WILLIAM DRAPER HARKINS:
AN EARLY ENVIRONMENTAL CHEMIST IN MONTANA (1900-1912)

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William Draper Harkins (1873-1951) is no longer the household name among chemists that it was earlier this century. As a physical chemist at the University of Chicago for nearly forty years, he was well known for his research in nuclear and atomic structure and isotope separation, as well as surface chemistry, for which he received the Willard Gibbs gold medal from the ACS Chicago Section in 1928(1). In a posthumous tribute to Harkins, the Nobel laureate Robert S. Mulliken recalled (2):

When I came to Chicago as a graduate student in 1918, it was because I had read about Harkins' pioneering work toward the understanding of nuclear structure, a subject ignored at that time by American physicists. In fact, during the period 1913-1928, Harkins and his students were the only Americans engaged in work relating to the structure of the atomic nucleus.

Scientists outside Harkins' area of research also recognized the importance of his work; for example, in 1923 Harvey W. Wiley grouped him with Soddy, Aston, and Rutherford in connection with his knowledge of "the constitution of the atom" (3).

Prior to his career at Chicago, however, Harkins spent a dozen years a the University of Montana in Missoula, where for much of that time his research interests were directed towards what would now be called environmental chemistry. After receiving his B.A. in chemistry from Stanford University in May, 1900(4), he became Instructor in Chemistry and Physics (1900-1901) and the Professor and Head of Chemistry (1901-1912) at Montana. Chemistry prospered under Harkins' leadership, and his first departmental report outlined the changes he had already made or was planning to make in the curriculum: a new course in physical chemistry; expansion of introductory chemistry from one semester to a full year; new courses in inorganic preparations, organic analysis, and gas analysis once the necessary equipment arrived from Germany; a new course in industrial chemistry in conjunction with the Department of Mechanical Engineering; and a lecture course in analytical chemistry to supplement the existing laboratory work(5).

The University of Montana had begun offering graduate study before the turn of the century—the first master's degree was awarded in geology in 1899 (6)—and in his report for 1902-1903 Harkins mentioned the three graduate students then studying chemistry (7):

Two of these work in the laboratory from eight to ten hours per day, Saturdays included. The third, Mr. Martin Jones, spends most of his time in the chemical laboratory working upon the analysis of Montana Ores, his thesis for the Masters Degree being upon this subject.

Another candidate for the master's degree was George Westby, a 1901 graduate of the University and subsequently Chief Chemist of the Washoe Smelter at Anaconda. The topic of his thesis, which was apparently
never completed, “An Examination of the Waters of Montana,” prompted Harkins to write (7):

It is of great importance to the people of any community to know whether the water they are using is pure or impure. If the former, no one need be afraid of moving into the community and using the water in abundance; if the latter, steps should be taken at once to purify the water, or to obtain a new source of supply.

Interestingly, while he was directing graduate students in chemistry, Harkins held no advanced degree himself, though in the summer of 1901 he had enrolled in some graduate courses at the University of Chicago: Advanced Experimental Physics, Special Methods in Quantitative Analysis, and Inorganic Properties. He returned to Chicago again during the summer of 1904 to take three more graduate courses: Kinetic Theory, Hertzian Waves, and Chemical Research (8). During the fall semester of 1905, he took a leave of absence from his teaching duties at Montana to register as a graduate student at Stanford. In his report for that academic year Harkins wrote about himself in the third person (9):

During the last half of the year 1905, the Professor of Chemistry was absent on leave without pay, and spent the time in research work at Leland Stanford, Jr., University. It is impossible, at the present time, for any college teacher of science to keep from growing rusty in his own line of work, unless he is given frequent leaves of absence in order that he may learn what other workers in the same subject are doing. This is particularly true in the Rocky Mountain states, where, especially in the case of Chemistry, there are very few scientists of note. . . . It would be, then, good policy for the institution, as is already done in most of the other leading institutions, to give the instructors a leave of absence on pay each seventh year, on condition that this year be spent in research or study at some great university, or in some laboratory in which first class research work is done.

