# METALS IN AGRICULTURAL SOILS OF ONTARIO

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Farm fields (296) in all agricultural areas of Ontario were sampled to a depth of 15 cm and analyzed for 10 metals and one non-metal. Metal additions to soils in the form of pesticides, trace elements, fertilizers, feed additives and non-agricultural depositions were reviewed. Arsenic and lead levels were elevated in fruit orchard soils as a result of using lead and calcium arsenate over the past 65 yr. Apple orchard soils had higher As and Pb levels than cherry soils, and these were higher than peach soils, correlating with the length of usage and the annual rates of application. Arsenic levels were slightly increased in potato soils due to the use of sodium arsenite. Mercury content in apple orchard soils was slightly elevated by the use of phenyl mercuric acetate over a 20-year period. The treatment of seed grain with methyl mercurials over a 40-yr period was not reflected in the content of farm soils. Organic soils had higher levels of mercury than mineral soils. Copper levels in soils were highest in organic soils following several years' treatment with copper as both a trace element and a fungicide. Copper concentrations in orchard and vineyard soils were raised only slightly by the application of copper fungicides over an 80-yr period. Widespread application of manganese as a trace element and fungicide in the production of vegetables and bean crops was not detected in soils on which these crops were grown. A much smaller use of fungicide containing iron and zinc likewise was not evident in these soils where these fungicides were used in crop production. Cadmium, cobalt, chromium, iron, and nickel levles were not affected by agricultural practises, especially those involving the use of general fertilizers and barn yard manures; however, serious inputs were found on a small number of soils from industrial activities, especially near a nickel–cobalt smelter and the disposal of sludge. Mean natural background levels of metals in agricultural soils of Ontario in order of increasing magnitude were mercury, 0.08; cadmium, 0.56; cobalt, 4.4; arsenic, 6.3; lead, 14.1; chromium, 14.3; nickel, 15.9; copper, 25.4; zinc, 53.5; manganese, 530; and iron, 14.470 ppm. Most metals increased with increasing clay or organic matter content of the soil.

On a prélevé dans 296 champs représentant toutes les zones agricoles de l'Ontario des échantillons des 15 premiers centimètres de sol, dont on analysé la teneur en 10 éléments métalliques et en 1 métalloide. Ces analyses ont été reliées aux applications de pesticides, d'oligo-éléments, d'engrais, ainsi qu'à l'emploi d'additifs alimentaires et aux dépôts de source non agricole. Dans les vergers, l'emploi prolongé d'arséniate de plomb et de calcium au cours des 65 dernières années a relevé la teneur en As et en Pb du sol. Les niveaux les plus hauts ont été observés dans les vergers de pommiers, puis dans les cerisaies et enfin dans les vergers de pêchers, ce qui s'explique à la fois par la durée d'emploi de ces produits et par les taux annuels d'application. Dans les sols à pomme de terre, la teneur en As a été légèrement haussée par suite de l'emploi d'arséniate de sodium. L'emploi d'acétate phényl mercurique pendant 18 ans s'est soldé par une légère augmentation de la teneur en Hg du sol. Par ailleurs, l'utilisation depuis 40 ans de traitements des semences aux fongicides mercuriels n'a pas laissé d'effets observables. Les sols organiques contenaient plus de mercure que les sols minéraux. La teneur en Cu la plus forte a été celle des terres organiques où l'on avait appliqué pendant plusieurs années cet élément comme oligo-complément et comme fongicide. Dans les sols de vergers et de vignobles, la teneur en Cu n'a été haussée que légèrement après 80 années d'emploi de fongicides cupriques. L'application généralisée de Mn comme oligo-élément et comme fongicide dans les cultures de légumes et de haricots ne s'est pas manifestée dans les sols en question. De même, l'emploi, il est vrai beaucoup moindre, de fongicides à base de Fe et de Zn n'a pas laissé de traces dans les sols ainsi traités. Les pratiques agricoles, notamment l'usage d'engrais ordinaires et de fumier, n'ont pas eu de suite sur les teneurs en cadmium, en cobalt, en chrome, en fer ou en nickel du sol. Toutefois, quelques sols ont révélé des augmentations inquiétantes de source non agricole: proximité d'une fonderie de nickel–cobalt et épandages de boues d'égout. Par ordre d'importance croissante, les teneurs de base moyennes naturelles de ces divers éléments dans les sols agricoles de l'Ontario s'établissent comme suit: Hg, 0.08 ppm; Cd, 0.56; Co, 4.4; As, 6.3; Pb, 14.1; Cr, 14.3; Ni, 15.9; Cu, 25.4; Zn, 53.5; Mn, 530, et Fe 14,470. La concentration de la plupart des métaux s'accroît avec la teneur en argile ou en matière organique du sol.

The agricultural soils of Southern Ontario have developed upon glacial deposits during the last 10,000 yr. They are derived from Paleozoic sedimentary rocks with inter-mixtures of Precambrian and igneous rocks. The sedimentary rock is mainly limestone with lesser amounts of red shale, especially at the foot of the Niagara escarpment. Northern Ontario soils are largely developed from Precambrian rocks.

Southern Ontario soils have been cleared and used in agricultural production for 150 yr or more, Metal additions to soils over this period have come from a number of sources. These include: (i) pesticides containing metals; (ii) fertilizers with metal contaminants; (iii) trace element fertilizers; (iv) manures with metals derived from additives to animal diets; (v) sewage sludge disposal, and (vi) aerial fallout from urban, transportation and industrial activities.

(i) PESTICIDES. The first recorded Ontario Ministry of Agriculture and Food recommendations were made in 1895 for the control of insects and diseases in fruit and vegetables (Eastman and Caesar 1911; Caesar 1948). At that time a Paris green (copper acetoarsenite)–Bordeaux (copper sulfate–calcium hydroxide) mixture was recommended for use on apples and cherries. By 1910 both calcium and lead arsenate were introduced to replace this mixture which caused foliar injury. Calcium and lead arsenate were used in increasing quantity up to the advent of DDT. Calcium arsenate applications stopped in 1952 but lead arsenate usage was continued at a reduced level until 1956 in peaches, 1971 in cherries, and to the present in apples (Table 1). In the past, amounts as high as 4 kg/ha/annum of arsenic and 20 kg/ha of lead were applied to apple orchards. In 1975 one application of lead arsenate was recommended on early ripening apples and two applications for late ripening apples, giving up to 0.5 kg/ha of arsenic and 2.3 kg/ha of lead per application (Ontario Ministry of Agriculture and Food) (OMAF) 1975).

