Levels of Chromium and Lead in the Taconic Golf Course Williamstown, Massachusetts

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Introduction

In this investigation, levels of chromium and lead in the soils of the Taconic Golf Course were measured. Golf courses are carefully maintained environments- to insure its natural beauty. Many golf courses in more metropolitan areas practice pest prevention- which is applying large amounts of pesticides to prevent any possibilities of destruction by insects, weeds, or fungi. However, in Williamstown, a small and quaint New England town, there is less pressure from the community to maintain a flawless golf course. Peter Lund, the owner of the Taconic Golf Course, practices pest elimination by applying pesticides only when there is actual evidence of damage.

In this research, it was thought that the source of chromium and lead was from the pesticides. In the past, many metal based pesticides and fertilizers were used. However, the use of these metal based compounds have become less common due to strict governmental regulations. In the Taconic Golf Course, the majority of pesticides used were organic compounds; the pesticides which were metal based had metals which were not analyzed in this research. To account for the presence of lead and chromium, literary research was done on possible sources of these two heavy metals.

Materials and Methods

To measure the amounts of chromium and lead in the soils of the Taconic Golf Course, samples were collected on Monday, April 27, 1992. The weather that day was sunny with very little wind. The temperature was about 60°F and samples were collected in the afternoon.

In the Taconic Golf Course, the greens and fringe are the most heavily treated with pesticides followed by the tees and fairways followed by the rough, which is treated least. The reason why the greens and fringe are the most heavily treated areas is because the grass in these areas are the shortest and most susceptible to disease or pests. All of the samples were collected in the northeast corner of the golf course. Since the greens are all treated exactly the same, as well as the tees and fairways, ect., it was unnecessary to sample the entire golf course. This sampling was done before knowing that the pesticides did not have chromium and lead in their composition.

Seven sites were chosen covering the three different levels of pesticide treatment. At each site, two samples were taken, one right underneath the grass and one 20cm below the surface. Professor Art suggested taking three samples: one beneath the surface, one 30cm beneath the surface, and one 60cm beneath the surface in order to have a soil horizon. Unfortunately, due to lack of strength, this was nearly impossible.

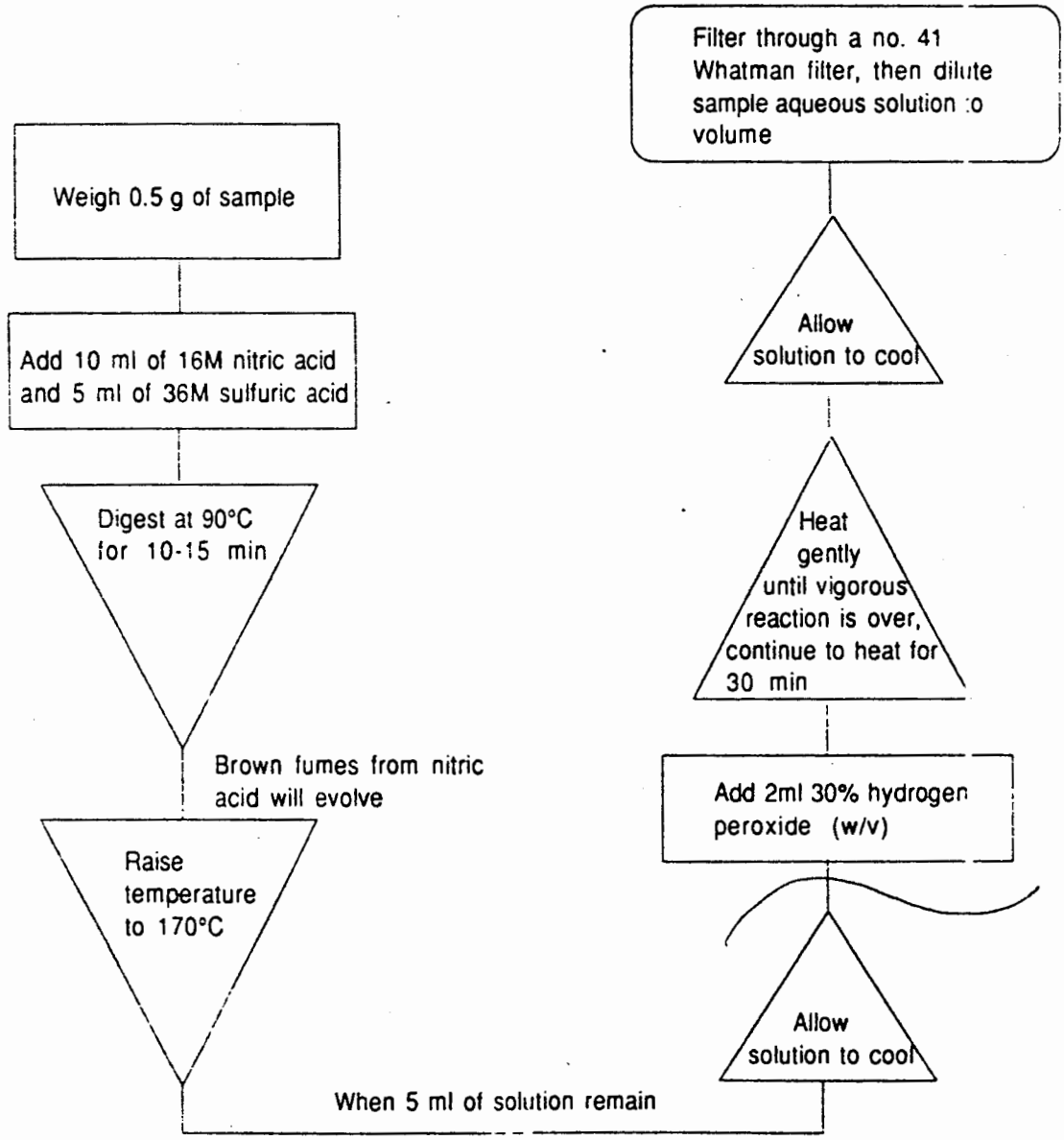
Sites were labelled from 1 - 7. Since two samples were collected from each site, an "A" following the site number denoted the layer right beneath the grass and "B" denoted the layer that was

20cm below the surface. Therefore, a total of fourteen samples were collected. To collect the soil samples, a soil auger and a small spade were used and samples were placed in 16 x 7cm whirly-bags. The layer just beneath the grass was collected by removing the top layer of grass and carefully scooping enough soil to fill the whirly-bag. The second layer was collected by drilling the auger into the ground to a depth of 20cm. The spade was used again to carefully scoop the soil into the whrily-bag. A map of the sampling sites can be found in the appendix as figure 1.