At nearly the same time that Harkins wrote this appeal, he was negotiating for the position of Head of Chemistry at the University of Nevada, and one of his major negotiating points, along with a significant increase in salary, was the possibility of paid leaves of absence (10). As a graduate student at Stanford, Harkins carried out his research under the direction of Robert Eckles Swain (1875-1961), who had received his B.A. from Stanford only a year before Harkins. Awarded a Ph.D. in biochemistry in 1904 by Yale University (11), where he studied with the physiological chemist Lafayette Mendel (1872-1935) (12), Swain had become interested in the effects of industrial pollutants on human health and the environment. He undertook several surveys and
investigations of smelter operations for the Federal government and acted as a consultant to many large-scale pollution studies (13). From 1905 to 1907 he worked with Harkins on the effects of the smelter emissions at Anaconda on nearby plant and animal life. On January 10, 1908, Stanford University awarded Harkins its first Ph.D. in chemistry (14). His thesis was published in 1907-1908 as a series of three papers under the general heading *Papers on Smelter Smoke* (15).

Harkins was again on leave from his regular teaching duties during the fall semester of 1909. In May of that year, he sailed from New York to Liverpool on the *Lusitania*. First, he attended the International Congress of Applied Chemistry in London (16), and then he spent the summer doing research with Fritz Haber at the Institut für physikalische Chemie in Karlsruhe, where he was given a project on surface tension. For the fall semester he was at the Massachusetts Institute of Technology, working with Arthur Amos Noyes and Gilbert Newton Lewis on electrolyte solubility (17). In his acceptance speech for the Willard Gibbs medal nearly twenty years later, Harkins recalled (18):

As an undergraduate, research appealed to me as one of life’s great adventures . . . While the study of the atom and of radioactivity, then a new subject, had an extreme fascination, there were two subjects of investigation in physical chemistry which seemed to me of such minor importance that I took a firm resolution never to be enticed into working on either of them. These two fields of work were surface tension and solubility.

Luckily for Harkins, Haber and Noyes overcame his undergraduate resolution since these two fields proved influential in shaping his later research interests (19).

From MIT Harkins returned to Montana for only two more years before leaving for the University of Chicago. In addition to his academic duties during his twelve-year stay in Missoula, Harkins was also president of the Missoula Board of Health and acted as a consulting chemist for the U.S. Justice Department, the Mountain Copper Company, and the Deer Lodge Valley Farmers’ Association (20). The latter two organizations were specifically mentioned by Ebaugh (21) for their roles in the growing "number of damage suits brought against smelting companies" beginning about the turn of the century. In another well-known case involving pollution by two copper companies near Ducktown,
Tennessee (22), Harkins was called to testify as an expert witness (23). Although publications on smelter problems in the U.S. at this time usually cited work carried out in Germany in the second half of the nineteenth century (24), there was increasing scientific interest in such work in America as evidenced by the more than seventy entries of articles and patents under the subject heading "Fumes, smelter" in the First Decennial Index (1907-1916) of Chemical Abstracts.

Of all of Harkins' consulting work, however, his longest and most extensive was with the Deer Lodge Valley Farmers' Association, for which he investigated the effects of smelter emissions at Anaconda on plant and animal life during the years 1902-1910 (25). Anaconda had been the site of smelting operations since 1884, when Marcus Daly, Montana's "Copper King," built the first smelter there for the Anaconda Copper Mining Company (26). Emissions from these operations had denuded the surrounding area of vegetation, which consisted mainly of shrubs that were considered useless, so their loss was not seen as a serious problem (27).

In January 1902, however, the Anaconda Company replaced its two existing smelters, which had a combined capacity of 4,000 tons of ore per day, with a much larger single facility, the Washoe Smelter, with a capacity of 12,000 tons per day and four 225-foot smokestacks. In less than a year farmers in the vicinity of the new smelter reported the deaths of hundreds of sheep and cows, along with nearly 2500 horses (28).

In November 1902 Harkins began measuring arsenic concentrations in plants and soils at numerous locations within fifteen miles of the new smelter, and for these analyses he successfully modified the Marsh method for his samples, which contained iron (29). By heating the Marsh generator (Fig. 4) to 100°C, he was able to eliminate the interference of iron in the quantitative reduction of arsenic oxides to arsine. His arsenic determinations on a series of eleven test samples, each containing 1.88 mg of arsenic and varying amounts of iron up to 0.4 g, all show an error of less than about 4% (30).

