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A-01 Metals in Stormwater Runoff Evaluation

by

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DISCLAIMER

A-01 METALS IN STORMWATER RUNOFF EVALUATION

EXECUTIVE SUMMARY

As a part of the A-01 investigation required by the NPDES permit, an investigation was performed to ascertain the concentrations of metals specifically copper (Cu), lead (Pb), and zinc (Zn) in stormwater being discharged through the outfall. This information would indicate whether all water being discharged would have to be treated or if only a portion of the discharged stormwater would have to be treated.

A study was designed to accomplish this. The first goal was to determine if the metal concentrations increased, decreased, or remained the same as flow increased during a rain event. The second goal was to determine if the concentrations in the storm water were due to dissolved. The third goal was to obtain background data to ascertain if effluent credits could be gained due to naturally occurring metals.

Samples from this study were analyzed and indicate that the copper and lead values increase as the flow increases while the zinc values remain essentially the same regardless of the flow rate. Analyses of samples for total metals, dissolved metals, TSS, and metals in solids was complicated because in all cases metals contamination was found in the filters themselves. Some conclusions can be derived if this problem is taken into account when analyzing the data. Copper concentrations in the total and dissolved fractions as well as the TSS concentrations followed the hydrograph at this outfall but the copper in solids concentration appeared to peak in the first flush and decline to nondetectable rapidly over the course of the storm event. Lead was present in the total analysis but not present in the dissolved fraction or the solids fraction of the samples. The data for zinc was interesting in that the dissolved fractions were higher than the total fraction in three out of four samples. This is probably due to the high zinc concentrations on the filters being transferred to the dissolved faction of the sample. Analysis of background samples indicate that there are concentrations of lead and zinc in stormwater runoff due to naturally occurring concentrations or to roadway runoff. This is not the case with the Copper concentrations. Analysis indicates that there is no detectable copper concentrations in the background water analyzed.

This study indicates that all the water discharged through the A-01 outfall including the stormwater should be included in calculations for wetland or treatment facility sizing.

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PROJECT DESCRIPTION

To ascertain the quantity of metals in stormwater at the A-01 outfall, an Isco sequential sampler, rain gauge, and flow meter was set up at the outfall. This equipment was programmed to collect samples when a rain event occurred and the water elevation increased a specific amount. The system then collected an aliquot of sample at each time a specified quantity of water was discharged through the outfall. The stripchart of the flow meter was set up to record the headheight of water and record when each sample was collected. This allowed a specific flowrate to be associated with each sample. The individual samples were then analyzed and the data recorded. Data from seven storm events were evaluated and a need to discriminate between the total and dissolved fractions became evident. To accomplish this, samples were collected in the same manner but analyzed in a different manner. Each sample aliquot was split and one portion preserved and analyzed for total metals. The other portion was filtered and the resulting filter weighed for a total suspended solids analysis. The filter and preserved filtrate were then analyzed for metals. This analytical technique gave the following results: the total quantity of metals in the sample in mg/l, the amount of dissolved metals in the sample in mg/l, the total suspended solids in the sample, and the quantity of metals in solids in the sample in mg/kg. A final portion of the project involved a background location for the same metals to ascertain if these metals exist in the environment naturally and in what quantities. A location was chosen in the Tims Branch drainage area and background samples take. This sample point was located on SRS road 1 approximately 100 yards north east of the junctions of SRS roads 1 and 1A where a dry watercourse which drains to Tims Branch crosses under SRS road 1. A composite sampler was set up at this point and samples collected. Due to an equipment malfunction, both a grab was taken on the first day of the storm event and a composite was taken on the second day of the storm event after the equipment was repaired. These samples were analyzed for total metals, dissolved metals, metals in the solids and total suspended solids. Data from all samples are given in the following section.

RESULTS

Copper

The total copper analyses given in the table below indicate that the concentrations increase as the flow increases. This is illustrated in the accompanying graph. The X-axis is an instantaneous flowrate in million gallons per day (MGD) and the y-axis represents the copper concentrations in mg/l.

