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To: The Lead Health and Safety Committee

Re: Paper given at the American Association for the Advancement of Science meeting on December 29, 1966, at Washington, D. C.

Attached for your information is a copy of a paper entitled "HEAVY-METAL CONTAMINATION OF SOILS" by Dr. John V. Lagerwerff. This copy was obtained for us by Hill and Knowlton unofficially and may have some mistakes and unclear passages. Please excuse.

We are writing to the author in an attempt to obtain a complete and official copy of this paper.

Of great interest to us are some of the comments that Dr. Lagerwerff makes about lead in that section.

Very truly yours,

Don O. Fowler

DOF:sw
attachment

Lead Mixed with Lead

# HEAVY-METAL CONTAMINATION OF SOILS[1]

Dr. John V. Lagerwerff[2]

Contamination of a soil occurs when foreign substances are introduced into the plow layer which adversely affect the quantity or quality of crops produced. The Environmental Pollution Panel of the President's Science Advisory Committee, in a recent report (137), emphasized the health hazards resulting from heavy metals entering the food cycle by way of the soil. There are at least 5 multiple sources of heavy metals[3] that may cause soil contamination, viz. aerosols, pesticides, limestones and phosphates, sewage sludges, and mine wastes (table 1).

Aerosols derive most of their heavy metals from oxidation processes, e.g., gasoline combustion, coal burning, and metal smelting. Contamination and local pollution of soils may then occur when smelting plants daily discharge into the atmosphere 2 tons of lead, 2 tons of copper, and 3 tons of zinc, as reportedly occurred in Montana (6). Airborne contaminants charged with heavy metals may decisively influence the heavy-metal composition of such slow growing plants as lichen, which is staplefood to reindeer, a main constituent of the Eskimo diet (75, 87). In weighing the potential hazard even of seemingly minute amounts of metals, it is well to remember that by passing through the consumption chain associated with plant and animal life, otherwise harmless concentrations may increase to injurious levels ("biological magnification").

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1/ Contribution from the U.S. Soils Laboratory, Soil and Water Conservation Research Division, ARS, USDA, Beltsville, Maryland. To be presented at the Symposium on "Agriculture and the Quality of Our Environment," sponsored by Section O (Agriculture) of the American Association for the Advancement of Science on December 29, 1966, at Washington, D.C. To be published in the Proceedings of that Symposium.

2/ Research Soil Scientist

3/ The term "heavy metals" in this paper has been used broadly to include certain metals not formally belonging to this group.

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(While the text gives references in parentheses, no list was attached.)

In view of current interest in accumulation, translocation, and degradation of pesticides in soils and waters, it is in order to examine the heavy-metal components of pesticides with respect to their potential as environmental pollutants. In a group of more than 200 different pesticides listed as current in the United States (112), heavy metals occurred 141 times in 112 different products (Hg, 45; Cu, 28; Zn, 24; Cd, 13; Mn, 12; Cr, 7; Sn, 5; Ni, 4; Fe, 3; and Pb, 1). This is because in 29 cases two metal species were present in the same compound. Metals like Pb, Cu, and Hg have been applied to soils since long before the advent of chlorinated hydrocarbons after the Second World War. In 1964, the U.S. production of copper sulfate, lead arsenate, and mercury-containing pesticides amount to about 41.8, 9.0, and 1.6 million lbs, respectively.

The application of limestones and phosphates, or their products, to soil always implies the addition of an array of heavy metals. The situation has been examined for rockphosphate (54), superphosphate (10, 23) and limestone (149). The presence of uranium in many phosphate deposits (113) is important because of the ensuing radioactivity in plants grown on phosphate-fertilized soil (109). This issue will be referred to later.

Sewage sledge, both activated and digested, likewise is a pool of heavy metals (4). In general, the 400,000 odd tons per day of solid wastes produced nationally by urban communities (61), constitute a veritable mine of heavy metals. The agricultural application of treated waste material, therefore, calls for careful chemical evaluation and control (8).

