Analysis of Heavy Metals in Soil Along Strawberry Creek

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Introduction

Hazardous wastes produced on the Berkeley campus are increasingly becoming an important issue. This problem is especially critical for Berkeley, because it is one of the largest research institutions in the country. Researchers and students at this campus produce a variety of toxic substances, which may enter the campus environment when improperly disposed of.

Past water quality studies indicate that Strawberry Creek has been contaminated by campus pollution (Phillips, 1986). The extent to which toxic substances are entering the campus environment and possibly posing a public health threat can be studied by regularly monitoring the Creek.

Heavy metals, one form of pollutant, often collect in the sediment in areas where water runs slowly. Strawberry Creek mainly flows above ground through campus, and is thus highly vulnerable to this pollution. There are three primary sources for contamination of the creek on campus: surface run-off, discharge from UC laboratories through drain pipes, and the possible leakages of substances from the sanitary sewer system (Phillips, 1986).

The purpose of this paper is to determine the degree to which selected heavy metals are being deposited in the soil along Strawberry Creek. The study focuses on the concentration and effects of cadmium, chromium, copper, lead, and zinc. It is being coordinated with a current water quality study assessing heavy metal pollution in the creek (Morales, this report).

Past Studies

Recently, the campus office of Environmental Health and Safety (EH&S) did an extensive water quality study of Strawberry Creek (Charbonneau, 1987). As part of their study, they tested for heavy metals in the water and sediment around selected drain pipes. Heavy metals in soils have also been monitored in other parts of the East Bay (e.g. Bisio, 1986; MacDonell, 1986; Sutton, 1987). Bisio's study looks at concentrations of cadmium, copper, lead, and zinc at the Brickyard on the Berkeley Waterfront. She does not find any significant build-up of these metals in the soil. MacDonnell examines the trends in metal concentrations in Aquatic Park, as it relates to the distance from the road. She also looks at cadmium, copper, lead, and zinc. Sutton looks at the concentration of cadmium, chromium, and lead in the sediments along the South Richmond Shoreline. He does not find any significant levels of these metals in the soil

Metals in the Environment

Metals occur naturally in our environment and often serve an essential function in biological systems. Their value, however, becomes complicated by their persistence and possible toxicity to human life (Oehme, 1979). This threat becomes especially serious because most metals become more concentrated as they move up the food chain.

Soil contamination is an especially critical problem, because pollutants tend to persist in this medium (Lepp, 1981). The residence time of pollutants in other components of the biosphere is generally shorter. In the case of heavy metals the pollutant is diminished only slowly by leaching, plant uptake, or erosion (Lepp, 1981).

Health Effects of Heavy Metals

Cadmium (Cd) is a natural constituent of most soils. It is usually found in very small concentrations, averaging only 0.15 - 0.20ppm in the earth's crust (Waldron, 1980). Cd shares very similar chemical properties with zinc. Its occurrence in nature will almost inevitably be found in association with zinc (Friberg *et al.*, 1974). The smelting of zinc, lead, and copper is the primary contributor of excess Cd in the soil. Other sources for Cd pollution in soil are sewage sludge and phosphate fertilizers (Waldron, 1980).

Cd does not seem to display any beneficial values for natural systems, and, in fact, may produce toxic effects (Bisio, 1986). The most serious problems associated with this metal that human beings encounter are chronic intoxications due to inhalation or ingestion (Piotrowski and Coleman, 1980). Inhalation may cause lung damage, such as emphysema. Other effects include bone damage and possible disturbance of a person's mineral metabolism (Piotrowski and Coleman, 1980). Usually, the real consequences of Cd only become apparent after a long period of exposure. Thus, due to critical health affects associated with Cd, it is crucial that the occurrence of this metal in the environment be monitored.

Chromium (Cr) as a metal is not harmful to human beings. However, in its hexavalent form, Cr can pose a serious health threat to human beings. Hexavalent Cr is an irritating and corrosive compound, which may severely damage the nasal system when inhaled (NRC, 1974).

