

May 2007

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Collins, Douglas (2007) "Trace Metal Trends in Payne Creek," *Colgate Academic Review*. Vol. 1 , Article 15.
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Trace Metal Trends in Payne Creek

Douglas Collins

GEOL 203

Payne Creek, located in Hamilton, NY, runs through both the Seven Oaks Golf Course and the grounds of Colgate University before being subjected to the effluent of the municipal sewage treatment facility. Trace metal analysis was performed using ICP-MS to identify contamination sources. The golf course and the fields of Colgate University were identified as a non-point sources, due to fertilizers. At a site on the golf course, cadmium was recorded at 0.6 ppb ± 0.1 ppb, and nickel at 10.2 ppb ± 0.1 ppb. All measurements yielded concentrations below NYSDEC surface water limits except for one; cobalt (6.7 ppb ± 0.3 ppb) exceeded the state limit of 5 ppb. The water treatment plant was an expected point source, and yielded relatively elevated concentrations of zinc (26.8 ppb ± 0.9 ppb), copper (16.6 ppb ± 0.3 ppb), lead (2.0 ppb ± 0.4 ppb), and chromium (2 ppb ± 1 ppb). This analysis provides a basis for understanding the effect of landscape management and anthropogenic interaction with surface waters. Trend analysis shows distinct areas of pollution, and more detailed sampling and analysis could yield accurate identification of pollution sources.

Introduction

Aqueous trace metals may occur naturally or come from anthropogenic sources. Some of these metals are biological nutrients, while others are considered toxic.(Bunce, 1994a) The EPA has set distinct limits for many metals and contaminants in drinking water, but leaves determination of environmental hazard to individual states to determine on a case-by-case basis.(Turner, 2005)

Presence of certain heavy metals like cadmium or lead in surface water can indicate anthropogenic contamination, due to the scarcity of these metals in nature.(Bunce, 1994a) Identifying sources and confirming with trace metal analysis provides confident identification of pollutant origin. Many fertilizers and household chemicals contain metal complexes, where the ligand is the active ingredient and the metal center is something of a spectator.

This study quantifies the concentration of a set dissolved solids in the Payne Creek system in Hamilton, NY. This stream system runs through the Seven Oaks Golf Course, the heavily-groomed grounds of Colgate University, and is subjected to effluent from the municipal sewage treatment facility. Each of these areas is a possible source of trace metal contamination. In some cases, the presence of the metals suggest the presence of other contaminants that are more directly harmful to the environment.

Analysis of these waters by inductively coupled plasma mass spectroscopy (ICP-MS) seeks to identify sources along the stream and the contribution of each. Concentrations of naturally occurring macro-nutrients and micro-nutrients, as well as toxic heavy

metals were quantified. Instrument limitations exclude the possibility of studying the oxidation states of the metals found.

Agriculture's impact on surface water is analogous to the situation in Payne Creek, as the main pollutants are soil additives made of synthetic chemicals. Other studies have concluded that increased pH and presence of metals in surface water is a direct result of agriculture upstream. It concluded, however, that the presence of agricultural activity upstream pollutes at a low level, and that it would not jeopardize the health of biota downstream. (Collins and Jenkins, 1996)

It is clear that the environmental state of a stream does not land solely in the hands of trace metals; however, they are an important tool to root out sources of contamination. A later study could be conducted to examine the stream further; a further survey could look to correlate metal concentration to water temperature, pH, and time-of-day. Sediment and soil samples could be included to broaden the scope of such a study and provide more factual and conclusive evidence for the conclusions.

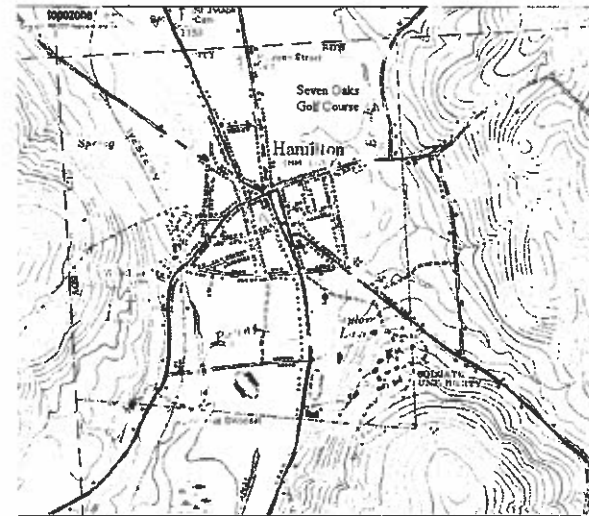
The effect of human activity on the environmental state of the creek is of particular importance to this analysis. Significant chemical additions resulting from