Soil contamination occurs in mining areas. Naturally, the soil near the mining operation is contaminated as a result of the disposal of liquid or solid wastes. Contamination of land by spoil bank drainage,

however, may involve large areas. Depending on the minerals that are mined, the heavy-metal concentration of these liquid wastes may be very high indeed (110), as will be discussed in passing.

The following metals will be examined individually: copper, zinc, manganese, nickel, aluminum, mercury, cadmium, and lead. Whereas the soil chemistry of the first 5 metals has many characteristics in common, that pertaining to the latter 3 deviates in important respects. In addition, hazards associated with mercury, cadmium and lead are far more serious than those typical of the other metals. Not considered are tin, which rarely contaminates soils, and iron, chromium, and cobalt, which are not known to contaminate soils, although the latter two have often been related to soil infertility. In each case, existing information shall be summarized on sources of contamination, occurrence and availability of the metal in the soil, and possible abatement programs. Metal concentrations in plant and soil associated with toxicity symptoms have been quoted in isolated instances only. For each combination of variables, these criteria are unique and of little general value.

Copper

Three sources of contamination with Cu prevail, viz., industrial dusts (47, 87), effluents from mines (48), and from sewage treatment plants (29), and copper-containing fungicide sprays. The latter have been particularly damaging in Florida's sandy citrus belt (143), and in wine-growing areas in France and Italy. Old vineyards near Bordeaux, France, contained up to 845 ppm of total Cu in the topsoil, 25% of which was considered exchangeable (37). Vineyards in the Alsace reportedly contained up to 400 ppm of total Cu in the topsoil (5). Apple orchards

in England with a long copper-spray record contained more than 1500 ppm in the surface mat (78). Concentrations of copper in the soil which exceed 50 ppm may already be harmful in Florida to citrus seedlings (141). In the United States, pesticides containing Cu now mostly hold the metal in an organic, less harmful form.

Copper often accumulates in the topsoil (38, 78, 144), strongly absorbed to silicate mineral surfaces (39, 114), or chelated by organic matter (18, 80). Thus, Cu is rendered less available to plants (98). Where the chelate is soluble, however, it may move to the B-horizon (176). In spite of exhaustive leaching, not more than 25% could be removed from $CuSO_4$ applied at a rate of 90 lbs/acre to columned soils (70). It follows that surface-rooting crops grown on certain orchard soils may suffer severely. Clover and alfalfa are particularly sensitive to excessive amounts of Cu, but so are citrus seedlings. Stunted growth, chlorotic foliage and dieback may result (141).

In determining the equilibrium between the mobile, monovalent, cuprous ions and less mobile, divalent, cupric ions, the soil chemistry of copper is intimately related to the acidity of the soil. Soil treatments or climatic conditions increasing soil acidity to $pH < 7$ favor the cuprous form, thereby causing copper toxicity symptoms where previously there were none. This may partly be caused by a breakdown of the complex between Cu and organic matter as the pH decreases (45). Such conditions may come about by heavy applications of superphosphates (144, 157), gypsum (134), or N-fertilizers (55). The application of phosphates, *per se*, seems to have had little effect in suppressing the availability of Cu to plants (86). Neither did it increase the retention of Cu

in topsoil (145). In order to increase the soil pH, the soil has been dressed with lime (13) or alkaline fertilizers like potassium bicarbonate (45). Although this treatment usually suppresses the uptake of Cu by plants, it failed to happen in studies with trefoil and barley (133).

Cu is known to promote the oxidation of ferrous ions to ferric ions, thereby obstructing Fe-translocation, and inducing Fe-chlorosis, in many plants (58, 73). In overcoming the effects of Cu-toxicity, therefore, application of Fe-EDTA to soil or foliage has met with considerable success (106, 155). In the case of citrus trees, a dosage of one-quarter to one-half pound of Fe-EDTA per tree, and enough lime to raise the pH above 7, have shown good results (160). In Europe, foliar application of Fe-EDTA in conjunction with liming (36), and the use of such Cu-complexing agents as $Ca(Ch)_2$ or $_{\lambda}Fe(Ca)_6$ (146) (???) have been tested with good results in overcoming the adverse effects due to contamination of soils with Cu.