Cu Mg/L	Flow MGD	Cu Mg/L	Flow MGD	Cu Mg/L	Flow MGD
0.0530	0.1355	0.0550	5.7558	0.2700	51.2912
0.0930	0.1355	0.0360	6.4787	0.1480	53.1042
0.0460	0.1355	0.0560	6.7273	0.1310	56.8595
0.0600	0.3373	0.0620	7.2472	0.1190	58.8028
0.0240	0.6476	0.0260	7.6683	0.2960	60.7462
0.0640	0.8036	0.1780	7.6683	0.1090	60.7462
0.0330	0.9218	0.0990	7.8052	0.2760	62.4303
0.0520	1.0746	0.1020	8.3838	0.1410	64.7015
0.1000	1.2336	0.0550	8.8356	0.2430	66.7445
0.0480	1.2336	0.1310	10.3367	0.1310	66.7445
0.0750	1.6161	0.0240	14.5865	0.2470	68.7789
0.1690	1.6762	0.0210	18.5567	0.1680	68.7789
0.0330	1.7500	0.0240	23.8406	0.2070	70.8936
0.0550	1.7938	0.1910	25.5405	0.1800	70.8936
0.0450	2.2576	0.1480	29.9748	0.2190	72.9732
0.0940	2.5177	0.1750	30.6486	0.1630	72.9732
0.0510	3.4013	0.2510	30.6486	0.1820	75.1134
0.0500	3.4013	0.0730	32.1704	0.1500	75.1134
0.0430	3.7406	0.0270	32.9174		
0.0600	4.7122	0.1850	32.9174		
0.0520	4.8808	0.1330	39.1770		
0.0510	5.3090	0.1290	45.9239		

Analysis of background samples for copper indicate that with one exception which is at the detection limit copper is not present. This data is given below. The samples were split in the lab for quality control reasons and both composite and grab samples were duplicated.

Sample Type	Total Cu Mg/L	Dissolved Cu Mg/L	Cu in TSS Mg/Kg	TSS Mg/L
Grab	0.0050	<0.005	<0.250	69.0
Grab	<0.005	<0.005	<0.250	87.0
Composite	<0.005	<0.005	<0.250	18.0
Composite	<0.005	<0.005	<0.250	25.0

Several quality control samples were run with the analyses to determine if the analytical method introduced copper to the analytical results. During the A-01 sampling for total, dissolved and sediment copper analyses, deionized water was treated in the same manner as the sample and analyzed. A filter that had been prepared for TSS analysis by seating it in the crucible with 20 mls of deionized water was also analyzed. These results are given below. During the background analyses, the same procedure was followed except that an unprepared filter was used and all QA samples were done in duplicate. A complicating factor occurred when three of the filters used as QA for the background samples showed measurable quantities of copper. This would become important if there were measurable quantities of copper in the dissolved or solid fractions of the analyses. This is not the case with the copper analyses and this contamination does not affect interpretation of the analytical results. The generated Quality control data are also listed below.

QA Data from A-01 Sample

	Deionized Water Data		Filter Data		
	Diss. Mg/L	Filter Mg/Kg	TSS Mg/L	Filter Mg/Kg	
Cu	<0.005	<12.4	<1.0	Cu	<12.2
Cu	<0.005	<13.3	<1.0	Cu	<15.0