the maintenance of the golf course and the lawns of Colgate University are expected. An earlier study concluded that phosphate fertilizer was contaminating the waters of Payne Creek, and special attention was paid to collect samples from some of the exact sites used in that analysis. (Collins, 2006)

Experimental Procedure

Sampling was conducted on Payne Creek and Taylor Lake in Hamilton, NY. Water was collected at a total of sixteen sites along the creek system (Figure 1). Spacing was determined by eye and was decided upon regardless of debris presence or anthropogenic modification of the stream (i.e. drain pipes, screens, etc.). Where possible, water was taken from the fastest moving areas of the stream at each site. Latitude and longitude coordinates were recorded using GPS, along with observations about the area. One sample from each site was collected and stored in a 250mL plastic bottle. Collection was conducted starting farthest upstream and continuing downstream. Numbered samples are in order of stream flow.

Figure 1: Map of Sampling Area. Site DC2201 is northern-most and DC2306 is southern-most.



Instrumental analysis was performed using a Hewlett-Packard 4500 Series ICP-MS with quadrupole mass analyzer. Two sets of standards were prepared for calibration. The first solution, called "Standard A," is an aqueous solution with composition shown in Table 2. A three point calibration series was constructed with successive 10-fold dilutions of the stock. The second standard solution, called "Standard B," is

Table 1: Coordinates of Sample Sites

Site	Latitude	Longitude
DC2201	42°49.13	75°32.34
DC2202	42°50.01	75°32.20
DC2203	42°49.89	75°32.19
DC2204	42°49.76	75°32.17
DC2205	42°49.63	75°32.18
DC2206	42°49.53	75°32.22
DC2207	42°49.44	75°32.25
DC2208	42°49.34	75°32.28
DC2209	42°49.20	75°32.37
DC2210	42°49.17	75°32.43
DC2301	42°49.14	75°32.47
DC2302	42°49.11	75°32.41
DC2303	42°49.11	75°32.41
DC2304	42°49.11	75°32.85
DC2305	42°49.02	75°32.94
DC2306	42°48.90	75°32.95

an aqueous solution of calcium (500 ppm) and magnesium (100 ppm). A two-point calibration series was prepared with a 10-fold dilution of the stock. An internal standard of 1 ppb indium, tungsten, and cesium was added for drift adjustment. Background correction is based on a deionized water blank. Triplicate measurements were performed for all samples.

Table 2: "Standard A" Concentrations

Element	Concentration
Aluminum	200
Vanadium	50
Chromium	20
Manganese	50
Iron	100
Cobalt	50
Nickel	50
Copper	25
Zinc	50
Silver	5
Cadmium	5
Barium	200
Lead	50
Beryllium	5

Data

Each element was adjusted to the internal standard to account for drift using Equation 1. Masses lighter than 115 mass

$$counts_{corrected} = counts_{raw} \left(\frac{counts_{std}}{average_{std}} \right) \quad [1]$$

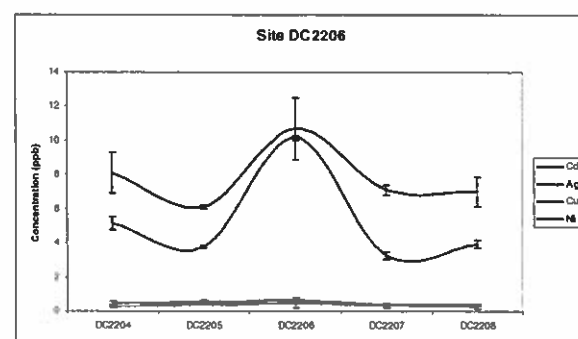
Calibration curves for each element were calculated using a linear least squares regression that yielded an R^2 value of about 0.99 for each mass. Calculations and data analysis were conducted using Microsoft Excel. See Appendix 1 for concentration data in tabular form.

