HEAVY METALS AND ARSENIC IN THE BIOSPHERE

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INTRODUCTION

This paper reviews some of the information on excesses of the "heavy metals" and arsenic in the soil-plant system. No attempt is made to deal with the effect of inbalances of heavy metals in man or in animals. Instead, use will be made of permissible levels in food as outlined by the Food and Drug Administration and the Saskatchewan Water Resources Commission.

The colloquial term "heavy metal" has been applied (Lagerwerff, 1967) to the following metals: aluminum (2.7), cadmium (8.7), copper (9.0), iron (7.9), lead (11.4), manganese (7.4), mercury (3.6), nickel (8.9), and zinc (7.1). These metals are present in soil and some have essential roles in plant nutrition. They become soil pollutants when for some reason they alter significantly in amount or form, and thus upset the balance of soil composition. Soil pollution, therefore, has been defined (Rennie, 1966) as follows: "Any substance that is common or foreign to the soil system which, in addition to soil either directly or indirectly, adversely affects the productivity of the soil is termed a soil pollutant. Soil productivity includes both yield parameters and the quality of the food products produced".

In the last decade the interest in contamination has caught most soil scientists off guard. Previously, it was not considered important to know the normal levels of non-essential elements such as mercury in the soil; neither was the significance of mercury levels known nor the forms in which mercury was used by plants. Methods had to be developed to measure even the total amount of these elements in soil, but it was well known that the total value of an element in the soil had very little relation to plant uptake values. Similarly,

government food and drug administrations have had to scramble
to provide information on toxic effect in animals and maximum
permissible levels in food and in water. In many cases the
maximum permissible levels in human diets is extrapolated
from the "no-Observed-adverse effect level" in animals with a
safety factor of 100 being employed. Figure 1 taken from
Oser, B.L. (1971), stresses the fact that the acceptable daily
intake (A.D.I.) for man calculated using a safety factor of
100 of the "no-effect" level in animals is more reliable when
the slope of the gradient is steep than when it is gradual,
as it may be at the low growth region where effects are minimal
in degree or instance. Table 1 gives the maximum permissible
levels in food and drinking water of a number of elements.
This careful type of approach means that the agronomist who is
accustomed to elements in the ppm range is required to work
in the nanogram per g region and to examine elements whose soil
chemistry is virtually unknown. Reliable techniques to do this,
first had to be developed.

CONTAMINATION PROBLEMS

As far as contamination is concerned, there are at least
five sources of "heavy metal" contamination in soil. These
have been reported by Lagerwerff (1967) (Table 2) as being
aerosols, pesticides, limestone, and phosphatic fertilizers,
manure and sewage sludges, and mine wastes. One could add
to this contamination resulting from a local deposit or outcrop
of an ore as has been described by Lag et al. (1969). To
understand the effect of an accumulation of any one element in
the soil, it is necessary to review the known soil chemistry
of each in turn. Before doing so, one can generalize that most
of the "heavy metals" will exist as cations in the soil, will
be held on the cation exchange complex, will be less available
at high pH levels than at low pH levels and that only 1 to 10%
of the total metal content will be available to plants.

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Aluminum

Aluminum is the third most abundant element of the accessible parts of the earth's surface following oxygen and silicon. Aluminum comprises approximately 15% of the earth's crust and exists in soils and its immediate environment as undecomposed fragments of alumino silico rocks, alumino silicate complexes (clays), colloidal and undispersed hydroxides, aluminum salts (phosphates), and as a true solution in soil water. The amount of aluminum in the soil solution is related to soil composition and the soil pH. This relationship has been well documented (cf. Soil Acidity and Liming, edited by R. W. Pearson and F. Adams, Agronomy Series No. 9). The mobility of aluminum in crop plants is low, and it tends to accumulate in plant roots, although some accumulator plants have been noted. Aluminum toxicity in acid soils is generally felt to be through the effect of aluminum associated with soil roots blocking the uptake of some other element. In most cases aluminum toxicity can be avoided by raising the pH of the soil by liming. Deposits of fly ash can cause toxicity but the availability of aluminum may decrease as the ash weathers.