After sampling was finished, the samples were brought back into the lab and the soils were transferred from the bags into large crucibles so the soils could be dried. The sediment was dried for twenty-four hours at 100°C in the Precision Scientific Thelco oven to remove any moisture from the samples.

To measure the amounts of chromium and lead in the soils, the metals first had to be extracted from the soil. This was done by digesting 5g of each sample in highly concentrated nitric and sulfuric acids. The concentrated acids digested the organic matter of the soils and this allowed the metals present in the samples to go into solution with the acids. The protocol for the metal extraction is from Arafat and Glooschenko. A flow chart of the protocol can be found on the next page. The digestion took about fourteen hours. Along with the fourteen samples, a blank and three standards, from the National Institute of Standards and Technology's Buffalo River Sediments, were digested, making the total number of samples eighteen.

Extraction Procedure for Sediment Samples From Arafat and Glooschenko (9)



All eighteen samples were filtered using Whatman 41 filters. Each filtered solution was diluted to 100mL using a volumetric flask and stored in plastic containers. Since this was not a bacterial analysis, refrigeration was not necessary.

To measure the amounts of chromium and lead, the Williams College Atomic Absorption Spectrophotometer (AAS) was used. To determine the concentration of a metal in a sample, a standard was run first to establish a curve to which the samples could be compared to. The samples were heated until the metal reached its gaseous phase. A light, whose source is usually a hollow cathode lamp, was passed through a monochrometer so that the wavelength that corresponds to the energy the specific metal absorbs is isolated. This monochromatic light is then passed through the gaseous sample. A detector measures the amount of light absorbed by the sample and sends the information to a computer which plots the absorbance vs. time. The absorbance peak is linearly proportional to the concentration. A schematic of the AAS can be found as figure 2 in the appendix

To test for chromium, a 10:1 dilution had to made for all the samples because the concentration of chromium was too high for the AAS to measure. Only 1A and 7A had to be diluted for the lead test.

Results

The results can be found in table and graph form in the appendix.

Discussion

A. Results

There are many problems with the data. The three controls were standards from the National Bureau of Standards. In the standard, the concentration of Cr should have been 135 ppm. The average of the controls in this experiment was 71 ppm. For lead, the concentration should have been 161 ppm and the average of the three controls in this experiment was 4.95 ppm. With such a huge discrepancy in numbers, it is difficult to believe that the data collected is of any significance. However, for the sake of this research, the values obtained in this research will be used as a very gross estimation of the concentrations of lead and chromium in the soils of the Taconic Golf Course.

Since the controls were so much lower than what they were supposed to be, it can be assumed that the concentrations of chromium and lead in the samples are higher than what was determined in this research. The data was separated by levels of pesticide application, but since the number of samples were so few, any inferences that can be made will be highly questionable as to its validity.

Since there was such a wide range of concentrations of lead and chromium, and since there were so few samples analyzed, it is difficult to make any statistical analysis. There might have been something inherently wrong in the procedure because Clair Sibley also had problems with her data.

First of all, there were possibilities for human error in the methods. The samples were all heated for different amounts of time because in the procedure suggested by Arafat and Glooschenko, the samples were heated until 5mL of the solution remained. Each sample took a different amount of time to evaporate to 5mL, so differences in heating could have affected the amounts of chromium and lead that went into solution with the acids.

Another source of error was possibly during filtration. After the samples cooled, they were filtered through 41 Whatman filters. Because the solutions were so acidic, they ate through the filter, making a huge hole. Thus, the sample had to be refiltered and some losses of metals could have occurred. Since the controls were filtered first, this problem occurred with the three controls.

After realizing that the solutions were too acidic for the filters, the samples were diluted to about 50mL before being filtered. This solved the problem of the samples eating through the filter. However, half of the filtration was done on Friday, May 1 and the rest on Monday, May 4. On Friday, all of the samples were diluted before being filtered and about half were filtered that day. On Monday, it was noticed that 7A was accidently not diluted, and the solution was much more yellow as compared to the rest of the samples. It is possible that since 7A was in a much more acidic medium over a 48 hour period, more chromium and lead could have went into solution.

As mentioned before, it would be difficult to make any sort of statistical analysis with the data obtained in this experiment.

However, the concentrations measured can be evaluated relative to the other samples.

The hypothesis as to why the levels of chromium and lead in sample 7A were so high is probably a viable one because both the lead and chromium were significantly higher than the rest of the samples.

Other irregularities in levels of chromium were in samples 2A, 3B, and 5A; and in levels of lead, in samples 1A and 7B. If procedural error account for these irregular values, and therefore, they can be disregarded, the range of concentrations of lead is 0.93-2.86 ppm and for chromium is 22.91-47.63 ppm. By taking the difference of the average concentration of the controls from the theoretical concentrations of the metals of the Buffalo River Sample, the average loss can be calculated. If the very irregular values of lead and chromium concentration are ignored, the average concentrations of lead in the soils, adding on the error from the control, is about 150-155 ppm and the average concentrations of the of chromium in the soils is about 83-107 ppm.

B. Pesticides

Pesticide is a general term for substances such as insecticides, herbicides, fungicides, fumigants, algacides, aviacides, and rodenticides (1, p. 321). On golf courses, the primary pesticides used are insecticides for insects, herbicides for weeds, and fungicides for fungi.

Insecticides enter insects through its stomach walls or respiratory systems and interfere with its biological mechanisms,

thus killing it. Insecticides can be divided into four major groups: inorganic, oil, botanical, and synthetic (1, p. 321). Presently, the golf course uses mostly synthetic insecticides, which are organic compounds with sulfur, chlorine, nitrogen, and/or phosphorus.

In the past, inorganic compounds were used although today they have been largely replaced by more efficient organic compounds. Arsenic based compounds used to be the most widely used group of stomach poison for insects (2, p. 7). Some examples are Paris Green [$(CH_3COO)_2Cu \cdot 3Cu(AsO_2)_2$], sodium arsenite ($Na_3AsO_3$) and lead arsenite.

Herbicides come in both inorganic and organic forms. Again, on the golf course, most of the herbicides are organic with the additions of halogens, sulfur, oxygen, and/or nitrogen. Some of the inorganic herbicides used in the past included copper sulfate in the late 1800's, iron sulfate in the 1940's, and sodium tetraborate. Like the insecticides, inorganic herbicides are gradually being replaced by organic compounds. Intensive EPA restrictions have been placed on inorganic herbicides because of their persistence in the soils (3, p. 80).

