

Cadmium Levels of Golf Green Soils

J. L. LEFTON and J.L. AHLRICHS

Agronomy Department

Purdue University

Introduction

Cadmium is not an essential element for either plants or animals. The need for information about cadmium levels in soils and plants has come with the environmental and health concerns associated with heavy metals. The soil represents a vast natural sink where cadmium and other heavy metals eventually are deposited either directly or indirectly. Once in the soil the metallic ions tend to accumulate although there is limited downward movement and some plant uptake.

A normal soil cadmium range of 0.01-0.70 ppm is quoted in the literature, the average being 0.06 ppm (Bowen, 1966). Values reported 15 Indiana sites by Pietz et al. (1978) range from <0.05 at Lafayette to 0.60 at a site near Gary where contamination is expected. The average content of cadmium in sandstone was reported by Bowen (1966) as 0.05 ppm, in limestone as 9.04 ppm, and in shale as 0.03 ppm. Cadmium is also geochemically associated with zinc materials such as ZnS (Lagerwerffs, 1972).

One of the land use situations receiving great doses of added cadmium is that of golf greens. Fortunately this use of soil is not typical and the crop is not harvested for human consumption. The high concentrations of cadmium expected in golf green soils can be attributed to the heavy use of cadmium fungicides, activated sewage sludge as a fertilizer source, and the use of phosphate fertilizers. In addition, there are natural sources of contamination from the air and rainfall, especially near cities and industrial areas. One would expect heavy accumulation of cadmium on greens to come primarily from the fungicide use in the 1950's and 1960's. Recent use has decreased because of a resistance of the pathogens to cadmium and with the advent of new controls.

Cadmium carbonate, cadmium chloride, cadmium sebacate, and cadmium succinate have been used as fungicides (Couch, 1962). The most commonly used cadmium fungicide for the control and prevention of the disease, dollar spot, *Sclerotinia homoeocarpa*, was a commercial product, Cadminate. It contained 60% cadmium succinate as the active ingredient, thus the product had 29% total cadmium. The manufacturer recommends that 0.5 oz Cadminate per 1000 sq ft (15g/100m²) per month be used on a preventative fungicide schedule. It was used extensively as a turf fungicide beginning about 1950. Today it is used less due to cadmium-resistant dollar spot strains.

Additional contributions of cadmium to agricultural or turf soils could come from some phosphate fertilizers and from activated sewage sludge fertilizers. Schroeder and Balassa (1963) reported 9-36 ppm Cd in the phosphate fraction of five fertilizers. The cadmium is primarily found in rock phosphate and super phosphate. Activated sewage sludges sold as slow-release sources of

nitrogen have only about 6% nitrogen so application rates of up to 100 lbs per 1000 sq ft (50kg/100m²) per year are not uncommon for golf greens. The trade name commonly used in turf management is Milorganite. The manufacturer reports that a representative sample of Milorganite contains 79 ppm Cd. Representative values from anaerabically-digested sludge produced by 10 different Indiana cities varied from 3 to 810 ppm and average 170 ppm Cd (Sommers et. al., 1973).

Thus golf greens were expected to be heavily contaminated with cadmium. The cadmium would be well equilibrated with the soil-plant system since much of the cadmium was added 10 or 20 years ago. The contaminated greens could therefore provide an excellent source of soil and plant material for cadmium research studies.

The objectives of this study were to develop simplifying modifications in a procedure for determining Cd in plant and soil material and to use the method to assay cadmium levels in representative golf greens to determine both the content and the vertical distribution.

Methods and Materials

Sampling Procedures:

The three main sampling locations were the Lafayette Country Club, Elks Country Club and The Purdue North Course, all in the Lafayette, IN vicinity. Three greens were randomly selected at each and four, one inch, cores were taken with a soil probe at random locations on each green. An additional sampling of three random cores were taken on the Purdue Experimental Green. The cores were separated into 0-3, 3-6, 6-9, and 9-12 inch layers and each analyzed separately.

To verify the prevalence of cadmium on golf course greens in general, seventeen greens from twelve different golf courses located all across the USA were sampled at 0-1" or 0-2" depths.

