levels from road dust during the winter months (MCCHD, 1991).

Until the winter of 1990/1991 the City of Missoula used sand for traction control and roadway deicing. The sanding material is typically mixed with 5% to 10% sodium chloride (road salt). During the winter of 1990/1991 the City began using a magnesium chloride based liquid deicer on an experimental basis. Early applications were mainly on bridges and usage was limited. The first product used was FREEZGARD™+Polymeric Corrosion Inhibitor (PCI)™. Prior to its initial use, the Missoula Water Quality Advisory Council reviewed the potential water quality impacts. The Council concluded that "a switch from salt and sand application to the proposed de-icing compound will not significantly impact water quality" (MWQAC, Oct., 1991).

Starting in the winter of 1991/1992 the City of Missoula Public Works Department and the Montana Department of Transportation began substituting liquid deicer for the traditional sand and salt mixture for roadway deicing throughout the Missoula area. The full scale switch from sand with salt to liquid deicer raised questions about the potential water quality impacts from the

Figure 1
Study Area and Storm Water Sampling Locations

liquid deicer. The concerns raised included possible heavy metals present in the liquid deicers, mobilization of heavy metals from the environment, impacts from the corrosion inhibitors added to the liquid deicers and impacts from the major ions of the liquid deicers.

3.0 REGULATORY SETTING

3.1 Air Quality

Regulations adopted by the Missoula City-County Air Pollution Control Board include the following definition for approved deicer:

Rule 1401 (1) (b); "Approved deicer" means a magnesium chloride based product treated with a lignin based corrosion inhibitor. A substitute deicer and corrosion inhibitor shall be considered an approved deicer when approved for use by the City Public Works Department and the Missoula City-County Air Pollution Control Board.

The use of approved deicers is also regulated based on weather conditions as described in Rule 1401 (11), which states:

No person shall apply street sanding materials other than an approved deicer when the ambient temperature is above 0 degrees Fahrenheit to public roadways in the required deicing zone, except under extraordinary circumstance.

Road sanding materials are also regulated within a specified area of Missoula, and are required to have a silt content of less than 2.5%. Figure 2 shows the areas of Missoula where approved deicers must be applied, and the areas where regulated sanding materials must be used. Outside these areas the types of deicers and sanding materials are not regulated.

3.2 Water Quality

The use of liquid deicers and sanding materials impact storm water quality, which in turn may impact ground water and surface water quality. Currently the City of Missoula does not have a population base large enough to be regulated under the Clean Water Act for discharge of storm water to ground waters or surface waters. As the City grows, this may change. In the future the City of Missoula may have to apply for and obtain a municipal storm water discharge permit. This permitting process would be through the Montana Department of Environmental Quality, and would require that the City of Missoula obtain a Montana Pollution Discharge Elimination System (MPDES) permit.

Figure 2
Area of Regulated Sanding Materials and Liquid Deicer

4.0 EVALUATION OF DEICER PRODUCTS

The District completed independent analysis of four magnesium chloride based liquid deicers, one calcium chloride based liquid deicer, and road sanding material used locally. Literature research was also conducted to review and evaluate other possible deicing products. For the liquid deicers that were submitted for review and approval to the Missoula City-County Air Pollution Control Board, the Missoula Water Quality Advisory Council also evaluated the liquid deicers.

4.1 Liquid Deicers Reviewed by the Air Pollution Control Board

Five liquid deicer products have been reviewed by the Board since 1990. The products reviewed, the primary salt component, the corrosion inhibitors used and the review decisions of the Board are presented in Table 1.

Table 1
Liquid Deicers Reviewed by
Missoula City-County Air Pollution Control Board

Product	Primary Salt	Inhibitor	Status
Freezgard/PCI™	Magnesium Chloride	calcium lignin sulfonate	Approved
CG-90™	Magnesium Chloride	sodium citrate	Approved
Ice Stop™	Magnesium Chloride	Zn phosphate, Na hexametaphosphate	Approved
Hicothaw™	Calcium Chloride	Na hydroxide and phosp. acid	Not Approved
Freezgard/lowt-herm™	Magnesium Chloride	Phosphate Ester	Approved

The only liquid deicer that the Board did not approve was the calcium chloride based Hicothaw™. This product was not approved by the Board because it was not considered to be a significant improvement over the existing approved magnesium chloride based products, and because of the potential impacts of increased phosphorus loading to surface waters.

4.2 Other Chemical Deicers Evaluated

In addition to the products reviewed for the Air Pollution Control Board, literature on other chemical deicers was obtained and reviewed to conduct a preliminary evaluation of the pros and cons of each type of product. The literature indicates that the chloride ion is the most harmful component of the chloride salts to plants (sodium chloride, magnesium chloride, calcium chloride). The following information was obtained on other products.

Calcium Magnesium Acetate;

A significant amount of research has been conducted on the effectiveness and environmental impacts of Calcium Magnesium Acetate (CMA). This deicer is manufactured using acetic acid and is a granular solid. It currently is not available in mass quantities, and is expensive relative to other available deicer products. The literature indicates that CMA has very little environmental impact. The magnesium and calcium ions are not known to harm soils or vegetation, and may be beneficial. The acetate anion is less mobile in soil than chloride ion, and is readily degraded. It is reportedly less corrosive than rain water. Because there is no chloride in the material, there are no water quality impacts from chloride ions. The primary disadvantage is that the material is more than 20 times more expensive than sodium chloride, mainly due to the cost of manufacturing acetic acid.

Potassium Acetate;

Information from only one distributor was found for potassium acetate, and it does not appear to be in wide spread use. Chemically it is very similar to CMA, and appears to have similar advantages and disadvantages.

Corrosion Inhibited Salt;

Products are available that are manufactured by treating sodium chloride (road salt) with magnesium chloride solution and a corrosion inhibitor. One product, manufactured under the name Qwiksalt+PCITM, is a blend of approximately 83% sodium chloride, 10% magnesium chloride and 7% PCITM corrosion inhibitor. This product is less corrosive than untreated sodium chloride, but still presents most of the environmental impacts of sodium chloride, and is more corrosive than straight magnesium chloride.