The fungicides used on the golf course are mostly organic compounds. Historically, fungicides were copper and mercury compounds. However, copper was found to retard growth in some plants, and, as a result, the organic fungicides were developed (3, p. 103). As in the other two pesticides, inorganic compounds typically are very persistent to the environment.

In the Taconic Golf Course, some examples of the pesticides used are (4, 5):

Insecticides: Turcam ($C_{11}H_{13}NO_4$)

Oftanol ($C_{15}H_{24}NO_4PS$)

Herbicides: Embark ($C_{11}H_{13}F_3N_2O_3S$)

Tempo ($C_9H_{10}Cl_2N_2O_2$)

Fungicides: Tersan ($C_6H_{12}N_2S_4$)

Dyrene ($C_9H_5Cl_3N_4$)

The practice of using mostly organic compounds as pesticides is common all over the United States (1, p. 323). Chromium and lead were not present in any of the pesticides used by the golf course. Therefore, the source of chromium and lead can either be from atmospheric pollution, fertilizers, or persistence from the days when lead or chromium based pesticides were used.

C. Possible Sources of Chromium and Lead Pollution

Heavy metals are commonly defined as the group of metals that are associated with pollution and toxicity- chromium and lead being examples of heavy metals. Studies of heavy metals in the soils have indicated that many areas near urban area, metalliferous mines, or major road systems contain high concentrations of heavy metals (7, p.4).

Chromium is an abundant mineral in the earth's crust and is present in low concentrations in sea water. The range of concentrations of chromium in the continental crust is 80-200ppm (6, p. 9). In the natural cycle of chromium, it goes from the soils, into plants and animals, and back into the soil again when organisms die and decay. Soils naturally contain low levels of chromium (1, p. 40).

Sources of chromium in soils today may be from the combustion of materials such as coal and wood. Chromium is also used as a protective coating on cars to prevent rusting (1, p. 40). In the 70's, chromium was a common metal in fungicides and fertilizer (6, p. 85). Another common source of chromium is sewage sludge (7, p. 133). When ingested or inhaled, chromium enters the bloodstream and into the liver and spleen. At high levels, chromium has shown to cause skin lesions, gastrointestinal ulcers, and lung cancer.

In this research, to extract the metals from the soils, the soils were heated in a very acidic solution and this allowed the metals to separate from the organic matter and go into solution with the acids. In Williamstown, it has been measured by the Environmental Studies 102 class in March that the pH of rain in this area is about 4.3. A pH of 4.3 is acidic and it is possible that the chromium present in the air, as a result of combustion, were dissolved in the acidic rainwater and ended up in the soils.

In the Taconic Golf Course, the pH of the soil is around 6.5, much more neutral than the rain. Therefore, the chromium from the rain probably remained in the soil because the pH of the soil was higher than the rain.

Lead is mostly found in the earth's crust. However, through the use of leaded gasoline, 98% of the lead present in the atmosphere is from the combustion of gasoline products. Other sources of lead are solders for pipes, paints, pigments, ammunition, storage batteries and as a protective shielding for radioactive substances. Lead has a long residence time compared with most other pollutants. As a result, lead tend to accumulate in soils and sediment (7, p. 177).

Plants obtain lead from soil, water, and air. Animals obtain lead from food, water, and air. When humans consume lead, a small portion is absorbed by the digestive tract, while 40% is absorbed by the lungs. Lead then enters the blood vessels where it can come into contact with cells and poison enzymes. Lead can also bind to hemoglobin and impair oxygen transport. At high enough levels, lead can kill people. Lead is also toxic to kidneys and can cause nervous systems disorders (1, p. 39).

Most farming soils or city soils have lead concentrations in the range of 2-200ppm, with soils being found in the range of 5-25ppm. In concentrations higher than this, it is almost certain that there has been lead pollution. The concentrations of lead in general decreases as depth increases, due to lead deposition from the air on the top layer of soil (8, p.132). In this research, the samples taken from 20cm below the surface did not have lowere concentrations than its corresponding "A" sample. It is possible that 20cm below the surface is not deep enough to prove that the concentrations of lead decrease as depth increases.

Since lead is very persistent, it is not uncommon for soils to have high levels of lead present. Plants also take up lead from their roots, and when they die, their decaying matter goes back into the soil, creating a lead cycle.

Although the exact concentrations of lead and chromium in the golf course are not known, there is evidence of their presence. It is most likely that the source of lead and chromium present in the soils of the Taconic Golf Course are from the atmosphere.

