EFFICIENCY OF ROADSIDE SWALES IN REMOVING HEAVY METALS FROM HIGHWAY ASSOCIATED NONPOINT SOURCE RUNOFF

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ABSTRACT: During the past decade, a substantial amount of research has accumulated relating to the water pollution caused by the operation of motor vehicles. This concern has been based mainly on the potential aquatic toxicity of heavy metals such as lead, zinc and chromium.

One of the most common management techniques for highway runoff is the roadside swale. These swale systems are usually designed as a conveyance mechanism for transporting runoff from the roadway to the receiving water body. However, little information has been collected on the efficiency of these swale systems in reducing pollutant concentrations. Therefore, a series of controlled experiments were designed and conducted to investigate the fate of nutrients and heavy metals discharged to swale areas located at two sites in the Orlando area.

Runoff water from adjacent retention ponds was dosed with various concentrations of nutrients and heavy metals and pumped continuously into the swale test areas, ranging in length from 53 to 170 m. Samples of the swale flow were collected at various distances along the flow path at specified time intervals for a period of 4-6 hours. Concentrations of heavy metals and nutrients were measured and removal efficiencies were quantified.

Removal of heavy metals was found to be closely associated with the pH of the runoff water and the corresponding chemical speciation of the metal ions. Heavy metals which existed at the test pH as a free metal ion were found to be removed to a much larger degree than metals which existed predominantly as an uncharged ion or as an ion with a diffused charge. The presence of organic complexing agents, such as humic acid, reduced the removal efficiency considerably. The removal of phosphorus was found to be much less than that observed for heavy metals. Concentrations of nitrogen forms were not changed to any significant degree during passage through the swale area.
(KEY TERMS: stormwater; heavy metals; swales.)

INTRODUCTION

Within the past decade, a substantial amount of research has accumulated relating to air and water pollution caused by the operation of motor vehicles. This concern is based mainly on the potential aquatic toxicity of heavy metals such as lead, zinc, and chromium. Heavy metals have been proposed by several researchers as the major toxicant present in highway runoff samples (Shaheen, 1975; Winters and Gidley, 1980).

Many heavy metals are known to be toxic in high concentrations to a wide variety of aquatic plants and animals (Wilber and Hunter, 1977). Even at sub-toxic levels, the presence of harmful metals such as mercury or cadmium can render commercially valuable fish and shellfish unmarketable.

The State of Florida currently requires that stormwater originating within a new project or development be managed and treated within the boundaries of the development. Most of the available management techniques, however, are based on hydraulic considerations of the flow and either ignore or minimize quality parameters. One of the most popular stormwater management techniques in use today is the roadside swale. Roadside swales are designed to drain, transport and control highway runoff waters from paved surfaces.

Although swales have become popular stormwater treatment alternatives, little qualitative data has been collected to determine the fate of pollutants, especially heavy metals, in these systems. The purpose of this research was to investigate the movement and attenuation of heavy metals in roadside swales. Two swale sites were selected and on-site investigations were conducted to answer these questions.

FIELD INVESTIGATIONS

A series of field investigations were conducted at two locations in the Central Florida area to investigate the efficiency of roadside swales for removal of heavy metals in highway runoff. The study areas included: (a) an older established swale area near an Interstate-4 interchange with Maitland Blvd. north of Orlando, Florida; and (b) a sandy, newly constructed swale which receives stormwater runoff from the main exit road to EPCOT Center of Disney World. Field investigations were divided into two phases. During one phase, a stormwater sampling program was established at six stations at the Maitland Interchange site. Three of the stations were selected so that direct highway runoff could be collected with the remaining three in swale areas to collect highway runoff after passing through the swale. Selection of these locations

assisted in differentiating between runoff quality from highways before and after flowing over adjacent swales. Plexiglass sample collection devices were installed at each station so that a flow weighted composite sample could be collected during flow events. A total of 17 storm events were sampled between August 1982 and March 1983, although a collectable amount of runoff did not occur at some locations on specific dates.

In the second set of field investigations, a series of controlled, continuous flow experiments were conducted to estimate the removal of dissolved heavy metals in swales during continuous flow. Three experiments were conducted at the Maitland site and two were conducted at the EPCOT site. A typical experiment consisted of pumping water from nearby stormwater holding ponds at a continuous flow rate to the upland region of the swale areas. A concentrated solution of heavy metals was dosed into the water flow at a constant rate to produce a solution with dissolved metal concentrations similar to those normally detected in highway runoff. The spiked water flowed by gravity flow through the swale area and was ultimately discharged either into a retention pond or wetland area at the end of the swale. A sharp-crested 90° V-notch weir was placed before the outlet at both sites so that the flow leaving the swale area could be monitored. Water samples were collected at various distances from the flow inlet at 30-minute intervals for time periods ranging between 3 and 5.5 hours. Average measured heavy metal concentrations at each of the sample collection points over the entire test period were used to estimate removal of dissolved metals during continuous flow through the swale area. Average hydraulic characteristics of the five swale experiments are presented in Table 1.