Calcium Chloride;

The advantage of calcium chloride over magnesium chloride is that it is an effective liquid deicer at very cold temperatures. The main disadvantage is that it is the most corrosive of the common salts (Washington DOT, 1989). To overcome the high corrosivity, a higher concentration of inhibitor compounds must be added.

Like magnesium chloride (MgCl₂), each calcium chloride (CaCl₂) molecule has two chloride ions. Sodium chloride (NaCl) in comparison only has one chloride ion per molecule. Mole for mole both magnesium chloride and calcium chloride add twice as much chloride to the environment as sodium chloride. In addition, calcium chloride is applied at a higher concentration (30%) than magnesium chloride (27%). The net result is that more chloride is

added to the environment.

Urea;

Urea is an organic fertilizer that is also used as a deicer (CH₄N₂O). It is often used on airport runways because it is not corrosive to aircraft. Like CMA, urea also reportedly has no adverse effect on soils and vegetation (Moran et al., 1992). It's primary disadvantage is that it contributes significant quantities of nitrogen to surface waters, and its breakdown in water consumes oxygen.

4.3 Corrosion Rates of Deicers

The available literature was reviewed to determine the relative corrosion rates of deicer chemicals. In general the most corrosive deicer was uninhibited calcium chloride, followed by uninhibited sodium chloride. The inhibited magnesium chloride products had the lowest corrosion rates. Table 2 shows corrosion rates in mils/year for various products, based on a study completed by the Washington State Department of Transportation (1989).

**Table 2
Corrosion Rates for Deicer Products**

PRODUCT	MILS/YEAR	COMMENTS
Cargill CG-90	1.15	W/sodium phosphate inhib.
Freezgard+PCI	1.99	
Urea	3.71	48% nitrogen fertilizer
CMA	4.07	Calcium Magnesium Acetate
Quiksalt+PCI	5.19	With improved PCI
Quiksalt	9.53	12%MgCl ₂ , 7%PCI, 81%NaCl
Quiksalt	12.61	3%MgCl ₂ , 7%PCI, 90%NaCl
Road Salt	17.26	Uninhibited NaCl
Super Melt	21.21	Improved Calcium Chloride
Calcium Chloride	26.00	

Washington DOT (1989)

5.0 CHEMICAL ANALYSIS OF LIQUID DEICERS AND SANDING MATERIALS

For each liquid deicer evaluated, the distributor was asked to provide a Material Safety Data Sheet (MSDS), available chemical data for the product and a sample of the product for independent chemical analysis. The District submitted the samples to an independent laboratory and had the samples analyzed for general chemistry and heavy metals. The distributor was also asked to provide information on the chemistry of the corrosion inhibitors used in the liquid deicers. The exact chemistry of the corrosion inhibitors is considered to be a trade secret, but enough data was obtained to evaluate the potential impacts. The data obtained for each liquid deicer reviewed is included in Appendix A.

5.1 Analytical Testing of Liquid Deicers

The liquid deicers used in Missoula are manufactured by evaporating salt solutions from either the Great Salt Lake in Utah or sea water. This process may concentrate heavy metals present in the salt water used to make the products. Arsenic was a contaminant of concern because it was detected at 2.8 mg/l in the first product tested (FREEZGARD™+PCI™), a level above the maximum contaminant level for drinking water of 0.050 mg/l, the Montana WQB-7 groundwater quality standard of 0.018 mg/l, and the Missoula Aquifer background for arsenic of approximately 0.03 mg/l. The primary concern was that heavy metals in the deicers would degrade surface waters and ground waters.

Each deicer was tested for arsenic, cadmium, chromium, iron, manganese, copper, and lead. (See Table 3. As shown in Table 3, the levels of heavy metals present in the liquid deicers were highly variable. The variability may be a characteristic of the products or may be due to laboratory matrix interference. FREEZGARD™+PCI™ was the most extensively tested, and had the highest levels of arsenic, cadmium, chromium, iron and manganese. Lead was detected in the FREEZGARD™+PCI™ at 2 mg/l, and the HICOTHAW™ at 7.6 mg/l. In comparison, the Montana WQB-7 groundwater standard is 0.015 mg/l.

5.2 Analytical Testing of Road Salt and Bulk Sanding Materials

The bulk sanding material and road salt used locally were also sampled and analyzed for heavy metals to compare with the sampling results for the liquid deicers. A sample of the bulk sodium chloride (road salt) was analyzed for arsenic, cadmium, chromium, copper, lead, and magnesium. The results are summarized in Table 4, and the laboratory data is included in Appendix B. As with the other deicer samples, the laboratory detection limits were increased due to matrix interference, and hydrite generation was used to obtain a lower detection limit for arsenic. Magnesium was the only metal detected at a low level, and no arsenic was detected in the salt.

Table 3
Heavy Metals Concentrations in Deicer

PRODUCT	DATE	As	Cd	Cr	Fe	Mn	Cu	Pb
FREEZGARD+ PCI™	11/91	<.5	19.8	<2	50.0	15.0	NT	NT
FREEZGARD+ PCI™	12/91	NT	0.2	NT	NT	NT	NT	NT
FREEZGARD+ PCI™	01/92	2.8	<.2	<.2	62.6	NT	NT	<.1
FREEZGARD+ PCI™	02/92	<5	<.4	<8	31	18	NT	<4
FREEZGARD+ PCI™	02/92	<5	<.4	25	63	24	NT	<4
FREEZGARD+ PCI™	02/92	<5	<.4	50	87	29	NT	<4
FREEZGARD+ PCI™	11/92	0.65	<.2	<1	135	22	6	2
CG-90™	11/92	0.6	<0.1	<1	<3	<2	14	<1
CG-90™	11/92	1.40	<.2	<1	<3	1	9	<1
Ice-Stop™	06/94	0.5	<.05	<.5	3.1	<.5	<.5	<.05
Hicothaw™	07/94	0.03	0.44	<.1	0.82	<.1	3.6	7.6
Hicothaw™	02/93	<.2	<.03	<.1	1.0	<.1	<.13	<.25
FREEZGARD+ Lowtherm™	03/95	2.2	<.1	<1	<3	<1	<1	<1

NT=(Not Tested), Units=milligrams per liter (mg/l)

Table 4
Heavy Metals in Sodium Chloride (road salt)

Metal	Detection Limit (mg/l)	Sample Result (mg/l)
Arsenic	0.5	<0.5
Cadmium	1	<1
Chromium	3	<3
Copper	5	<5
Lead	5	<5
Magnesium	5	6

To determine if the bulk sand could be a source of heavy metals due to leaching by storm water, a sample of the bulk sanding material was analyzed using the Toxicity Characteristic Leaching Procedure (TCLP) method, which measures the concentration of metals present in leachate derived from the washing of the sample. The results are presented in Table 5. The original laboratory report is also included in Appendix B.

