Arsenic Residues in Agricultural Soils of Southwestern Ontario

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Determination of arsenic residues in farm soils in southwestern Ontario showed the highest residue levels in orchard soils. Residues in four apple orchards were 10.2, 23.1, 39.4, and 107 p.p.m. of arsenic between the trees, and 15.6, 44.9, 67.0, and 121 p.p.m. under the trees. One vegetable soil contained 26.6 p.p.m. of arsenic. The remainder of the 32 farm soils sampled contained residues of less than 10 p.p.m. of arsenic, the normal range for untreated soils. Strata studies conducted on one orchard soil showed a fairly uniform vertical distribution of arsenic residues in the top 6 inches of soil. An improved standard-taper all-glass apparatus, for more efficient absorption of arsine gas in the arsine–molybdenum blue method for arsenic is described.

Arsenic accumulation in soils has been reported and reviewed by a number of authors (Albert, 1933; Bishop and Chisholm, 1962; Blodgett, 1941; Vandecaveye, 1943). The U. S. Department of Agriculture Yearbook of Agriculture (1938) states, "Arsenic is present in all soils, varying from a few tenths of one part per million to over 500 parts per million. Most soils contain less than 10 parts." Bishop and Chisholm (1962) reported finding up to 124 p.p.m. of arsenic in orchard soils in Nova Scotia. They also discussed the relation of total arsenic to soluble arsenic and phytotoxicity. No reports were found on arsenic levels in the agricultural soils of Ontario. There is some evidence (U. S. Department of Agriculture, 1957) that arsenic residues will remain in soils for some years after being deposited from crop sprays. Lead arsenate was used for a number of years for hornworm control on tobacco in Ontario, but has been replaced by organic insecticides. However, lead arsenate is still recommended in Ontario for insect control on apples, cherries, pears, plums, currants, and gooseberries. This paper reports on arsenic residues in orchard, vegetable, grain, and tobacco soils in southwestern Ontario.

METHOD

Soil samples, 0 to 6 inches deep, were collected in October and November 1964, and April 1965. Soil types included sand, sandy loam, clay, clay loam, and muck. Location of the farms and description of sampling procedure are included in the paper by Harris *et al.* (1966), which reports on the complete assay of organochlorine residues in these soils.

Five-gram air-dried soil samples were digested in concentrated sulfuric acid with dropwise additions of 50% hydrogen peroxide as described by Polley and Miller (1955). From one highly contaminated orchard, strata soil samples were taken from 0- to 2-, 2- to 4-, and 4- to 6-inch depths in order to assess the vertical distribution of the arsenic residues. Arsenic analyses on the extracts were carried out by the arsine–molybdenum blue method of Hoffman and Gordon (1963) with modification of the evolution and absorption apparatus as described below.

Modification of Arsine–Molybdenum Blue Apparatus. The arsenic apparatus described by Hoffman and Gordon (1963) was modified because leaks of arsine gas occurred at the rubber-stoppered joints. An apparatus was constructed using a 60-ml. ⅎ reagent bottle as the evolution chamber. The trap and absorber were also fitted with ⅎ ground joints. This apparatus, which used a ⅎ 19/38 outer ground joint as the absorber, eliminated the leakage. However, in subsequent tests, only 82.5% recovery (up to 30 μg. of As) was obtained. Above 30 μg., recovery was erratic. Since it appeared that the poor recovery was due to lack of height of the absorbing liquid, new absorbers were constructed using Quickfit 14/23 inner joints (i.d. 1.0 cm.). When these absorbers were filled with glass beads, and the recommended volume (3.0 ml.) of sodium hypobromite solution was used, the effective absorbing height was increased 2.5 times. The complete apparatus is shown in Figure 1. A glass plug was used at the bottom of the absorber to prevent the glass beads from closing the opening to the capillary tube. Glass wool was first used at this position, but frequently siphoned over into the volumetric flask. The glass plug was made by breaking a piece about 7 mm. long from a 7-mm. diameter glass rod. The ends were left rough, so the flow of gas and liquid would not be blocked. With this modification, recovery was 96.3%, and standard curves were linear up to at least 50 μg. (Figure 2).