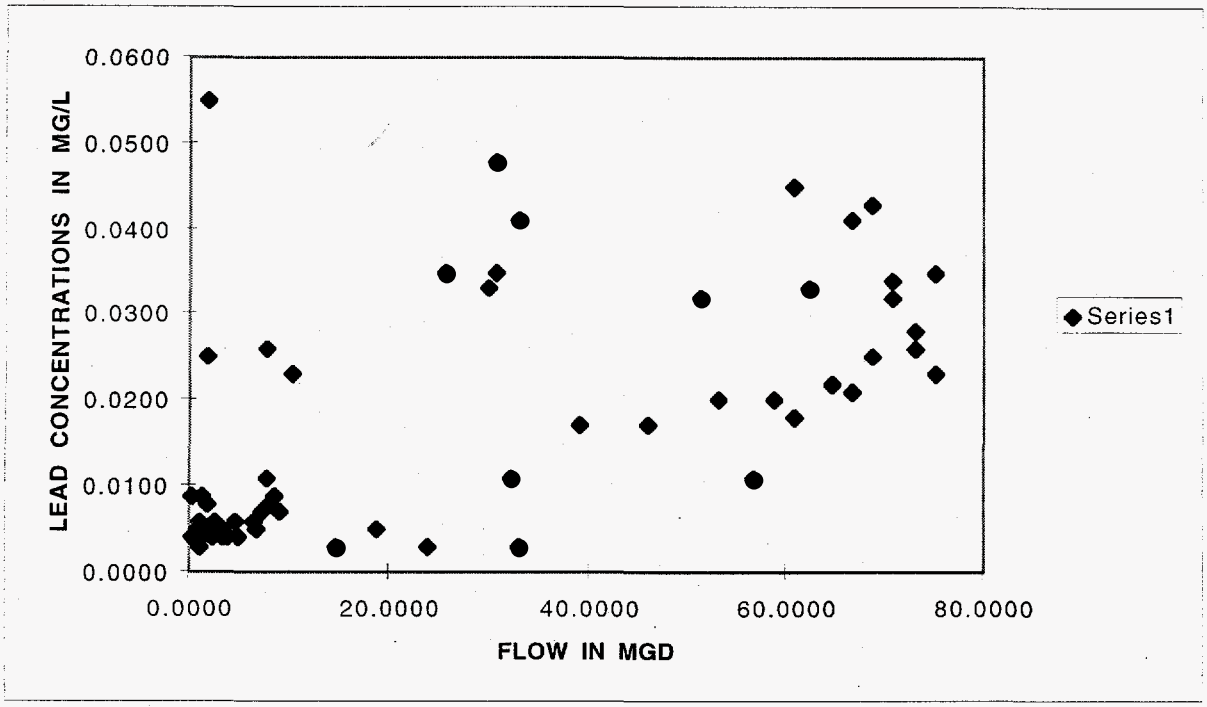
Quality Control From Background Samples

Filter-No Preparation	Cu Mg/Kg	Blank Filter	Cu Mg/Kg
TB- Filter -1	12.40	TB- Blk Filter -1	13.20
TB- Filter -2	<0.25	TB- Blk Filter -2	<.25
Filter -Preparation Only	**Cu Mg/Kg**	**Filtered H20**	**Cu Mg/L**
TB- Filter -1	12.40	TB-Blk Dissolved-1	<0.005
TB- Filter -2	<0.25	TB-Blk Dissolved-2	<0.005

Lead

The total lead analyses indicate that during a storm event, lead values increase as the flow values increase. This is illustrated in the following Table and accompanying graph. The X-axis is an instantaneous flowrate in million gallons per day (MGD) and the Y-axis represents the lead concentrations in mg/l.

Flow MGD	Pb Mg/L	Flow MGD	Pb Mg/L
0.1355	0.0040	14.5865	0.0030
0.1355	0.0040	18.5567	0.0050
0.1355	0.0090	23.8406	0.0030
0.3373	0.0040	25.5405	0.0350
0.6476	0.0050	29.9748	0.0330
0.8036	0.0040	30.6486	0.0350
0.9218	0.0060	30.6486	0.0480
1.0746	0.0030	32.1704	0.0110
1.2336	0.0040	32.9174	0.0030
1.2336	0.0090	32.9174	0.0410
1.6161	0.0050	39.1770	0.0170
1.6762	0.0250	45.9239	0.0170
1.7500	0.0080	51.2912	0.0320
1.7938	0.0550	53.1042	0.0200
2.2576	0.0040	56.8595	0.0110
2.5177	0.0060	58.8028	0.0200
3.4013	0.0040	60.7462	0.0180
3.4013	0.0050	60.7462	0.0450
3.7406	0.0040	62.4303	0.0330
4.7122	0.0060	64.7015	0.0220
4.8808	0.0040	66.7445	0.0210
6.4787	0.0060	66.7445	0.0410
6.7273	0.0050	68.7789	0.0250
7.2472	0.0070	68.7789	0.0430
7.6683	0.0110	70.8936	0.0320
7.6683	0.0260	70.8936	0.0340
7.8052	0.0080	72.9732	0.0260
8.3838	0.0090	72.9732	0.0280
8.8356	0.0070	75.1134	0.0230
10.3367	0.0230	75.1134	0.0350



