

**“Only Rain Down the Drain”
Evaluation of Elemental Analytes in Street Sweeper and
Catch Basin Sediment in Holland, MI**

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Advanced Environmental Seminar, Fall 2011
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Introduction

During the fall semester of 2011 at Hope College, the Advanced Environmental Seminar class conducted research projects related to the Macatawa Watershed. Team B, which consisted of Sioned Sitkiewicz, Dean Hazle, and Rachel Medina, focused on the evaluation of elemental analytes of street sweeper and catch sediments in Holland, MI.

Currently in the city of Holland, the streets are swept weekly and additionally after major rain events. There are two primary pieces of equipment that are used to maintain the streets. The Elgin Pelican is used to collect sediment lining the curbs using large brushes. The Vactor trucks draw sediment out of the catch basins. A catch basin is a concrete structure below the storm drain with an elongated bottom where sediment settles, as opposed to flowing through the elevated pipes to Lake Macatawa. There are hundreds of storm sewers and miles of streets that must be maintained. There is a necessity for street maintenance because all street pipes lead directly to Lake Macatawa without being treated. Without maintenance of streets, catch basins would be overwhelmed. Increasing the sediment influx to Lake Macatawa would exacerbate the current problems with sediment loading (MACC, 2011).

State regulations classify street sweeper and catch basin sediments as low hazardous waste, according to Section 299.4122 of Solid Waste Management Act (2005). These regulations state that the street cleanings and catch basin sediment must be relocated to a licensed landfill (DEQ, 2005). Specifically, the landfill must be a Type 3 landfill, which holds low to non-hazardous waste. Fortunately, cities have the ability to appeal these regulations (DEQ, 2011). If a state licensed laboratory determines street and catch basin sediment samples below state threshold for inorganic and organic constituents, a city may be exempt from classifying street sweepings as low hazardous solid waste.

The city of Holland currently stores its street sweepings in an above-ground storage lot, located at the intersection of 29th Street and Ottawa, in Holland, MI. Its catch basin sediments are stored nearby in a settling pond. The street sweeping piles are transported to Autumn Hills landfill in Zeeland, MI, at a rate of approximately \$20-22 per ton. The total cost of moving the street sweeping piles to Autumn Hill costs several thousand dollars per year. Last year, the city of Holland used up the allocated funds for moving street sweeping piles in about two months. The city plans to double these funds in the future in order to meet the relocation demand.

Team B's project considered two main objectives. The first objective assessed whether Holland's street sweeping and catch basin sediments were above state threshold elemental levels, such that it would be necessary for the sediments to be relocated to landfills. The second objective was to determine if there was any seasonal variation between the chosen analytes.

Methods

In order to collect control samples, two locations were chosen based on the lack of anthropogenic impact on the area. Stu Visser Trails and two different ponds at the Outdoor Discovery Center were chosen. At each of these locations, three replicate samples were taken to create a representative sample. The samples were collected from the edge of ponds, as stated in literature from Townsend et al. (2002). The sediment samples were then dried in trays in the greenhouse. Once dried, the sediment was sieved

through a 1 mm sieve and the three replicate samples from each location were then mixed together in equal proportions. To collect the samples from the fall, spring, and summer piles, three replicates were collected from each season and placed in plastic bags. The samples were then dried in trays, sieved through a 1 mm sieve, and combined in equal proportions.

Our method for determining the leachable concentration of inorganic constituents is based on the EPA Test Method 1311: Toxicity Characteristic Leaching Procedure (TCLP) (EPA, 1992). This is the standard method used by the Michigan Department of Environmental Quality (DEQ) for determining both organic and inorganic constituents of solid waste. Team B adapted the TCLP procedure to fit Hope College's laboratory supplies and time requirements. The EPA method was reproduced to a reasonable quality standard. Analytes (Table 1) were chosen based on literature precedents and state thresholds (DEQ, 2005; Walch, 2006; Townsend et al., 2002; Western Michigan Environmental Services, 1995).