Future Research

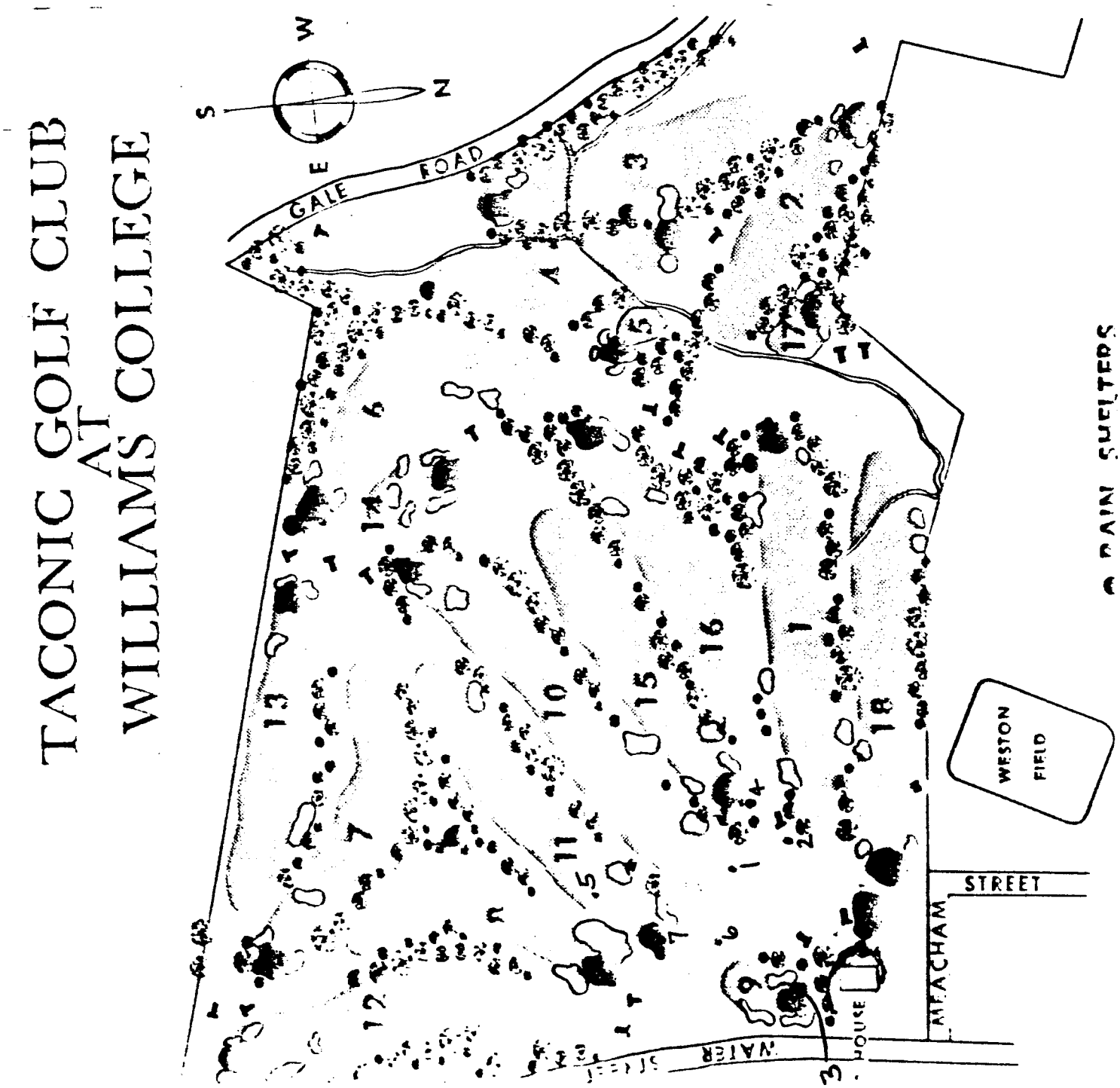
For future work, more samples should be collected, and more than one trial should be run so that the data becomes more valid. It seems as though most of the chromium and lead are coming from the atmosphere, and so taking samples at different elevations might be useful in determining if the concentration of metals are different at higher elevations. This might be due to the fact that metals are heavy so there might be higher levels of metals at lower elevations.

Different instrumentation for determining the concentration of metals in the samples other than just the AAS might be useful in getting better results. In Nathalie Weicker's thesis, she used both the AAS and an Inductively Coupled Argon Plasma Emission Spectrophotometer. Different instrumentations measure different metals or different levels of concentrations better than others. It is possible that the AAS of Williams College was not a good instrument to use for the analysis that was done in this research because the samples had to be diluted, and by diluting, some of the metals could have been lost.

Different techniques of extracting the metals from the soils might also yield better results.