Zinc

The following sources of soil-contamination with Zn prevail: sewage effluents (9), industrial wastes (69), particularly from mines (7, 148), superphosphates (118) and pesticides (59). A few instances have been reported of Zn-toxicity due to protective wire caging around young trees (66) or flax (117).

Chelation of Zn by organic matter in the topsoil, although to a lesser degree than Cu (80), has been repeatedly shown to occur (77, 116). Chelation may render Zn less available to plants. Where the chelate is soluble, it may move to the B-horizon (176). A correlation coefficient of 0.81 (?) has been reported to exist between the distribution of Zn

and organic matter in a number of soils (88). Furthermore, Zn, like Cu, is strongly absorbed by silicate mineral surfaces (49, 120). Where Zn accumulates, therefore, surface-rooting plants like mustard suffer more than deep-rooting plants like peas (95).

The pH of the soil influences the state of oxidation of Zn, as well as the solubility of the hydroxide and of several salts of Zn. This relationship may be limited due to organic-matter complexing of Zn (21). Partly because of the breakdown of organic Zn-chelates, toxic amounts of Zn may be released if the soil pH decreases (172). On the other hand, increasing the soil pH by the application of lime (151, 174), or hydrated lime (159), strongly counteracts the availability of Zn to plants. In bentonite-clay systems, Zn solubility has been observed to reach a minimum in the pH-range of 6 to 8 (92). Yet, maximum uptake of the chelate, Zn-EDTA, was observed at pH 7, which may characterise a physiological optimum (161).

The possibility of a reduction of Zn-toxicity upon the application of phosphate fertilizers to the soil would follow from many a report involving a number of crops (50, 101). No effect of phosphate application on Zn-toxicity was observed, however, with beans (12). Likewise, heavy dressings with superphosphate did not influence the retention of Zn in the topsoil (145). Earlier evidence indicated that Zn is not necessarily precipitated when phosphates are added to the soil (86, 132). It has been pointed out with regard to ion-uptake by excised barley roots that competition between Zn and Ca, rather than precipitation of Zn as the phosphate, may explain reduction in Zn-uptake in the presence of calcium phosphate (131).

In some cases, the possible effect of phosphate fertilizers on Zn-uptake may well have been obliterated by the concentration in which this metal occurred as inperity in these fertilizers. Values as high as 1430 ppm Zn have been measured in superphosphate (18) and up to 2400 in triple superphosphate (12). Rock phosphates from the Eastern USA may contain no more than about 150 ppm Zn; but those from the Western area may have as much as 1050 ppm (29) (cf. table 1). Superphosphate in Australia may also contain large amounts of Zn (170, 126).

Zn-toxicity symptoms appeared to be alleviated by enriching the soil with Fe-chelate (101), or the nutrient solution with Cu-salts (125). The use of Cu-salts, like that of Ca-salts, however, may cause Fe-chlorosis, a hazard also brought about by Zn itself (20, 146).

From experiments carried out in Florida (142) one may deduce that orange trees would be able to overcome toxic symptoms due to Zn by the application of N and K fertilizers to the soil. In contrast, N-containing fertilizers have also been observed to increase the availability of Zn (125). The matter, of course, strongly depends on accompanying changes in soil acidity.

Manganese

Reported instances of contamination of soils with Mn are few. Mine seepage (166), fly ash (140), Mn-containing fertilizers (145), and impure phosphate fertilizers (41) were held responsible.

Although Mn has occasionally been observed to accumulate in topsoils (40), it generally occurs throughout the soil profile (176). Where accumulation occurs, chelation of Mn by organic matter (88), even involving the manganic ion (67), may be a possible explanation. Chelation decreases the availability of Mn (95).