During the experimental period, the Maitland swale area was covered with a thick crop of grasses, predominantly Bahia. Of the two experiments conducted at the EPCOT site, one was conducted shortly after construction of the swale when the bottom and sides were in a predominantly earthen state before establishment of vegetation. The other experiment was conducted several months later after vegetation had become established. Gross cover was estimated at approximately 20 percent in the first experiment and 80 percent in the second. The swale test area at the Maitland site was approximately 53 m in length while the EPCOT test area was 170 m in length.

The EPCOT area was originally a wetland forest before construction, and as a result, natural groundwater in the area is high in organic content, as evidenced by the dark color of surface water. Normal seepage flow through the swale at the start of both experiments was also highly colored and this background flow was presumed to be rich in humic organic materials.

During both the stormwater sampling program and the continuous flow swale experiments, water samples were collected in polyethylene bottles and preserved at 4°C. Heavy metal analysis was conducted following sample digestion using argon plasma spectroscopy with a Spectrometrics, Inc. Spectrospan III Plasma Emission Spectrophotometer. Dissolved metal samples were prepared by filtration through a 0.45 micron filter.

RESULTS

Stormwater Sampling Program

In order to make a comparison and analysis of the various collection locations, it was necessary to group the data collectively into two categories, according to the source of stormwater runoff: (1) locations 1, 5, and 6 grouped together collectively as "highway runoff;" and (2) locations 2, 3, and 4 grouped together as "swale flow." A comparison of average concentrations for highway and swale areas is given in Table 2. It can be seen that the concentrations of both total and dissolved forms of every heavy metal analyzed are lower in the swale flow than in the highway flow.

Zinc concentrations were decreased to the greatest degree by passage through a swale area, with an average of 82 percent reduction in dissolved and 90 percent reduction in total species. Concentrations of total lead and nickel were reduced approximately 90 percent with a 50 percent reduction in dissolved forms. Iron and aluminum were removed less efficiently with a 75 percent reduction in total forms and a 20-40 percent removal of dissolved species. Cadmium, copper and chromium were removed to the smallest degree with 30-40 percent removal of total forms and only a small removal of dissolved species.

TABLE 1. Hydraulic Characteristics of Swale Experiments.

Experiment				Swale Characteristics				Flow (m³/min)		Average Calculated Velocity (m/min)
No.	Location	Date	Duration (hr)	Length (m)	Average Cross Section Area (m²)	Average Top Water Width (m)	Average Hydraulic Depth (m)	Into Swale Area	Output From Swale	
1	Maitland	1/24/83	3.0	53	0.063	1.67	0.038	0.227	0.098	2.58
2	Maitland	2/07/83	4.0	53	0.045	1.35	0.033	0.086	0.038	1.37
3	Maitland	2/21/83	5.5	49	0.014	0.85	0.017	0.026	0.000	0.90
4	EPCOT	3/23/83	4.2	170	0.059	1.47	0.040	0.162	0.125	2.44
5	EPCOT	5/16/83	4.0	170	0.063	1.59	0.040	0.168	0.138	2.46

TABLE 2. Comparison of Highway Runoff and Swale Flow During 1982-1983 at Maitland Interchange.

Heavy Metal	Highway Runoff		Swale Flow		Change in Concentration Through Swale (percent)	T-Test Probability for Unequal Means
	Average Concentration (ug/l)	Percent Dissolved (percent)	Average Concentration (ug/l)	Percent Dissolved (percent)		
Cadmium						
Dissolved	1.1	79	0.9	90	−18	81.2
Total	1.4		1.0		−29	98.2
Zinc						
Dissolved	89	35	16	64	−82	99.9
Total	255		25		−90	99.9
Copper						
Dissolved	27	61	22	85	−19	42.9
Total	44		26		−41	90.1
Aluminum						
Dissolved	66	7	53	23	−20	86.5
Total	970		233		−76	99.9
Iron						
Dissolved	52	6	29	12	−44	87.3
Total	830		240		−71	99.7
Lead						
Dissolved	36	9	18	50	−50	99.7
Total	417		36		−91	99.9
Nickel						
Dissolved	3.4	17	1.8	75	−47	97.2
Total	21		2.4		−88	78.2
Chromium						
Dissolved	3.2	39	2.8	61	−13	54.3
Total	8.2		4.6		−44	99.3
Average pH	5.75		5.54			
No. of Samples	47		25			

Continuous Flow Investigations

Three swale experiments were conducted at the Matiland Interchange during which the removal of dissolved heavy metals was investigated in a continuous flow situation at three different swale flow velocities ranging from 2.58 m/min to 0.90 m/min. A summary of the data for these experiments is presented in Table 3.