The use of Bordeaux mixtures was largely replaced by fixed copper introduced in 1940; however, both are still recommended in 1975 (OMAF 1975). Mercury, in the form of methyl mercurials, was used as a seed treatment between 1932 and 1972 and the maximum amount of mercury applied was approximately 0.002 kg/ha. Inorganic mercury sulfate (calomel) was used as a root dip for cruciferous crops between 1930 and 1950. The use of phenyl mercuric acetate for scab eradication on apples was discontinued in 1973 and replaced by other eradicant fungicides. Sodium arsenite was used as a potato top killer between 1930 and 1972 (Table 1).

(ii) FERTILIZERS. Analytical data presented by Agriculture Canada on fertilizers sold in Ontario indicate low levels of 10 metals in fertilizers (Agriculture Canada 1974). The range of mercury was 4–47 ppb; lead, 5–26 ppm; cadmium, cobalt and nickel, 1–70 ppm; chromium and zinc, 1–800 ppm; manganese, 1–3,000 ppm; and iron, 5–14,000 ppm. Fertilizer rates vary from $10^2$ to $10^3$ kg/ha/annum; hence additions of metals would be:

1. less than 50 mg/ha/annum — mercury
2. less than 26 g/ha/annum — cadmium, cobalt, nickel and lead
3. less than 800 g/ha/annum — chromium and zinc
4. less than 3 kg/ha/annum — iron.

(iii) TRACE ELEMENTS. Copper sulfate (40% Cu) is used for trace element deficiencies in vegetable crops, especially on organic soils at 2.2–11 kg/ha, and manganese sulfate (42% Mn) for the same reason on vegetables and bean crops at 1.1–2.2 kg/ha (OMAF 1975). Other metals have been used but not on a regular or widespread basis.

(iv) MANURES. Rations for livestock are usually adequate in essential metals; however, in the production of milk and pork, copper and cobalt may be added to the diet as 1% copper sulfate and as 1% cobalt

Table 1. Pesticides containing metals recommended in Ontario, (OMAF 1892-1975)

| Chemical | Metal composition of product | Period of recommendation | Crops |
|---|---|---|---|
| | *Insecticides* | | |
| Copper aceto-arsenite | 2.3% As, 39% Cu | 1895–1920 | Apples & cherries |
| (Paris green) | | 1895–1957 | Vegetable & small fruit (foliar & bait) |
| Calcium arsenate | 0.8–26% As | 1910–1953 | Fruit & vegetables |
| Lead arsenate | 4.2–9.1% As | 1910–1975 | Apples |
| | 11–26% | 1910–1971 | Cherries |
| | | 1910–1956 | Peaches |
| | | 1910–1955 | Vegetables |
| Mercuric chloride | 6% Hg | 1932†–1954 | Cruciferous crops |
| Zinc sulfate | 20–20% Zn | 1939–1955 | Peaches |
| | *Fungicides* | | |
| Copper sulfate–calcium salts (Bordeaux & Burgundy mixtures) | 4–6% Cu | 1892–1975 | Fruit & vegetables |
| Fixed copper salts | 2–56% Cu | 1940–1975 | Fruit & vegetables |
| Ferbam | 0.5–12% Fe | 1947–1975 | Vegetables |
| | | 1948–1975 | Fruit |
| Maneb | 1–17% Mn | 1947–1975 | Fruit & vegetables |
| Mancozeb | 16% Mn, 2% Zn | 1966–1975 | Fruit & vegetables |
| Methyl& phenyl mercuric salts | 0.6–6% Hg | 1932–1972 | Seed treatment |
| Phenyl mercuric acetate | 6% Hg | 1954–1973 | Apples |
| Zineb & ziram | 1–18% Zn | 1947–1975 | Vegetables |
| | | 1957–1975 | Fruit |
| | *Topkiller* | | |
| Calcium arsenite | 30% As | 1930†–1972 | Vegetables |
| Sodium arsenite | 26% As | 1930†–1972 | Vegetables |

†Exact year not available.

iodized salts (OMAF Agdex 1971). Bates et al. (1974) reported levels of 18–205 ppm copper, 45–381 ppm manganese, and 30–737 ppm zinc in animal and poultry manures.

(v) SLUDGES. Much literature indicates high metal levels can exist in sewage sludges that are applied to agricultural land and this can lead to metal accumulations (Chaney 1973). Black and Schmidtke (1974) reported that approximately 19.5 × $10^6$ liters (2–9% solids) of sewage sludge is produced per day in the Province of Ontario. Approximately 41% of this volume is disposed of on farmers' fields.

(vi) AERIAL FALLOUT. Metal accumulations in soils have been reported for many metals as a result of aerial fallout from industrial and transportation activities (Friberg et al. 1971, National Research Council of Canada 1973).

A 3-yr survey into metal levels in agricultural soils was conducted between 1972 and 1975 to determine the levels of 10 metals (Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, and Zn) and one non-metal (As). The purpose of the survey was to try and determine background levels of metals in agricultural soils and correlate elevated levels to agricultural, industrial, or other activities.

Table 2. The soil texture, location and crop production where 296 soils were collected in Ontario

| Soil, texture, location and crop | Number of soils |
|---|---|
| Organic | 13 |
| Sand | 125 |
| Loam | 98 |
| Clay | 60 |
| Total | 296 |
| South Western | 66 |
| Niagara | 102 |
| Western | 82 |
| Central | 20 |
| Eastern | 23 |
| Northern | 3 |
| Total | 296 |
| Pasture and unimproved land | 15 |
| Cash crops: | |
| corn, soybeans, grain, tobacco | 126 |
| Vegetable and nurseries | 69 |
| Tree fruit | 70 |
| Vineyards | 16 |
| Total | 296 |

## METHODS AND MATERIALS

### Field

Soils were collected from different agricultural areas of Ontario so as to include all types of crop production. Each sample was a composite of samples taken randomly from 10–20 sites to a depth of 15 cm at each location. A total of 296 soils were collected: 86 from orchards and vineyards, 82 from vegetable producing farms, 126 from hay and cash crop farms, and 15 from unimproved pastures. Sample sites were located in 34 of the 42 counties and 4 of the 13 districts of Ontario (Table 2). A comprehensive study of orchard soils is reported elsewhere (Frank et al. 1976).

### Metal Analysis

For the analysis of Cd, Co, Cr, Cu, Mn, Fe, Ni, Pb and Zn, 1.000 g of oven-dried soil was digested with 10 ml of conc. $HNO_3$. The flask contents were gently boiled for 5 h, 20 ml of water were added, and the contents were warmed for 2 h. The mixture was filtered through a coarse porosity, sintered glass filter and made up to 100 ml with distilled water.