The most grave effect is its role in increasing the chances for lung cancer (NRC, 1974). In most instances, industrial exposure has been the primary cause for these adverse effects.

Research on the influence of Cr on ecological systems is inconclusive (Waldron, 1980). Its role in producing harmful health effects, however, has begun to focus attention on levels accumulating in the environment (Waldron, 1980).

Copper (Cu) is essential in most biological systems and makes up about 70ppm of the earth's crust (Page *et al.*, 1981). The primary man-made source for this metal in the soil is mining and smelting. Other sources more relevant to Strawberry Creek are automobile exhaust, urban development, contaminated dust and rainfall, and fertilizers and pesticides (Nriagu, 1980).

Though Cu is essential to human life, it can be toxic at high concentrations. Human beings may suffer from Cu toxicosis by topical exposures, inhalation, or ingestion of this metal. Topical exposure can induce allergic reaction, and in some cases, turn a person's hair green. Inhalation can cause congestion and ulcerations of the nasal septum. Workers exposed to fumes and dust may suffer from "metal fume fever" (a condition referring to sudden chills and fever). Ingestion may cause liver damage, renal toxicity, and in some extreme cases, it may affect the central nervous system, and induce a coma (Cohen, 1979).

Though this metal is inherently toxic, human beings have developed an internal defense mechanism, which diminishes the effects of copper toxicosis from ingestion. The lethal effects of copper seem to occur more often in lower life forms. This is especially true for fish populations, which may be adversely affected by copper concentrations well below the lethal level.

Of the metals being studied, lead (Pb), has perhaps the worst reputation for causing environmental poisoning (Piotrowski and Coleman, 1980). Excessive exposure to Pb may pose a variety of serious health threats. Among these, the most widely documented include: interference with certain metabolic functions, anemia, damage to the nervous system, renal deterioration, and possible adverse effects on the reproductive cycle (Piotrowski and Coleman, 1980).

Pb enters the environment primarily from automobile exhaust (Waldron, 1980). Ingestion of this metal, however, poses a much more serious health risk than inhalation. Eventually Pb is deposited in the soil, and then may enter the food chain through plant uptake. Once in the food chain, this metal becomes concentrated in the tissues of animals. As it moves up the food chain to human beings, the Pb concentration exceeds the level at which it was initially introduced (Waldron, 1980). Because Strawberry Creek flows directly to San Francisco Bay, a concentration of Pb in the creek has the potential for becoming biomagnified in the Bay's ecosystem.

Zinc (Zn) is much less toxic than the other heavy metals discussed (Shuman, 1979). Excessive amounts of Zn, however, can induce adverse effects for human beings, as well as for the rest of the ecosystem. The most common health effect associated with Zn ingestion is anemia. This condition results from the excess Zn interfering with the natural metabolism of copper and iron in the body (Oehme, 1979). Other symptoms of Zn toxicity include dehydration, abdominal pain, nausea, and dizziness (Shuman, 1979). Industrial workers exposed to fumes may also suffer from "metal fume fever" (Shuman, 1979).

Methods

Samples were collected at six sites along Strawberry Creek in November 1987 (Figure 1). The soil samples were taken from the area surrounding drain pipes where a concurrent water quality study is being conducted (Morales, this report). The sites Morales chose to test correspond to those in a previous study (Charbonneau, 1987). I collected soil samples near these sites in order to determine if there is a correlation between metal concentration in the water and that of the soil.

On November 15, 1987, approximately 450 grams of soil was taken from each site. After rocks and organic material were removed, the soil was air-dried, ground and sieved through a 2-millimeter mesh screen. Five grams of soil were digested at 70°C in 4N nitric acid and diluted to 100 milliliters (See Appendix I for detailed methodology). The possibility for experimental error is inherent in the nature of this procedure. For example, the preparation of the soil samples for analysis requires several dilutions. Although extreme care was taken in handling the solutions, the possibility for error existed at any point in this process. Metal concentrations were determined using a Perkin-Elmer 360 Atomic Absorption Spectrophotometer. There is a 10% uncertainty in the data obtained from a spectrophotometer, which should be taken into account when the results are interpreted.