The TCLP is a basic solid sample extraction procedure. Since natural rain water and landfills are often mildly acidic, the TCLP is meant to mimic these conditions and characterize how contaminants leach from a solid sample. Leaching was defined as whatever small amount of sample may be dissolved by an acidic solution. To perform a TCLP extraction, the initial pH of sediment stirred in water is determined. Based on the resulting pH, an aliquot of sample is washed in an acidic solution of either dilute glacial acetic acid, or dilute glacial acetic acid (CH_3COOH) and some sodium hydroxide (NaOH). The acid wash is performed by continuously rotating the sample end-over-end for 18 hours.

The sediment is separated from the extract by vacuum filtration. The vacuum filtration was set up under a fume hood and utilized a standard two trap vacuum filtration system and a seven micron glass fiber filter (Figure 1). During the filtration, filter papers became progressively clogged with fine sediments. In several instances, filtration was paused in order to wash the filter paper. In total, vacuum filtrations took approximately thirty minutes.



Figure 1: Vacuum filtration set up using 7 micron glass fiber filters.

Inorganic constituents (Table 1) of the TCLP extract were determined using Inductively Coupled Plasma (ICP) Emission Spectroscopy. The instrument used was a PerkinElmer Optical Emission Spectrometer, Optima 4300 DV. Samples were prepared with internal standards using the Method of Standard Additions as presented by Harris in Quantitative Analytical Chemistry (Harris, 2010). Standard additions were performed by adding successive amounts of a multielemental standard to an amount of TCLP extract. Each volumetric flask was diluted to a final volume of one hundred milliliters. The wavelengths chosen for each analyte were based on literature values and selected to minimize any light interference from other elements (Asha, 1991). The detection limits of each analyte were determined using the standard method from the instrumental handbook for the ICP (WinLab32 instrument control software: Software guide, 2000). In order to disassociate any remaining mineral complexes which may have bound analytes, samples were acidified with 2-3drops of 18M nitric acid (HNO₃) before each was run on the ICP.

Table 1: Inorganic constituents measured by ICP spectroscopy, using internal standards.

Analyte	Wavelength (nm)	Detection Limit (ppm)
Ba	493.408	0.00130
Cd	228.802	0.02200
Cr	205.56	0.08320
Cu	327.393	0.00450
Fe	259.939	0.00370
Pb	220.353	0.12000
Mn	257.61	0.00033
Ni	221.648	0.04700
Zn	206.2	0.01000

Concentrations of each analyte were determined using a best fit line for the linear region of a plot of standard added and each corresponding light intensity. In the method of standard additions, the unknown concentration is found by back extrapolating the best

fit line to the x-axis. A more linear correlation between the concentration of standard added and light intensity results in a more accurate calculation of the unknown concentration. The concentration of an unknown sample is equal to the difference between the x-intercept and the y-axis. This calculation is made using the equation for a best fit line, and solving for the x-intercept. Error was propagated through this calculating using the calculated uncertainty for slope and the y-intercept. The calculated uncertainty associated with the least squared regression includes y-variance for each point on the calibration. Figure 2 is an example of a standard addition calibration curve for manganese, where the amount of standard added is plotted on the x-axis, and the corresponding light intensity is plotted on the y-axis. The calculated concentration of each unknown sample was multiplied by twenty to account for the dilution factor.