RESULTS AND DISCUSSION

The arsenic residues found in the agricultural soils are given in Table I. Since 10 p.p.m. of arsenic is considered

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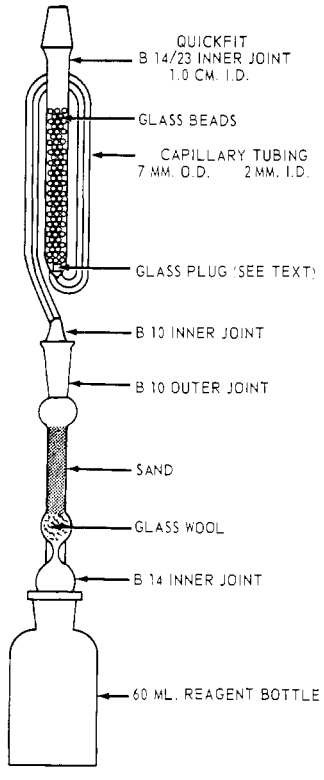

Figure 1. Modified arsenic apparatus

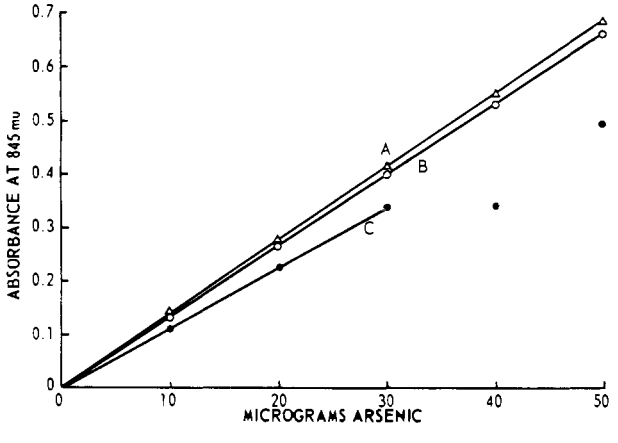

Figure 2. Standard curves

A. Developed directly in 25-ml. volumetric flasks (no evolution step)
B. AsH_3 evolved into new taller absorbers (see Figure 1)
C. AsH_3 evolved into shorter absorbers as per Hoffman and Gordon (1963)

Table I. Arsenic Residues in Farm Soils of Southwestern Ontario

Sample No.	Soil Type	Crop	Arsenic in Soil, P.P.M.[a]
1	Sand	Onions, lettuce	3.2 ± 0.2[b,c]
2	Clay loam	Corn	4.4 ± 0.1
3[a]	Sandy loam	Greenhouse	5.9 ± 0.3
3[b]	Sandy loam	Greenhouse	6.9 ± 0.2
4[a]	Sandy loam	Greenhouse	2.3 ± 0.0
4[b]	Sandy loam	Greenhouse	5.3 ± 0.3
5	Muck	Onions	5.5 ± 0.0
6	Muck	Radishes	3.2 ± 0.3
7, 8	Loam	Corn, beets, carrots	1.1 ± 0.0
9	Clay	Corn, sugar beets	8.6 ± 0.5
10	Clay loam	Corn, sugar beets	2.3 ± 0.2
11	Loam	Corn, soybeans, sugar beets	1.5 ± 0.3
12	Clay loam	Corn, alfalfa	5.5 ± 0.2
13[a]	Loam	Apple orchard (under trees)	15.6 ± 0.8
13[b]	Loam	Apple orchard (between trees)	10.2 ± 0.5
14	Muck	Celery, onions	6.0 ± 0.3
15	Loam	Corn, beans	1.8 ± 0.2
16	Sandy loam	Oats, alfalfa, sugar beets	2.9 ± 0.1
17	Sandy loam	Tobacco, rye, potatoes	1.4 ± 0.2
18	Sand	Tobacco, rye, wheat	4.5 ± 0.1
19	Sandy loam	Tobacco, wheat	4.7 ± 0.5
20	Sandy loam	Tobacco, rye	5.7 ± 0.2
21[a]	Sandy loam	Apple orchard (under trees)	121.0 ± 2.0
21[b]	Sandy loam	Apple orchard (between trees)	107.0 ± 2.0
22[a]	Clay loam	Apple orchard (under trees)	67.0 ± 0.9
22[b]	Clay loam	Apple orchard (between trees)	39.4 ± 0.9
23[a]	Sandy loam	Apple orchard (under trees)	44.9 ± 1.9
23[b]	Sandy loam	Apple orchard (between trees)	23.1 ± 0.6
24	Loam	Corn, turnips, wheat	3.2 ± 0.2
25	Sandy loam	Radishes	3.3 ± 0.2
26	Clay	Oats, turnips	1.7 ± 0.2
27	Muck	Lettuce, onions, carrots	26.6 ± 0.2
28	Loam	Grain	6.0 ± 0.4
29	Clay loam	Grain	1.3 ± 0.2
30	Silt loam	Pasture	3.7 ± 0.4
31	Sand	Rye, tobacco, corn	6.9 ± 0.4
32	Sandy loam	Corn, all vegetables, tobacco	4.5 ± 0.2