The behavior of Mn in the soil depends largely upon the relative equilibrium between the mobile, divalent manganous and the less mobile, trivalent manganic ions. This equilibrium is determined by oxidation-reduction conditions, which may be chemical or biological by nature (107) and are related to the pH (127). From a soil-pH of 6.5 on up, the oxidized form generally prevails. More acid conditions promote the occurrence of the reduced form (171). The amount of untractable Mn of 26 Louisiana soils increased 6-fold upon submergence (139). Manganous ions are readily available to plants, whereas manganic ions are not (153). Consequently, reducing conditions such as generally exist in poorly aerated soils (17), and such as may exist in the $A_0$-horizon of podzol and podzolic soils (96), may lead to an increase in Mn-uptake by plants. On the other hand, the same conditions also promote loss of Mn by leaching (9).

Soils suffering from contamination with Mn can be readily reclaimed by liming (63, 85). On one occasion, liming a soil from pH 4.5 to 6.5 reportedly decreased the exchangeable Mn by a factor of 20 to 50 (28). With cotton (1) and beans (52) the problem could be controlled by liming the soil to a pH of only 5.4. On one occasion, a recuperative effect has been reported of $MgSO_4$ with regard to Mn-toxicity (104).

Conflicting results have been obtained with regard to the effect of phosphates on the availability of Mn to plants. On the one hand, reports dealing with pineapple (93), and tomatoes (97) indicate that phosphates tend to counteract effects due to toxic concentrations of Mn. On the other hand, phosphates have been mentioned to stimulate the uptake of Mn by leguminous and non-leguminous forage plants (3) and oats (128). Application of superphosphate to soil cultures of lettuce lowered the pH on an alkaline soil, leading to increased uptake of Mn. On an acid soil, however, the pH was raised, thereby reducing Mn-uptake (115).

The oxidation-reduction conditions that determine the equilibrium between manganous and manganic ions are known to be subject to bacterial activity (60, 98). Microbiological oxidation of manganous ions has been observed (19). Fumigation of soils with 1,3-dichloropropane resulted in a decrease in Mn-uptake by Brussels sprouts (102). Steam-sterilization (56, 115), as well as drying (153) of soils, however, resulted in an increased availability of Mn. Bacteria that oxidize Mn increased in number when straw mulch was added to a soil (164).

An excess of Mn is known to cause Fe-chlorosis in plants (51, 124). On the basis of this antagonistic relationship, the decrease in Mn-injury can be explained following application of Fe-salts to the root substrates of tobacco (74), rice (129), and red clover (65). Cobalt has been mentioned as an antidote to Mn in the case of tomatoes (2), and oats (57), but it may cause Fe-chlorosis by itself (72).

Nickel

Until recently, superphosphate containing nickel impurities appears to have been the only known cause of contamination of soil with this metal (54). Currently, Ni has replaced Pb as anti-knock agent in certain gasolines. As plants generally show much less tolerance to Ni than to Pb (cf. 72), this trend should be looked upon with due concern. It may be pointed out that infertility due to Ni is of concern in serpentine soils in Scotland (147, 158), and in Southern Rhodesia (83). The metal here occurs as a native constituent, sometimes accompanied by chromium (147, 156). Whereas Ni occurs throughout the profile in serpentine soils, its presence in certain podzolic soils is limited to the topsoil (44). The possibility of chelation by organic matter has been suggested (32).

Because the availability of Ni to plants is inversely related to the pH of the soil, application of lime has resulted in a reduction of toxic symptoms (25, 32). A 70% reduction in Ni-uptake by sugar beets resulted when the soil pH was raised from 4.8 to 6.3 by liming (84).