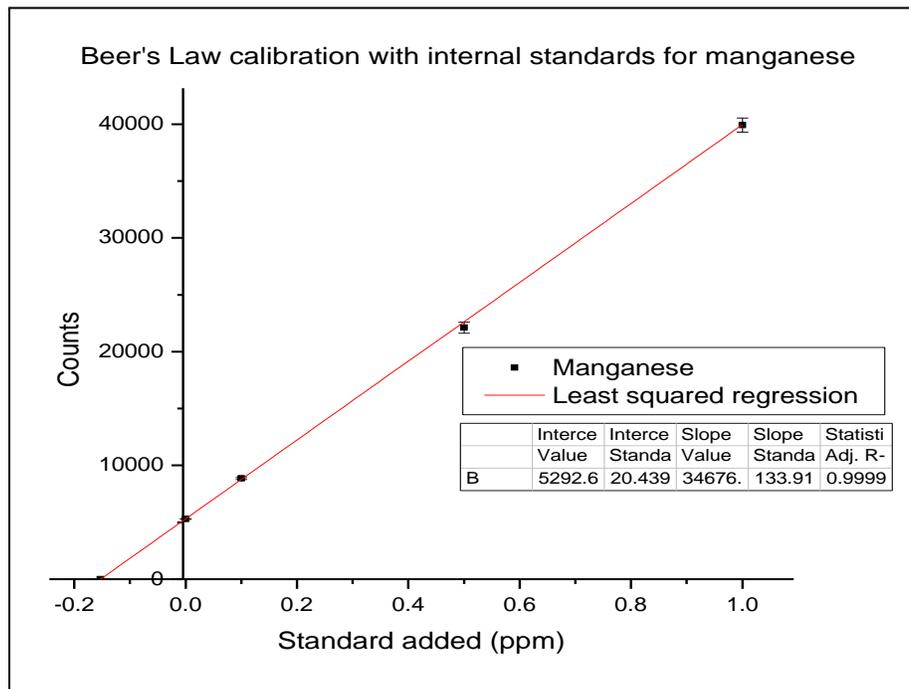


Figure 2: Internal standard calibration for manganese.

Phosphate concentrations were determined by colorimetry using a Seal Analytics Auto Analyzer II Spectrophotometer. Phosphate concentrations of each sample are determined by external standards. Sediment samples are first pulverized, and then analyzed in three stages. An aliquot of pulverized sediment is first washed with 1M potassium chloride (KCl) to release water soluble phosphates. The same aliquot is dried and washed with 1M sodium hydroxide (NaOH) to release iron bound phosphates. The same aliquot is dried again and washed with 0.5 M HCl to release calcium bound phosphates. Results from each stage are summed for a total phosphate concentration.

Results

The following are results of elemental analyses determined by the TCLP and ICP analysis. Each figure compares the chosen analytes in each sample to the state threshold. It should be noted that zinc is not included on any of the following figures, because in all cases it was below the state threshold of 50 ppm by at least one order of magnitude. Figure 3 displays data from the homogenized control sample. Each analyte of interest is below the state threshold, with the exception of manganese and possibly cadmium

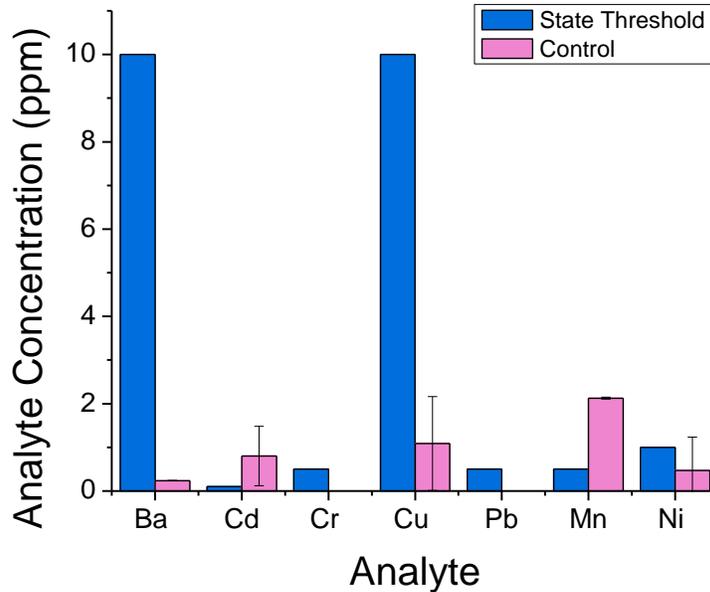


Figure 3: Plot of analytes from the homogenized control sample compared to the state threshold limits.

