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Arsenic and Lead in an Orchard Environment

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During this century substantial amounts of arsenic and lead compounds have been redistributed in the environment through agricultural sprays and smelting operations. Lead has also become widespread from automobile exhausts. Analysis of background concentrations in the range 0.1 to 30 ppm As/g soil and 1 to 100 ppm Pb/g soil as well as contaminated soil concentrations about 10 times larger are typical (FRANK et al. 1976, MOTTO et al. 1970, and WOOLSON et al. 1971).

Both arsenic and lead are nearly immobile in soil. Vertical concentration gradients are apparently stable for tens of years with pollutant arsenic and lead usually found in the surface 10 cm of soil (FRANK et al. 1976, PAGE and GANJE 1970). Another measure of immobility is the difficulty of extracting As and Pb species from soils. JACOBS et al. (1970) extracted 2 and 15% of added arsenate from a loam and a sandy soil, respectively, with neutral 1 $\underline{M}$ NH_4OAc. MACLEAN et al. (1969) extracted 5 to 37% of added lead from roadside soils with the same reagent.

The distinction between the total concentration of arsenic or lead in soil and the concentration available to plants is important. High, rapid uptake of each element from solution has been shown (SACHS and MICHAEL 1971 and JARVIS et al. 1977). Various extraction solutions have been used to approximate the available concentration of arsenic or lead in soil (WALSH and KEENEY 1975, and MACLEAN et al. 1969). In addition, airborne lead may be available to plants near highways (TERHAAR (1970).

The extent to which arsenic and lead enter our food supply is a matter of concern. Such entry may be either direct through food we eat or indirect through grass and meat. JELINEK and CORNELIUSSEN (1977) present average levels of arsenic in various foods in the United States for the period 1967-1974. SULEK (1978) cites mean values for lead in raw and canned food. Both surveys found concentrations in fresh foods of the order of 10^{-2} μg element/g food. The distribution of substances within the plants, however, is relevant to the entry of heavy metals into our food. Plants grown in soils (rather than in nutrient solutions) have shown marked differences in arsenic and lead concentrations in their different parts. Various studies of arsenic or lead in vegetables (tomato, bean, pea, carrot, beet, onion, corn)

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have found substantially lower concentrations in the edible parts of the plants than in the remainder (ELFVING et al. 1978; TER HAAR 1970; MOTTO et al. 1970). Thus, the presence of heavy metal pollutants in soils does not necessarily mean they will be taken into food to a large extent.

In this work we have taken samples of soil, apples, grass and vegetables fron an apple orchard which was started in 1929. The orchard has been sprayed heavily with lead arsenate and retains a substantial residue. Samples were analyzed for total arsenic and lead, the distribution of arsenic and lead in the soil and plants, and the fractions of these elements that could be extracted by neutral ammonium citrate from soil.

EXPERIMENTAL

Sampling. Samples were taken from Orchard 17 at the New York State Agricultural Experiment Station, Geneva. This orchard is approximately 9 acres and contains 19 rows of 47 apple trees per row. The west edge of the orchard is bordered by a ditch and a public highway, the other edges border other apple orchards. The surface is flat. The orchard continues to be sprayed routinely with herbicides around the trees, and the grass between the trees is mowed. The ground is not now tilled.

At each of ten trees, selected at random, composite samples of leaves, apples, native grass and soil were taken. Leaves, apples, and grass were taken in late summer by walking around each tree and sampling at random. Ten soil cores were taken in a circle at each tree's dripline for the horizons 0-5 and 5-10 cm. Composite grass and soil cores were taken at eight locations from the bottom of the highway drainage ditch along the west side of the orchard.

Six sites in the orchard where trees were recently removed were rototilled and used for growing vegetable samples. Each site was approximately 3 m x 5 m. The vegetables grown were: radish (Cherry Belle), carrot (Danvers half-long), onion (yellow), potato (Katahdin), tomato (Golden Boy), green snap beans (Greenway), cabbage (Savoy), Brussels sprouts (Jade Cross). The vegetables were planted in June and harvested at maturity. After harvest, the vegetables and plant parts were washed thoroughly with tap water and distilled water. Plant parts of each type from each site were grouped together and stored in a cold room until analysis. At each of these six orchard sites 10 soil cores were taken in 5 cm increments to a depth of 25 cm. The samples at each horizon in each plot were grouped together.