Cadmium

Although some reports in the literature claim that cadmium must be considered to be an essential trace element, it is generally not regarded as such. Most recent references, (John et al. 1972); Lagerwerff, 1971; Lagerwerff and Specht, 1970) deal with the pollution aspects of cadmium particularly in soils and in plants in the vicinity of industrial areas where cadmium contamination may occur because of its presence in car exhaust fumes or through the processes of smelting, roasting, and plating of metals. There have also been reports (Lagerwerff, 1967) that show that cadmium in the range of 9 to 36 ppm had been found in the phosphate fractions of fertilizers. The original source of cadmium in the phosphate is thought to be sea water for natural phosphate rock is partly composed of the hard parts of marine animals of the plio-pleistocene or tertiary times.

Man is thought to have a low tolerance for cadmium (cadmium accumulates with age in the human kidney and liver), and the principle sources of cadmium sources for man are mollusks, crustaceans, and grains. There has been a large number of papers dealing with cadmium in the last few years. For instance, Schroeder and Balassa, (1963), examined the uptake by vegetables of cadmium from superphosphate containing 7.25 ppm cadmium that was applied to the soil. Their results showed that the application of this superphosphate to soil did increase the concentration of cadmium in vegetables grown in that soil. The allowable level of cadmium in food stuff, set between 1 to 2 ppm, may be easily exceeded when certain soils are contaminated.

In recent work carried out by John et al. at the CDA Research Station, Agassiz, B.C., found that when 100 ppm of cadmium was added to soil, the cadmium concentration of edible portions of radishes and lettuce averaged 387 and 138 ppm respectively. This very high level of cadmium pollution produced toxicity symptoms and reduced yields. Liming partially reduced this effect. Although comparable levels of cadmium are rarely found in agricultural soils (average cadmium level ranges from 200 to 750 ppb) except in the vicinity of a smelter, this study emphasized that careful evaluation of the cadmium contamination from industrial and waste waters should be undertaken when such is used for agricultural purposes. Lagerwerff (1970) showed that large changes in the content of cadmium due to contamination by traffic caused only small changes in the content of the metal in radish grown in samples partly contaminated soils. However, at 200 meters from a busy highway aerial contamination accounted for greater than 40% of the cadmium content of the radish tops. This material was not translocated to the roots to any significant extent.

Another source of cadmium contamination that has been investigated, Ross and Stewart (1969) is the effect of using cadmium chloride as a cover spray in apple, fruit and foliage. It was found that cadmium accumulated in the leaves and persisted through the growing season and suggest that it may be

translocated from the foliage to the fruit. An interesting
sideline in connection with cadmium is the fact that cadmium-109
has been detected (McCallum and Woodward, 1966) in rainwater
collected in New Zealand following the high altitude nuclear
detonation carried out in 1962. As this material had a half life
of 470 days, and as the cadmium accumulates in bodies, this
radiation was carefully monitored.

Lead

The average lead content of the earth crust has been
established at roughly 16 ppm with the majority of agricultural
soils varying between 2 and 200 ppm (Stevenson, 1971).
Much of the high values have been recorded in densely populated
areas near industrial sites, (Alloway and Davis, 1971), and in
areas of geochemical deposits. For instance, John and co-workers
in B.C. examined 700 surface samples, most of them from farmland
and found that the level of soluble lead was found to vary from
0.5 to 180 ppm. Soil samples taken near a battery smelter contained
50,000 ppm. Surface samples of cultivated soils in eastern
Canada (MacLean et al., 1969) contained 6 to 14 ppm. Warren et al.
1968) conducted analysis of 60 Canadian soils and indicated that
they all contained lead usually between 0.5 and 5 ppm, except soils
that were developed over or near lead-containing rocks which run
as high as 25 to 300 ppm.

The soluble or readily available lead in soils probably
accounts for as little as 1 to 10% of the total lead present.
There is evidence to show that lead is rapidly fixed in soil as a
metal ion form complex with soil humic or fulvic acid fractions.
This means that lead will generally accumulate in the organic
rich surface horizons with concentrations rapidly decreasing with
increased soil depth. The availability of soil lead to plants
is dependent on a number of factors. The addition of organic
matter, lime and phosphate to soils, reduces the available lead
content and its subsequent uptake by plants. The mineralization
of soil lead has been found to be increased under acidic conditions
and to be greater in soils with low organic matter content.