The metals were measured with a carbon rod atomizer attached to Techtron Model AA-5 atomic absorption spectrophotometer and the response recorded with a Varian Model G-2000 recorder. The method used is only slightly modified from the procedure described by Amos et al. (1971). The wavelengths used to measure the metals were Cd 228.8, Co 240.7, Cr 428.9, Cu 327.4, Fe 392.0, Mn 403.1, Ni 352.4, Pb 283.3, Zn 307.6 nm. High-purity nitrogen gas was used to protect the carbon rod at a flow rate of 3.5 liters/min.

### Total Mercury Analysis

A 1.000-g sample of oven-dried soil was digested with 20 ml of concentrated sulfuric and nitric acids (4:1) for 1 h in a shaker bath at 60 C. The digested samples were cooled over ice and 25 ml of saturated potassium permanganate was slowly added until the color remained dark purple; an excess was then added. The contents were incubated for 2 h in the shaker at 60 C.

A 0.1- or 0.2-g aliquot was made up to 100 ml with distilled water. Hydroxylamine sulfate solution (2%) was added and the contents were allowed to stand until the color disappeared. Stannous sulfate solution (5 ml of 10%) was added and the effluent was passed through a mercury analyzer as a cold vapor. Mercury content was determined from peaks produced by an atomic absorption spectrophotometer set at 253.7 nanometers and attached to a recorder (Hatch and Ott 1968).

### Arsenic Analysis

Soils were analyzed for arsenic according to the procedure of Ishida and Braun (1974) based on the spectrophotometric measurement of the chromogenic complex formed between arsine gas and molybdate.

## RESULTS

### Arsenic

The arsenic content of 296 soils varied from 1.1 to 126 ppm (Table 3 and Fig. 1.). There were 207 soil samples where no actual or potential uses of arsenic were recognized and these soils contained from 1.1 to 16.7 ppm arsenic with a mean of 6.27 ± 2.67 ppm.

The use of lead arsenate on apples and cherries, and sodium arsenite on potatoes grown on mineral and organic soils was reflected in higher soil content of arsenic.

Table 3. Arsenic content of agricultural soils in Ontario

| | Soils analyzed (no.) | Arsenic content in dried soil (ppm) | | |
|---|---|---|---|---|
| | | Mean | Range | SD |
| *Crop production* | | | | |
| General crops | | | | |
| Unimproved | 15 | 4.74 | 1.77–15.3 | 3.79 |
| Field crops | 126 | 5.69 | 1.10–15.7 | 3.00 |
| Vegetables | | | | |
| Mineral soils | 39 | 5.45 | 1.28–16.7 | 3.43 |
| Organic soils | 13 | 14.1 | 1.77–66.5 | 17.8 |
| Potatoes | 17 | 9.47 | 1.66–28.9 | 7.86 |
| Fruit | | | | |
| Apples | 31 | 40.5 | 3.20–91.6 | 25.8 |
| Sweet cherries | 16 | 30.2 | 12.1–62.6 | 13.4 |
| Sour cherries | 12 | 22.9 | 6.2–63.0 | 20.8 |
| Peach | 11 | 9.90 | 4.17–15.4 | 3.84 |
| Grape | 16 | 7.71 | 4.40–12.0 | 2.32 |
| Totals & means | | | | |
| Apples, cherries, potato & vegetables on organic soils | 89 | 26.5 | 1.66–91.6 | 22.8 |
| Other crops | 207 | 6.27 | 1.10–16.7 | 2.67 |
| *Soil types* | | | | |
| Organic | | | | |
| Vegetables | 13 | 14.1 | 1.77–66.5 | 17.8 |
| Sandy soil | | | | |
| Apple, cherries | 34 | 29.7 | 7.8–63.0 | 16.7 |
| Other crops | 91 | 5.84 | 1.10–28.9 | 4.60 |
| Loam soils | | | | |
| Apple, cherries | 23 | 38.3 | 3.20–91.6 | 29.2 |
| Other crops | 75 | 6.14 | 1.66–16.7 | 3.13 |
| Clay soils | | | | |
| Apples, cherries | 2 | 61.0 | 57.4–64.6 | 5.09 |
| Other crops | 58 | 6.43 | 1.33–15.3 | 3.69 |
| Totals & means | 296 | 12.4 | 1.10–91.6 | 15.7 |