No arsenic, cadmium, chromium, lead or copper was detected in the leachate from the bulk sand. Elevated levels of calcium were found in the leachate, probably due to the dissolution of calcium carbonate in the sand by the acidic leaching solution.

Table 5
Metals in Leachate from Sanding Materials

Metal	Detection Limit (mg/l)	Sample Result (mg/l)
Arsenic	0.5	<0.5
Cadmium	0.1	<0.1
Chromium	0.5	<0.5
Lead	0.5	<0.5
Copper	not reported	<0.5
Potassium	not reported	3.2
Calcium	not reported	190

Magnesium	not reported	19
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5.3 Evaluation of Corrosion Inhibitors

The exact formulation of the corrosion inhibitors used in the liquid deicers is considered a trade secret. However, each of the product distributors provided sufficient information to evaluate if the inhibitors posed an environmental risk. The most distinctive inhibitor was calcium lignin sulfonate used in FREEZGARD+PCI™. This product is derived from wood pulp, and gives the deicer a dark oily appearance. One concern with this inhibitor was the possible presence of dioxin. Dioxin can be formed during the wood pulping process when chlorine and organic compounds are co-mingled under high pressure and temperature. This concern was addressed by the manufacturer of FREEZGARD+PCI™ reporting that the calcium lignin sulfonate was derived from the wood pulping process prior to any bleaching, eliminating the possible mixing of chlorine and organic compounds.

The inhibitors used in the other deicer products studied were comprised primarily of phosphate and zinc compounds. Three liquid deicers (FREEZGARD+LOWTHERM™, ICE-STOP™, and HICOTHAW™) contain phosphate compounds as corrosion inhibitors. ICE-STOP™ also contains zinc in the form of zinc sulfate. Phosphate is considered a primary compound of concern due to existing nutrient pollution in the Clark Fork River. The concentration of zinc sulfate in ICE-STOP™ of 120 mg/l, as reported by the manufacturer, was not considered high enough to result in aquatic organism toxicity.

6.0 SNOW REMOVAL AND DEICER APPLICATION PRACTICES

Within the 22 square mile study area (see Figure 1), the Street Division of the Missoula Public Works Department plows, deices and sands most of the streets. The only major exception is a four mile stretch of Interstate 90 on the north side of Missoula, which is plowed and deiced by the Montana Department of Transportation (DOT). The Street Division maintains approximately 200 miles of City streets and 29 miles of state routes under contract with DOT. The Public Works Department has drafted a *City of Missoula Snow Plan*, which is included as Appendix C. The plan presents the snow removal and deicing priorities, equipment used and personnel.

6.1 Liquid Deicer and Sand Application Data

The Street Division applies sanding materials using five sander trucks. Two trucks are tandem axle sander/plows, two are single axle sander/plows and one is a single axle front discharge sander. Six trucks are used for application of liquid deicer. Four of the units are dump trucks fitted with snow plows and twin 600 gallon deicer tanks. In addition a 1000 gallon tanker truck and a 3000 tanker truck are used to apply liquid deicer. Snow removal is accomplished using the four sander/plow units, four deicer/plow units, two graders and three front end loaders.

Currently all deicer application trucks pump deicer under pressure to spray distribution pipes

which have restricting orifices to control flow. The discharge rate can not be metered to adjust for vehicle speed, deicer is applied at a constant rate. The Street Division has purchased two computerized metering devices to measure control applications rates. Current application rates are only estimates due to the lack of metering equipment on the trucks. The Street Division estimates the application rates vary from 100 to 150 gallons/lane mile, depending on road conditions and vehicle speed. All liquid deicers applied in the Missoula area between 1990 and 1997 have been magnesium chloride based deicers. In areas with steep grades and during periods when the temperature is below 0 degrees fahrenheit, sand is still applied.

6.2 Total Annual Usage and Environmental Loading

Table 6 summarizes the data obtained from the City Street Division on the annual amounts of liquid deicers, sand, and road salt applied by the Street Division between 1988 and 1996. The application data is also presented in graphic form in Figure 3. During the winters of 1990/91 through 1994/95 the amount of sanding materials applied decreased as more liquid deicer was applied. The amount of liquid deicer used each winter since 1990/91 has steadily increased. The winters of 1995/96 and 1996/97 were wetter than most, and a record amount of liquid deicer was used. The amount of sanding material used also increased during the winter of 1995/96, but decreased somewhat in 1996/97.

Table 6: Liquid Deicer and Sand Application Data

Winter	Deicer - MgCl ₂ (gallons)	Sand (tons)	NaCl - 5% (tons)
1988/89	0	6200	310/620,000
1989/90	0	4200	210/420,000
1990/91	26,280	2400	120/240,000
1991/92	88,325	1600	80/160,000
1992/93	154,785	1750	87.5/175,000
1993/94	149,550	1316	65.8/131,600
1994/95	255,240	2000	100/200,000
1995/96	340,740	9550	477.5/955,000
1996/97	413,660	5210	260.5/521,000

Figure 3
Annual Liquid Deicer and Sand Usage

To evaluate total loading of the major salt components, the quantities of sanding materials and liquid deicers applied were used to calculate annual loading of chloride, sodium and magnesium ions to the environment for the winters of 1988/89 to 1996/97. Table 7 summarizes the loading calculations for contributions from the road salt. The following assumptions and conversion factors were used:

Assumptions: The percentage of NaCl mixed with sand varies from 5% to 10%, and the purity of the product is unknown, but probably ranges from 85% to 95%. For calculations, a 5% mixture in sand was assumed, and the product was assumed to be 100% pure.