APPENDIX

FIGURE 1:
Location of
Sample Sites



SCHEMATIC DIAGRAM OF THE INDUCTIVELY COUPLED ARGON PLASMA SPECTROPHOTOMETER

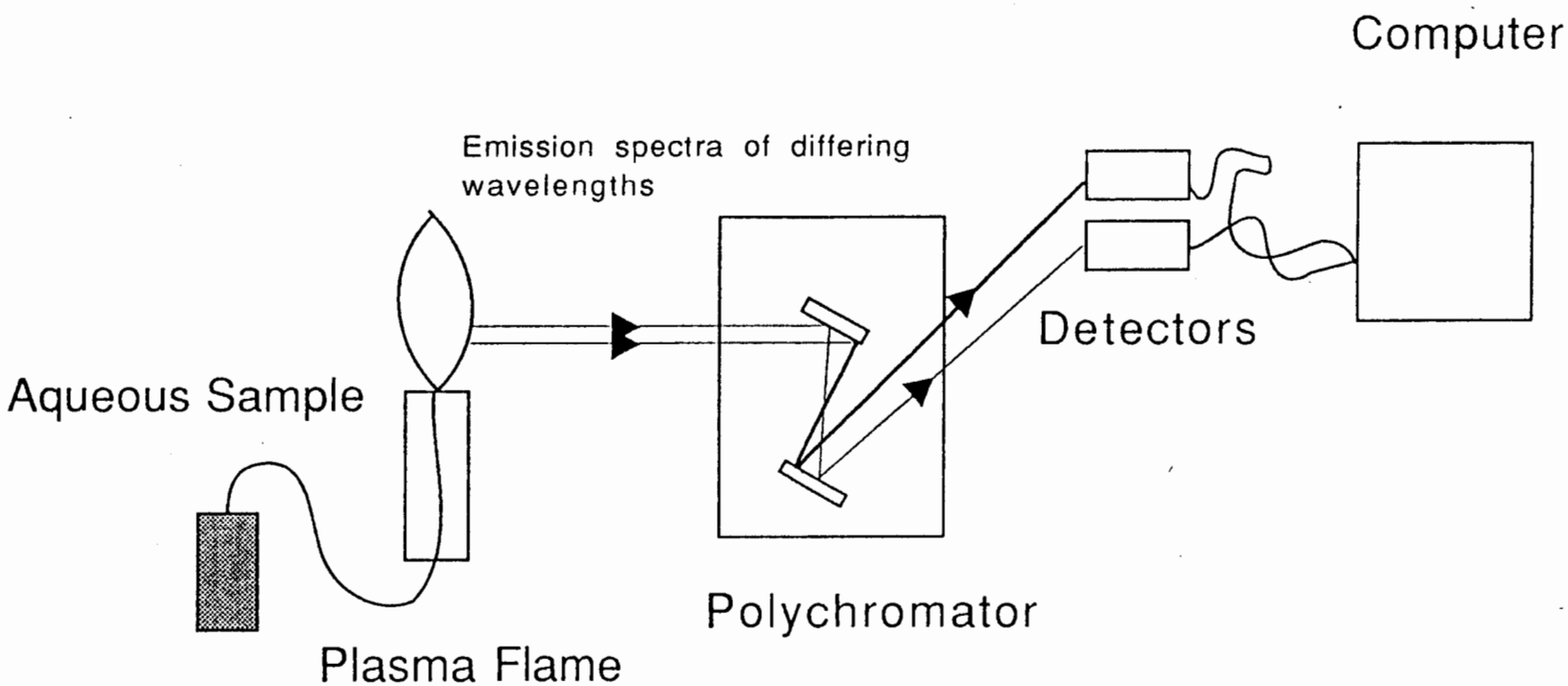


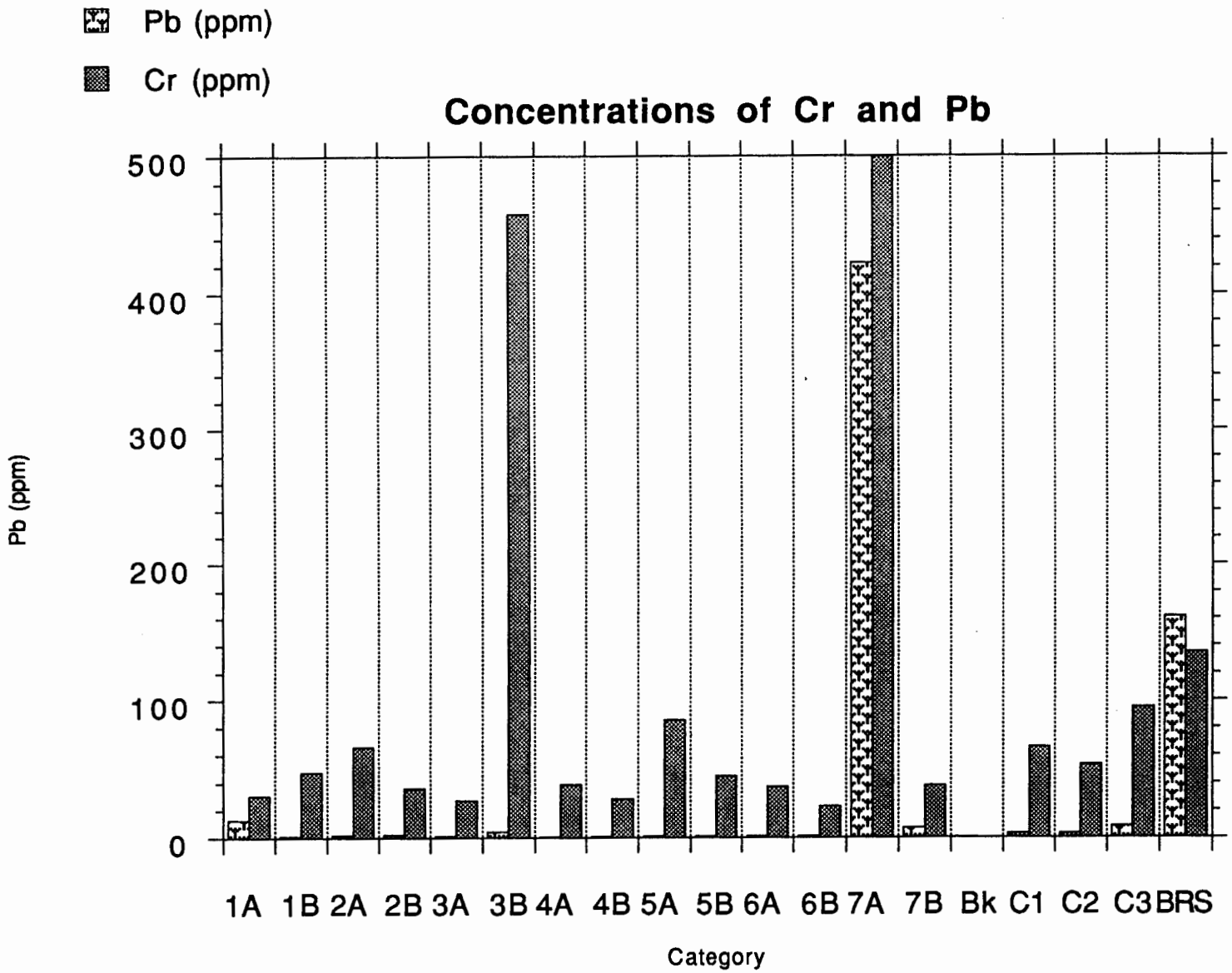
Figure 2

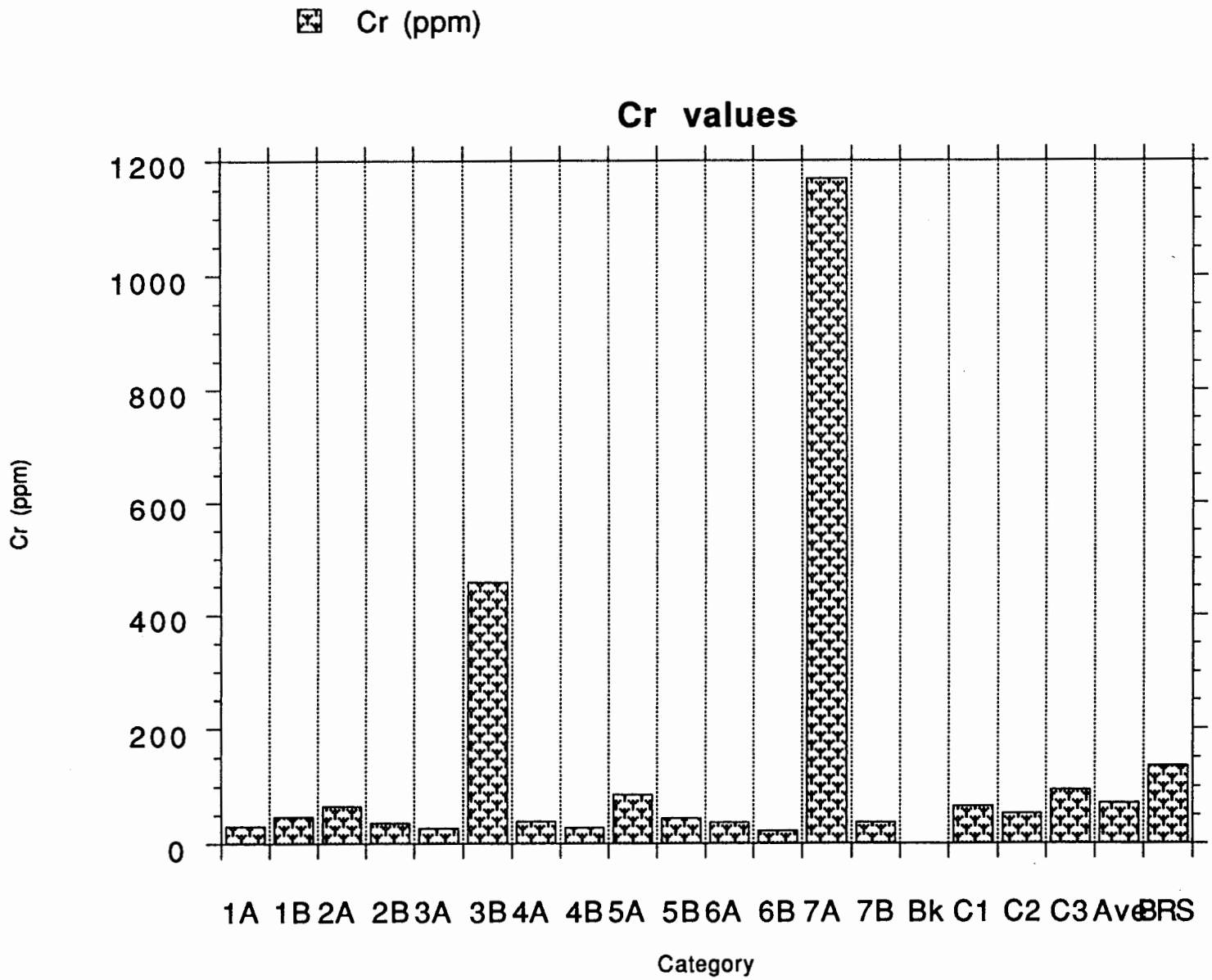
	Sample #	Pb (ppm)	Cr (ppm)
1	1A (rough)	13.080	30.590
2	1B	1.2700	47.630
3	2A (tee)	1.9400	66.030
4	2B	2.6800	36.150
5	3A (greens)	1.2700	27.140
6	3B	4.7000	458.18
7	4A (fringe)	0.93000	38.910
8	4B	1.0000	28.240
9	5A (fairways)	1.4700	85.490
10	5B	1.2800	45.000
11	6A (rough)	1.2600	36.980
12	6B	1.2700	22.910
13	7A (greens)	422.46	1169.2
14	7B	7.4000	37.800
15	Blank	0.47000	0.22000
16	Control 1	3.2000	66.270
17	Control 2	3.2000	53.210
18	Control 3	8.4600	94.400
19	Ave of Control	4.9500	71.290
20	BRS	161.00	135.00