As a result of the deaths of so many animals and the high arsenic concentrations found in grass and hay in the valley around Anaconda, the company shut down the new smelter from July through September of 1903 in order to install a new system of flues and a 300-foot smokestack, which were expected to reduce the amounts of arsenic, copper, and sulfur dioxide in the emissions.
Animal deaths decreased dramatically, at least for a while, and in early 1905 the company announced that the modifications to the smelter had achieved their objective. The farmers, however, were not so sure; they believed that the problems had merely been altered, not eliminated, as the taller smokestack spread the smelter's emissions over a different—and larger—area than before (31). Their lawsuit against the Anaconda Company, filed in May 1905, eventually resulted in a small monetary award, but the judge refused to issue an injunction against the company, ruling that the smelter operation was of greater importance to the region than agriculture. The considerable attention generated by the case sparked several scientific investigations into the area's problems, including the studies of Harkins and Swain (32).

Beginning in mid 1905, Harkins and Swain carried out velocity determinations and chemical analyses on the smelter emissions from the 300-foot smokestack. On the basis of four samplings in July and August, they found that the smoke moved at an average velocity of 52.88 feet per second and that the stack emitted nearly 2.3 billion cubic feet of smoke per day (measured at an average outside temperature of 17°C). Their chemical analysis of the smoke, based on the same four samplings, is given as an average daily discharge in Table I (33).

As an indication of the extreme amounts that these figures represent, current EPA standards for primary copper smelters require that gaseous emissions contain no more than 0.065% sulfur dioxide by volume (34), whereas the average percent determined by Harkins and Swain was 1.493% (33). These same EPA standards also limit the particulate matter emitted to 50 mg/m$^3$ and arsenic to 75 kg/h (34), considerably less than the values of 1000 mg/m$^3$ and 848 kg/h, respectively, calculated from Harkins and Swain's data for the Washoe Smelter.

Harkins and Swain (35) concluded that while the new flue system had indeed reduced arsenic and copper emissions to the atmosphere, significant amounts of arsenic trioxide, which condensed to the solid state in the flue, were still being discharged because it was too fine to settle out of the smoke moving at the observed velocities. They also concluded that the taller smokestack had decreased the amount of arsenic deposited in the immediate vicinity of the smelter but spread it over a greater area instead, just as the farmers had claimed. This was true for all the substances examined, and thus the damage to trees and other vegetation from sulfur dioxide extended to areas that had previously escaped its effects. By 1910 emissions from the Washoe Smelter had affected approximately 570 square miles of surrounding territory, a considerably larger area than that affected before the operation of the taller smokestack (36).

Harkins and Swain also investigated the amounts of arsenic and copper in vegetation, especially hay and wild grasses (37), and the arsenic poisoning of herbivorous animals (38) in the area surrounding the Washoe Smelter. Table II (39) lists some of Harkins' analyses carried out prior to the installation of the flue system and the construction of the taller smokestack (samples 1-5), and then shortly after the smelter resumed operation (samples 6-9). Harkins collected samples 2 and 5 from the same farm, but the former had been exposed to smelter emissions for approximately six months, while the latter, cut in July and stacked, had been exposed for less than three months. This difference in arsenic values was "fairly representative of a condition which will be found to prevail with notable uniformity throughout the analyses" (40). Samples 6 and 7 were collected shortly after the smelter had been restarted following its three-month shutdown, while sample 8 was exposed to smelter emissions for an additional month during a very dry period. The large arsenic value for sample 9 suggests that because of "its peculiar matted growth the moss may have collected the arsenic which fell upon it like a natural fiber, and held on to it from the previous year" (40).
Both by himself and in collaboration with Swain, Harkins continued to collect samples of vegetation from the vicinity of Anaconda for arsenic analysis at least through October 1907. Although these analyses by themselves did not justify any conclusions about the distribution of arsenic throughout the area, they did, in conjunction with arsenic analyses of soils and of the “finely divided dark-gray powder” (41) that collected everywhere in the vicinity of the smelter, lead to “only one interpretation, which is that the smelter smoke is the source of the arsenic found in such excessive amounts in the vegetation of the region around Anaconda” (42).

The final article in Harkins and Swain’s series Papers on Smelter Smoke(15) focused on the large number of deaths of sheep, cows, and horses around Anaconda after the start-up of the new smelter in 1902. Harkins himself observed the carcasses of hundreds of animals during his travels over 100 square miles of territory surrounding Anaconda in November 1902. Many of these and other animals were dissected, and almost all of them gave evidence of acute or chronic arsenic poisoning (43). After tabulating the arsenic analyses of 82 organs, tissues, and fluids from nearly as many animals, Harkins and Swain tried to relate the amounts of arsenic ingested by some of the animals to the amounts found in their livers. This proved extremely difficult, however, and their attempt was unsuccessful. On average, they found larger amounts of arsenic in those animals kept closer to the smelter, but concluded that the condition of any particular animal was a more important factor in the retention of arsenic in the various tissues (44).