Removal efficiencies for dissolved heavy metals in the first Maitland swale experiment conducted on 1/24/83 at a flow velocity of 2.58 m/min are presented in Figure 1. Dissolved zinc was removed at the fastest rate with 77 percent being removed over a distance of 53 meters. As seen in Figure 1, the removal rate for zinc was approximately linear, and the shape of the curve suggests that additional removal could have been obtained if the swale test length had been increased. Excellent removal was also noted for dissolved iron, although the concentration increased slightly during the first 10-15 meters. Although lead was removed to only 40 percent of its original concentration after a travel distance of approximately 20 m, a significant increase in lead concentration was observed in the 53 m sample. Removals of dissolved copper, aluminum, and

chromium were much less with an average of approximately 80 percent remaining after 53 m. Although nickel and cadmium were included in the spike solution, measured concentrations of these metals in the flow stream were too low to accurately comment on removal efficiencies for these two metals.

A summary of average removal efficiencies for the second Maitland experiment, conducted at a slower average flow velocity of 1.37 m/min, is given in Figure 2. Dissolved zinc was again removed at the fastest rate with a calculated removal of 92 percent over the test distance of 53 m. Approximately 70 percent of the iron and 60 percent of the copper was also removed. Lesser removals averaging between 25 and 40 percent were noted for aluminum, lead and chromium. It is interesting to note that lead, aluminum and iron did not exhibit increases in the first 10 m at this slower velocity as they did in the first experiment which was conducted at a velocity almost twice as great. Final removal efficiencies for each of the metals listed in Table 3 exceeded those of the previous experiment. Measured concentrations of nickel and cadmium were again

TABLE 3. Summary of Average Dissolved Heavy Metal Concentrations in Continuous
Flow Swale Experiments Conducted at the Maitland Interchange Site.

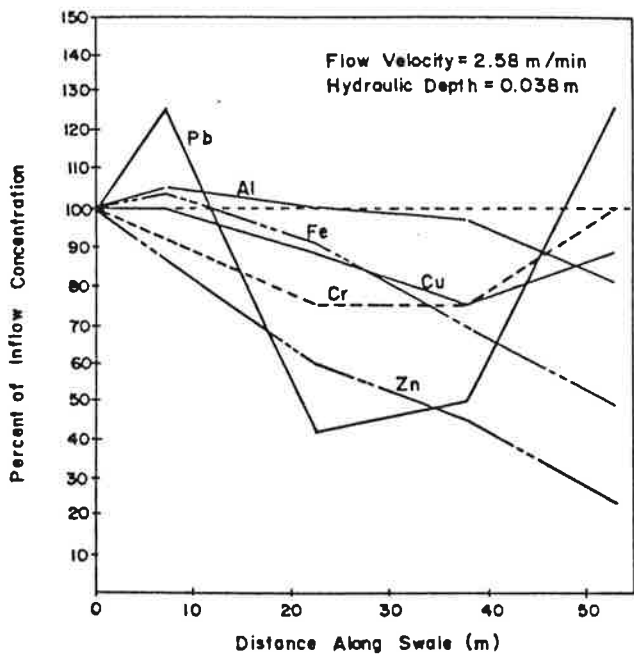| Date | Flow Velocity (m/min) | Heavy Metal | Average Dissolved Metal Concentrations in Swale Flow (ug/l) | | | | | Average pH |
			0 m (Input)	7.5 m	23 m	38 m	53 m	
1/24/83	2.58	Zn	22	19	13	10	5	6.5
		Cu	8	8	7	6	7	
		Al	131	136	131	127	106	
		Fe	35	36	32	24	17	
		Pb	12	15	5	6	15	
		Cr	12	11	9	9	12	
2/07/83	1.37	Zn	26	23	9	6	2	6.5
		Cu	7	7	6	4	3	
		Al	123	92	93	91	75	
		Fe	469	342	190	168	143	
		Pb	8	8	5	8	6	
		Cr	6	6	2	4	4	
2/21/83	0.90	Zn	18	6	5	2	*	6.5
		Cu	2	2	4	4		
		Al	37	8	8	10		
		Fe	277	86	84	83		
		Pb	6	4	5	6		

*Flow did not reach this distance.

Figure 1. Changes in Concentration of Various Heavy Metals During Flow Through a Grassy Swale at Maitland on 1/24/83.
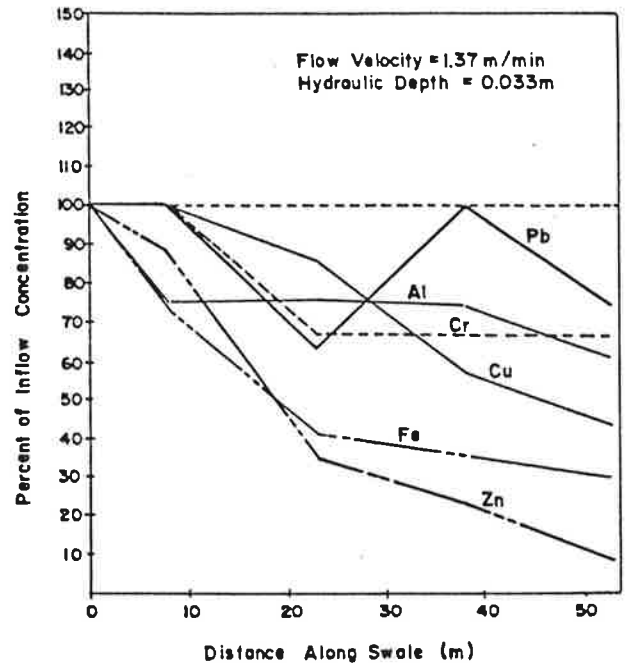