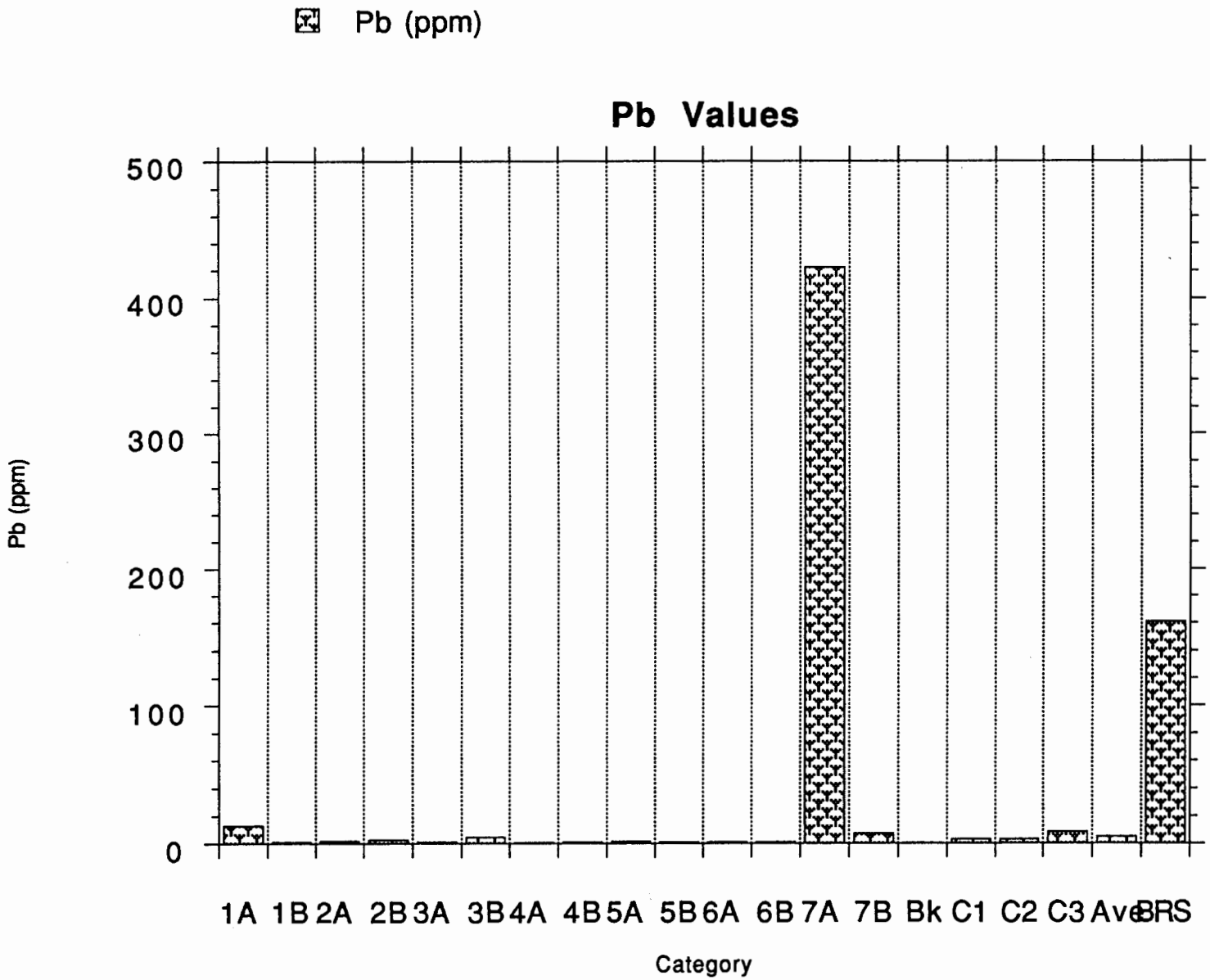
	Sample #	Pb (ppm)	Cr (ppm)
1	1A	13.080	30.590
2	6A	1.2600	36.980
3	Ave	7.1700	33.790
4	Std Dev	8.3600	4.5200