Conversion Factors: NaCl: Molar Weight NaCl = 58.44277 g/mole, Na = 22.98977 (39.335%), Cl = 35.453 (60.665%)

1 pound = 453.59 grams, 1 ton = 2000 pounds, **1 ton = 907,180 grams**

1 ton NaCl = .39335 tons Na + .60665 tons Cl

1 ton NaCl = 786.6 pounds Na + 1213.2 pounds Cl

**Table 7
Sodium and Chloride Loading from Road Salt**

Winter	NaCl (pounds)	Na - 39.335% (pounds)	Cl - 60.665% (pounds)
1988/89	620,000	243,877	376,123
1989/90	420,000	165,207	254,793
1990/91	240,000	94,404	145,596
1991/92	160,000	62,936	97,064
1992/93	175,000	68,836	106,164
1993/94	131,000	51,529	79,471
1994/95	200,000	78,670	121,330
1995/96	955,000	375,649	579,351
1996/97	521,000	204,935	316,064
TOTAL	2,382,000	936,959	1,445,040

The magnesium chloride based deicers typically contain 24% to 27% magnesium chloride by weight. The MSDS sheet for Ice-Stop™ indicates the product weighs 10.5 pounds/gallon and contains 25% magnesium chloride. A local distributor of FREEZGARD+LOWTHERM™ reports that the product weighs 10.8 pounds/gallon and contains 26% magnesium chloride by weight. An average of these values was used to calculate the total loading of magnesium and chloride to the environment. Table 8 summarizes the loading calculations for contributions from the liquid deicers, and describes the assumptions and conversion factors used.

Using the values from Tables 7 and 8, the annual combined loading of chloride from the road salt and the liquid deicer was calculated for the period from the winter of 1990/1991 through the winter of 1996/1997. Figure 4 summarizes this data. For the period an estimated total of 4,335,102 pounds of chloride was applied to the environment. The data show that overall two-thirds of the total chloride applied was from the liquid deicers.

The data from Tables 7 and 8 were also used to compare the annual loading of sodium and magnesium for the period from the winter of 1990/91 through 1996/1997. This data is summarized in Figure 5. For the period, the total loading of the two cations were similar with a total of 990,673 pounds of magnesium and 936,959 pounds of sodium applied to the environment.

Table 8
Magnesium and Chloride Loading From Liquid Deicers

Winter	Deicer Applied (gallons)	MgCl₂ - 2.7165 lbs/gal (pounds)	Mg - 25.528% (pounds)	Cl - 74.472% (pounds)
1990/91	26,280	71,389	18,224	53,165
1991/92	88,325	239,935	61,250	178,684
1992/93	154,785	420,473	107,338	313,135
1993/94	149,550	406,253	103,708	302,545
1994/95	255,240	693,359	177,001	516,358
1995/96	340,740	925,620	236,292	689,328
1996/97	413,660	1,123,707	286,860	836,847
TOTAL	1,428,580	3,880,736	990,673	2,890,062

Assumptions: The percentage of MgCl₂ in the deicers used is 25.5% by weight and the average weight MgCl₂ in a gallon of deicer is 2.7165 pounds/gallon.

Conversion Factors: MgCl₂: Molar Weight = 95.211 g/mole, Mg = 24.305 g/mole, Cl=35.453 g/mole; weight percent Mg = 25.528; weight percent Cl = 74.472

Figure 4
Combined Total Chloride Loading

Figure 5
Annual Loading of Sodium and Magnesium

7.0 STORM WATER SAMPLING

Grab samples of storm water were collected from storm sewer out falls and storm water injection wells within the study area to determine the variation in concentration of the major ions and metals. Commercial and residential sites were sampled. Storm sewer samples were collected to represent the cumulative loading of storm drains to the Clark Fork River. Storm water injection well samples were collected to represent single point discharges to the Missoula Aquifer. A control site was established in an area where liquid deicer was not applied to document changes in storm water quality in areas where deicer was applied. Historical storm water sampling data was reviewed where available and appropriate.

7.1 Sampling Methods

Storm water samples were collected from eight locations shown on Figure 1. Two sites were selected for each type of site, with sites being characterized as composite commercial, composite residential, injection well commercial and injection well residential. Table 9 summarizes the sampling sites, and the number of samples taken. Storm water laboratory sampling reports are included in Appendix D.

Table 9
Storm Water Sampling Site Data

SITE NAME	SITE TYPE	# OF STORM DRAINS	# OF SAMPLES TAKEN
Orange Street Outfall	Composite Commercial	54	9
5th & 6th St. Outfall	Composite Residential	36	5
South Higgins Outfall	Composite Commercial	7	5
39th St. & Hillview	Comp. Residential (control)	12	6
Stephens and Mount	Injection Well Commercial	1	3
Russell and Brooks	Injection Well Commercial	1	1
Park and Agnes	Injection Well Residential	1	1
Franklin and Woodford	Injection Well Residential	1	1

A total of 31 storm water samples were collected from the eight sites on eight different dates between January 1993 and March 1995. Samples were collected during the winter, spring and fall. The winter and spring samples were collected to represent storm water quality during times of deicer use. The fall samples were collected to represent storm water quality during times of no deicer use. The rationale was that by the fall the streets would have been flushed several times and residual salts from winter deicing would not be present.

All samples were collected in polyethylene bottles, and refrigerated until they were shipped to the laboratory. Samples were analyzed for the major ions (sodium, magnesium, calcium, potassium and chloride), and metals (arsenic, cadmium, chromium, copper and lead). For most sampling events filtered samples for dissolved metals and unfiltered samples for total metals were collected. The metals samples were preserved in the field with nitric acid, where appropriate. Samples were filtered using a 0.45 micron filter.

7.2 Chloride Concentrations

The storm water sampling data for chloride, other anions and cations, and metals is summarized in Table 10. The chloride concentrations varied significantly, ranging from 3870 mg/l to less than detection. Concentrations of chloride at a level above the Montana WQB-7 acute and chronic standard for surface water of 860 mg/l and 230 mg/l were detected in storm water sampled on January 21, 1993 and March 6, 1995. The March 6, 1995 sampling event was conducted during an initial runoff event associated with a spring snow storm. The January 21, 1993 sampling event represents runoff after heavy snows and deicer application.