Analytical Methods. Arsenic was determined by the flameless atomic absorption spectrophotometer (AAS) (Perkin Elmer 305B) method of THOMPSON and THOMERSON (1974). In this method 1 ml of sample solution was mixed with 1 ml 0.5% $NaBH_4$ to generate AsH_3. The arsine was carried in a nitrogen stream into a hot Vycor tube in the AAS light path, and the absorbance measured at 194 nm. Lead was determined by aspirating the sample solution directly into a hydrogen/air flame in the AAS and measuring the absorbance at 283 nm. The accuracy and precision of the methods is approximately ± 5% for As and ± 3% for Pb. These numbers represent the usual scatter in our calibration graphs and sample replications. Each standard and each sample was run three to five times. Standards were routinely run with the samples. Some samples were spiked with arsenic and lead to check the recovery of the elements. Lead recoveries were quite uniform at 81% for soils or plant materials. Arsenic recoveries varied between 21 and 31% for soils and between 20 and 100% for plant materials.

Each soil sample was dried in air, ground to a coarse powder and stored in a cardboard box. Four 2 g subsamples and a fifth subsample spiked with lead and arsenic from each soil sample were analyzed. The soil was first digested with HNO_3 and $HClO_4$. After digestion and dilution the sample was analyzed for lead. An aliquot of the solution was then further digested with H_2SO_4 to remove all HNO_3 and $HClO_4$, diluted and analyzed for arsenic.

The soil samples from the garden plots were extracted with neutral ammonium citrate (NAC) and water to estimate the available arsenic and lead (ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS, 1965). Ten gram samples of soil were shaken with 35 ml NAC for 10 min. The liquid was decanted and the extraction repeated once with 35 ml NAC and again with 30 ml water. The extracts were combined and analyzed as described above.

The pH of slurries of the soils were also measured. Two parts water and one part soil by weight were agitated for 30 minutes, allowed to settle, and the pH of the liquid determined.

The plant materials (except apple juice) were oven dried at 100°C to constant mass. In most cases one composite sample of 10 to 20 g dry weight of each type of material for each site was analyzed for lead and arsenic. The largest samples of each type were divided and one part was spiked with both lead and arsenic. The dried material was digested in HNO_3, diluted and analyzed for lead as described above. An aliquot of the solution was then digested in H_2SO_4 and H_2O_2 and analyzed for arsenic as described above. Apple juice was digested directly with HNO_3 without drying.

RESULTS

The results obtained for the tree-sites and ditch are summarized in Table 1. Soil analyses for the garden plots are given in Table 2. Results for vegetable plant materials are presented in Table 3 along with some comparable published results. As described above, the analyses were carried out with composite samples from each site with the expectation that there would be a correlation with the soil concentration. However, in most cases

TABLE 1

Summary of results for 10 apple tree sites and ditch

		Arsenic (ppm)		Lead (ppm)		pH	
		Range	Average	Range	Average	Range	Average
Orchard Soil	0-5 cm	31-109	72	171-512	339	4.51-5.77	5.32
	5-10 cm	21-109	47	43-200	116	4.62-6.34	5.78
Apple	Pomace	0.015-0.080	0.043	1.08-9.28	2.52		
	Juice		<0.005	0.037-0.085	0.063		
	Leaves	0.15-0.34	0.25	0.9-12.6	6.9		
Orchard Grass		0.10-0.53	0.21	5.0-13.0	9.4		
Ditch Soil	0-5 cm		9.4		316		7.56
	5-10 cm		10.5		159		7.87

TABLE 2

Analyses of soil in garden plots

Horizon (cm)	Arsenic (ppm)[1]					Lead (ppm)[2]				
Site[3]	0-5	5-10	10-15	15-20	20-25	0-5	5-10	10-15	15-20	20-25
2-19	18.7	13.9	10.4	13.5	5.8	103.1	79.7	33.1	31.2	23.4
5-7	25.6	24.1	19.2	17.0	9.8	130.1	109.3	60.8	37.3	20.7
5-27	16.3	15.9	15.4	8.7	5.9	75.3	65.7	47.8	26.3	24.7
7-13	37.1	22.5	17.1	16.7	7.4	121.7	84.0	55.7	34.4	26.4
13-24	75.7	62.6	55.8	31.5	31.7	370.6	235.4	134.6	92.0	82.6
16-40	68.8	62.1	82.2	35.6	15.2	276.4	268.1	250.4	108.2	44.2
Average soluble[4] fraction for each horizon	0.069	0.086	0.050	0.053	0.051	0.40	0.30	0.25	0.24	0.16
Pb/As	4.47		2.95							
pH	5.55	5.35	5.60	6.13	6.45					

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[1] ± 5%

[2] ± 3%

[3] Row number - tree number

[4] ± 0.031 for arsenic; ± 0.05 for lead

TABLE 3

Concentrations of As and Pb (ppm, dry weight) in vegetable plants averaged over six plots.