The results generated by the stormwater samples analyzed for total metals, dissolved metals, TSS, and metals in the sediment indicate that lead is present in the total analyses but in only one case present in the dissolved fraction. The total lead quantities also follow flow quantities though in small increments. No lead was found in the solids fraction analyzed. These data are given in the following table;

		Total Mg/L	Diss. Mg/L	TSS Mg/L	Filter Mg/Kg	Flow MGD
A-01-1	Pb	0.004	0.005	8.0	<12.3	1.9
A-01-2	Pb	0.006	<0.003	85.0	<12.1	25.4
A-01-3	Pb	0.006	<0.003	35.0	<12.0	20.9
A-01-4	Pb	0.004	<0.003	16.0	<12.3	5.6

Analysis of background samples for lead are given below. The samples were split in the lab for quality control reasons and both composite and grab samples were duplicated. Lead was found in both the grab and composite background samples in both the total and dissolved fractions at levels that exceed the monthly average limit (0.005 mg/l) proposed for the A-01 outfall.

Sample Type	Total Pb Mg/L	Dissolved Pb Mg/L	Pb in TSS Mg/Kg	TSS Mg/L
Grab	0.012	0.008	7.31	69.0
Grab	0.009	0.004	8.90	87.0
Composite	0.031	0.006	2.10	18.0
Composite	0.006	0.005	4.58	25.0

Several quality control samples were run to determine if the analytical method introduced lead into the analytical results. Deionized water was treated in the same manner as the sample and analyzed. A filter that had been prepared for TSS analysis by seating it in the crucible with 20 mls of deionized was also analyzed. These results are given below. During the background analyses, the same procedure was followed except that an unprepared filter was also analyzed and all QA samples were done in duplicate. Those results are also listed below. The data indicates that there is lead in the filters used in the dissolved and solids analyses and though none appears in any of the liquid fraction results, all positive results for dissolved and solids fractions should be viewed as suspect.

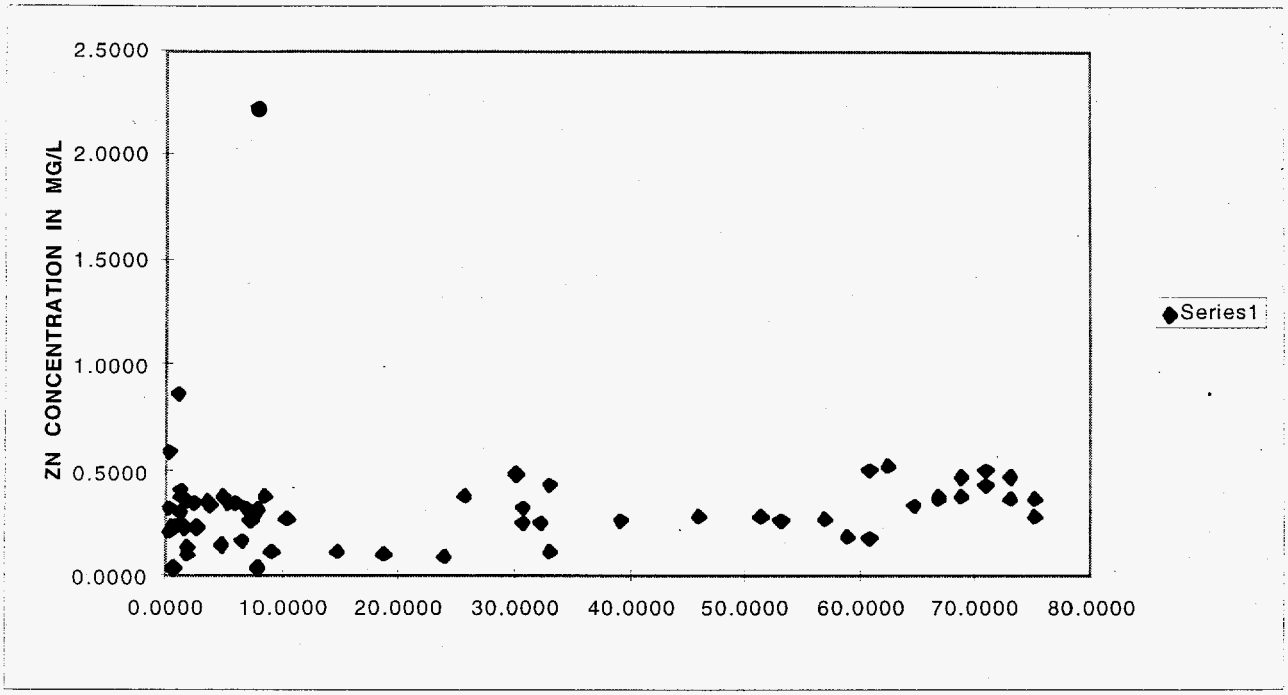
	Deionized Water Data		Filter Data	
	Diss. Mg/L	Filter Mg/Kg	TSS Mg/L	Filter Mg/Kg
Pb	<0.003	12.400	<1.0	PB <12.2
Pb	<0.003	<13.3	<1.0	PB <15.0