Addition of phosphate to solutions containing $NiCl_2$ has been observed to decrease significantly the solubility of Ni at pH> 6.5 (136). On the other hand, application of phosphates to Scottish serpentine soils increased toxicity symptoms due to Ni in the case of oats (33). With soil cultures of tomatoes, application of phosphate fertilizer did not alter the extent of injury due to Ni (121). The matter may depend very much on the pH of the system. Because Ni and Fe are somewhat antagonistic in the nutrition of certain plants, such as barley (38), application of Fe may counteract Ni-toxicity. In fact, in the presence of sufficient Fe, a decrease in pH reportedly stimulated the uptake of Fe by oats at the expense of Ni (31). Where liming is preferred, especially in the case of serpentine soils, attention should be paid to the Fe-nutrition of plants (169).

Aluminum

About the only reported type of contamination of soil with Al, outside of mining areas, occurs when certain kinds of fly-ash settle down (140). As weathering of the ash proceeds, the availability of Al may decrease by the formation of crystalline Ca-aluminate (91). The toxicity of fly-ash to plants has also been ascribed to boron rather than Al (81).

Natural infertility of acid soils due to Al falls beyond the scope of this paper. Soil amendments recommended in this case, however, should be applicable also to soils contaminated with fly-ash. Pertinent literature is voluminous.

Mercury

Fungicides containing Hg abound (112). They seem to be the only presently known source of contamination of soil with Hg. Reports indicate that Hg-containing paints, used for their wood-preserving properties in greenhouses, may constitute a source of contamination when ventilation is inadequate (42).

Under conditions normally prevailing in soils, Hg is readily reduced to the metallic form, thereby disengaging itself from the original compound if the latter were a simple salt. No such behavior has been reported for complex organic Hg-compounds. The toxic nature of mercury vapor has long been known (16). Potted roses did not suffer any damage when grown in soil treated with $HgCl_2$, and placed in a well-ventilated greenhouse. Damage did occur, however, in the absence of ventilation, especially when the soil was mixed with tankage (177). The same was observed to happen with a variety of truck crops (15). In the case of 10 plant species, $HgCl_2$ mixed with soil or tankage that was placed in the immediate environment of, but not in contact with, these plants, caused foliar absorption of Hg and reduction of growth. No translocation of Hg was observed from the leaves to other plant parts (178). Hg did not seem to be taken up by the roots of plants from soil treated with $HgCl_2$ and tankage. The damage was limited to the leaves (79). Reports indicate that the vapors of Hg and $HgCl_2$ affected the growth of roses (138) and that of wheat, beans and lettuce (14) in equal measure in each case. As the vapor pressure of $HgCl_2$ is significantly lower than the one of metallic Hg, it is likely that the chloride salt indeed had broken down, releasing metallic Hg.

Deposited in the form of spray or leaf litter, Hg occurs mostly in the topsoil. The only effective measure against contamination of soil with Hg seems to be the appliation of lime sulfur or of elemental sulfur. Sulfur and Hg react effectively in vapor form (175).

Cadmium

Although there are no known instances of contamination of soil with Cd, a few remarks regarding this eventuality are in order. They are prompted by a recent report on relatively high atmospheric concentration of Cd in 11 Eastern U.S. cities (24), in conjunction with the known low mammalian tolerance of Cd. The latter partly results from the lack of a homeostatic mechanism, i.e. Cd is absorbed virtually irrespective of the existing concentration in the body. It accumulates in soft tissues, and causes cardio-vascular disturbances (30). Distribution of Cd in the atmosphere occurs through processes of smelting, roasting, and plating of metals. Cadmium also reaches the soil as an impurity in phosphates (table 1). It is usually present in soft water flowing through welded pipes. The matter is of concern to soil chemists because Cd is known to be absorbed readily by at least a number of plants such as mint (62), vine (43), lettuce, parsnips, beets, peas, and grain crops (150). In the latter case, the concentrations range from 4 to 14 µg per 100 g wet weight. There is no known information on the soil chemistry of cadmium.