	As		Reference		Pb		Reference	
	Conc.[1]	σ(%)[1]	4	5	Conc.[1]	σ(%)[1]	4	6
Brussels Sprout	0.11	26			1.8	23		
Leaf	0.21	27			3.9	25		
Stem	0.16	25			2.5	18		
Cabbage Inner	0.38	29	<0.1	0.4-1.2	2.6	21	1.4	
Leaf Outer	0.31	40			1.8	37	(1.5)	
Bean Pod	0.17	88	<0.1	0.4-5.2	2.2	18	1.4	
Leaf	1.23	69			10.9	13	(1.0)	
Stem	1.11	55			4.2	20		
Tomato Fruit	0.03	55	<0.1	0.54-0.66	1.4	30	0.8	3-7
Leaf	1.12	82	(0.1)		16.1	25	(0.9)	37-276
Stem	0.48	71			12.1	48		19-166
Potato Tuber	0.02	50	0.1		0.6	67	0.4	3-10
Leaf	1.37	98	(0.1)		19.9	26	(0.9)	95-368
Stem	0.43	48			13.3	41		
Onion Top	0.53	36	0.4		8.4	28	0.8	
Bulb	0.07	31	(0.1)		0.9	23	(1.0)	
Carrot Top	0.42	56	0.9		7.7	22	7.1	25-80
Bulb	1.11	34	(<1.0)		7.5	25	(1.0)	8-24
Radish Top	0.78	59			11.5	25		
Bulb	0.74	35		0.5-26	15.0	10		

[1] This work; concentration in µg element/g dry plant,σ is relative standard deviation.

[4] ELFVING et al. (1978). Old orchard (control).

[5] WOOLSON (1973). Calculated for 1.0 and 10 ppm available As in soil.

[6] MOTTO et al. (1970).

the results fitted a simple average value better than a functional relation with the soil concentration. Each result listed is the average over the six plots, and its relative standard deviation.

DISCUSSION

There is an approximate mass balance between the lead arsenate applied to the orchard and that which we have found. The orchard was planted in 1929 and then sprayed with lead arsenate through 1965. The spray program is known in detail from 1954 to 1966; usually 2 applications of 9 lb/100 gal. per year for a total of 2236 lb during 12 years. Earlier publications from this Station cite 3 or 4 applications of 3 to 6 lb/100 gal. as a normal spray program (HARMON 1940). If we assume the same rate of application during the period 1929-1953 as for the period 1954-1965, the total was approximately 6900 lb. FRANK et al. (1976) point out that lead arsenate formulations varied considerably, with the mass ratio Pb/As between 2.8 and 4.6. Our results lie within these limits: Pb/As is 2.95 in the depth range 10-25 cm and 4.47 in the 0-10 cm range (Table 2). The depth profiles (Table 2) suggest that the background level for As is practically 0 ppm at 30 cm while the background for Pb is about 20 ppm at 25 cm. Both elements have approximately constant vertical concentration gradients. Taking these background concentrations with the average surface concentrations in Table 1 and the orchard area as 9 acres, and assuming a soil density of 2 g cm^{-3}, the total mass of arsenic in the top 30 cm is 1700 lb and the total mass of lead is 6000 lb over the background. The estimated total application of 6900 lb is equivalent to 1500 lb As and 4100 lb Pb for the compositin $PbHAsO_4$. The agreement is very satisfactory and implies that the entire application of lead arsenate is still in the surface 25 cm of soil.

The results for apples (Table 1) are rather similar to those for vegetables (Table 3). In the apple juice arsenic was below our detection limit while the lead concentrations were comparable to those found in commercial fresh foods (SULEK 1978). Our values for lead in pomace are comparable to two collaborative studies of MARCUS (1974); 7.2 ± 1.2 and 0.4 ± 1.0 µg Pb/g dry apple. The similarity between uptake by our trees and vegetables is rather surprising since ATKINSON (1974) reported that most absorption of phosphorus by roots of apple trees took place at depths between 15 and 90 cm depending on the age of the tree and time during the growing season. At these depths, both the concentration and availability of lead and arsenic are much smaller than near the surface where the vegetable roots grew.

The results from our six vegetable plots do not correlate well with either the total element concentrations in the soil or with the neutral ammonium citrate extractable concentration. The edible parts of the plants, usually seed bearing or storage parts, have uptakes less than the leaves and stems. Brussels sprouts, cabbage, carrots and radishes are exceptions. The arsenic concentrations in the edible parts of the plants studied, except carrots and radishes, are similar to those reported by JELINEK and CORNELIUSSEN (1977). However, the lead concentrations, 0.6 to 3 ppm/dry weight) are 10 to 100 times larger than those given by SULEK (1978) but are still well under the U.S. Public Health Service interim action guidelines of 7 ppm (fresh weight). Apparently the availability to plants of old arsenic and lead residues in loam soil is low enough that there is no particular health hazard in apples, tomatoes, beans, cabbage, Brussels sprouts, onions, and potatoes.

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