Lead has not been shown to be an essential element for plant growth, although it is commonly found in most vegetation. Some plants display extremely high tolerance of lead in the soil whereas others appear to be killed off. For instance, Lag et al., (1969) described a lead poisoned barren area at Kastad in Norway. The soil samples of the barren area had a high lead content approximate 1,600 times as high as that of adjoining areas, and the apparently normal vegetation of the poisonous area had a lead content in the dry matter of the order of 1,000 ppm, while the dying vegetatio averaged 3,000 ppm with a maximum of 5,000 ppm. Such concentrations of lead must also affect the fauna of the area.

The prime sources of lead contamination are combustion product of gasoline, liquid and vapour wastes from coal burning, and metal smelting establishments, lead arsenate pesticides, phosphate fertilizers, and naturally occurring lead ores. Lagerwerff (1971) states that the amounts of lead discharged into the atmosphere by the U.S. by motor vehicles in 1964 amounted to 100,000 tons or 10% of the total lead consumed industrially in that year. Lagerwer and Specht (1970), Page and Ganji (1970), and others reported by Stevenson (1970) have examined the accumulation of lead in soils for regions of high and low motor vehicle traffic density. They found that where the motor vehicle traffic density was less than 18 motor vehicles per square mile, no lead accumulations were observed. But when the motor vehicle traffic density was greater than 580 motor vehicles per square mile, the lead concentration in the surface 2.5 cm of the soil increased by a factor of 2 to 3 times. This, of course, does not mean that this lead is necessaril available to plants.

Schuck and Locke (1970) analyzed cauliflower, tomatoes, cabbage, strawberries, and oranges, in addition to the soil water and air in contact with these crops. They found that the lead content of 4 of these 5 crops was not altered by the amount of lead in the atmosphere. In some cases, (Dedolph et al., 1970) lead was present as a dust coating which could simply have been removed by washing with water. In another study on applied uptake, reported by stevenson, the emergence, plant height, and grain yielc of corn were not affected by added lead. Lead content of grain averaged 0.45 ppm and was not affected by the added lead. There

was an increase in the straw of stover for the 0 and 3,200 kg
hectare treatments of 2.4 and 37.8 ppm for young whole plants,
3.6 and 27.6 ppm for leaves at tasseling, and 4.2 and 20.4 for whole
plants at grain harvest.

Lead arsenate has been extensively used for insect control,
principally for a control of apple maggots and other chewing
insects in fruit trees. It has also been used for control of
earthworms and other soil inhabiting insects of golf green and
lawns and on airport turf adjoining runways. From an appraisal
of the limited information available, Stevenson (1971) stated that
the use of lead arsenate as a pesticide does affect soil and plant
levels in lead. However, in view of the restricted use of this
compound in special areas, it is doubtful if it constitutes a
serious threat. Another minor source of lead pollution can be
found in the fact that additives such as limestone, phosphatic
fertilizers, sewage sludge and peat contain lead. Limestones
have frequently been found to contain as much as 60 ppm of lead and
sewage sludge may contain extremely high lead levels. This area
needs further research.

In summary, it can be said that despite the fact that lead
has shown to be toxic in solution plant culture at concentrations
of 30 to 100 ppm, the available lead content in soil is unlikely
to be that high. The edible portions of crops such as grains
generally show the smallest lead content, but Mitchell and
Reith (1966) found that the lead content of herbage varied
markedly with season. Care has to be taken with vegetation grown
near busy highways, where much of this lead is present as
surface contamination and with enough rainfall, it will be partially
de-activated in the soil. In the soil, lead is rapidly
immobilized with as little as 1 to 10% of the total lead
present being in an available form. As the immobilization of
lead occurs in the organic matter, there tends to be an
increase in lead at the surface. Some consideration has to
be given to lead levels in soils adjacent to the very busy
highways. Stevenson (1971) concluded that it is doubtful
if man's activities contribute markedly to lead in the food

chain through contamination of soil and subsequent uptake in
vegetation.