Figure 2. Changes in Concentration of Various Heavy Metals During Flow Through a Grassy Swale at Maitland on 2/7/83.

TABLE 4. Summary of Average Dissolved Heavy Metal Concentrations in Continuous
Flow Swale Experiments Conducted at the EPCOT Site.

| Date | Flow Velocity (m/min) | Heavy Metal | Average Dissolved Heavy Metal Concentrations in Swale Flow (ug/l) | | | | | | Average pH |
			0 m (Input)	30 m	60 m	90 m	120 m	170 m	
3/23/83	2.44	Cd	11	9	8	8	8	7	5.95
		Zn	256	188	158	140	122	102	
		Cu	22	25	22	22	20	19	
		Fe	489	454	403	410	458	503	
		Pb	91	46	53	44	44	31	
		Ni	112	92	80	74	62	50	
		Cr	11	8	8	8	10	8	
5/16/83	2.46	Cd	2	2	1	1	1	1	7.00
		Zn	23	19	15	14	11	8	
		Cu	29	34	38	36	36	27	
		Fe	91	125	127	112	94	116	
		Pb	44	40	42	39	32	28	
		Ni	28	26	21	20	17	16	
		Cr	8	10	11	11	10	9	

DISCUSSION

Removal of Dissolved Heavy Metals

Upon review of the data for the three Maitland experiments, it becomes evident that not all dissolved metals were removed at the same rate. Zinc and iron were consistently removed rapidly while copper, aluminum, lead and chromium were removed consistently less rapidly. One of the first possible explanations to this question is to examine the solubility of each of these metals in the test waters. A survey was conducted of all known inorganic equilibria for zinc, copper, iron, lead, chromium, nickel and cadmium, and reactions which were through to be important in aerobic surface waters were listed. Solubility diagrams including all important soluble and insoluble species were then constructed for each of the seven heavy metals for situations with and without significant organic complexation. A summary of these diagrams is given in Table 5.

A review of soluble concentrations measured during the swale study for iron, zinc, copper, lead, cadmium and nickel revealed that only iron was initially present in concentrations sufficiently high to cause formation of a precipitate at the experimentally measured pH of approximately 6.5. It is, therefore, probable to assume that the iron removal was, at least in part, due to formation and settling of a precipitate. However, zinc, which was present in concentrations in the range of 10^{-7} M and 10^{-8} M, was clearly in the soluble region, yet excellent removal was obtained.

It is a well known fact that negatively charged particles in the soil and organic litter layer have the ability to adsorb cations from solution in an exchange reaction. If this phenomenon were to be responsible for heavy metal removal in swales, then the charge and size of the cationic species would
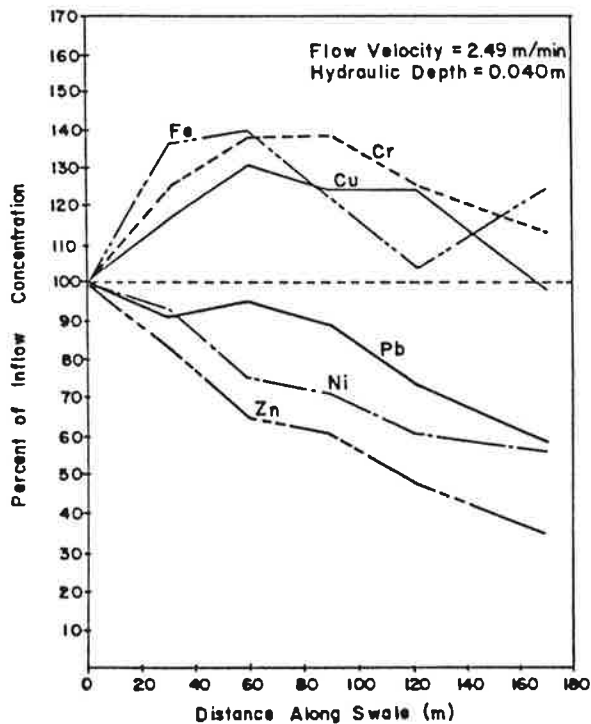

Figure 5. Changes in Concentration of Various Heavy Metals During Flow Through a Grassy Swale at EPCOT on 5/16/83.

determined to be too low to accurately comment on removal efficiencies.