Filter-No Preparation	Pb Mg/Kg	Blank Filter	Pb Mg/Kg
TB-Filter-1	1.33	TB- Blk Filter -1	1.65
TB- Filter -2	1.74	TB-Blk Filter -2	2.40
Filter-Preparation Only	Pb Mg/Kg	Filtered H20	Pb Mg/L
TB- Filter -1	1.52	TB- Blk Dissolved-1	<0.003
TB- Filter -2	2.01	TB- Blk Dissolved -2	<0.003

Zinc

The total zinc analyses indicates that during a storm event, zinc values remain essentially the same as the flow values increase. This is illustrated in the following Table and accompanying graph. The X-axis is an instantaneous flowrate in million gallons per day (MGD) and the Y-axis represent the lead concentrations in mg/l.

Flow MGD	Zn Mg/L	Flow MGD	Zn Mg/L
0.1355	0.2140	10.3367	0.2730
0.1355	0.5910	14.5865	0.1110
0.1355	0.3280	18.5567	0.1050
0.3373	0.2300	23.8406	0.0990
0.6476	0.0470	25.5405	0.3780
0.8036	0.2470	29.9748	0.4880
0.9218	0.8640	30.6486	0.2490
1.0746	0.3060	30.6486	0.3240
1.2336	0.4150	32.1704	0.2580
1.2336	0.3760	32.9174	0.1150
1.6161	0.2280	32.9174	0.4310
1.6762	0.1350	39.1770	0.2620
1.7500	0.1030	45.9239	0.2800
1.7938	0.3620	51.2912	0.2830
2.2576	0.3520	53.1042	0.2650
2.5177	0.2340	56.8595	0.2700
3.4013	0.3560	58.8028	0.1910
3.4013	0.3450	60.7462	0.5060
3.7406	0.3390	60.7462	0.1830
4.7122	0.1450	62.4303	0.5300
4.8808	0.3790	64.7015	0.3410
5.3090	0.3480	66.7445	0.3780
5.7558	0.3460	66.7445	0.3640
6.4787	0.1740	68.7789	0.4780
6.7273	0.3220	68.7789	0.3760
7.2472	0.2670	70.8936	0.4290
7.6683	0.0380	70.8936	0.5040
7.6683	2.2300	72.9732	0.4740
7.8052	0.3160	72.9732	0.3640
8.3838	0.3810	75.1134	0.3650
8.8356	0.1150	75.1134	0.2800



The results generated by the stormwater samples taken and analyzed for total metals, dissolved metals, TSS, and metals in the sediment are given in the following table. It is interesting to note that in three out of four samples that the dissolved fraction contains more zinc than the total fraction.