Below, Figure 4 shows catch basin sample analyte concentrations compared to the state threshold concentrations. Again, the analytes are below state threshold limits, except for manganese. Although manganese was measured above the state threshold, the experimental error encompasses the state threshold.

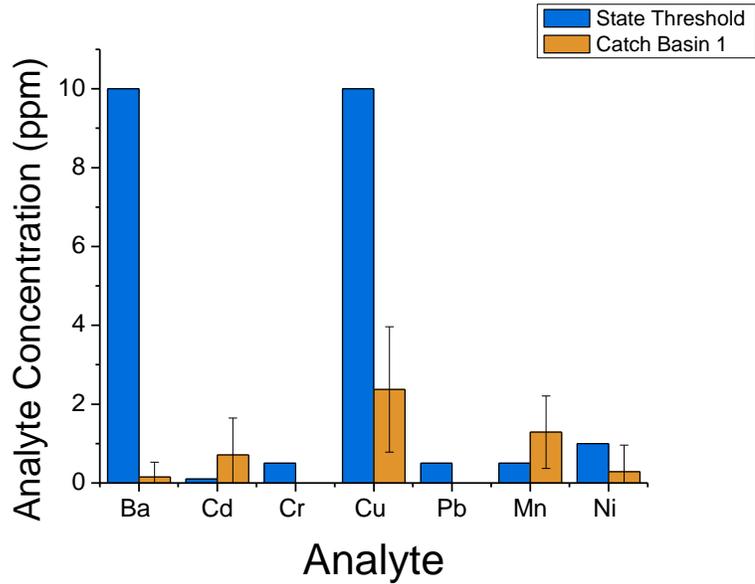


Figure 4: Plot of selected analytes from the combined catch basin samples compared to the state threshold limits.

The data from the spring 2011 sample is displayed in Figure 5. Manganese and cadmium are elevated. However, the experimental error for cadmium encompasses the state threshold.

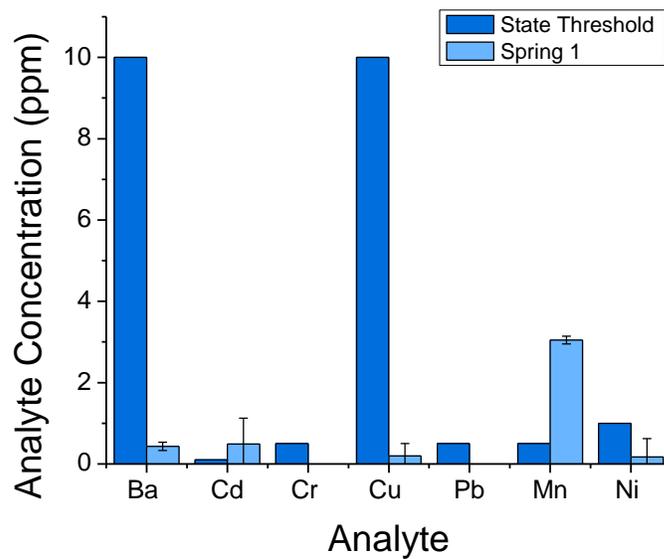


Figure 5: Plot of selected analytes from the spring 2011 sample compared to the state threshold limits.

Figure 6 displays data from summer 2011. Again, all analytes are below the state threshold limit. Manganese and cadmium are elevated, but cadmium may lie below the state threshold limit as evidenced by the error bar. In this sample, the concentration of copper is slightly higher than the rest of the seasonal samples.