Another experiment conducted at Matiland Interchange was designed to test the effect of a very low velocity on removal efficiencies. A velocity of only 0.90 m/min was maintained throughout the experiment. Since the flow rate was very slow, infiltration losses were quite large, and the flow only reached the 38 m station. As seen in Figure 3, dissolved forms of zinc and iron were again removed most rapidly. Approximately 90 percent of the dissolved zinc and 70 percent of the dissolved iron were removed during overland flow at this velocity over a distance of 38 m. Aluminum was also removed to a large degree with an average final removal of approximately 75 percent. Concentrations of dissolved nickel, copper, lead and cadmium were very low in the simulated stormwater flowing through the swale. At these concentrations, accurate analysis becomes difficult, and the significance of measurement errors increases considerably.
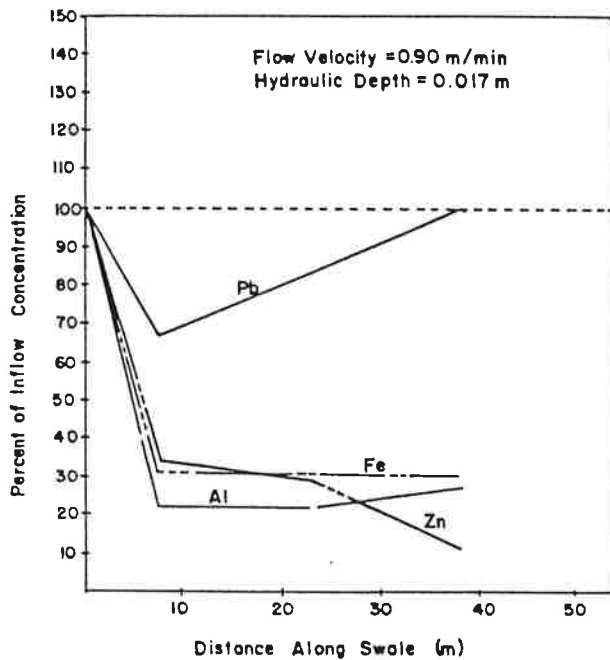

Figure 3. Changes in Concentration of Various Heavy Metals During Flow Through a Grassy Swale at Maitland on 2/21/83.

A summary of average dissolved heavy metal concentrations for the two EPCOT experiments is given in Table 4. Removal efficiencies for the first experiment conducted on 3/23/84 at an average flow velocity of 2.44 m/min with a 20 percent plant cover are presented in Figure 4. As seen in the previous experiments at the Maitland site, zinc was removed from solution rapidly with a total removal of 61 percent over 170 m. Removal of dissolved nickel and lead closely followed that observed for zinc. Approximately 54 percent of the dissolved nickel and 65 percent of the dissolved lead were removed in the 170 m test area. It appears that cadmium was removed to

a lesser degree with 64 percent still remaining at the end. Removal of copper, iron and chromium by passage through the earthen swale seemed to be minimal, and as seen in Figure 4 concentrations of iron may have actually increased after a distance of 90 m.
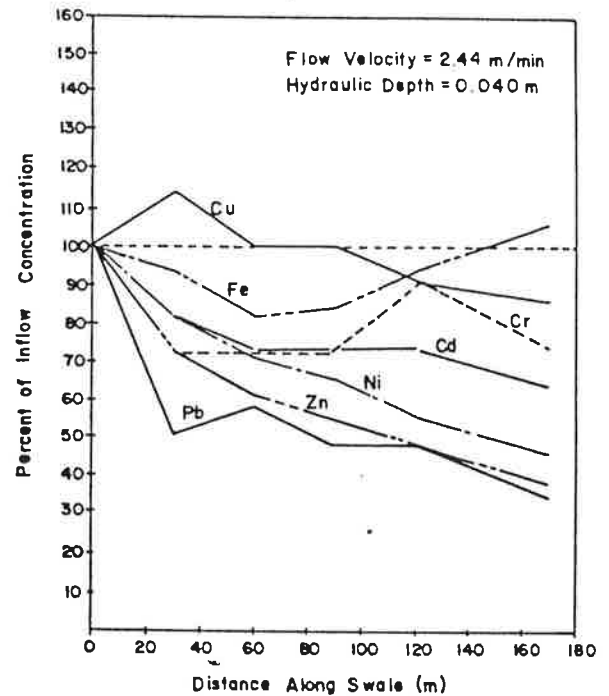

Figure 4. Changes in Concentration of Various Heavy Metals During Flow Through in Earthen Swale at EPCOT on 3/23/83.