The level of chloride in storm water increases with the application of salt or liquid deicer. The variation in the chloride levels may reflect changes due to varying sample collection times with respect to deicer application and whether or not the sample was collected during the first street flushing. Higher levels of chloride would be expected during the first flushing of the street, with lower concentrations being present after subsequent flushes. How much deicer is applied to the road prior to sampling should also effect the amount of chloride present in the storm water. The amount of deicer applied is unknown since it was not metered by the street department at the time of sampling.

7.3 Sodium and Magnesium Concentrations

The sodium and magnesium sampling data shows that storm water quality varies significantly from location to location and that in general the use of liquid deicer increases the concentration of these salts in storm water. The concentrations of sodium and magnesium for each site are presented in Table 10 and Figure 6. The highest concentrations of sodium and magnesium were detected on January 21, 1993 and March 6, 1995, the same dates elevated chloride and metal concentrations were detected. The non-control sites had a proportionally higher concentration of magnesium than the control site. By contrast, the control site (Hillview) had a higher level of sodium compared to the non-control sites. The higher concentrations of salts during spring

Table 10

Storm Drain Sample Results
Trace Metal and Cation/Anion Concentrations

Location	As	Cd	Cr	Cu	Pb	Cl	Mg	Na	Su
ORANGE ST. OUTFALL									
1/21/93	t-<5 d-<5	t-3, d-2	t-20 d-<10	t-30, d-20	t-110 d-<10	1240	362	199	na
2/14/94	t-<5	t-<1	t-20	t-40	t-80	35	572	93	3
4/22/94	t-<5 d-<5	t-<1 d-<1	t-10 d-<10	t-40 d-10	t-80 d-<10	5	3	2	5
5/20/94	t-7 d-<5	t-1 d-<1	t-20 d-<10	t-60 d-<10	t-470 d-<10	5	3	2	7
10/11/94	t-<5 d-<5	t-<1 d-<1	t-10 d-<1	t-30 d-30	t-70 d-<10	7	3	4	9
3/6/95	t-<5 d-<5	t-1 d-1	t-20 d-<10	t-20 d-10	t-20 d-<10	1030	399	58	88
4/13/95	t-9	t-2	t-60	t-60	t-330	11	5	3	na
HILLVIEW									
1/21/93	t-<5 d-<5	t-<1 d-<1	t-20 d-<10	t-70 d-<10	t-70 d-<10	290	20	139	na
4/22/94 (SS)	t-<5 d-<5	t-<1 d-<1	t-<10 d-<10	t-30 d-<10	t-30 d-<10	1	1	1	2
5/20/94	t-<5 d-<5	t-<1 d-<1	t-20 d-<10	t-40 d-<10	t-40 d-<10	4	5	6	7
10/11/94	t-<5 d-<5	t-<1 d-<1	t-<10 d-<10	t-20 d-<10	t-20 d-<10	2	2	2	5
3/6/95 (SS)	t-8 d-<5	t-<1 d-<1	t-60 d-<10	t-190 d-<10	t-190 d-<10	1080	133	440	49
4/13/95	t-12	t-2	t-70	t-220	t-220	9	5	7	na
5TH/6TH OUTFALL									
1/20/93	t-5 d-<5	t-4 d-1	t-<10 d-<10	t-120 d-<10	t-240 d-<10	344	97	na	68
2/14/94	t-<5	t-<1	t-10	t-10	t-20	na	na	na	na
4/22/94	t-<5 d-<5	t-3 d-<1	t-20 d-<10	t-10 d-<10	t-60 d-<10	7	4	2	5
5/20/94	t-<5 d-<5	t-<1 d-<1	t-<10 d-<10	t-<10 d-<10	t-<10 d-<10	2	7	12	3
10/11/94	t-<5 d-<5	t-<1 d-<1	t-20 d-<10	t-<10 d-<10	t-100 d-<10	4	2	7	2
3/6/95	t-<5 d-<5	t-5 d-4	t-<20 d-<20	t-<20 d-<20	t-<20 d-<20	3630	1320	310	65
STEPHENS/MOUNT									
4/22/94	t-<5 d-<5	t-<1 d-<1	t-<10 d-<10	t-<10 d-<10	t-30 d-<10	2	<1	2	<1
10/11/94	t-<5 d-<5	t-<1 d-<1	t-20 d-<10	t-<10 d-<10	t-50 d-<10	1	<1	3	2
3/6/95	t-21 d-14	t-11 d-13	t-70 d-<20	t-60 d-<20	t-200 d-<20	3260	1390	331	71
PARK/AGNES									
4/22/94	t-<5 d-<5	t-<1 d-<1	t-<10 d-<10	t-<10 d-<10	t-40 d-<10	<1	<1	<1	<1
10/11/94	t-<5 d-<5	t-<1 d-<1	t-<10 d-<10	t-<10 d-<10	t-<10 d-<10	<1	<1	1	<1
S. HIGGINS OUTFALL									
3/6/95	t-7 d-<5	t-6 d-5	t-30 d-<20	t-30 d-<20	t-100 d-<20	3870	1480	75	309
4/13/95	t-7	t-2	t-50	t-40	t-220	8	4	3	na
FRANKLIN/WOODFORD									
5/20/94	t-<5 d-<5	t-<1 d-<1	t-10 d-<10	t-<10 d-<10	t-30 d-<10	<1	<2	<1	<1

na-not analyzed; t-total; d-dissolved; As-arsenic; Cd-cadmium; Cr-chromium; Cu-copper; Pb-lead; Cl-chloride;
Mg-magnesium; Na-sodium; Su-sulfate; ppb=parts per billion; ppm=parts per million
Bold-concentration exceeds aquatic life and/or human health standard published in MDEQ WQB-7

runoff and the higher magnesium concentration in non-control sites may be attributed to deicer

use. The higher sodium concentration at the Hillview control site may be attributed to a reliance on sand (NaCl) for traction on roads in this area of Missoula.