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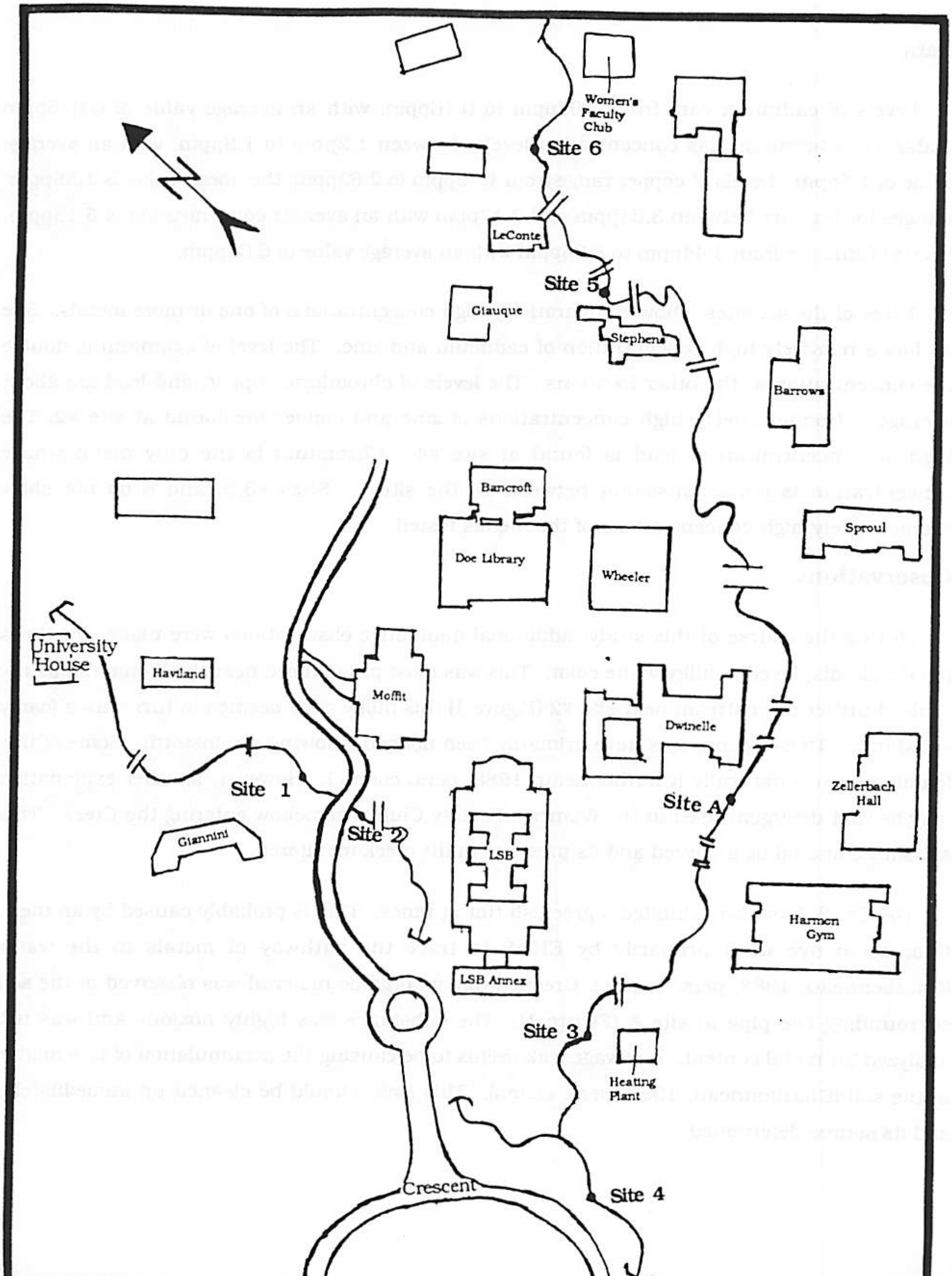

Figure 1: Strawberry Creek, Sampling Sites

Data

Levels of cadmium vary from 0.05ppm to 0.16ppm, with an average value of 0.075ppm (Table 1). Chromium has concentration levels between 1.2ppm to 1.8ppm, with an average value of 1.5ppm. Levels of copper range from 1.15ppm to 2.62ppm; the mean value is 1.55ppm. Ranges for lead are between 3.64ppm and 7.17ppm with an average concentration of 5.13ppm. Levels of zinc are from 3.44ppm to 8.65ppm with an average value of 6.02ppm.