A summary of removal efficiencies for the second EPCOT investigation conducted on 6/15/83, after the establishment of a grass cover, is presented in Figure 5, as seen in all previous experiments, dissolved zinc was removed from solution at a rapid rate. A total removal of 65 percent was calculated and compared to the removal of 61 percent obtained in the earthen channel. Dissolved lead was also removed from solution, particularly at the 120 m and 170 m sites with only 59 percent remaining at the end of the test area. Removal of nickel was also found to occur and, as seen in Figure 5, exhibited removal efficiencies approximately midway between the removal of zinc and that of lead. Concentrations of iron, copper and chromium, however, exhibited initial increases and remained near or above their original concentrations throughout the test area. It should be noted that in the first EPCOT experiment, conducted in the earthern channel at the same site, significant removals of both copper and chromium were found. Concentrations of cadmium throughout the experiment were too low to form accurate conclusions.

TABLE 5. Summary of Inorganic and Organic Speciation of Heavy Metals at Various pH Ranges in Natural Aquatic Systems.

Heavy Metal	Inorganic Complexation Only			Inorganic + Organic Complexation		
	$pH < 6.5$	$6.5 < pH < 7.5$	$pH > 7.5$	$pH < 6.5$	$6.5 < pH < 7.5$	$pH > 7.5$
Cd	Cd^{+2}	Cd^{+2}	Cd^{+2} $CdCO_3^{\,o}$ $Cd(OH)_2^{\,o}$	Cd^{+2} Cd-Fulvate	Cd^{+2} Cd-Fulvate	Cd^{+2} $CdCO_3^{\,o}$ $Cd(OH)_2^{\,o}$
Zn	Zn^{+2}	Zn^{+2} $ZnCO_3^{\,o}$	$ZnCO_3^{\,o}$ $Zn(OH)_2^{\,o}$ $Zn(OH)_4^{-2}$	Zn^{+2}	Zn^{+2} $ZnCO_3^{\,o}$	$ZnCO_3^{\,o}$ $Zn(OH)_2^{\,o}$ $Zn(OH)_4^{-2}$
Fe	$Fe(OH)_2^{\,+}$	$Fe(OH)_2^{\,+}$ $Fe(OH)_3^{\,o}$	$Fe(OH)_3^{\,o}$ $Fe(OH)_4^{\,-}$	Numerous Species		
Pb	Pb^{+2}	Pb^{+2} $PbCO_3^{\,o}$	$PbCO_3^{\,o}$ $Pb(CO_3)_2^{-2}$ $Pb(OH)_3^{\,-}$ $Pb(OH)_4^{-2}$	Pb^{+2}	Pb^{+2} $PbCO_3^{\,o}$	$PbCO_3^{\,o}$ $Pb(CO_3)_2^{-2}$ $Pb(OH)_3^{\,-}$ $Pb(OH)_4^{-2}$
Cu	Cu^{+2}	Cu^{+2} $CuCO_3^{\,o}$ $Cu(OH)_2^{\,o}$ $Cu(OH)_2^{\,o}$	$Cu(OH)_2^{\,o}$	Cu^{+2} Cu-Fulvate Cu-Humate	Cu^{+2} $CuCO_3^{\,o}$ $Cu(OH)_2^{\,o}$ Cu-Fulvate	$Cu(OH)_2^{\,o}$
Ni	Ni^{+2}	Ni^{+2} $NiCO_3^{\,o}$	$NiCO_3^{\,o}$ $Ni(CO_3)_2^{-2}$ $Ni(OH)_3^{\,-}$	Ni^{+2}	Ni^{+2} $NiCO_3^{\,o}$	$NiCO_3^{\,o}$ $Ni(CO_3)_2^{-2}$ $Ni(OH)_3^{\,-}$

determine to a large degree the magnitude of removal observed. This relatively simple ass-mption is complicated by the fact that both inorganic as well as organic species of metals can exist in solution. However, investigations of Yousef (1984) using Anodic Stripping Voltametric (ASV) analysis techniques have shown that, with the exception of copper, heavy metal complexes in actual stormwater collected at the Maitland Interchange as well as in the retention pond water, which was used as a water source for these experiments, are almost totally inorganic in nature. Copper was divided approximately 50-50 between inorganic and organic species. The assumption will, therefore, be made that the chemistry of removal of heavy metals at the Maitland site is based on inorganic reactions.

Assuming that inorganic species are the major heavy metal forms present, differences in the dominant species for a particular metal should help to explain the variability in removals. As seen in Table 5, the dominant species of zinc present at the experimentally measured pH is the Zn^{+2} ion. Since this ion is relatively small, the net effective charge should be relatively large, and zinc removal as predicted by the assumed adsorption model should be possible. This explanation corresponds well with the observed results. If the adsorption model is valid, then an increase in removal should be observed for zinc at lower velocities of flow since contact time is increased. If removals are compared in the three experiments at a distance of 38 meters, since the last Maitland experiment did not reach the 53 m point, it is evident that removal efficiencies increased from 55 percent to 77 percent to 89 percent as the flow rate is decreased. It appears, therefore, that the assumption of removal by adsorption of Zn^{+2} ions onto soil and organic particles is appropriate for zinc removal at this site.