Arsenic

Although arsenic is not a heavy metal, it has been associated
with heavy metals in pollution and would appear to fit into
this review. Arsenic is widely distributed in nature as
oxygenated compounds of sulfide. Deposits of arsenic tri-
oxide are known and arsenic sulfide As_4S_4 and As_4S_6 are mined.
The average of arsenic content of soils of various parts of
the world is approximately 5 ppm although Woolson et al.
(1971a, 1971b) report soil arsenic values from 0.4 to 40 ppm.
There appears to be no clear relation between climate and arsenic
content of soil groups, no uniformity of distribution in soil
profiles, and no clearly defined relation between total arsenic
content and plant material. Little is known about the arsenic
compounds formed in soil although their formation has been
assumed to be similar to that of phosphate compounds. If this
is so, factors which affect the behaviour of phosphate in soil
will also affect the behaviour of arsenate. Thus, iron,
aluminum, calcium, phosphorus and humus in soils might be
expected to influence the fixation of arsenic in soil and thus
its vital toxicity.

It has been noted, for instance, that heavy soils require
much more sodium arsenate ($NaAsO_2$) to sterilize than do light
textured soils, as it has been found that the ability of soil
to fix arsenate is proportional to clay content. Further-
more, the solubility product constant of calcium arsenate
($Ca_3(AsO_4)_2$) is greater than that of iron and aluminum
arsenates Fe_x and $Al_x(AsO_4)_x$. Calcium is therefore not as
important in fixation as iron and aluminum are. (Woolson
et al., 1971).

Arsenic toxicity in plants, variously described as leaf
wilting, root discoloration, micosis of leaf tips and margins,
and root plasmolysis, indicate a limitation in the movement

of water in the plant which may result in death. The soluble arsenic levels in soils which cause injury vary from 1 ppm for peas to 9 ppm for peas and beans. Barley is injured by 2 ppm, rice by 7 ppm, but in another series of experiments it has been reported that neither alfalfa or barley were injured with soluble arsenic levels up to 6 ppm. Woolson et al., (1971) found that arsenic accumulated in soil from repeated applications of insecticides, herbicides, soil sterilants, etc. When the reactive iron content of the soil was high, iron arsenate was the predominant form of residual arsenic in most soils. It may also accumulate in soils as aluminum and calcium arsenate if the reactive aluminum or exchangeable calcium is high. It can be leached from the soil if the level of reactive iron, aluminum and exchangeable calcium are low. Application of phosphate could displace adsorbed or fixed arsenic from the soils, thereby initially increasing the amount of arsenic in the soil solution and the plant content. The effect of arsenic toxicity is such that plant growth is limited before large amounts of arsenic are absorbed or translocated to the top.

Woolson et al. (1971) examined the toxicity of 72 contaminated soils from 12 states by a corn bioassay. Total arsenic levels which gave increased toxicity ratings averaged 43 ppm arsenic, none, 89 ppm arsenic slight, 115 ppm arsenic, moderate, 182 ppm arsenic, severe, 345 ppm arsenic, extreme. When the soils greater or equal to 6.5 were extracted with 0.5 N sodium bicarbonate or pH of less than 6.5 were extracted with 0.5 N HCl, and 0.025 N H_2SO_4, the arsenic values for the same five toxicity rankings averaged 4, 9, 15, 30 and 26 ppm arsenic. Woolson did note that there was variability in the data and that this was related to the ability of the soil to hold arsenic in a form unavailable to plants. Data on Saskatchewan soils (Huang, 1972) indicated that As levels in a small sample of Saskatchewan soils were generally low. However, this study which was initiated after animals on a Meadow Lake farm were found to have been poisoned by As

was a preliminary one, and there is a need to know details of
the variations in As in different soils, and factors which
affect arsenic availability.