Three of the six sites show comparatively high concentrations of one or more metals. Site #1 has a relatively high concentration of cadmium and zinc. The level of cadmium is double the concentration at the other locations. The levels of chromium, copper, and lead are about average.. Comparatively high concentrations of zinc and copper are found at site #2. The highest concentration of lead is found at site #4. Chromium is the only metal whose concentration is fairly consistent between all the sites. Sites #3,5, and 6 do not show comparatively high concentrations of the metals tested.

Observations

During the course of this study, additional qualitative observations were made. At times the Creek displayed a milky white color. This was most pronounced near the Women's Faculty Club. Further downstream near site #2 (Figure 1) this milky color seemed to turn into a foamy substance. These occurences have primarily been noticed following a rainstorm. Some of this foaming occurs naturally (Charbonneau, 1988, pers. comm.). However, another explanation may be that detergent used in the Women's Faculty Club is somehow entering the Creek. This substance should be analyzed and its presence in the creek monitored.

The Creek has also exhibited a greenish tint at times. This is probably caused by an inert, fluorescein dye used primarily by EH&S to trace the pathway of metals in the water (Charbonneau, 1988, pers. comm.). Greenish-brown organic material was observed in the soil surrounding the pipe at site A (Figure 1). The substance was highly noxious and was not analyzed for metal content. A sewage leak seems to be causing the accumulation of this matter in the soil (Charbonneau, 1988, pers. comm). This leak should be cleaned up immediiately, and its source determined.

Metal Concentration (PPM Dry Weight)

Site	Cd	Cr	Cu	Pb	Zn
1	0.16	1.4	1.17	3.64	7.80
2	0.08	1.7	2.62	5.56	8.65
3	0.05	1.3	1.65	5.89	5.56
4	0.05	1.2	1.52	7.17	4.75
5	0.05	1.16	1.15	3.97	3.44
6	0.06	1.8	1.20	4.54	5.90

Table 1. Concentrations of heavy metals in soil samples at sites along Strawberry Creek

Comparative Sediment Analysis

Metal	Range
Cadmium	0-3.0
Chromium	10-1200
Copper	10-180
Lead	0-1000
Zinc	20-810

Table 2. Concentrations of heavy metals in soils around the Bay Area
Source: Adapted from EH&S study (Charbonneau, 1987)

Discussion

The results of this study do not indicate any significant build-up of heavy metals in the soil along Strawberry Creek. The concentrations of the metals tested are all below the average concentrations of comparable soils in the Bay Area (Table 2) and are also below the natural background levels of various soils (Table 3). Although the metal concentrations are below these levels, the distribution of each metal (with the exception of Cr) is not uniform from site to site. For each metal the highest concentration is almost double the lowest one. This discrepancy may be explained by improper disposal of the metals down campus drains.

The elevated levels of Cd and Zn at site #1 may be attributed to the effluent from the pipe near this sampling location. The source point for this pipe is Giauque Hall (Charbonneau, 1987). Thus, laboratory activities in Giauque Hall may be contributing to the concentrations of Cd and Zn. It is, however, beyond the scope of this report to determine if these metals are currently used in research in Giauque Hall. The highest concentrations of Cu and Zn are at site #2. The effluent from the pipe located at this site flows directly out of LeConte Hall (Charbonneau, 1988, pers. comm.). LeConte Hall contains research facilities for the Physics Department, which use Cu and Zn for experimental purposes. Since at least some of the effluent from this hall flows directly into the Creek, a relationship might exist between concentrations in the soil and activities in the building. However, since the concentrations in the soil are below natural background levels (Table 3), this link is difficult to establish. Furthermore, the two water quality studies conducted at this pipe do not show any significant concentrations of Cu or Zn (Morales, this report; Charbonneau, 1987).