Lead

Prime sources of soil contamination with Pb are combustion products of leaded gasoline, liquid and vapor wastes from coal-burning and metal-smelting establishments, lead arsenate pesticides and phosphate fertilizers. Lead naturally occurs as a family consisting of a number of labile/(radioactive) and stable isotopes. The terminal parts of the thorium and, especially, of the uranium radioactive series are of concern in the case of soils and plants. In the uranium-series, bismuth, tellurium and polonium (Po-210) are the intermediates occurring in the transition from radioactive lead (Pb-210) to stable lead (Pb-206). The transition from Pb-210 to Po-210 is accompanied by beta and gamma radiation, whereas Po-210 transmutes to

Pb-206 producing alpha radiation (46). Lead readily assimilates in the bone, and polonium in the soft tissues (muscle, kidney, spleen) of the mammalian system (76, 123).

Car-exhaust fumes currently are the dominant source of soil contamination with Pb. Between 1950 and 1964, the volume of lead arsenate handled annually by agricultural cooperatives in the United States dwindled from 38 to 9 million lbs. In the same period, the production of leaded gasoline almost doubled from 36 to 70 billion gallons per year. Due to the addition of Pb-tetraethyl or Pb-tetramethyl to gasoline, the radioactivity may be as high as 30 pc/gallon[b/] (108).

The amount of Pb discharged into the atmosphere above the U.S. due to motor vehicles in 1964 amounted to 100,000 tons, or 10% of the total lead industrially consumed (167). It has here been assumed that the proportions of premium and regular gasoline are 30% and 70% of the total gasoline used. The average Pb-contents are taken to be 2.1 and 1.5 g per gallon, respectively (11), with 25% of the lead never reaching the atmosphere. In the entire northern hemisphere, the average annual motor vehicle exhaustion of lead is estimated to be about 240,000 tons. This estimate is conservative (cf. 130). The average atmospheric content of Pb for cities with a population $< 0.1$, 1 to 2, and $> 2$ million increases in the same order from 1.5 to 2.0 and 2.9 $ug/m^3$ of ground-level air (26). Current attempts at improving the combustion of leaded gasoline may result in a decrease of the average particle size of aerial lead compounds. Thus, the concentration of air-borne Pb, and the contaminating capability of the atmosphere with regard to this metal, may increase.

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b/ pc = picocurie = $10^{-12}$ curie = 2.22 atomic desintegrations per minute.

Partially equilibrated mixtures consisting of Pb-210, Po-210 and stable Pb eventually reach the surface of land and ocean by the precipitating action of rainwater, snow, or dusts of various kinds. The steady increase in the Pb-content of the air in the course of this century follows from the fact that the Pb-content of Greenland snow has risen from 0.16 to 2.6 ug/liter between 1904 and 1964 (119). A study of the composition of snow in Lassen Volcanic National Park, California, indicates not only a higher content of lead than calculated on the basis of current lead-alkyl production in the northern hemisphere, but also an isotopic composition similar to that of Los Angeles aerosols. This composition, in turn, is practically identical to the one typical of regular gasoline (27).

The influence of motor vehicle exhaust is directly reflected in the Pb-content of plants as a function of urban proximity, or of distance from and density of, traffic (table 2). Thus, the Pb-content of trees growing near the London, England, metropolitan area was higher than that of specimens growing the countryside by a factor of 7 for ash, 25 for oak, and 26 for hazel (173). Grass sampled as a function of distance from the roadbed contained up to 4 times as much Pb within 25 feet from traffic as that collected more than 500 feet away (22). The Pb-content of grass collected at the leavard side of a road was much higher than that of grass growing at the windward side (47). An increase in traffic density by a factor of 2 or 3 caused an increase in the Pb-content of the tops of roadside grass by a similar factor (94). When rye and potato plants growing within 15 feet of traffic were compared with plants located more than 300 feet away, the Pb-contents of kernel and tuber were smaller by a factor of about 2, but those of chaff and green tops were about the same in the case of each crop (100). Ocean contents of lead also appear to reflect the proximity of industrial establishments (163).