Unlike zinc and iron, copper was not removed from solution at a significant rate. Maximum removal of dissolved copper observed during these investigations was approximately 50 percent. Solubility diagrams indicated that at a pH of approximately 6.5, the major inorganic copper irons in solution are Cu^{++} as well as $CuCO_3^{\,o}$. Organic species of copper are also present. Assuming the adsorption model to be valid, then only Cu^{++} is available for adsorption while $CuCO_3^{\,o}$, which has a net charge of zero, will not be available. This explains the lower removal efficiency observed for copper. If this assumption is correct, then copper could be more easily

removed in waters with lower pH values where Cu^{++} is the major species.

As seen in Figures 1 through 3, average concentrations of lead measured at various distances during swale flow in each Maitland experiment appear to be somewhat erratic. A great deal of this inconsistency can be explained by experimental error since measurement of lead at the low concentrations found in these experiments is subject to extreme variability. However, it appears that little or no removal of lead was achieved. Examination of Table 5 reveals that at a pH of 6.5 the dominant lead species would be $PbCO_3^o$ and Pb^{+2}. $PbCO_3^o$ species carries no charge and would not be expected to be affected by adsorption processes.

As stated previously, the concentrations of cadmium and nickel measured during these investigations were quite low and, in most cases, approached the limits of detection for our measurement technique. Therefore, no reliable data is available from which the behavior of these two metals in a swale environment can be analyzed. However, assuming that these two elements would follow the general trends observed for other metals, some predictions as to their expected behavior can be made. As seen in Table 5, the major soluble cadmium species at a pH of 6.5 would be the Cd^{+2} ion. If this ion exhibits behavior similar to the Zn^{+2} ion in the absence of significant organic concentrations, then removal of cadmium would be expected to occur. As seen in Table 5, the dominant dissolved forms if nickel at a pH of 6.5 would be both the Ni^{+2} and $NiCO_3^o$ ions. This situation is very similar to that observed in the case of copper. Removal of nickel would be expected to occur but not to the extent exhibited by zinc. It is expected that the removal of nickel should increase at lower pH values where Ni^{+2} becomes the dominant species.

It can be concluded, therefore, that heavy metal removal in this series of investigations was predominantly an adsorption phenomenon. The ability of a heavy metal to be removed was found to be closely related to the dominant inorganic species present.

As seen previously, several of the heavy metals measured exhibited significantly lowered removal efficiencies at the EPCOT site in spite of the fact that the swale test length increased from 53 m to 170 m. The presence of organic acids was indicated at this site by the dark stain which characterized ground water and the water pumped for use in the experiments. Therefore, at this site, organic as well as inorganic complexation must be considered. The measured pH for the first EPCOT experiment was approximately 6.0, while the pH for the second investigation was approximately 7.0.

As seen in previous experiments at the Matiland site, zinc was removed from solution rapidly during both EPCOT experiments. No significant organic complexes are known to form between humic or fulvic acids and zinc at a neutral pH. Therefore, according to Table 5, the dominant zinc species will still be Zn^{+2} for a pH value less than 7.5, and removal should occur.

Contrary to the results observed in previous experiments at Maitland, significant removal of iron did not occur at EPCOT even though the dissolved concentration exceeded the solubility product for iron at a pH of 6.0. It has been reported by numerous researchers that iron can form quite stable complexes with humic substances. Evidently, the formation of these complexes increased the solutility of iron and no removal was possible. In the second EPCOT experiment, conducted on 5/16/83 with a grass cover, the concentrations of dissolved iron actually increased by passing through the swale. Presumably, iron which had been previously deposited in the swale was present in a loosely bound form, and was able to be mobilized by the force of the flow.

As observed in the previous Maitland experiment, copper was not removed to any significant amount and, in fact, may have exhibited increased solubility in the EPCOT experiments, particularly in the second experiment with the gross cover. Copper can form significant organic complexes with both fulvate and humate even at low organic concentrations. As seen in Table 5, $Cu(OH)_2^o$ is the dominant inorganic copper species in the pH range between 7.0 and 13.0 with Cu^{+2} becoming an important species at pH values less than 7.0. However, at pH values less than neutral, organic complexation also becomes more significant. Copper, therefore, seems to exist in the presence of organic complexes in a number of organic and uncharged inorganic species over a wide range of pH values. Neither organic complexes of copper nor the inorganic $Cu(OH)_2^o$ forms are suitable for adsorption, and removal is not expected to occur. As noted previously for iron, copper concentrations also increased by passing through the grassed swale, presumably due to mobilization or solubilization of previously deposited species.