An apparent sewage leak at site A, located upstream from site #4, may be contributing to the high concentration of Pb at site #4 The water from the sewage leak shows the highest concentration of all the metals tested by Morales (this report, site #3) and Charbonneau (1987, site #68). It is possible that the other metals may have been retained in the soil surrounding the sewage leak. This may explain why these metals do not have elevated concentrations at site #4. Since soil samples were not taken at site A, this possibility cannot be confirmed. Alternatively, the elevated levels of Pb at site #4 may be caused by automobile exhaust. Of all the sampling sites, this location is the closest to the roadway, and thus most vulnerable to automobile pollution.

Since the concentrations of Cr are fairly uniform between the sites, there is no indication that it is entering the campus environment from improper disposal. The metal concentrations

Metal Concentration (PPM Dry Weight)

Metal	Range	Mean
Cadmium	0.41-0.57	----
Chromium	11.6-189	50
Copper	3-300	26
Lead	<10-70	26
Zinc	13-3	73.5

Table 3. Average concentration of heavy metals in various soils
Source: Adapted from Kabata-Pendias and Pendias, 1984: Tables 41, 57, 63, 96, 122

Metal Concentration (PPM Dry Weight)

Metal	North Fork	South Fork
Cadmium	<0.5	<0.5
Chromium	27	21
Copper	31	37
Lead	52	35
Zinc	150	110

Table 4. Sediment Analysis of Strawberry Creek
Source: Adapted from EH&S study (Charbonneau, 1987)
Notes: Samples were taken 8/13/87 on lower reaches of central campus

found at sites on the north and south forks along the lower reaches of campus do not show the same patterns as found in a previous sediment analysis (Table 4). In the earlier study most of the metals occurred in higher concentrations at the north fork, whereas in this study, the concentrations at the south fork are comparatively higher than at the north fork. However, the difference in concentrations between the two forks is so small that one cannot make a conclusive assessment that one site is more contaminated than the other.

Conclusion

This study suggests that heavy metals are not entering the campus environment from improper disposal. This is good news considering the extent to which toxic substances are used on campus. If significant concentrations of heavy metals had been found, the source would need to be determined, and the soil may have required excavation. Both these measures would have been time consuming and costly. Fortunately, the results of this study do not warrent that such measures be taken. In the future, the Creek should be periodically monitored for the presence of metals in surrounding soils as a precautionary measure.

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Appendix I: Detailed Methodology

I. Sampling

a. Approximately 450g of soil were taken at 6 sites (Figure 1) with a hand shovel. The samples were taken from the upper two inches of the soil.
b. Time and Date: 2-3:30pm on Sunday, November 15, 1987, following a rain on Friday, November 13, 1987.
c. Other variables: The outside temperature was warm, approximately 75°F. The samples were taken close to and occasionally in the water and were thus fairly wet.
d. Samples were stored in a plastic bag.
e. On Saturday, November 21, 1987, the samples were air dried under a fume hood. Large rocks and organic material were removed.

II. Sample Preparation

a. Weighed out 5g of dry sample from each site.
b. Ground sample using a mortar and pestle.
c. Sieved sample through a 2mm mesh screen.
d. Added 35ml of 4N HNO3--made from 8.75ml of 16N HNO3 and 26.25ml of H2O.
e. Heated sample with acid at a temperature of 70°C for 24 hours. This process digested the soil.
f. Added enough water to make 100ml of final solution.

III. Standard Solution Preparation

a. Took an initial reading of the samples using the Atomic Absorption Spectrophotometer in order to determine the range for the standards.
b. Prepared standards using "high" and "low" values.

IV. Analysis using Atomic Absorption Spectrophotometer

a. First ran standards to determine range of concentration.
b. Then ran sample solutions to determine range of concentration.