At the time of Harkins’ work, there was not much data available on the arsenic poisoning of livestock, and the little that was available was often contradictory. Therefore, to compare the arsenic concentrations in tissues of the autopsied animals and also to try to determine lethal amounts of arsenic, Harkins and Swain fed known amounts of arsenic to horses and sheep and then analyzed various tissues for their arsenic concentrations after the animals’ deaths. These results, as well as those of other experiments they undertook toward the same ends, proved inadequate to provide much insight into their study of the effects of arsenic on animals in the Anaconda region. As Harkins and Swain somewhat ruefully concluded (45):

> The question of the amount of arsenic which will kill a farm animal, if fed daily, is a very important one to the chemist who undertakes to investigate the conditions existing in smelter regions. The effects depend so greatly upon the conditions that even after such an extensive investigation as that carried out by the veterinarians, pathologists, bacteriologists, and chemists, upon the present case, no very definite statements can be made in regard to this point. A study of Table I [Arsenic and Copper in Grass and Hay] of the second paper of this series will give some idea of the poisonous dose, for on almost all of the ranches listed, animals have been supposed to die from arsenical poisoning. On the other hand, there is almost no place in the farming district where some of the animals will not survive.

Despite the inconclusiveness of their investigations into the deaths of animals in the Anaconda region, Harkins and Swain gathered and published a large amount of valuable scientific data about a smelter region at a time when such conditions were not usually recognized as environmental problems nor generally considered appropriate topics for scientific investigations. Their work helped establish Swain’s reputation in this field and led directly to his participation in a subsequent study of the Anaconda area for the Department of Justice (46).

For Harkins, however, these investigations represented only the opening chapter in a long and distinguished research career. By 1909 his attention was already shifting toward some of the topics that would occupy him for the rest of his life, and within the next two years his top priority was to find an academic position more conducive to his new interests. In 1912 he moved...
to such a position at the University of Chicago, leaving behind the smelter problems at Anaconda and his career as an early environmental chemist in Montana.

REFERENCES AND NOTES


10. Correspondence between Harkins and J. E. Stubbs, President of the University of Nevada, August 1906. Harkins' inquiry about leaves of absence is in the copy of his telegram dated August 12, 1906. Box 1, Folder 3 of the William D. Harkins Papers in the University of Chicago Library Special Collections. Harkins decided against accepting the position at Nevada.


14. Miscavage, Ref. 4; Hutchinson, Ref. 4, p. 87.


16. The article "University Honored," Weekly Kaimin, April 28, 1909, pp. 1+, contains this information, but also mistakenly reports that Harkins would be "doing research work with Professor Nernst in the University of Berlin." Whether this was simply a mistake on the part of the student reporter or a later change in Harkins' plans for some reason is unknown.

24. See, for example, the references to German literature given in footnotes in Harkins and Swain, 1907, Ref. 15, pp. 970, 998.


27. Taskey, Ref. 25, p. 20.


30. Harkins, Ref. 29, Table III, p. 522.

31. Harkins and Swain, 1907, Ref. 15, pp. 973, 996.

32. Taskey, Ref. 25, pp. 6, 22; Wells, Ref. 26, pp. 8-11.

33. Harkins and Swain, 1907, Ref. 15, p. 994.


35. Harkins and Swain, 1907, Ref. 15, pp. 995-996.

36. This area is estimated from the extent of damage in different directions from the smelter as given by Taskey, Ref. 25, p. 49.

37. Swain and Harkins, Ref. 15.

38. Harkins and Swain, 1908, Ref. 15.


40. Swain and Harkins, Ref. 15, p. 920.

41. Swain and Harkins, Ref. 15, pp. 923.

42. Swain and Harkins, Ref. 15, p. 926.

43. Harkins and Swain, 1908, Ref. 15, p. 928.

44. Harkins and Swain, 1908, Ref. 15, pp. 932-934.

45. Harkins and Swain, 1908, Ref. 15, p. 939.


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