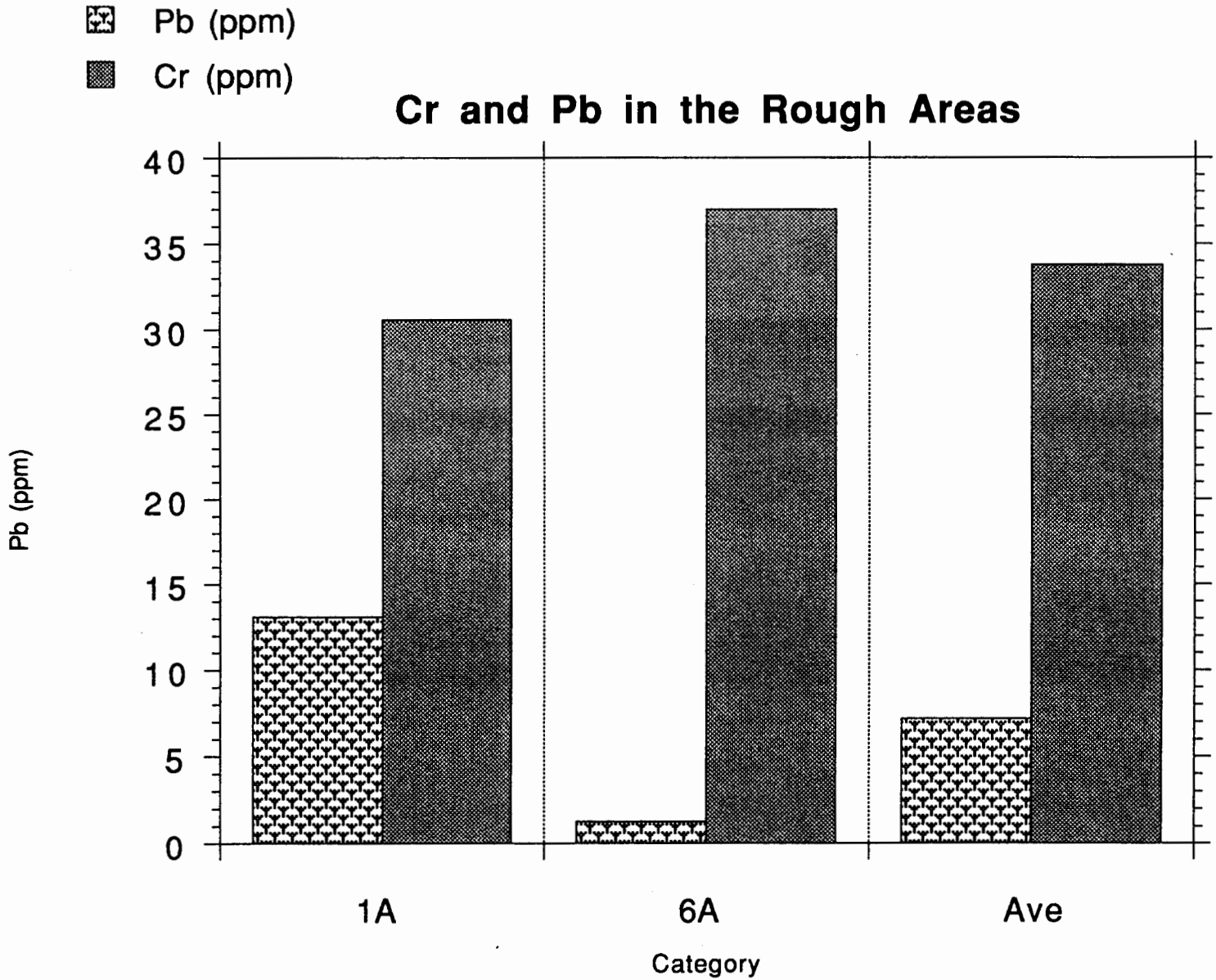
	Sample #	Pb (ppm)	Cr (ppm)
1	2A	1.9400	66.030
2	5A	1.4700	85.490
3	Ave	1.7100	75.760
4	Std Dev	0.33000	13.760

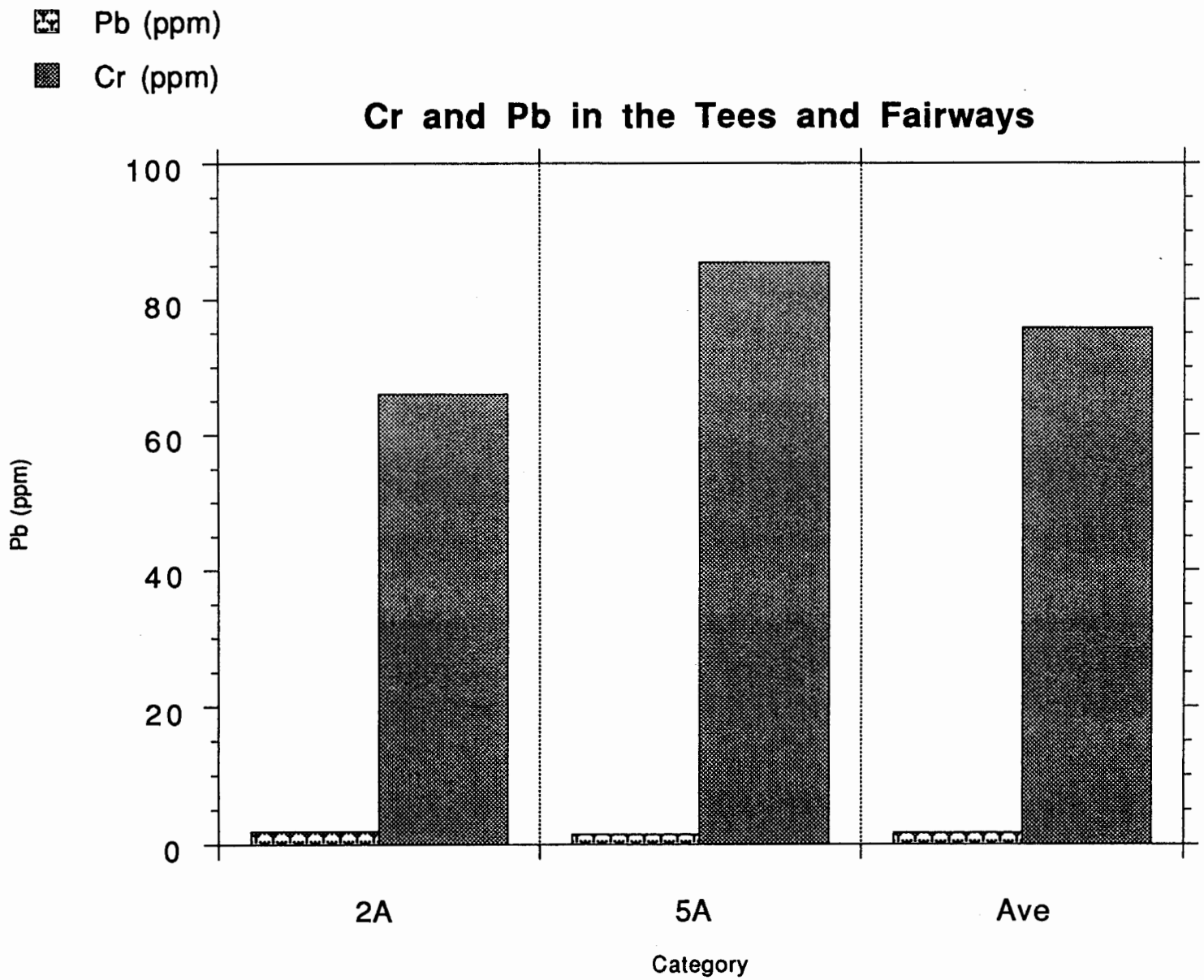
	Sample #	Pb (ppm)	Cr (ppm)
1	3A	1.2700	27.140
2	7A	422.46	1169.2
3	Ave	211.86	598.18
4	Std Dev	297.83	807.58