Uncertainty was obtained from the relative standard deviation in the triplicate

$$\%difference = \frac{counts_1 - counts_2}{counts_1} \times 100 \quad [2]$$

Several of the metals have peaks in concentration that coincide at certain sites. At site DC2206, which is amidst the golf course, levels of silver, cadmium, copper, and nickel reach a local maximum, and decrease quickly before the next sample site

Figure 2: a. Site DC2206 Trends in cadmium, silver, copper, and nickel.

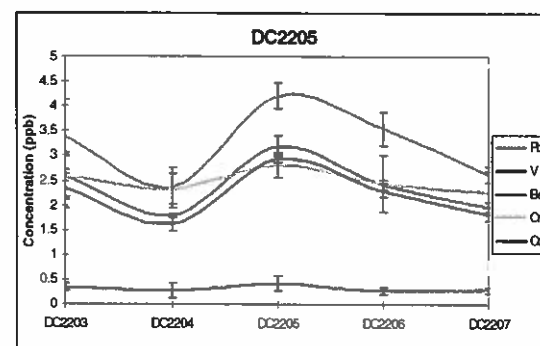


units were adjusted to indium-115, while barium-137 was adjusted to cesium-133 and lead-208 was scaled to tungsten-182.

measurements reported by the ICP-MS. It is represented as 2 standard deviations. The degree of uncertainty is small, which is expected with ICP-MS measurements and indicates the instrument's high analytical precision. A validation standard was measured at the end of the analysis and the percent difference in the counts was calculated (Equation 2, Appendix 1).

(Figure 2a). Cadmium and silver are in much lower concentrations, hence the smaller change, though equally significant. Another coincidence occurs at site DC2205 with lead, cobalt, vanadium, chromium, and beryllium (Figure 2b).

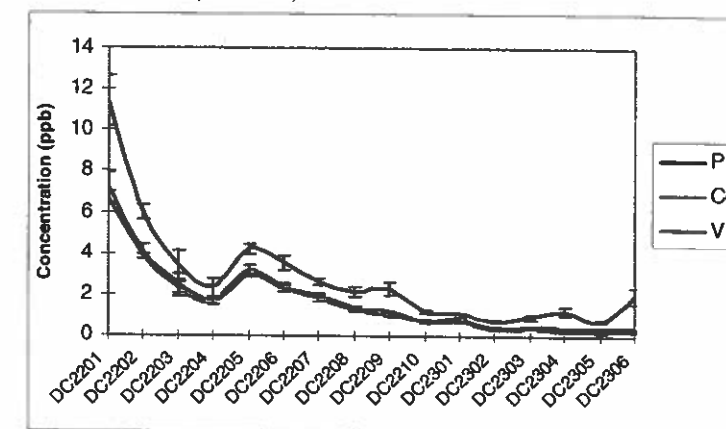
b. Site DC2205: Trends in lead, vanadium, beryllium, chromium, and cobalt



Throughout the analysis, concentrations of lead, cobalt and vanadium parallel each other closely (Figure 3). Other coincidental peaks occur at DC2301 and DC2304. Concentrations of calcium and magnesium were mostly constant

along the stream. These two elements were present on the scale of parts per million, while other metallic contaminants were on the order of parts per billion.

Figure 3: Trends in lead, cobalt, and vanadium



Discussion

On the whole, the analysis was successful in determining trends among trace metals in Payne Creek. Peaks in some metals coincide, while others have concentrations that change independently. There are sources of contamination along the stream in several places, and they are supplying distinct combinations of metals.

Sampling began upstream at the northern end of the Seven Oaks Golf Course (Figure 1). This area is directly south of a virtually inaccessible wetland area. The trends of many of the metallic elements, with the exception of manganese, are on a steep decline at the upstream end of the analysis, as exemplified by Figure 3. A further survey of the wetland could determine the cause of this high concentration of metals. This feature in the analysis is not deemed a systematic error, due to the inconsistency of the trend across all of the analyzed elements. Cobalt, with a concentration of $6.7 \text{ ppb} \pm 0.3 \text{ ppb}$ at this site, is above the New York State Department of Environmental Conservation

limit for surface water contamination (5 ppb). (NYSDEC, 1999)

Toxic heavy metals seem to vary widely in this analysis, compared to the more abundant nutrient elements. Thus, the remainder of the discussion will focus mainly on these more toxic elements, as they occur less in nature and suggest anthropogenic pollution.