Various methods of detoxifying soils have been suggested.
Some of these use an increase in acidity either by the appli-
cation of aluminum or iron compounds or by adding sulphur to
the soils to increase the active aluminum and iron content.
Others use the application of phosphorus which displaces arsenic
from the soil colloids. The latter method though will initially
increase the amount of arsenate in the solution.

Copper

Lagerwerff (1967) reports four sources of contamination of
copper as being the most important. These are the industrial
dusts, mine effluents, sewage treatment wastes, (including
effluent from some piggeries) and copper containing fungicides.
As copper is chelated by organic matter and can be held on the
exchange complex, it will accumulate in the top soil. Therefore,
spray treatments of fungicide have been found to be particularly
damaging in the sandy citrous belt in Florida, and in some of the
vine growing areas in Franc and Italy. It has been reported
(Lagerwerff, 1967) that levels of 845 ppm of total copper was found
in the top soil of a vineyard in Bordeaux, France, and that 25% of
this would be exchangeable or plant available. Similar levels
have been found in apple orchards in England with a long copper
spray record. Copper concentrations in the soil over 500 ppm
may be harmful to citrous seedings in Florida. However, this
type of data is of little use unless we know the form in
which the copper is held in the soil and how much of this is
available. For instance, the total copper value of a variety
of Saskatchewan soils was found (Stewart and Tahir, 1972) to
average 88 ppm in the top 15 cm and 76 in the 15-30 cm.
However, only an average of 2 to 3 ppm of this was found to
be extractable by EDTA or DTPA solutions.

The soil chemistry of copper is related to the acidity of
the soil and to the percentage of organic matter. Soil
treatment of climatic conditions increasing soil acidity to

a pH of less than 7 favour the cuprous form, thereby causing copper toxicity symptoms where previously there was none. This may be caused partly by the breakdown of the complex between copper and organic matter as pH increases. Increasing the soil pH by liming usually reduces the uptake of copper by plants. Other means of overcoming the effects of copper toxicity have been the application of organic matter to soils, and as copper is known to promote the oxidation of ferrous to ferric irons, an application of Fe - EDTA to soil or foliage has reduced the effects of copper toxicity. The availability of copper in the soil can be easily measured by use of either EDTA or DTPA reagents. It is this measurement of copper that will be important in determining the effects of copper toxicity.

Zinc

Zinc contamination may be caused by sewage effluents, industrial wastes, particularly from irons, super phosphates and pesticides (Lagerwerff 1967). The chemistry of zinc in the soil is somewhat similar to that of copper, and zinc may be held by the organic matter in the top soil. The availability of zinc would appear to be related to cation exchange capacity of the soil and to the pH of the soil. Deficiency of zinc may be caused by the precipitation of zinc phosphates on the application of phosphate fertilizers. However, phosphate rock may contain large amounts of zinc.

In normal soils the total zinc values range from 30 to 140 ppm. In prairie soils Stewart and Tahir (1971) found that the main 24 soils in the 0-15 cm depth was 126 ± 38 ppm zinc, and in the 15-30 cm depth, it was 119 ± 47. Despite this the amount of zinc that could be extracted in a EDTA or a DTPA solution averaged 1.5 ± 1.2, and 1.6 ± 1.5. This means that approximately 1% of the zinc in soils is in the form available to plants. The chemistry of zinc in soils has been worked out in some detail, and it would appear that the toxicity symptoms due to zinc may be modified by increasing the soil pH or by increasing the organic matter content

in the top soil. A further method has been to enrich the soil with iron chelates and some experiments in soil depth show that toxic symptoms due to zinc may be overcome by the application of N and K fertilizers. However, nitrogen containing fertilizers have also been observed to increase the availability of zinc. This no doubt is due to the form of N applied and subsequent change in soil acidity.

Manganese

There are only a few reports of contamination of soils with manganese, and in general mine seepage, fine ash, and superphosphate fertilizers have been held responsible. Another source of manganese toxicity has been noted in paddy soils (Stewart, Friaz, Lapid (1972), when attempts were made to grow corn on gently sloping concretionary fan terraces during the dry season. The behaviour of manganese in the soil depends on the dynamic equilibrium between exchangeable divalent manganese, which is present as an adsorbed cation on the soil solution, to trivalent manganese, which exists as a highly reactive oxide Mn_2O_3, and tetravalent manganese, which exists as the very inert MnO_2. It has been shown that in soils high in organic matter near neutrality in reaction,

some crops, particularly legumes and small grains, exhibit varying degrees of manganese deficiency. Considerable amounts of organic matter frequently cause the deficiency symptoms to appear at lower pH values.