Indications have been gathered in England that the radioactivity of grass remained confined to the aerial parts, and that the fraction of the total Pb that was radioactive Pb-210 was 20 times higher than it was in the soil. These findings suggest that most of the Pb-210 in this grass originated from aerial sources. The Po-210 and Pb-210 apparently were deposited on the grass blades from the air, rather than absorbed by the plants from the soil and translocated to the blades (75, 111). Under the high rainfall conditions prevailing in England, radioactivity of grass amount to 10 pc/g dry matter is reported not to be uncommon (76). There are indications that grasses would absorb alpha-radioactive Po-210 with preference to beta-gamma-radioactive Pb-210 (82). The biological effectiveness of alpha-radiation is 4 times greater than that of gamma-radiation (46).

The much discussed topic of contamination of soil with Pb due to spraying or dusting of plants with Pb-arsenate must remain limited to one pertinent example (90). Eight different plant species were grown for 3 years as rotation crops on commercial orchard soils at 4 different locations in Oregon. Between plants from sprayed and unsprayed soils, the Pb-contents differed by a factor of 1.2 for the tops, 1.6 for the edible portions, and 3.1 for the roots. It had been noted in what probably was one of the earliest studies involving the biological use of radio-isotopes (71) that Pb, when absorbed by the roots, tends to accumulate in that plant part.

The average uranium-content of U.S. phosphate deposits is equivalent to 0.1% $U_3O_8$ (105). It follows that soils dressed with phosphate fertilisers may render plants radioactive due to uptake of Pb-210 and Po-210. Thus, the radioactivity of the bones of sheep raised on fields fertilised with basic slag was 25% of comparable values of animals pastured on fields supplied with superphosphate (109).

Pb originating from contamination tends to be retained in the topsoil. For example, the Pb-content of the $A_0$-horizon was 3.2 times that in the $A_1$-horizon of soils of the Charlotte-town series, and 9.1 times that in the $A_2$-horizon of soils of the Armadale series (176). The possibility of Pb-chelation by organic matter seemed(?)/not likely in a study covering a variety of soils (154). It has been suggested (163) that precipitation of Pb and PbS(?) due to organic matter is instrumental in Pb-retention by the topsoil. Because of the surface accumulation, surface-rooting plants such as cover crops are affected to a greater extent than deep-rooting plants such as orchard trees (89). This may pose a special threat to livestock that is kept on old orchard or potato land (103).

The toxicity of lead to plants has been related to the pH of the soil (34). The uptake of Pb by kidney beans has been counteracted by adding $CaCl_2$ to culture solutions (135). In the case of legumes growing on soils adjacent to mines in England, heavy dressings with lime have been applied with good results to counteract toxicity due to Pb (64).

Concluding Remarks

The majority of the metals discussed in this presentation appear to have a number of properties in common. First, the equilibrium between the more mobile lower-valency forms, and less mobile higher-valency forms depends on oxidation-reduction conditions, pH, and occasionally on microbial activity. These factors may all be interrelated. Second, to some extent they occur as chelates, either by accumulating biologically in living systems, or by reacting with soil organic matter. This generally decreases their availability, though not necessarily their mobility. Third,

to different degrees the heavy metals are competitive with iron. The general order of decreasing competition seems to be: Cu > Co > Ni > Cr > Zn > Mn > Pb (35, 51, 72, 155). The order here given is approximate, and the transposition of any two adjoining metals should be held possible. The toxicity of these metals to plants does not necessarily follow the same order. Fourth, the phosphates of the heavy metals are rather insoluble, especially under alkaline conditions.

It thus follows that unfavorable effects of heavy metals on plants can generally be alleviated by one or more of the following operations: A. Increasing the soil pH to above 6, such as by liming. B. Organic-matter treatment of soil (stubble mulching, green manuring), the pH being near or above 6. C. Application of Fe, particularly as the EDTA-chelate, either foliarly or to the soil. D. Application of phosphates, provided the soil pH is managed properly. Absolute values for the different treatments depend entirely upon species of plants involved and ecological conditions in topo.