Samples were air-dried and crushed with a wooden roller to pass a 16-mesh aluminum screen.

*Digestion Procedures:*¹

1. A. 3.5 gram air-dried samples were placed in graduated 50 ml Folin-Wu N.P.N. tubes (Kimax 47125 or Corning 7940).
2. N-octyl alcohol (1 ml) was added to each to reduce frothing during digestion.
3. The samples were then placed in an aluminum heating block constructed as described by Nelson and Sommers (1972).
4. One Folin-Wu tube centrally located in the block contained mineral oil and a thermometer to determine the operational temperature of the block.
5. Twelve ml of concentrated HNO₃ (70%) was added and 25 mm diameter funnel was placed on top of each tube to maintain a constant reflux of the liquid.

¹ A modification of the procedure for total cadmium used by the Analytical Lab, Bionucleonics, Purdue Univ., W. Lafayette, Indiana 47907.

6. The aluminum block was then placed on an electric hot plate at a temperature of 110 C for approximately 15 hours of predigestion.
7. After the pre-digestion the samples were cooled to room temperature, three ml of fuming HNO_3 (90%) was added and they were reheated to 100 C. Digestion was considered complete when brown NO_2 fumes disappeared.
8. The samples were cooled to room temperature and diluted in the tubes to the 35 ml mark with distilled water.
9. The samples are then filtered through Whatman 42 filter paper into 50 ml Erlenmeyer flasks for reading on a Jarrell-Ash Model 82-526 Atomic Absorption Spectrophotometer.
10. Cd solutions were prepared containing 2, 1, 0.5 and 0.1 ppm for the standard curve.

TABLE 1. Cadmium Concentrations from 5 Different Samples. (A Comparison of the Results Obtained by the Method Described, and the Results Obtained by the Analytical Lab, Bionucleonics, Purdue University, West Lafayette, Indiana).

Sample Location	ppm Cd ^a	ppm Cd ^b
Purdue University Golf Course, G.11	15.3	19.2
Lafayette Country Club, Practice Green	9.1	10.2
Elks Country Club, G.9	2.3	2.5
Elks Country Club, G.18	1.8	ND ^c
Elks Country Club, G.18	43.5	50.3

^a Results from the method described in this paper.

^b Results from the method utilized by the Analytical Lab, Bionucleonics, Purdue University, West Lafayette, Indiana.

^c Not detectable.

Results and Discussion

Analytical Procedure

The development of an analytical procedure for total cadmium that would be rapid, easy to duplicate, and accurate was one of the objectives of this study. The low level of cadmium in most samples requires a digestion method which will handle several gram sample sizes with minimum dilution.

The accuracy of the tube digestion method with 3.5 gm sample was evaluated by comparison to the cadmium values obtained on five representative samples by the analytical lab for the cadmium project¹. The results (Table 1) of this investigation show a close agreement between the two procedures. The further substantiate the accuracy of the tube digestion method, recovery tests of added cadmium chloride ranged from 95 to 100%. This range was considered satisfactory for this particular study. Also the same check sample (Purdue North

¹The Analytical Lab, Bionucleonics, Purdue University, utilize a nitric acid digestion in Erlenmeyer flasks on a hot plate and determines cadmium on a Perkin-Elmer 304 atomic absorption Spectrophotometer.

Golf Course, Green 11, the 3-6 inch depth) was in each set of digestions run on the Lafayette vicinity samples. In each case the concentration of this sample did not vary measurably from the initial value of 2.5 ppm Cd.

The N-octyl alcohol and nitric acid used in the digestion procedure contained no detectable cadmium.

Since the accuracy of the volume calibration of the tubes is $\pm 0.8\%$, dilution directly in the digestion tubes was considered adequately precise. By diluting in the tubes, the chance for error in transferring digests is eliminated, and time and labor are reduced.

It is estimated that a technician could analyze 500-600 samples per week utilizing two aluminum blocks with the method described. Thus, the proposed method represents an accurate, rapid and simple method for determining total cadmium in soil samples.

Cadmium Levels in Golf Green Samples.

The results (Table 2) show that the highest concentration of cadmium is in the top movement of cadmium vertically in the profile. Lagerwerff et al. (1970) found a similar situation for roadside soils contaminate with cadmium.