Figure 6
Sodium and Magnesium Levels at Control Site and Application Areas

7.4 Metals Concentrations

Storm water samples were analyzed for total and dissolved arsenic, copper, cadmium, chromium and lead. Results are presented in Table 10. The results indicate that metals found at elevated levels were primarily detected as total metals not dissolved. An exception to this trend were arsenic and copper, which were detected as both total and dissolved metal. Montana WQB-7 standards for arsenic, copper, lead, and cadmium were exceeded in storm water samples collected during this study. Most exceedances were seen on March 6, 1995, a date considered to represent storm water quality after deicer use. Lead was consistently detected at all sampling sites at elevated concentrations suggesting that the source of lead may not be deicer. Copper concentrations varied by sample location. The Orange Street outfall and the Hillview site consistently showed elevated concentrations of copper, whereas the 5th/6th Street outfall and Stephens and Mount site did not show elevated levels of copper. The reason for this locational difference at the Orange Street outfall may be the percentage of copper pipe in contact with the

storm water. Storm water in the downtown area is comprised of both precipitation and heating and cooling water. Heating and cooling is often in contact with copper pipe, allowing the copper to leach into the water. The reason for the high copper levels at the Hillview sampling site is unknown. Cadmium was detected at elevated concentrations on March 6, 1995 at the South Higgins outfall and the 5th/6th Street outfall. The primary source of cadmium is thought to be automobiles.

8.0 MAPPING OF STORM SEWERS AND STORM WATER INJECTION WELLS

Most storm water (approximately 85%) in the study area is disposed of using shallow injection wells (dry wells). Approximately 15% is disposed of using storm sewer systems that discharge into the Bitterroot and Clark Fork Rivers.

8.1 Storm Sewers

The City of Missoula Public Works Department mapped the locations of all public storm sewer systems in the study area. This map is included as Attachment A. This map also shows the locations of storm water injection wells on public streets.

8.2 Storm Water Injection Wells

Aerial photographs were used to map the locations of storm water injection wells on public and private property. This data was used to determine the density of storm water injection wells per quarter/quarter section. A map showing the density of injection wells is included as Attachment B. Within the study area a total of 6,107 injection wells were mapped. The maximum density was 152 injection wells per quarter/quarter section in the area of Southgate Mall.

9.0 SURFACE WATER AND GROUND WATER IMPACTS

9.1 Surface Water Impacts

Surface water samples were not collected from the Clark Fork or Bitterroot Rivers to directly measure impacts from the deicers. Storm water quality data suggests that the rivers do receive chlorides, phosphorus, and metals. Copper and lead, in particular, are loaded to the river at concentrations that exceed Montana acute and chronic aquatic life standards. However, based on the volume of water in the river at the time of deicer use in comparison to the volume of storm water discharged to the river, acute impacts to the river from deicer application are considered to be minimal. Chronic impacts to aquatic life from metals loaded to the river from deicers may be more significant when they combine with existing sources of metals pollution. Metals present in deicers can be persistent and/or bioaccumulative in river systems.

Phosphate loading estimates were made to the Clark Fork River since the river is a phosphorus limited stream. Estimates were based on the use of HICOTHAW™, which contains the highest concentration of phosphate of all the deicers reviewed. It was estimated to contribute 682

pounds/year to the environment, and 136 pounds/year to the Clark Fork River (Dr. Garon Smith, personal communication). Based on this estimate, the total annual loading of phosphate compounds from deicers was found to be very low relative to river flows and other sources of phosphate. For example, based on data from 1991 through 1993 the Missoula Waste Water Treatment Facility discharged 186 pounds/day of phosphate, or 67,890 pounds/year.

9.2 GROUNDWATER IMPACTS

9.2.1 Chloride Levels in Mountain Water Company Wells

Water quality data from three Mountain Water Company public water supply wells were reviewed to determine if chloride levels were elevated or had changed since the start of deicer application. These wells are all relatively large, deep production wells that draw water from the lower portions of the Missoula Valley Aquifer. The laboratory reports obtained to evaluate chloride levels in the wells are included in Appendix F.

The Maurice Street well was selected as a control well because it is located upgradient of the area of most deicer application, and is in the recharge area for the Missoula Valley Aquifer. This well has been sampled eight times between 1978 and 1994. The chloride level in the well averaged 3.5 mg/l. The chloride level was 3.0 mg/l in 1978 and 1994, indicating that there has been no significant increase in chloride levels in groundwater located in the deeper zones of the aquifer at this location.

Two other Mountain Water Company wells, the Benton Avenue well and the Southgate Mall well were also used to evaluate chloride levels before and after deicer application. Both wells are located down gradient of the Maurice Street well in areas with high densities of storm water injection wells and heavy deicer usage. The Benton Avenue well is located near the intersection of Brooks, South and Russell streets, one of the busiest intersections in Missoula. This area receives significant deicer application, and contains high densities of storm water injection wells. Chloride levels in the Benton Avenue well averaged 3.7 mg/l between December, 1977 and June, 1994, indicating that levels have not increased in the deep aquifer at this location.

The Southgate Mall well is located directly downgradient of the mall parking lot area, which contains the highest density of storm water injection wells in the Missoula Valley. Chloride levels in this well averaged 3.96 mg/l between 1978 and 1994. One sample in 1978 showed a level of 3.8 mg/l, and five samples collected between 1984 and 1994 were all 4 mg/l. The results do not indicate a significant increase in chloride levels.

In summary, the chloride levels in the Mountain Water Company wells are low and have not significantly changed during the period of deicer application. This is probably due to the very high flow rate in the aquifer and the fact that the wells are all drawing water from the lower portions of the aquifer.

9.2.2 Chloride & Magnesium Levels in Shallow Monitoring Wells

Data collected from the Water Quality District monitoring wells from 1986 until 1997 were reviewed to evaluate whether any trend in chloride or magnesium concentrations could be seen in the shallow groundwater of the Missoula Aquifer. Data from the Madison Street, Blaine & Crosby Street and South and Bancroft Street wells were reviewed. The Madison street well is located near the Mountain Water Company Maurice Street well in an area upgradient of most deicer application, and within the main recharge area for the Missoula Valley Aquifer. The Blaine Street and the South Avenue wells were both originally installed to monitor storm water impacts from injection wells located next to the monitoring wells. The wells were installed by Wogsland (1987).