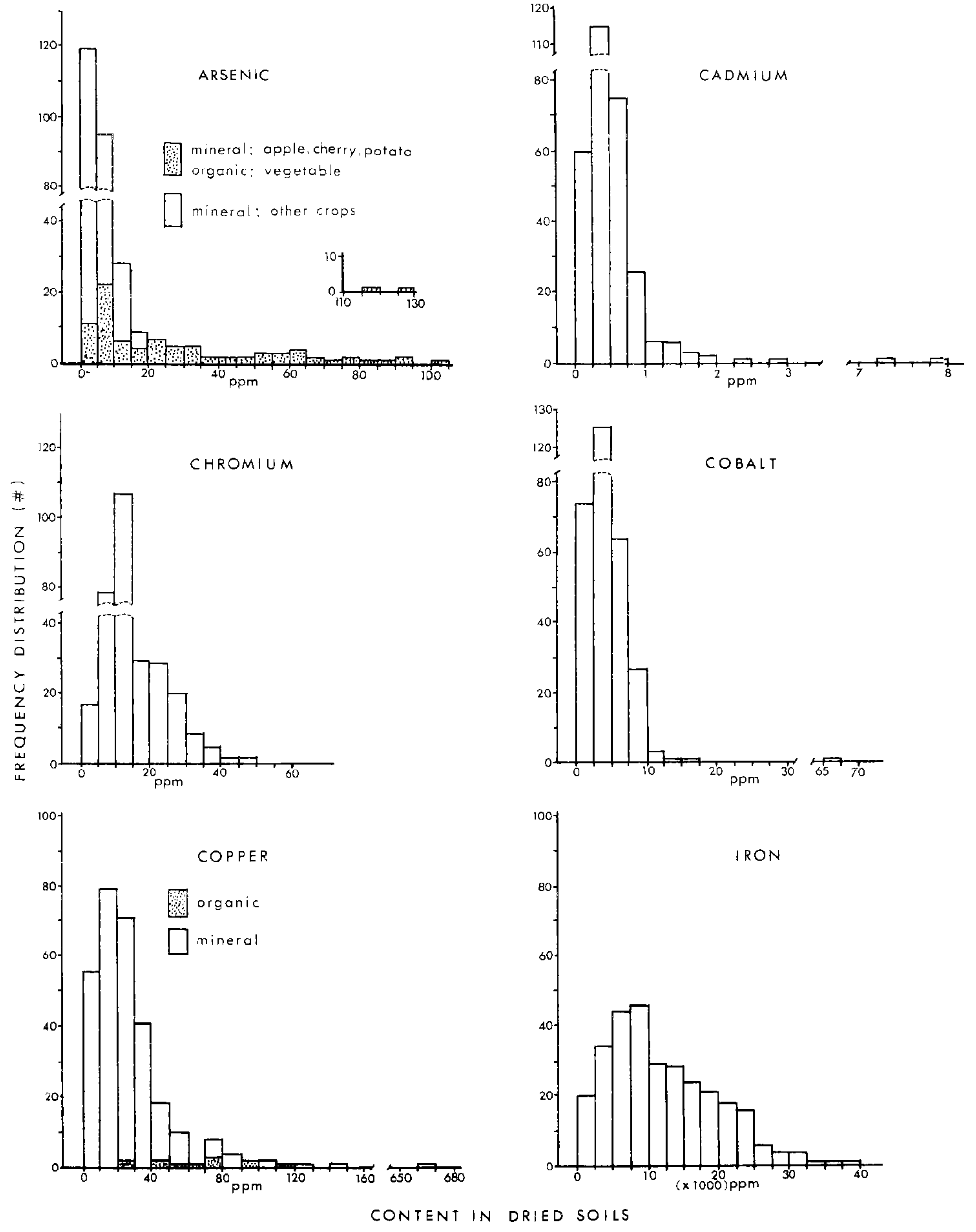


Fig. 1. Soil contents of arsenic, cadmium, chromium, cobalt, copper and iron in 296 soils collected from important agricultural areas of Ontario.

Soils from apple orchards ranged from 3.2 to 126 ppm As with a mean of 54.2 ± 35.4 ppm. Only five apple orchards had residues within the normal range (i.e., up to 8.94 ppm) and these were found to be newly planted orchards where little or no lead arsenate had been applied. The remaining 26 orchards had been in apples for up to 60 yr with past and present use of lead arsenate.

There were 16 sweet and 12 sour cherry orchard soils analyzed and their mean contents of As were, respectively, 30.2 ± 13.4 ppm and 22.9 ± 20.8 ppm. Five sour cherry orchards had contents below 8.94 ppm. Levels were not as high as in apple orchards because less lead arsenate was used per annum and because the recommendation for its use was discontinued in 1971.

Recommendation for the use of lead arsenate in peaches was discontinued in 1956; however, 6 of the 11 samples analyzed had arsenic contents above 8.94 ppm. Th mean content was 9.9 ppm, only slightly above the content where no known use had occurred.

There were 17 samples of soil analyzed from farms where potatoes were regularly grown in the rotation. Twelve of these samples had residues below 8.94 ppm and in nine of these cases no sodium arsenite had been used to kill vines over the past 10–12 yr. Where sodium arsenite had been used until 1972, arsenic contents ranged from 8.03 to 28.9 ppm. A study was conducted on one farm where a pasture had been plowed up and potatoes were grown and treated with sodium arsenite in alternate years from 1963 to 1972. When soil growing potatoes was compared with soil from pasture on the same farm, the arsenic content was observed to have risen from 5.2 to 28.9 ppm in the 10-yr period. On organic soils where a variety of vegetables including potatoes had been grown, 5 of 13 samples had As residues that ranged from 11.5 to 66.6 ppm. These residues were assumed to be the result of using sodium arsenite as a potato vine killer.

Arsenic content of uncontaminated soils increased slightly with increasing clay content (Table 3). Sandy soils had the lowest content with a mean of 5.84 ± 4.60 ppm and clay soils had the highest with a mean of 6.43 ± 3.69 ppm. These contents were considered to be the normal background levels for soil in Ontario. It was difficult to determine a background level for organic soils because past uses of arsenic were not remembered by growers. The three highest residues of 19.1, 32.4 and 66.5 ppm were associated with past potato production. If the remaining 10 were considered to indicate no, or very little, use of arsenicals then a mean of 6.53 ± 3.89 ppm (range 1.77–13.4 ppm) is very comparable with other soils.

## Cadmium

Cadmium content of soils ranged from 0.10 to 8.1 ppm; the mean was 0.56 ± 0.69 ppm, while the median content was 0.43 ppm (Table 4 and Fig. 1). Only 15 samples (5.1%) exceeded 1.25 ppm, and of these 8 were planted to general field crops, 2 to vegetables and 5 to tree fruits. None of these high cadmium contents could be associated with recent agricultural practises; however, in three cases sewage sludge had been accepted in past years. Two of these soils contained very high Cd concentrates of 7.32 and 8.10 ppm.

Sandy soils had the lowest mean content at 0.43 ± 0.29 ppm, while loam soils had the highest content at 0. 71 ± 1.11 ppm. Loams included six soils with the highest cadmium contents, including the two abnormally high values quoted above. If these latter two soils were removed then loam soils had average contents of 0.56 ppm or almost the same as clay and organic soils.

## Cobalt

The cobalt content of soils ranged from 1.0 to 65.8 ppm with a mean of 4.6 ± 4.3 ppm (Table 4 and Fig. 1). There were 15 soils with cobalt contents over 9.0 ppm; however, one had unusually high nickel and copper levels and was located close to a nickel–cobalt smelter. Hence these unusual levels were considered the result of industrial activity. Omitting this one soil, organic soils exhibited a mean Co content of 6.8 ± 2.7 ppm and the mean for all soils was 4.4 ± 2.5 ppm. Moreover, the cobalt content of organic and clay soils was similar.

## Chromium

The chromium content of soils ranged from 12.6 to 46.2 ppm with a mean of 14.3 ± 8.5 ppm (Table 4 and Fig. 1). Sandy soils had the lowest content at 10.0 ± 4.5 ppm and clay soils the highest at 22.3 ± 8.9 ppm. Only 12% of soils had chromium levels that exceeded 25 ppm and these were loam and clay soils. Those soils with Cr concentrations above 35 ppm were mainly located on the Canadian Shield or were soils with high clay content.

## Copper

The copper content of 296 soils ranged from 2.1 to 664 ppm (Tables 4,5 and Fig. 1). The soil with the highest Cu concentration was a composite of six samples taken from one farm where the content ranged from 486 to 2,190 ppm and was associated with stunted root growth and reduced crop production among vegetables. The same farm had high cobalt and high nickel levels and was situated close to a nickel–cobalt smelter.

Omitting this soil, the copper contents ranged from 2.1 to 144 ppm with a mean of 25.4 ± 21.5 ppm. Organic soils had the highest residues with 65.0 ± 26.9 ppm and sandy soils the lowest with 20.2 ± 27.8 ppm. The higher copper contents in organic soils reflected the production practises of adding copper sulfate once every 3 to 4 yr to combat copper deficiencies, and using fixed copper fungicides on vegetables (Table 4).