		Total Mg/L	Diss. Mg/L	TSS Mg/L	Filter Mg/Kg	Flow MGD
A-01-1	Zn	0.053	0.024	8.000	168.000	1.9
A-01-2	Zn	0.191	0.216	85.000	231.000	25.4
A-01-3	Zn	0.177	0.707	35.000	155.000	20.9
A-01-4	Zn	0.106	0.115	16.000	189.000	5.6

Analysis of background samples for zinc are given below. The samples were split in the lab for quality control reasons and both composite and grab samples were duplicated. Please note that three out of four dissolved analytical results are greater than the total metals results.

Sample Type	Total Zn Mg/L	Dissolved Zn Mg/L	Zn in TSS Mg/Kg	TSS Mg/L
Grab	0.039	0.037	126.0	69.0
Grab	0.059	0.067	135.0	87.0
Composite	0.045	0.105	151.0	18.0
Composite	0.030	0.050	135.0	25.0

Several quality control samples were run to determine if the analytical method introduced zinc into the analytical results. Deionized water was treated in the same manner as the sample and analyzed. A filter that had been prepared for TSS analysis by seating it in the crucible with 20 mls of deionized was also analyzed. These results are given below. During the background analyses, the same procedure was followed except that an unprepared filter was also analyzed and all QA samples were done in duplicate. These results are given below. Those results are also listed below. Please note that zinc concentrations are found in all phases of the quality control process. This may explain why dissolved fractions are higher than the total concentrations in the stormwater and background samples.

	Diss. Mg/L	Filter Mg/Kg	TSS Mg/L
Zn	<0.005	89.400	<1.0
Zn	<0.005	126.000	<1.0

	Filter Mg/Kg
Zn	128.000
Zn	84.600

Filter-No Preparation	Zn Mg/Kg	Blank filter	Zn Mg/Kg
TB-Filter-1	184.000	TB- Blk Filter-1	83.0000
TB-Filter-2	139.0000	TB-Blk Filter-2	153.000

Filter-Preparation Only	Zn Mg/Kg	Filtered H20	Zn Mg/L
TB-Filter-1	83.400	TB- Blk Dissolved-1	0.023
TB-Filter-2	193.00	TB- Blk Dissolved-2	0.051

CONCLUSION

Copper

The data indicates that the copper values increase as the flow increases in the liquid samples analyzed. This is true of both total and dissolved fractions. The samples analyzed for TSS indicated that the solids values also increased and decreased with flow whereas the metals found on the filters in solid form decreased over the duration of the storm. This would indicate that the copper is being resuspended in the first flush of the storm event rather than throughout the storm event. Background water samples indicated no detectable copper concentrations evident. This would mean no background credits could be used in calculation of copper limits for this outfall.

Lead

QA data indicate that the all solids results should be discounted due to Pb contamination inherent in the filters and that positive dissolved data should be reviewed carefully prior to acceptance though contamination is not evident in the QA samples run. The total lead data indicates that generally as flow increases the concentration of lead increases. This is ameliorated to a large degree by the amount of lead found in the background samples. The maximum amount of lead found in the stormwater samples taken at the A-01 outfall was 0.055 mg/l and the maximum amount of lead analyzed in an aliquot of the background sample was 0.031 mg/l. This comparison is made only to indicate that lead is naturally found in the environment at levels that are in excess of the average limit in the permit. This would mean that during rain events, lead level elevation will be contributed to by natural runoff.

Zinc

The data indicates that Zn concentrations remain essentially the same regardless of flow. It was interesting to note that in comparing the total and dissolved fractions of the four samples taken for this purpose that the dissolved fraction was higher than the total fraction. This may be caused by contamination of the dissolved fractions by the filters which contained significant quantities of zinc.
The QA data shows the filtered deionized water fraction as having 0.023 mg/l and 0.051 mg/l Zn concentrations. The total analyses for Zn in the background samples does indicate that it is present in the environment in quantities at levels (0.131 mg/l) approximately half that of the average effluent concentrations (0.341 mg/l) during a rain event.