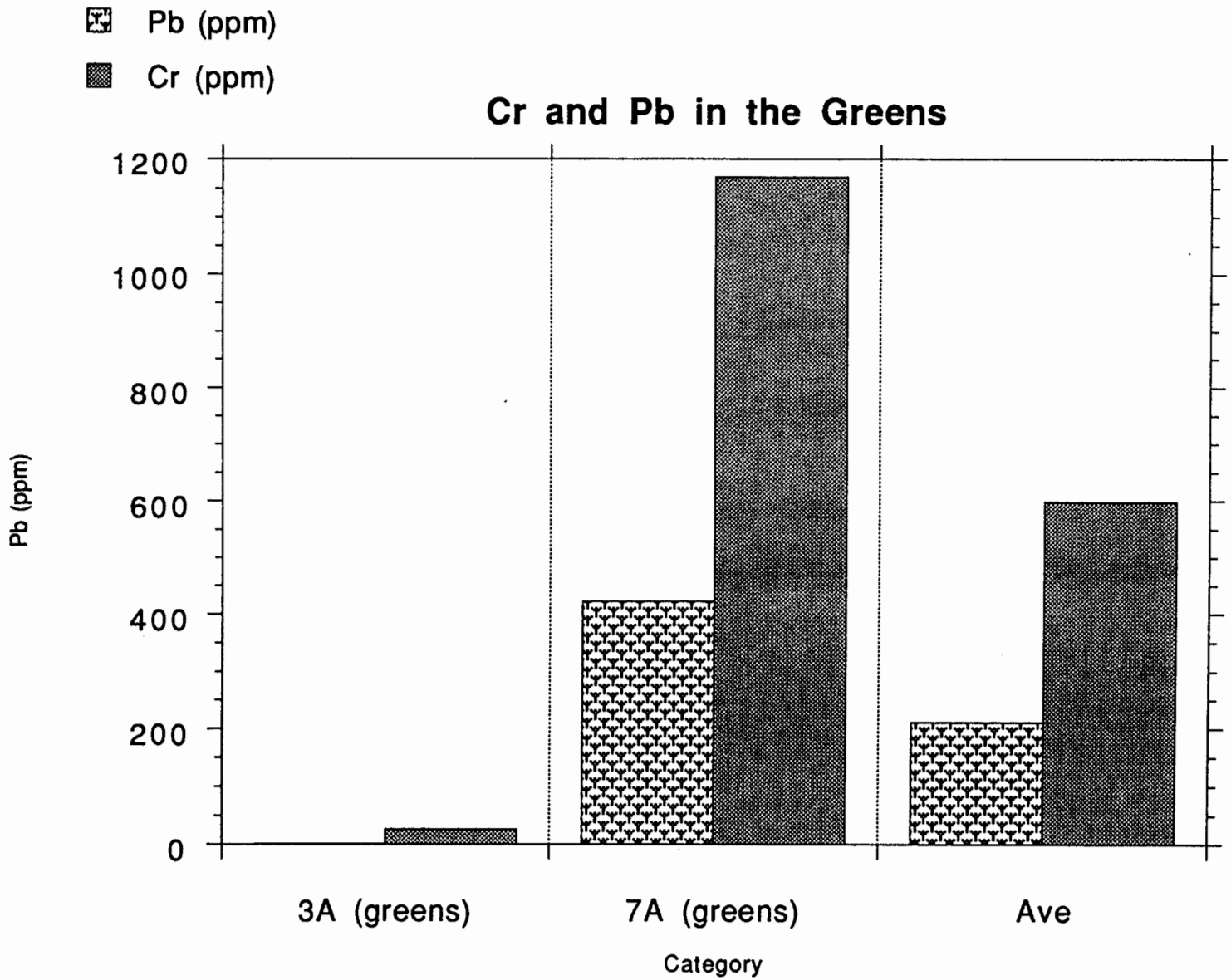

Pb (ppm)
Cr (ppm)
Concentrations of Cr and Pb
500
400
300
200
100
0
Pb (ppm)
1A 1B 2A 2B 3A 3B 4A 4B 5A 5B 6A 6B 7A 7B Bk C1 C2 C3 BRS
Category


Cr (ppm)
Cr values
1200
1000
800
600
400
200
0
Cr (ppm)
1A 1B 2A 2B 3A 3B 4A 4B 5A 5B 6A 6B 7A 7B Bk C1 C2 C3 Ave BRS
Category


Pb (ppm)
Pb Values
500
400
300
200
100
0
Pb (ppm)
1A 1B 2A 2B 3A 3B 4A 4B 5A 5B 6A 6B 7A 7B Bk C1 C2 C3 Ave BRS
Category


Pb (ppm)
Cr (ppm)
Cr and Pb in the Rough Areas
40
35
30
25
20
15
10
5
0
Pb (ppm)
1A
6A
Ave
Category


Pb (ppm)
Cr (ppm)
Cr and Pb in the Tees and Fairways
100
80
60
40
20
0
Pb (ppm)
2A
5A
Ave
Category


Pb (ppm)
Cr (ppm)
Cr and Pb in the Greens
1200
1000
800
600
400
200
0
Pb (ppm)
3A (greens)
7A (greens)
Ave
Category

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