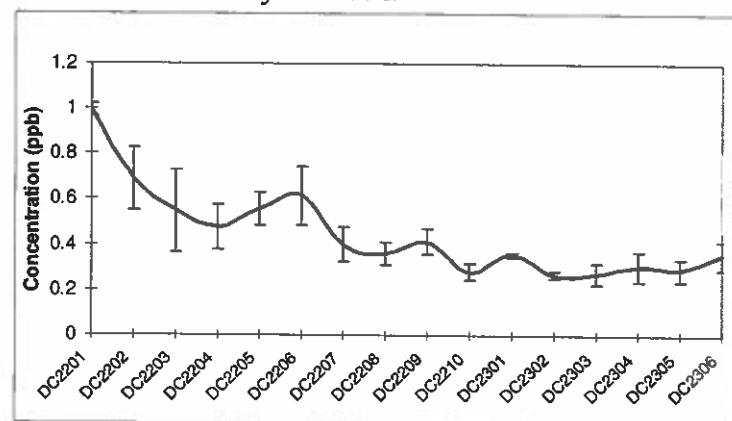
Cadmium is a toxic metal that bio-accumulates in the human body. This transition metal tends to be a raw water pollutant (Bunce, 1994b), as opposed to commonly contaminating drinking water. It occurs naturally along with zinc, copper, and lead sulfides in nature, and can occur as an industrial by-product of the isolation of other more commonly used metals. Phosphate fertilizers contain cadmium and may be a contributing source to the contamination of Payne Creek as it weaves through the golf course. A study done in the United Kingdom concluded that phosphate fertilizers on agricultural lands were the most important sources of cadmium in surface waters. (Fuge, 2005)

The highest concentration of cadmium found in the creek was $0.99 \text{ ppb} \pm 0.03 \text{ ppb}$. Normal aqueous cadmium levels are 10-times this amount.(Bunce, 1994a)

Concentration of cadmium in Payne Creek varies by about 30% in different areas of the stream. This degree of variance is consistent with trends quantified in a US Geological Survey study of diurnal variation of trace metals in streams.(US Geological Survey, 2003) Figure 4 shows the trend in cadmium concentration throughout the sampling area. The error bars are large, however, the degree of uncertainty does not invalidate the trend.

Locally high concentrations of cadmium at DC2206, DC2209, and DC2301 signify possible sources. Sites DC2206 and DC2209 are of particular interest. The former is a part of the Seven Oaks Golf Course near a heavily groomed area of the course. The ground was muddy and soft in a 50 meter radius about the sample site. As

Figure 4: Cadmium Trend in Payne Creek.

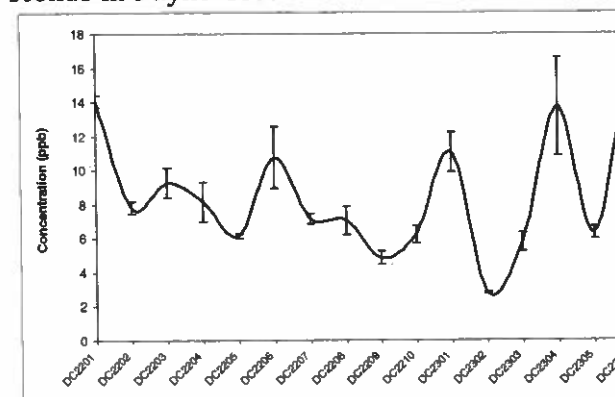


Copper, another metal found in phosphate fertilizers (Fuge, 2005), shows great variation throughout the stream. Concentrations were found as high as $16.5 \text{ ppb} \pm 0.3 \text{ ppb}$ and as low as $2.81 \text{ ppb} \pm 0.07 \text{ ppb}$. The spikes in the trend correspond with other metals, including cadmium. These results are consistent with the hypothesis that phosphate fertilizers are

for the latter location, a previous study ascertained that the phosphate level at this exact site was elevated compared to surrounding waters (Collins, 2006). This indicates that the heavily manicured fields of Colgate University may be playing a role in phosphate contamination in the Creek. As mentioned earlier, cadmium is used in phosphate fertilizer (Fuge, 2005), which this analysis concludes to be the pollution source in this case; a phosphate analysis of this water sample is required to fully support this conclusion. The high concentration at site DC2301, located at the effluent of Taylor Lake, is assumed to be elevated for the same reason as DC2209, which is located at the influent of the lake. A stream-like current flows through the lake, carrying majority of the waters directly to the lake's effluent; this explains the inconsistency in DC2210, taken from a more stagnant part of the water body.