[a] Based on oven-dry weight of soil.
[b] Mean, followed by standard error.
[c] $N = 2$ except $N = 3$ samples 11, 13a, 21b, 23a, and 31; $N = 4$ for 23b; $N = 6$ for 21a and 22b; $N = 7$ for 32.

to be a natural level, only four orchard soils and one vegetable soil can be considered as contaminated with arsenic in this study. Phytotoxicity could occur if the orchards were cleared and the land planted with crops susceptible to arsenic poisoning. Bishop and Chisholm (1962) report that soil levels of 50 to 125 p.p.m. of total arsenic may have a detrimental effect on the growth of beans and strawberries. Using these levels as a guide, two apple orchards, samples 21 and 22, would be unsuitable for growing these susceptible crops. The high residues found in samples 22a and b, and the even higher residues in 21a and b, are consistent with the spray history as given in Table II. The tobacco soils, samples 17 to 20 and 31, all have arsenic levels below 10 p.p.m., which indicates that lead arsenate sprays used some years ago for hornworm control on tobacco have not resulted in significant continuing residues in soil. No reason is known for the relatively high arsenic residue of sample 27 (a vegetable farm).

Table II. Spray History

Sample No.	Lead Arsenate Application	
	Year	Pounds/acre
1 to 12, inclusive		0
13a and b	Up to and including 1964	28
14, 15, 16		0
17, 18, 19. 20	Prior to 1947	Unknown
21a, and b	1932	63
	1933	60
	1934, 1935	63
	1936	60
	1937–1943	63
	1944–1947	75
	1948	71
	1949–1955	45
	1956, 1957	30
	1958	46
	1959–1964	38
22a and b	1932	63
	1933	60
	1934, 1935	63
	1936	60
	1937–1943	63
	1944–1947	75
23	Up to and including 1964	28
24 to 31		No record of arsenic treatment
32		0

The orchard strata samples (Table III) show very uniform distribution of arsenic to a 6-inch depth under the trees and indicate that, in orchards at least, sampling probably should have been deeper. In other studies (Harris and Sans, 1966) the vertical distribution of DDT residues has also been determined. These DDT levels, included here for comparison, show that the DDT is mainly concentrated in the upper 2 inches of soil, where the residue is more than three times greater than the DDT found in the 4- to 6-inch sample. The combined arsenic and DDT residues in this orchard total 240 p.p.m. when averaged over the 6-inch depth, but in the upper 2 inches were as high as 324 p.p.m.

Table III. Arsenic and DDT Residues in Strata Samples at Three Depths in an Apple Orchard Soil

	Arsenic, P.P.M.[a]	DDT, P.P.M.[a]
Under trees		
0–2 inches	109	215
2–4 inches	123	107
4–6 inches	111	60
Between trees		
0–2 inches	98	90
2–4 inches	116	74
4–6 inches	69	66

[a] Based on oven-dry weight of soil.

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