Historical chloride and magnesium groundwater concentrations from the three monitoring wells can be seen in Table 11. A background concentration for magnesium could not be established with confidence at this time due to the lack of sampling data; however, the March 1997 concentration for the Madison Street well was 5.70 mg/l. Assuming a background concentration for magnesium of around 6.0 mg/l, groundwater quality is degrading slightly as it moves through the shallow aquifer. This conclusion is made by comparing 6.0 mg/l to the range of magnesium found in downgradient wells of 11.0 to 17.5 mg/l. The increase in magnesium does not appear to be associated with increased deicer use, as magnesium levels have either decreased slightly or remained the same from 1986 till 1997 in the South Avenue and Blaine Street wells.

The chloride data shows very different results depending upon which downgradient well is compared to background chloride concentrations. Chloride levels appear to increase as groundwater flows through the aquifer when comparing data from the Madison Street well to the South Avenue well. Background concentrations for chloride (Madison Street Well) ranged from 2.49 to 7.00 from July 1995 to March 1997. Over the same period chloride levels in the South Avenue well ranged from 7.89 to 26.82 mg/l. The data from the South Avenue well also shows a cyclical pattern with the highest concentrations seen during the spring time months and the lowest in the summer or fall. This pattern was seen in 1987, 1994, 1995, and 1996. This cyclical pattern may be the result of increased loading of chloride from deicer and road salt use during the spring. The data from the Blaine Street well shows a completely different picture. No cyclical pattern can be seen, and chloride levels in the Blaine well were lower than the background well.

9.2.3 Trace Metal Levels in Shallow Monitoring Wells

Concentrations of arsenic, cadmium, chromium, lead in wells screened in the shallow zone of the Missoula aquifer were reviewed to evaluate the potential impacts of deicer use on groundwater quality. Groundwater analytical results from 1995 to 1997 are presented in Table 11. Data from the same three monitoring wells used to evaluate chloride and magnesium trends were reviewed

Table 11
Shallow Groundwater Monitoring Well Results

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Location & Date	Chloride	Magnesium	As	Cd	Cr	Pb
	units - mg/l			units - ug/l		
Madison Street						
7/6/95	5.00	ns	<0.10	<0.002	<0.004	<0.002
11/1/95	2.49	ns	3.04	<0.002	<0.004	0.158
2/15/96	3.30	ns	ns	ns	ns	ns
5/21/96	7.00	ns	ns	ns	ns	ns
8/15/96	4.00	ns	ns	ns	ns	ns
11/13/96	5.00	ns	ns	ns	ns	ns
3/17/97	5.43	5.70	2.20	<0.005	<0.005	<0.06
South Avenue						
6/13/86	5.30	15.3	ns	ns	ns	ns
10/10/86	7.90	17.5	ns	ns	ns	ns
5/17/87	8.00	15.9	ns	ns	ns	ns
3/24/87	25.20	16.1	ns	ns	ns	ns
6/24/87	6.86	15.4	ns	ns	ns	ns
7/7/94	10.00	15.0	ns	ns	ns	ns
9/29/94	7.00	14.0	ns	ns	ns	ns
6/29/95	15.00	ns	<0.10	<0.002	<0.004	<0.002
10/31/95	7.89	ns	2.39	<0.002	0.978	<0.002
3/13/96	19.20	ns	ns	ns	ns	ns
11/20/96	9.00	ns	ns	ns	ns	ns
3/13/97	26.82	16.24	1.6	<0.005	<0.005	<0.06
Blaine/Crosby Streets						
10/9/86	3.10	12.0	ns	ns	ns	ns
3/24/87	2.76	12.1	ns	ns	ns	ns
5/17/87	3.13	11.6	ns	ns	ns	ns
7/7/94	4.00	11.0	ns	ns	ns	ns
9/8/94	4.00	11.0	ns	ns	ns	ns
6/29/95	5.00	ns	<0.10	<0.002	<0.004	<0.002
11/1/95	2.50	ns	<0.10	<0.002	<0.004	<0.002
3/13/96	2.90	ns	ns	ns	ns	ns
6/10/96	6.00	ns	<0.005	<0.001	<0.01	<0.01
11/20/96	4.00	ns	<0.001	<0.001	<0.01	<0.01
3/13/97	4.55	12.34	1.4	<0.005	<0.005	<0.06

ns-not sampled; Cl and Mg pre-1994 data taken from Wogsland (1987).
Cl and Mg post-1994 data obtained taken from Missoula Valley Water Quality
District (MVWQD) database; Metals data from the MVWQD database

to look at trends in trace metal concentrations. The results show that groundwater does not appear to be adversely impacted from deicer use with respect to metals. Arsenic and lead were the only metals detected at low concentrations. Arsenic was detected in the Madison Street well, a well near the river and hydraulically upgradient of most deicer use. The slightly elevated arsenic in this upgradient well may reflect background conditions. Rattlesnake Creek and many Mountain Water Company wells not influenced by the Clark Fork River have shown arsenic levels around 3 ug/l.

10.0 CONCLUSIONS AND RECOMMENDATIONS

10.1 Conclusions

Deicer use in the Missoula Valley has increased each year since use began in the winter of 1990/91. (See Table 6.) An estimated 26,280 gallons of deicer was applied to the roads in 1990/91. During the winter of 1996/97, 413,660 gallons were applied. Sand usage declined from 1990 to 1994 as deicer use increase. However, the last two heavy snowfall years (1995/96 and 1996/97) resulted in an increase in sand usage to levels near or above pre-deicer years.

The deicers applied to Missoula roadways are manufactured by evaporating salt solutions from either the Great Salt Lake or sea water. Four magnesium chloride deicers have been approved by the Missoula City-County Air Pollution Control Board; Freezegard/PCITM, CG-90TM, Ice StopTM and Freezegard/LowthermTM. Freezegard/PCITM and CG-90TM have been the most commonly applied by the Public Works Department.

A shift from road sand to deicer results in an increase load of trace metals to the environment. Analytical testing of the deicers showed that arsenic, cadmium, chromium, copper, lead and manganese were present in the deicers. (See Table 3.) The concentrations were variable, possibly a characteristic of the products or laboratory matrix interference caused by the high salt content of the deicers.