TABLE 2. *Cadmium Contents of Golf Greens Sampled at Four Locations, and at Four Depths*^a

Sampling Location ^b		Soil Profile Layer, inches			
		0-3	3-6	6-9 (ppm Cd)	9-12
Elks C.C., West Lafayette, Indiana	G. 9	46.1	2.9	1.8	1.9
	G. 18	61.6	3.2	2.0	1.7
	P. G.	68.5	3.0	2.1	1.7
Purdue North Golf Course, West Lafayette, Indiana	G. 9	38.1	3.6	2.6	2.6
	G. 11	21.4	2.4	1.9	1.4
	G. 3	51.0	2.7	1.6	1.8
Lafayette C.C., Lafayette, Indiana	G. 7	35.5	3.9	3.5	2.3
	P. G.	8.3	7.4	2.8	1.8
	G. 9	33.0	3.0	2.4	2.1
Purdue Experi- mental Putting Green, West Lafayette, Indiana		17.1	3.6	2.9	1.9
	Average	38.1	3.6	2.4	1.9

^a Averages of triplicate samples and duplicate analysis.

^b Samples are identified according to country club, city, state, and G (green).

For golf greens, the higher concentrations of cadmium in the surface can be attributed to several factors. To maintain resiliency on the surface of putting greens it is common practice to maintain a 0.25-0.50 inch thatch layer. The thatch layer offers a vast sink for chelation as well as exchange sites for heavy metals added to the surface. In addition, the use of hard water on golf greens tends to make most putting greens calcareous at the surface. The excessively high levels of phosphorus¹ found in a majority of greens also increases the possibility of precipitating cadmium in the surface layer.

Only the practice green (Table 2) at the Lafayette Country Club was appreciable lower in total cadmium in the 0.3" layer, as compared to the other surface samples. This would be expected since this green was established recently. There has been less cadmium fungicide applied, less phosphorus fertilizer used, and less thatch build-up when compared to the other greens.

Statistical studies showed the cadmium levels to vary from green to green on the same golf course and between golf courses. For the Elks Country Club the mean value of cadmium² in the 0-3" layer varied from 46.1 to 68.5 ppm Cd. For the Purdue North Golf Course the variation was from 21.4 to 5.1 ppm Cd. For the Lafayette Country Club the variation was from 8.3 to 35.5 ppm Cd. This type of variation would be expected since golf greens vary in their construction, in slope, in compaction, in water application, and in the rate and frequency of cadmium fungicide application.

In addition, variation in the cadmium levels existed in the lower portion of the profile of the greens. This can be attributed to differences in the internal water movement, layering within greens, and a variation in internal porosity of greens. The mean value of cadmium² in the 3-6" layer ranged from 2.5 to 3.9 ppm Cd. An exception to this was the practice green at the Lafayette Country Club. The mean value for cadmium² for this layer was 7.4 ppm Cd. Since the green is fairly new, the reduced compaction and a corresponding greater porosity in the top 6 inches of the profile would yield high infiltration and percolation rates. Also contributing to the movement of cadmium in this particular sample is the lack of organic matter in the surface. The thatch layer for this green was minimal when compared to the other samples.

The cadmium content of samples within greens also varied significantly. The greatest source of error here would come from uneven application of the fungicide. In addition, variations in compaction, slope and moisture application on the same green could cause the varying cadmium contents.

The high cadmium levels in the 9-12" layer is of special interest. Even at this depth the cadmium level is still considerable above the normal soil cadmium level of 0.06 ppm (Bowen, 1966). Follow up studies on green 9 of the Purdue North Course showed that cadmium levels did not reach background levels until the 24" depth.

¹From the Midwest Turf Leaflet No. 16, 86% of the 1600 golf green samples tested by the Soil Testing, Laboratory of Purdue Univ. were excessively high in phosphorus (greater than 100 lbs. P/A).

²The mean cadmium level was determined from triplicate samples and duplicate analysis.