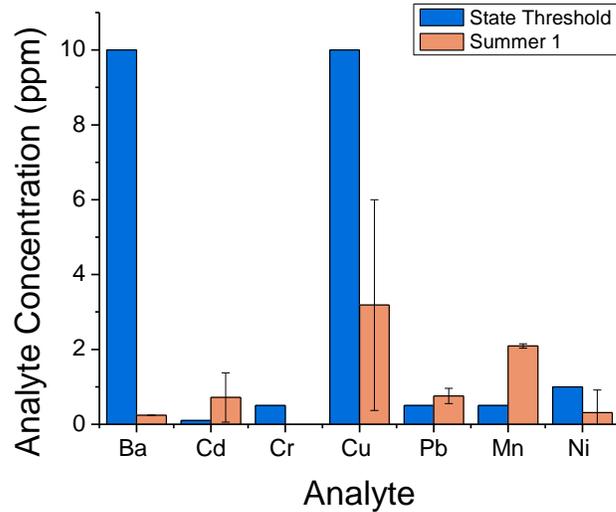


Figure 6: Plot of selected analytes from the summer 2011 sample compared to the state threshold limits.

Figure 7, below, shows data from fall 2011. This data indicates that all selected analytes are below the state threshold level, again with manganese and cadmium below the threshold after the addition of error bars.

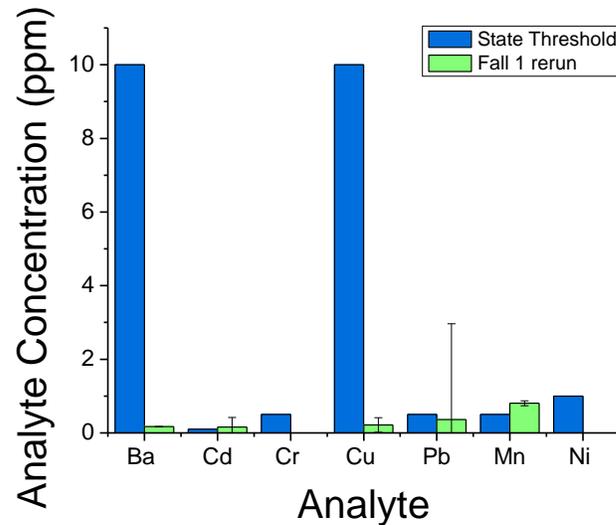


Figure 7: Plot of selected analytes from the fall 2011 sample compared to the state threshold limits.

In Figure 8, each sample taken from fall sediment piles (Fall 1 and Fall 2) is compared to the control sample on one plot. There is little variance between fall samples and also between fall and control samples.

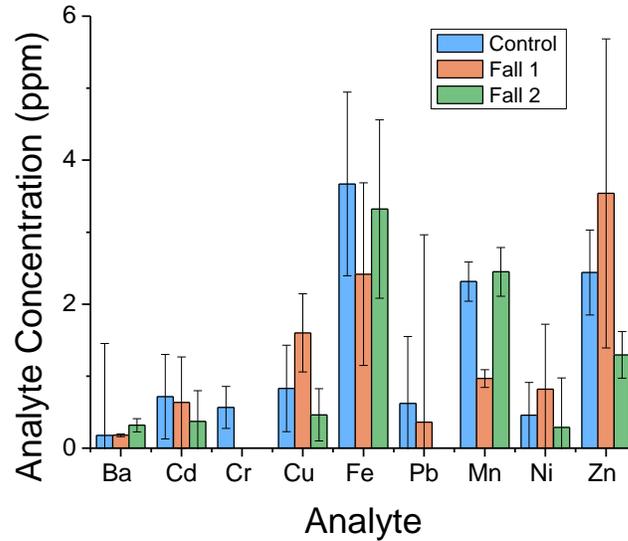


Figure 8: Plot comparing analyte concentrations of control, fall 1 and fall 2 samples.

Figure 9 shows samples from spring 2011, summer 2011, fall 2011, and catch basin compiled onto one plot. In general, Figure 9 shows that spring, summer, fall, and catch basin samples tend to have lower elemental levels compared to the control. Elements that are elevated above the control are less than one order of magnitude higher.