Table 4. Cadmium, chromium, cobalt and copper contents of agricultural soils in Ontario

| | Cadmium (ppm) | Chromium (ppm) | Cobalt (ppm) | Copper (ppm) |
|---|---|---|---|---|
| | | *Organic soils*† *(12 Co & Cu, 13 Cd & Cr)* | | |
| Mean | 0.57 | 14.6 | 6.8 | 65.0 |
| Range | 0.19–1.22 | 4.1–39.0 | 3.1–13.9 | 29.5–111.0 |
| SD | 0.29 | 11.0 | 2.68 | 26.9 |
| | | *Sandy soils (125)* | | |
| Mean | 0.43 | 10.0 | 3.4 | 20.2 |
| Range | 0.10–1.80 | 2.6–33.5 | 1.0–16.7 | 2.1–123.0 |
| SD | 0.29 | 4.5 | 2.1 | 27.8 |
| | | *Loam soils (98)* | | |
| Mean | 0.71 | 14.7 | 4.6 | 26.0 |
| Range | 0.12–8.10 | 3.9–46.2 | 1.2–12.1 | 3.8–144.0 |
| SD | 1.11 | 8.4 | 2.2 | 25.5 |
| | | *Clay soils (60)* | | |
| Mean | 0.57 | 22.3 | 6.4 | 27.1 |
| Range | 0.12–1.61 | 10.2–45.8 | 2.0–10.4 | 9.5–77.2 |
| SD | 0.32 | 8.9 | 2.2 | 16.7 |
| | | *All soils* | | |
| Mean | 0.56 | 22.3 | 4.4 | 25.4 |
| Range | 0.10–8.10 | 10.2–45.8 | 1.0–16.7 | 2.1–144.0 |
| SD | 0.69 | 8.5 | 2.5 | 21.5 |
| | | *Soils analyzed* | | |
| | 296 | 296 | 295 | 295 |

†One organic soil had a high concentration of cobalt (65.8 ppm) and copper (664 ppm) and was located near a smelter. These high readings were omitted from the means, ranges and SD of Co & Cu.

Among the tree and vine fruits, soils producing grapes had the highest copper content at 40.4 ± 21.7 ppm and peaches had the lowest at 29.6 ± 18.3 ppm. Fixed copper fungicides have been used on apples, cherries and grapes for almost 80 yr (Table 5).

Soils growing vegetables, pastures and field crops tended to have lower contents of copper than fruit soils and organic soils. A total of 35 soils contained copper levels above 25.4 ± 21.5 ppm and of these 12 were planted to vegetables (8 organic and 4 mineral), 3 to field crops and 20 to fruit.

## Iron

The iron content of soils ranged from 2,560 to 38,900 ppm with a mean of 14,470 ± 7,570 ppm. Sandy soils had the lowest iron content and clays the highest (Table 6 and Fig. 1). The addition of iron in the form of ferbam in fruit orchard soils had no apparent effect on the natural soil level.

## Lead

Soils exhibited lead levels that ranged from 1.5 to 888 ppm (Table 7 and Fig. 2). In the case of tree fruits, lead arsenate has been used for a varying number of years (Table 1). While recommendations for use of lead arsenate on grapes was discontinued in 1942, planting of grapes has occurred on old apple and cherry orchard soils, hence the 10.1 ± 7.9 ppm content. Lead arsenate applications to peach were discontinued in 1956; hence levels are much lower than for

Table 5. Copper, manganese and zinc contents of agricultural soils in Ontario

| | | Soils analyzed (no.) | Copper (ppm) | Manganese (ppm) | Zinc (ppm) |
|---|---|---|---|---|---|
| | | | *General crops* | | |
| Unimproved | Mean | | 23.0 | 490 | 48.5 |
| | Range | 15 | 7.3–36.7 | 91–1,190 | 5.3–116 |
| | Sd | | 9.7 | 262 | 36.2 |
| Field crops | Mean | | 16.6 | 560 | 56.7 |
| | Range | 126 | 2.1–103 | 90–3,000 | 6.3–158 |
| | SD | | 13.7 | 393 | 30.4 |
| | | | *Vegetable crops* | | |
| Organic soils | Mean | | 05.0 | 338 | 66.3 |
| | Range | 12 Cu† | 29.5–111 | 240–540 | 13.0–162 |
| | SD | 13 Mn & Zn | 26.9 | 92 | 61.4 |
| Mineral soils | Mean | | 25.1 | 415 | 51.7 |
| | Range | 56 | 3.1–144 | 111–1,790 | 5.9–150 |
| | SD | | 22.0 | 317 | 41.0 |
| | | | *Fruit crops* | | |
| Apples | Mean | | 39.0 | 317 | 31.7 |
| | Range | 31 | 11.3–110 | 120–861 | 5.4–117 |
| | SD | | 20.7 | 285 | 31.0 |
| Cherries | Mean | | 36.0 | 423 | 56.6 |
| | Range | 28 | 14.7–123 | 113–1,570 | 10.7–112 |
| | SD | | 17.7 | 329 | 29.0 |
| Peaches | Mean | | 29.6 | 416 | 27.6 |
| | Range | 11 | 17.0–81.4 | 120–1,074 | 4.6–65.2 |
| | SD | | 18.3 | 324 | 22.4 |
| Grapes | Mean | | 40.4 | 867 | 57.9 |
| | Range | 16 | 9.5–77.2 | 250–2,010 | 12.3–96.5 |
| | SD | | 21.7 | 494 | 28.5 |

†One organic soil had a high concentration of copper (664 ppm) and was located near a smelter. This high reading was omitted from the mean range and SD for copper in organic soils.

apple and cherry soils (26.4 ± 19.2 ppm). Lead contents were elevated in apple (247 ± 207 ppm), sweet cherry (109 ± 69.1 ppm), and sour cherry (71.2 ± 80.1 ppm) orchard soils. Sour cherry orchards received smaller annual applications than sweet cherry and sweet cherry less than apple orchards. The use of lead arsenate for cherries was discontinued in 1971, but continues to the present day for apples.

The lead content of 210 non-fruit soils was 14.1 ± 9.5 ppm and, of these, 22 soils had residues that ranged from 23.6 to 50.1 ppm. Nine of these soils were planted to field crops, five to vegetables, and one to pasture. No reason could be found for these high levels and it was assumed that they were either unusually high background values or that the fields had been orchards sometime in the past. All soils with residues over 50 ppm came from apple, cherry or peach orchards and reflect the additions of lead to these crops.

Assuming a normal lead level to be between 4.6 and 23.6 ppm, then 24 of the 31 apple orchards, 24 of the 28 cherry orchards, 5 of the 11 peach orchards and 4 of the 16 vineyards had elevated soil contents, indicating the use of lead arsenate.