It is quite interesting to note that, contrary to the results obtained at Maitland, lead was removed quite well in the EPCOT experiments. No significant organic complexes of lead are known to occur under the test conditions. Therefore, the removal mechanism must be based on a change in inorganic speciation. As seen in Table 5, the speciation of lead changes from $PbCO_3^o$ to Pb^{+2} at pH values below 6.5. Above a pH of 6.5, however, Pb^{+2} as well as $PbCO_3^o$ becomes dominant. In the first EPCOT experiment, the average laboratory measured pH was approximately 6.0, and the dominant lead species would be expected to be Pb^{+2}. If this is the case, the removal of lead should follow closely the removal exhibited by zinc. As seen in Figure 4, the removal curves for both zinc and lead are very similar. Thus, it appears that the decrease in pH from 6.5 at the Maitland site to 6.0 at the EPCOT site placed a portion of the dissolved lead in a form suitable for adsorption, and removal efficiencies were increased. In the second EPCOT experiment, the pH increased to approximately 7.0. At this pH, the dominant lead species should be Pb^{+2} as well as $PbCO_3^o$. Since $PbCO_3^o$ is not expected to be removed to a large degree, the overall removal at this pH should be less. As seen in Figure 5, the change in concentration of lead during passage through the swale test area at this pH was approximately one-half that observed at a pH of 6.0.

Effect of Cover Crop on Dissolved Metal Removal

It is also possible by using the data collected in the two EPCOT investigations to comment on the effect of a grass cover removal of dissolved heavy metals. A comparison of Figure 4, which represents removals obtained on an earthen channel with Figure 5, representing a grassed channel, reveals that the ultimate removal of every metal tested was greater in the earthen condition than in a grassed condition. Some heavy metals, iron, chromium, and copper, actually increased in concentration by passage through the swale. These conclusions fit precisely in line with the theory of heavy metal removal in swales. It is assumed that heavy metals are removed by adsorption onto exchange sites in the soil and on organic particles. The better removal efficiencies obtained on bare soil merely reflect the fact that more exchange sites are open and available than when a grass cover is present. The release of heavy metals into the swale flow is probably due to either decomposition of plant matter which had trapped heavy metals either by uptake or surface adsorption, or by change in speciation in adsorbed metals which results in a soluble species.

Comparison Between Steady State Flow and Actual Conditions

Although the removal of only dissolved species of heavy metals has been discussed previously, heavy metals in highway runoff often have significant particulate fractions as well. As seen in Table 2, zinc, aluminum, iron, lead, nickel and chromium all exist in highway runoff in predominantly particulate form with zinc, lead and nickel all approaching 90 percent particulate. With the exception of copper and nickel, flow through the swale was able to produce a significant decrease in the particulate fraction with t-test probabilities in excess of 98 percent. Swales, therefore, appear to be quite efficient in removing particulate forms of heavy metals.

If the combined data listed in Table 2 for highway runoff and swale flow is compared with the results from the swale experiments, it is apparent that the measured reductions in dissolved heavy metals over the eight-month sampling period are not as great as those observed in discrete continuous flow situations. It is possible that certain species are being released and remobilized in the swale area with time. This may be particularly important for metal species which change from the free metal state to a neutral ion such as $PbCO_3$. Copper, lead, zinc and nickel all change forms from Me^{+2} to a neutral ion in the pH range of 6.0-7.5. Changes in the soil pH between storm events could resolubilize certain species. It is also possible that the shearing action of the water flow could remove attached species, but the importance and significance of this phenomenon is not known. In any case, the actual obtained removal efficiencies for dissolved species over a long period would probably be less than that obtained in continuous flow experiments.

CONCLUSIONS

From the results obtained in these experiments, it appears that the chemistry of heavy metals in natural waters is a fairly complex and site-specific phenomenon. In the studies conducted at Maitland in which only inorganic species were assumed to be present, the solubility and removal efficiencies obtained for dissolved species were found to be directly related to the dominant inorganic complex present. Those metal species which were present as a charged ion, such as zinc and iron, were removed quickly. Those which were complexed with inorganic species and carried a diffuse charge or zero charge were not removed. Removal rates were found to increase as the velocity of swale flow decreased.

The importance of organic complexing in regulating solubility was demonstrated in the EPCOT experiments. Of the metal ions present, copper and iron are known to form significant metal-organic complexes and, as a result, no removal was found to occur. Other metals which formed no important organic complexes were regulated by their inorganic species.

It also appears that the removal of dissolved metal species occurs more rapidly in bare earth swales than in grass-lined channels. Concentrations of iron, copper and chromium were actually increased by passage through a grassed swale. Removal efficiencies presented in these investigations did not take into account losses by infiltration. If infiltration losses are considered, then the removal rate on a total mass basis can be increased in proportion to the amount of infiltration. If no water reaches the downstream discharge, then the removal efficiency is actually 100 percent.

Data collected over an eight-month period from both highway and swale areas indicates lower removal efficiencies than were obtained in the continuous flow situations. It is possible that certain metals may change forms between storm events and become solubilized. This is particularly likely in species which exhibit a change in speciation from a charged free ion to a neutral ion in the pH range of 6-7.5.

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