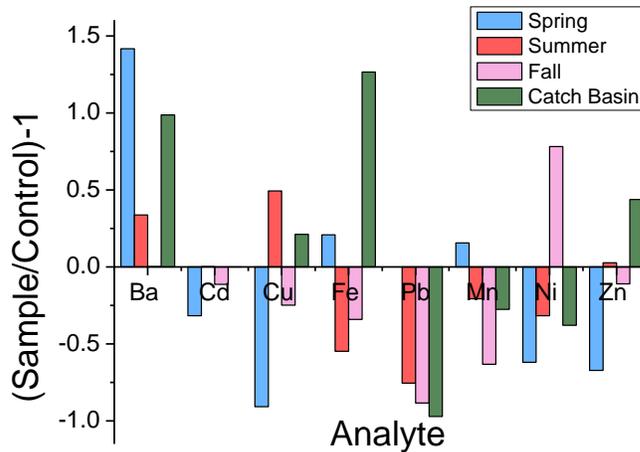


Figure 9: Plot of spring 2011, summer 2011, fall 2011, and catch basin samples compared to one another. The samples are normalized to the control.

Discussion

As supported by Figures 3 through 7, the street sweeper sediments of Holland, Michigan are similar to the control in terms of analyte concentration. This indicates that the samples are relatively similar to soil found in natural settings. Due to the elevated levels of manganese and cadmium in the homogenized control, it may be assumed that these elements naturally occur in higher levels in the Holland area. Therefore, elevated concentrations of these elements in the street sweeping and catch basin sediment are not a cause for alarm but rather reflect the components of local soil. Furthermore, a study by Grove and Ellis (1978) demonstrated that manganese is readily leachable from minerals commonly found in soil. Alternatively, the uniform high levels of manganese and cadmium could indicate that all the soil is affected by human activities.

As noted in Figure 6, copper is slightly more elevated in summer 2011 than in other seasonal and catch basin samples. This could be due to a variety of reasons. One possibility is that the high heat and little rainfall during the summer preserves elements on the street for a longer period of time after they have leached off automobiles or roof shingles. Copper has been shown to easily leach from automobiles by a dilute acidic solution (Rabah, 2000). Furthermore, it has been found that copper is leachable from disk brake wear using TCLP procedures (Hur, 2003).

Although the measured values for cadmium lead and nickel are often above or near the state threshold (Figures 4, 5, 6, 7), considering the experimental error associated with each measurement, these values often encompass their respective state threshold. Previous studies have shown that cadmium has a greater solubility in soils at a lower pH (Santillan-Medrano and Jurinak, 1975). Therefore, cadmium levels would be expected to be elevated following the acid wash during TCLP. Cadmium may also be naturally leached from soil by slightly acidic natural rain water. In general, the error associated with several analytes includes zero (Figures 4, 5, 6, 7). The relative size of these error bars is indicative of concentrations at or near the detection limit of the ICP, again indicating that the concentrations of these analytes are effectively zero.

Conclusion

Overall, both street sweeper and catch basin sediment was found to be below state regulatory limits with the exception of manganese and cadmium which has levels similar to those found in local soils. Therefore, above ground storage piles and settling ponds are adequate storage methods for holding street sweepings and catch basin sediment. Concerning future directions for this project, although the study is preliminary it does have the potential to support future decisions to appeal state regulations. Appealing state regulations could lead to the alternative uses of street sweeping and catch basin sediment rather than transporting them to a landfill. Ultimately, this would save the city of Holland thousands of tax dollars per year.

Acknowledgments

Special thanks to Dave Nowicki for his hours spent running the ICP for Team B. Also, to Brian White and Nick King at the City of Holland Department of Engineering for their help with coordinating sample collecting. Thank you to Mary Fales from MACC for help with brainstorming during the early stages of our project. Finally, Adam Maley ran phosphate samples for us, which might be used for later studies.

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