The mean lead content of organic, sandy, loam and clay soils not cropped with fruit ranged from 10.4 to 17.6 ppm lead; the loam soils were the highest and the organic soils were the lowest.

## Manganese

Manganese contents of soil varied widely from 90 to 3,000 ppm with a mean of 530 ± 531 ppm (Tables 5,6 and Fig. 2). No correlations were noted between cropping practise and manganese content in spite of

Table 6. Iron, manganese, nickel and zinc contents of agricultural soils in Ontario

| | Iron (ppm) | Manganese (ppm) | Nickel (ppm) | Zinc (ppm) |
|---|---|---|---|---|
| | | *Organic soils (13 Fe, Mn, Zn, 11 Ni)* | | |
| Mean | 13,480 | 338 | 28.6 | 66.3 |
| Range | 2,660–24,800 | 240–540 | 6.6–119 | 13.0–162 |
| SD | 8,770 | 92 | 32.3 | 61.4 |
| | | *Sandy soils (125)* | | |
| Mean | 9,030 | 428 | 7.6 | 39.9 |
| Range | 2,650–25,300 | 90–1790 | 1.3–34.2 | 5.3–111 |
| SD | 3,710 | 840 | 4.9 | 30.1 |
| | | *Loam soils (98 Fe, Mn, Zn, 97 Ni)* | | |
| Mean | 16,440 | 606 | 17.9 | 63.8 |
| Range | 5,400–32,300 | 138–2010 | 3.0–97.5 | 8.8–158 |
| SD | 5,900 | 375 | 15.1 | 31.8 |
| | | *Clay soils (60)* | | |
| Mean | 22,770 | 662 | 27.8 | 62.2 |
| Range | 9,900–38,900 | 140–3000 | 8.0–88.0 | 11.3–154 |
| SD | 6,760 | 469 | 18.4 | 33.5 |
| | | *All soils* | | |
| Mean | 14,470 | 530 | 15.9 | 53.5 |
| Range | 2,560–38,900 | 90–3000 | 1.3–119.0 | 4.6–162 |
| SD | 7,570 | 531 | 16.0 | 34.3 |
| | | *Soils analyzed* | | |
| | 296 | 296 | 293† | 296 |

†One loam and two organic soils had high concentrations of nickel (344, 381 and 6560 ppm, respectively) as a result of being close to a smelter. The high readings were omitted from the mean, range and SD for Ni.

the fact that manganese was used widely on certain bean and vegetable crops as a trace element and on vegetables as a fungicide. Grape soils had the highest manganese content; however, they are clay soils which are naturally high in manganese and which receive considerable amounts of mancozeb fungicide. Clay soils had the highest manganese content at 662 ± 469 ppm and organic soils the lowest with 338 ± 92 ppm. The low organic soil manganese concentrations were unusual, since manganese sulfate, maneb and mancozeb were used for vegetable production on these soils.

## Mercury

Mercury content of soils was very low compared to other metals, ranging from 0.01 to 1.14 ppm with a mean of 0.11 ± 0.18 ppm (Table 8 and Fig. 2). The use of phenyl mercuric acetate on apples was the only recommended foliar treatment made to a food crop. Soils from apple orchards had mean mercury contents of 0.29 ± 0.29 ppm. The past use of mercuric and mercurous salts as a root dip for vegetable crops (Table 1), especially cruciferous crops may explain certain high values obtained in both mineral and organic soils which now produce a variety of crops. Organic soils had the highest mean mercury contents (0.41 ± 0.41 ppm) which could be natural or the result of past practises with inorganic mercury salts.

The mean contents of 252 mineral soils (excluding 31 apple orchard soils) was 0.08 ± 0.08 ppm. If a normal soil range of 0.01–0.16 ppm is assumed, then 84.8% of

Table 7. Lead contents of agricultural soils in Ontario

| Agricultural practice & soil type | Soils analyzed (no.) | Lead content in dried soils (ppm) | | |
|---|---|---|---|---|
| | | Mean | Range | SD |
| *Crop production* | | | | |
| General crops | | | | |
| Unimproved | 15 | 12.5 | 3.2– 33.7 | 7.5 |
| Field crops | 126 | 11.4 | 2.3– 47.9 | 4.1 |
| Vegetables | | | | |
| Mineral soils | 56 | 13.3 | 1.5– 50.1 | 10.2 |
| Organic soils | 13 | 12.6 | 2.3– 42.4 | 11.0 |
| Fruit | | | | |
| Apples | 31 | 247.0 | 6.4–888.0 | 207.0 |
| Cherries sweet | 16 | 109.0 | 11.6–233.0 | 69.1 |
| Cherries sour | 12 | 71.2 | 4.4–235.0 | 80.1 |
| Peaches | 11 | 26.4 | 6.0– 69.0 | 19.2 |
| Grapes | 16 | 19.1 | 8.0– 35.5 | 7.9 |
| Total & mean | | | | |
| Tree & vine fruit | 86 | 123.0 | 4.4–888.0 | 165.0 |
| Other crops | 210 | 14.1 | 1.5– 50.1 | 9.5 |
| *Soil types* | | | | |
| Organic soils | 13 | 12.6 | 1.5– 50.1 | 11.0 |
| Sandy soils | | | | |
| Fruit | 43 | 129.4 | 4.4–888.0 | 178.4 |
| Other crops | 82 | 10.4 | 2.3– 47.5 | 8.4 |
| Loam soil | | | | |
| Fruit | 29 | 153.3 | 6.0–654.0 | 171.7 |
| Other crops | 69 | 17.6 | 4.0– 49.3 | 9.9 |
| Clay spil | | | | |
| Fruit | 14 | 43.5 | 8.0–208.0 | 59.0 |
| Other crops | 46 | 15.7 | 1.5– 50.1 | 15.8 |
| Total & mean | 296 | 45.8 | 1.5–888.0 | 102.0 |