contaminating the stream in certain places along the golf course. The additional spike in the trend at site DC2304 (Figure 5), may be due to fertilizer from the Hamilton Central School's athletic fields about 100 yards to the northeast, or from scrapmetal seen in the creek at the sampling site.

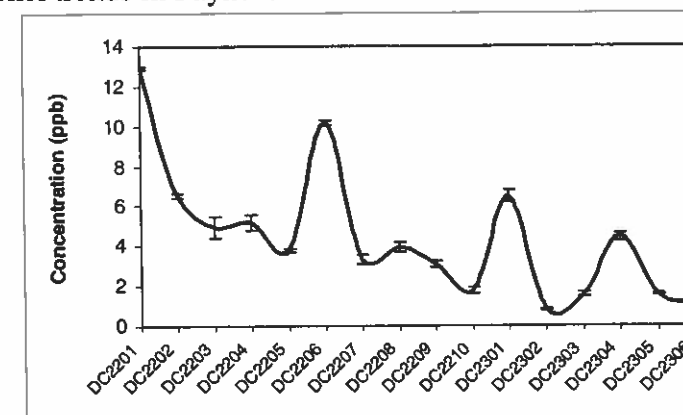
Figure 5: Copper Trends in Payne Creek



Other metals, like nickel, exhibit analogous trends, but have other spikes that can be attributed to other sources. Nickel concentrations indicate a source at the

effluent of Taylor Lake (Figure 6), which happens to be adjacent to a recently reconstructed bridge (site DC2301).

Figure 6: Nickel trends in Payne Creek

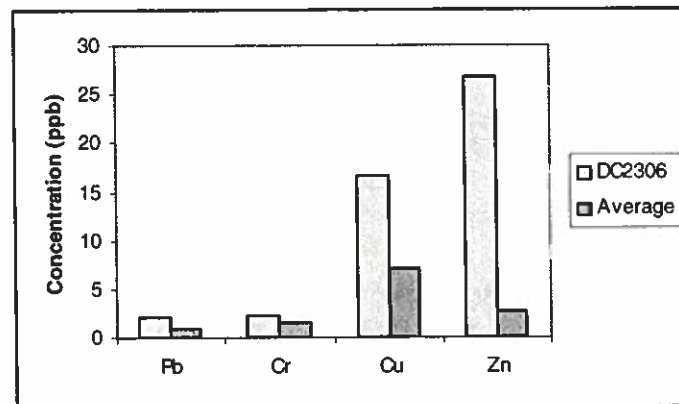


Nickel is a known component in steel, which was seen at the site and is used in some of the new dam and bridge construction. This spike in concentration is not the most severe in the sampling area; the analysis indicates a higher degree of contamination as a result of phosphate fertilizer from the golf course, as nickel, too, is used in some fertilizers (Fuge, 2005).

Most elements in the analysis, with few exceptions, show significant additions from the municipal sewage treatment plant at the south end of the sampling area. This was an expected

point source, and none of the quantified dissolved solids exceed surface water contamination limits set by the NYSDEC (1999), although some of the elements exist in higher concentrations than at any of the preceding sites (Figure 7). Other elements are elevated concentrations due to use in household applications. Copper and lead are elevated perhaps due to household plumbing and zinc is used commonly in galvanizing metals to protect from corrosion.(Bunce, 1994b) Chromium is a common component of alloys like stainless steel as well as in certain pigments, which can be found in the household.(EPA, 2006)

Figure 7: Contamination levels at sewage facility compared to average of four sample sites immediately upstream



Conclusion

The trend analysis was successful in quantifying the trends in trace metal concentration for Payne Creek. It determines fertilizer to be the source of contamination for this surface water system with point sources on the golf course and the grounds of Colgate University. The municipal sewage treatment plant is also a significant point source for contaminants in the stream.

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