The 17 greens representing 12 golf courses across the USA (Table 3) illustrate the prevalence of the cadmium enrichment. The lowest surface soil value found was 4.2 ppm which is much above normal levels. The high value is the 80 ppm of the University of Michigan country club green 16. This is the oldest green in the collection being over 40 years old. It represents the accumulation of cadmium from many years of use in a part of the country where its use for disease control started early.

Summary

Digestion of soil samples for cadmium requires a concentrated digestate to maintain sufficient cadmium concentration for analysis. The 3.5 gm samples were handled well in the Folin-Wu tube digestion by long digestions at low temperature, use of N-octyl alcohol as antifoaming agent and use fuming HNO₃ acid for final digestion. The advantage of this block digestion system is the great number of large samples that can be digested simultaneously with minimal attention.

TABLE 3. *Cadmium Contents of surface soil samples from Greens of 12 additional Golf Courses ^a.*

Sampling Location	Green No.	ppm Cd
Old Warson C.C., St. Louis, MD	10	7.8
Big Spring C.C., Louisville, KY	17	12.0
Point-O-Woods, Benton Harbor, MI	1	16.8
Browns Run C.C., Middleton, OH	15	10.4
Oakwood C.C., Cleveland, OH	15	31.0
Riverside C.C., Battle Creek, MI	2	4.2
Univ. of Mich. C.C., Ann Arbor, MI	16	80.0
Goodyear Golf & C.C., Litchfield Park, AR	15	5.2
Silver Lake C.C., Silver Lake, IL	10	6.1
Sunset C.C., St. Louis, MO	2	8.4
Sunset C.C., St. Louis, MO	10	10.4
Edgewood C.C., Cincinnati, OH	4	7.0
Edgewood C.C., Cincinnati, OH	16	10.3
College Park, MA	8	8.6
College Park, MA	10	7.0
College Park, MA	12	5.8
College Park, MA	15	7.8
Average		14.0

^a Results are averages of duplicate analysis on samples taken from 0-1" depth with thatch removed excepting College Park samples which were 0-2" depth.

Cadmium contents on old greens is particularly high in the surface 0-3 inches, is still above normal at 9-12 inch depths, and in one green which was studied to greater depths the cadmium levels returned to normal at 24 inches.

There is great variation in cadmium levels between golf courses, between greens on a course and within greens. These undoubtedly arises primarily from variation in rates of cadmium fungicide used and from movement patterns affected by physical and chemical properties of the green and its soil.

Samples from greens all across the USA showed modest to very great contamination with cadmium. The levels appear to be related to the age of the green and the use of cadmium salts as fungicides.

The soils, the microfauna, and the grass on the greens have been reacting with the cadmium for many years. Thus, we have an excellent source for high cadmium soil, microfauna and plant tissue from an already equilibrated system for future scientific studies.

Acknowledgements

The authors appreciate assistance received from R.P. Freeborg, A. Hegab, and W.P. Miller in the sampling and analytical work.

Literature Cited

1. BOWEN, H.J.M. 1966. Trace elements in biochemistry. Academic Press, New York. p. 179.
2. LAGERWERFF, J.V. 1972. Lead, mercury, and cadmium as environmental contaminants. Soil Science Society of America, Madison, Wisconsin p. 619-628.
3. LAGERWERFF, J.V., and A.W. SPECHT. 1970. Contamination of roadside soil and vegetation with cadmium, nickel, lead, and zinc. Environ. Sci. Technol. 4:583-586.
4. NELSON, D.W., and L.E. SOMMERS. 1972. A simple digestion procedure for estimation of total nitrogen in soils and sediments. J. Environ. Quality. 1(4):423-425.
5. PIETZ, R.I., R.J. VETTER, D. MASARIK, and W.W. MCFEE. 1978 Zinc and Cadmium Contents of Agricultural Soils and Corn in Northwestern Indiana. J. Environ. Quality (accepted for publication)
6. SCHROEDER, H.A., and J.J. BALASSA. 1963. Cadmium: uptake by vegetables from superphosphate by soil. Science 140:819-820.
7. SOMMERS, L.E., D.W. NELSON, J.E. YAHNER, and J.V. MANNERING. 1973. Chemical Composition of Sewage Sludge from Selected Indiana Cities. Ind. Acad. Sci. 82:424-432.