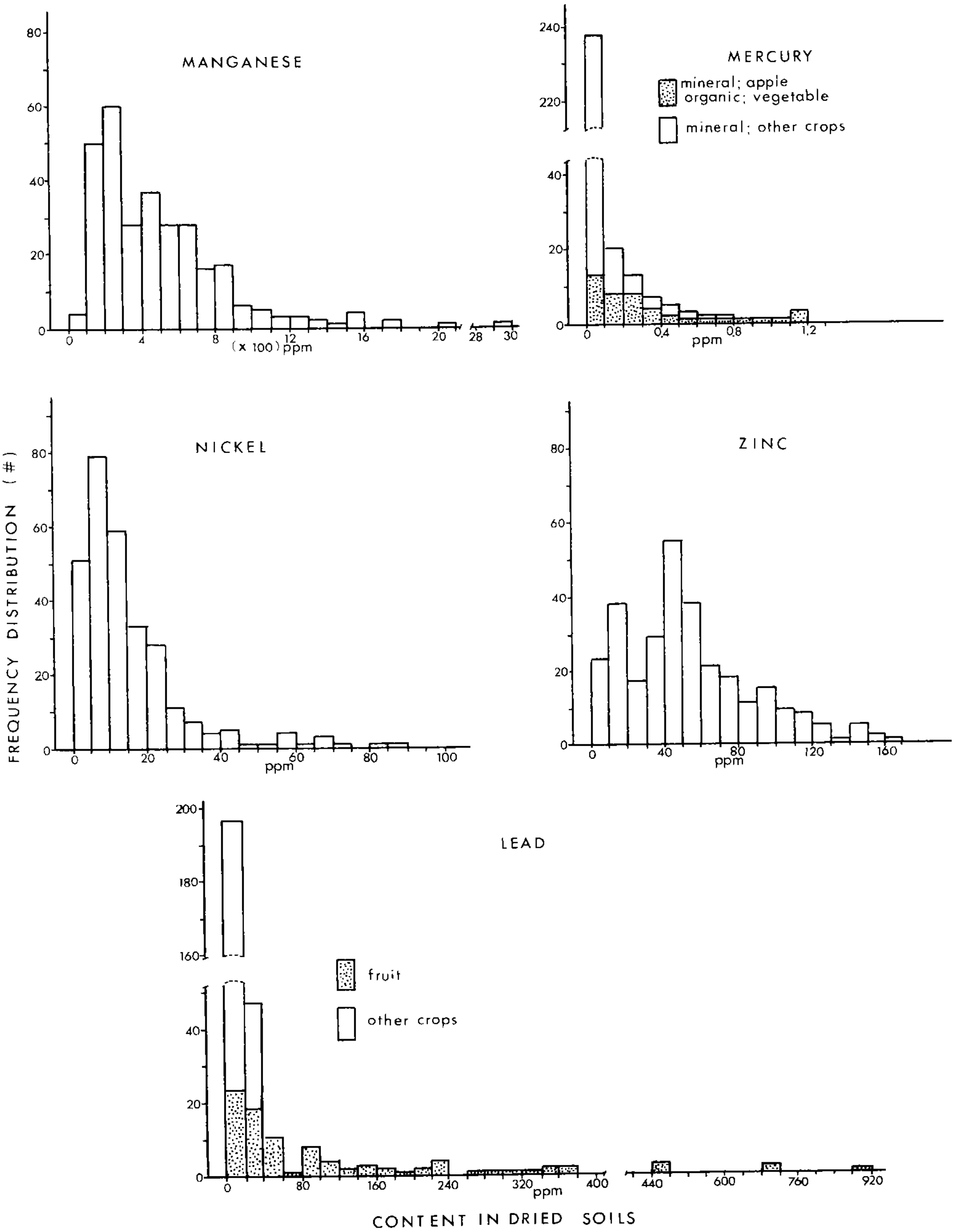


Fig. 2. Soil contents of lead, manganese, mercury, nickel and zinc in 296 soils collected from important agricultural areas of Ontario.

the 296 samples analyzed had mercury contents in that range. Of the remaining 15.2%, 19 were apple orchard soils, 9 were organic soils, and 17 were from a variety of soils and cropping practises that included vegetables (6), cash crops (5), grapes (3), peaches (1), cherries (1) and pastures (1). Investigation of these 17 soil samples revealed that in three cases, tobacco was grown in the rotation and soil from tobacco seedbeds that had been treated with mercury had been spread over the fields. The elevated Hg contents of other soils was not resolved but could be either natural contents or due to past uses of mercury salts.

The mercury content of the different soil types varied very little. The use of methyl mercuric salts as seed treatments over the past 45 yr was not apparent from soil analyses.

## Nickel

The nickel content of soils ranged from 1.3 to 6,560 ppm (Table 6 and Fig. 2). One organic soil had an unusually high nickel content (6,560 ppm). On further investigation the soil on this farm was found to have nickel levels that ranged from 3,260 to 14,890 ppm. It was also found that it was high in cobalt (65.8 ppm), and copper (664 ppm) and was located 1 mile from a nickel–cobalt smelter. Organic and loam soils on two other farms in the same general area exhibited levels of 381 and 344 ppm. These nickel contents appear to be the result of nickel fallout. In order to calculate a

Table 8. Mercury contents of agricultural soils in Ontario

| Agricultural practice & soil type | Soils analysed (no.) | Mercury content in dried soil (ppm) | | |
|---|---|---|---|---|
| | | Mean | Range | SD |
| *Crop production* | | | | |
| General crops | | | | |
| Unimproved land & pasture | 15 | 0.08 | 0.03–0.49 | 0.08 |
| Field crops | 126 | 0.07 | 0.01–0.70 | 0.09 |
| Vegetables | | | | |
| Mineral soils | 56 | 0.10 | 0.02–0.78 | 0.14 |
| Organic soils | 13 | 0.41 | 0.05–1.11 | 0.41 |
| Fruit | | | | |
| Apples | 31 | 0.29 | 0.03–1.14 | 0.29 |
| Cherries | 28 | 0.07 | 0.02–0.27 | 0.05 |
| Peaches | 11 | 0.06 | 0.02–0.18 | 0.05 |
| Grapes | 16 | 0.10 | 0.04–0.31 | 0.09 |
| Total & mean | | | | |
| Veg-organic soil | | | | |
| Apples | 44 | 0.33 | 0.03–1.14 | 0.33 |
| Other crops | 252 | 0.08 | 0.01–0.78 | 0.08 |
| *Soil type* | | | | |
| Organic soil | 13 | 0.41 | 0.05–1.11 | 0.41 |
| Sandy soil | | | | |
| Apples | 13 | 0.39 | 0.05–1.14 | 0.37 |
| Other crops | 112 | 0.06 | 0.01–0.70 | 0.08 |
| Loam soils | | | | |
| Apples | 16 | 0.18 | 0.03–0.42 | 0.13 |
| Other crops | 82 | 0.09 | 0.02–0.78 | 0.12 |
| Clay soils | | | | |
| Apples | 2 | 0.60 | 0.46–0.73 | 0.19 |
| Other crops | 58 | 0.08 | 0.03–0.46 | 0.08 |
| Total mean | 296 | 0.11 | 0.01–1.14 | 0.18 |

normal background level, these three soils were omitted. The mean nickel content then became 15.9 ± 16.0 ppm, as compared to 42.0 ± 382 ppm when they were included. The nickel content of soils increased from sandy soils with 7.6 ppm to clays with 27.8 ppm. Organic soils had the highest mean content at 28.6 ppm.