The road sanding material does not increase the load of trace metals to the environment. No arsenic, cadmium, chromium, lead or copper were detected in the bulk sand.

Total loading of chloride to the environment from deicer and road sand from 1990-1997 is estimated at 4,335,102 pounds. (See Figure 4) Almost two thirds (66%) of the chloride loading was from the liquid deicers. Over this same period, approximately 990,673 pounds of magnesium (deicer) and 936,959 pounds (road sand) of sodium were applied to the roadways.

Storm water sample analytical results showed that:

(A) Chloride, magnesium, and sodium concentrations were highly variable, with chloride levels exceeding the Montana WQB-7 standard for aquatic life after spring initial street runoff in spring 1995. The highest concentrations were seen during the initial flushing of the roadway after deicer application. Storm water sample concentrations of these salts decreased significantly after this initial flushing.

(B) The lead detected in storm water does not appear to be associated with deicer use. Lead was detected at elevated concentrations at all storm water sampling locations during all seasons. Lead was not seen at significantly higher concentrations when magnesium and chloride were seen at their highest concentrations. Other potential sources of lead which may account for the elevated concentrations include use of lead-based paints on the road and shoulder, leaded gasoline, and antifreeze and crank case oil spillage to the road.

(C) Arsenic, cadmium and chromium detected in storm water may be associated with deicer use. These metals were detected at their highest concentrations during the spring of 1995, the same time the highest concentrations of magnesium and chloride were detected.

(D) Copper concentrations in storm water appeared to be location specific, with the highest seen in discharges from the city urban core and the south hills area. Elevated concentrations of copper did not correlate with elevated chloride and magnesium concentrations. Possible reasons for locational differences in copper concentrations may be a higher percentage of non-contact heating and cooling water in the storm water discharge from the urban area and geologic differences in valley soils.

(E) Chloride, arsenic, copper, and lead were detected in storm water at concentrations above Montana WQB-7 standards. (See Table 10.) Chloride and copper were detected at concentrations above the acute aquatic life standards of 860 mg/l and 18 ug/l, respectively. Arsenic and cadmium were detected at a concentration above the human health protection standards of 18 ug/l and 5 ug/l. Lead was detected at concentrations above the acute aquatic life standard of 82 ug/l and human health standard of 15 ug/l.

Use of deicer increases the loading of salts and metals to the Clark Fork and Bitterroot Rivers. The resultant change in river salt and metal concentrations from deicer use is not known since surface water was not sampled during this study. Based on the volume of discharge to the rivers and the time of discharge (high flow), the resultant increase in salt and trace metal river water concentrations is expected to be minimal. However, conclusions concerning surface water impacts should be considered preliminary since river sampling was not done. Because metals associated with deicer use are persistent and/or bioaccumulative, significant chronic or cumulative impacts to aquatic life may result when they combine with existing sources of metals pollution.

A review of Mountain Water Company well sampling data and Water Quality District monitoring well data suggests:

(A) The increase in deicer use has not resulted in an increase in the concentration of arsenic, lead, cadmium, or chromium in groundwater. (See Table 11.)

(B) Localized seasonal increases of chloride near storm drains may be expected with

increased reliance on deicers. The chloride data from the South Avenue Well (Table 11) shows a seasonal increase during the spring months of the year. This well is located hydraulically downgradient of a storm drain approximately 30 feet away.

(C) In general there is a slight increase in magnesium and chloride concentrations in groundwater as it flows below the area of deicer use (from the Clark Fork River toward the Bitterroot River). Comparison of data from the Madison Bridge well (upgradient) and the South Avenue well (down gradient) supports this conclusion. (See Table 11.)

10.2 Recommendations

The increasing reliance on deicers to remove snow and ice from streets of Missoula results in increased loading of salts and metals to surface and groundwater in the valley. Each year since 1990/91 the amount of deicer used has steadily increased, resulting in an increased loading of salts and metals. At this time it does not appear that the increase in deicer use has resulted in a significant negative impact to groundwater, and based on the volume of storm water discharged and the time of discharge, immediate impacts to surface water are probably short-term, localized, and minor. However, because metals associated with deicer use are persistent and/or bioaccumulative, significant chronic or cumulative impacts to aquatic life may result when they combine with existing sources of metals pollution.

The following recommendations are intended to measure the effects or amend the way deicers are used in the Missoula Valley.

(A) Groundwater sampling for magnesium, chloride, and trace metals should be continued to evaluate trends in groundwater quality. The Water Quality District monitoring well network of wells currently being sampled appears to adequately cover the area of deicer application.

(B) Initiate sampling of the Clark Fork River upstream and downstream of Missoula to evaluate the in stream effects of deicer use. This study did not accomplish this task due to a belief that the volume and concentration of contaminants loaded to the river wouldn't alter in stream concentrations. This should be supported by hard data.

(C) Test the corrosivity of storm water after deicer application to evaluate the corrosive potential of deicer application.

(D) Consider a shift from magnesium chloride-based deicers to a calcium magnesium acetate (CMA) deicer every few years to minimize the potential environmental impact. Our research indicates that this product has the least potential for environmental impact; however, it is currently 20 times more expensive than magnesium chloride-based deicers.

(E) The continued development of homes on top and along the hillsides surrounding Missoula should be discouraged. The roads leading to homes placed on hills require a greater than normal amount of sanding material to ensure safe travel. With more sand comes more particulate problems. The winters of 95/96 and 96/97 showed an increase in sand usage to pre-deicers years. The main objective of using deicer was to lower the

amount of sand used on the streets. If homes continue to be built on hills, the decrease in sand usage may never be seen.

(F) Eliminate the use of lead-based paints on curbs and streets. Results of this study showed that storm water consistently contains elevated levels of lead during all times of the year. Lead-based paints are likely a major contributor to the quantity of lead detected.

(G) The use of deicers should be carefully managed and minimized to the maximum extent practicable, consistent with the need to protect public safety through improved winter road conditions. Deicers are contaminants, and the continued growth in use of them may result in impacts to groundwater and surface water.

(H) Construction of storm sewers that discharge to rivers should be discouraged.

(I) Use of infiltration swales should be required in new construction on roads and bridges that will discharge storm water directly to rivers.

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