**Zinc**

The zinc content of soils varied from 4.6 to 162 ppm with a mean of 53.5 ± 34.3 ppm (Tables 5,6 and Fig. 2). The median content was 47.6 ppm. Zinc content was related to soil texture and indirectly to agricultural practise. Sandy soils were much lower in zinc (39.9 ± 30.1) than loam, clay and organic soils which averaged 63.8, 62.2 and 66.3 ppm Zn, respectively. Peach growing soils are sandy and contained low levels of zinc, while those growing grapes were clay and contained high levels. The zinc contents of the soils were considered to be normal background levels and not elevated by agricultural or industrial activities.

## DISCUSSION

The arsenic, lead and mercury contents of fruit soils appeared to have been elevated from the use of inorganic pesticides over the past 80 yr. Records from 1895 to the present time indicate that at least three forms of arsenicals have been used on apples and cherries. Applications of arsenicals, especially those containing lead, occurred over the past 80 yr in apple production, 76 yr in cherry production and 46 yr in peach production. This use pattern is reflected in the Pb and As soil contents of the three tree fruits. The higher As and Pb contents in apple orchard soils reflects the annual application which was double the use on pome as compared to stone fruits. Miles (1968) analyzed soils from four apple orchards and reported contents of from 10.2 to 107 ppm As in soil between trees and 15.6 to 121 ppm As under trees. These ranges compare closely with the 3.2–91.6 ppm arsenic reported in this study (Table 3).

The source of the elevation of lead and arsenic appears to be mainly from lead arsenate, although it could include some calcium arsenate. The ratio of As to Pb in lead arsenate lies between 2.8 and 4.6 and most usually about 1:3.5. Calculating the mean contents for apple, sweet cherry, sour cherry, peach and grape soils the following ratios of As/Pb were obtained, respectively; 4.6, 3.6; 3.1; 2.7 and 2.5. The natural background levels of As to Pb on non-fruit soils was 2.2. The ratios for apple and cherries are indicative of lead arsenate additions. In both peaches and grapes, the elevation is small and indicates little use in recent years.

There were 26 apple orchards with elevated soil contents and 24 with elevated lead contents as compared to the normal background level. For cherries, the numbers were 23 and 24, for peaches 6 and 5, and for grapes 5 and 4, respectively. These data suggest that 81% of apple orchards and 82% of cherries received treatments of lead arsenate.

Mercury contents of soils were elevated by the use of phenyl mercuric acetate in apple production only. While the mean content appeared to be more than triple the background level of mercury of all other soils, the actual increase in the top 15 cm of apple orchard soils amounts to only about 100 g/ha. This accumulation could only have occurred over a 20-yr period of use. Among the orchards surveyed, 61% appeared to have used this foliar treatment. The highest levels of mercury were in organic soils. The findings by Chattopadhyay et al. (1972) indicated some elevation of surface layers of agricultural organic soils and quote 0.02 ppm as the level in virgin organic soils. Past uses of organic and inorganic mercuric salts as seed treatments, root dips, and seedbed treatment may explain the above mentioned elevated contents.

The use of mercurial seed treatments over the past 40 yr did not appear to be reflected in the soil content of agricultural mineral soils. The total possible mercury addition over 40 yr, if seed had been treated annually, would have amounted to 80 g/ha. This could have increased the soil content to 15 cm by only 0.02 ppm, an increase that could not have been measured in this study. Background soil contents of mercury reported in this paper are similar to the 0.08 $\pm$ 0.19 ppb reported by McKeague and Kloosterman (1974) for soils across Canada but slightly higher than those reported by Mills and Zwarch (1975) as present in Manitoba soils.

It was difficult to determine background levels of copper because of its widespread use either as a trace element, a fungicide or a feed additive. However, it is unlikely that unimproved land would have received copper treatment and , assuming the levels in these soils to be background, it is concluded that the levels in organic soils were elevated more than three times. Organic soils have been the main ones receiving copper additions. The use of copper fungicides in fruit production was greatest for apples, grapes and cherries and this is reflected by soil levels intermediate between organic and unimproved pasture. Copper contents in Manitoba soils as reported by Mills and Zwarich (1975) were only slightly lower than those contents herein reported in Ontario.

Chattopadhyay et al. (1972) reported arsenic, cadmium and zinc levels of 0.5, 0.2 and 50 ppm in virgin organic soils and 0.6–1.6, 0.5–1.5, and 325–682 ppm, respectively, in agricultural organic soils. In this study, the zinc levels were similar to those of virgin soils, arsenic levels were considerably higher background and cadmium levels fell within background.

Soil contents of cadmium, cobalt, chromium, iron, manganese and zinc appeared to be normal soil background levels similar to those reported by Hawkes and Webb (1972). In most cases, the metal content increased with increasing clay content of the soil.

Comparison between agricultural soils of Manitoba (Mills and Zwarich 1975) and Ontario soils revealed cadmium and lead were of very similar soil contents, while chromium, nickel and zinc were slightly higher in Manitoba soils.

In a very few soils, the levels appeared to be elevated from either the addition of sewage sludge or aerial fallout from a smelter. One organic soil had mean contents of 65.8 ppm Co, 664 ppm Cu, and 6,560 ppm Ni. These levels indicated serious contamination because normal background levels of these metals are 4.4, 25.4, and 15.9 ppm, respectively. Two other soils located near heavy industrial sites had nickel levels in the order of 300–400 ppm.

## CONCLUSIONS

In conclusion, the elevated metal contents in Ontario soils could be associated with any one of six main sources cited in the Introduction.

(i) PESTICIDES. The use of lead, and calcium arsenate is reflected in considerably elevated As and Pb contents in soils of apple and cherry orchards. Minor elevations of these two elements were observed in peach orchard and vineyard soils. Arsenic levels were elevated slightly from the use of sodium arsenite as a vine killer on potatoes. The use of phenyl mercurial acetate in apple production elevated the mercury content of apple orchard soils. Past uses of inorganic and organic mercury salts may explain higher mercury residues in organic soils and a few in mineral soils. The use of copper fungicides appeared to have raised soil contents on a few soils producing fruit and vegetables.

(ii) FERTILIZERS. The use of fertilizers supplying N, P and K did not appear to affect the metallic content of soils although this was difficult to ascertain.

(iii) TRACE ELEMENTS. The use of copper sulfate as a trace element on organic soils appeared to double normal soil levels.

(iv) MANURES. The use of manures could not be associated with increased metal contents in soil.

(v) SLUDGES. A few cases of high cadmium were associated with past applications of sludge.

(vi) AERIAL FALLOUT. Three farms had soils with nickel levels above normal and one of these farms had elevated cobalt and copper. These elevations were associated with fallout from a cobalt–nickel smelter close by.

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