As the effect of organic matter, lime and degree of soil moisture have been associated with manganese deficiency, it is reasonable to suppose that additions of organic matter and lime will counteract manganese toxicity. Levels of manganese in crops generally average about 50 ppm in cereals, while toxicity symptoms have been noted when the plant manganese value is greater than 500 ppm. A recent study of manganese in Saskatchewan soils (Stewart and Tahir 1972) showed that the average manganese content was 549 ppm, but that the available manganese as measured by EDTA or DTPA solutions averaged 22 or 35 ppm respectively. In summary, it

would appear that manganese toxicity would be rather rare in soils and that applied manganese would be quickly converted to a non-available form in soils near neutrality.

Mercury

Mercury in its elemental state is a silvery liquid metal approximately $13\frac{1}{2}$ times as heavy as water, and it is the only metal which occurred in liquid form at ordinary earth surface temperatures. Like other liquids, it vaporizes and condenses in a pattern determined by its own vapor pressure and by the temperature and biometric pressure of the environment in which it exists. It reacts with a great variety of inorganic and organic compounds to form simple and complex molecules ranging from mercuric sulfide (cinnibar), the most common ore mineral to the metallo-organic complexes which have received recently worldwide attention as potential water pollutants and biological toxicants (Jonasson 1970). The compounds of mercury are dispersed throughout rocks, soils, air, water and living organisms by a complex system of physical, chemical and bacteriological controls.

Mercury content of rocks in the earth's crust range from 10 to 20,000 ppb (U. S. Dept. Int. 1970). Igneous rocks are the basic source of the mercury and these generally contain less than 200 ppb of mercury averaging 100 ppb. Sedimentary rocks average less than 100 ppb and seldom exceed 200 ppb of mercury except for certain organic-rich shales which may reach concentrations of 10,000 ppb. As mercury can exist as a vapour, the atmosphere measured at ground level near mercury ore deposits may contain as much as 20,000 nanograms Hg per cubic meter of air. Rain washes mercury from the atmosphere, and tests have shown that the mercury content of the atmosphere over mercury ore deposits is essentially 0 immediately after a rainstorm. Tests in Sweden (Jonasson and Boyle 1971) have shown that mercury carried down by rain adds to each acre of land per year about the same amount of mercury one would expect to be added by mercury seed dressings for fungal control of cereal crops. Mercury from other

sources is partly held in the upper 2" or so of the soil.

Surface waters generally contain less than 0.1 ppb of
mercury. This reflects the relatively low concentration of
mercury in rainwater and the relatively tight bonding of
mercury in organic and inorganic materials over which the
water passes as it travels through the environment. A
recent reconnaisance of river water in 31 states in the
U.S. showed that 65% of the samples tested had mercury con-
tents below 0.1 ppb, 15% exceeded 1 ppb and only 3% were
more than 5 ppb, the maximum considered safe for drinking
water.

Underground waters are likely to contain higher concen-
trations of mercury because of the longer and more intimate
contact with the mineral grains. However, because of mercury's
tendency to sorb readily on a variety of earth materials
particularly organic matter, particulate matter suspended in
water, and bottom sediments of streams are more likely to
contain high concentrations of mercury than the water itself,
whatever the source might be. Sediments immediately down-
stream of mercury ore deposits and mercury contaminated
industrial discharges may contain from a few hundred to
several hundred thousand ppb of mercury. A recent survey of
the Saskatchewan River (Wobeser et al. 1970, Bailey et al.
1971) showed a similar trend in fish and sediment content.

Although mercury is not known to be an essential part
of the food chain, it is assimilated by organisms living in
the environment which contain it. This process proceeds
through the conversion of inorganic mercury by certain
anaerobes to methyl mercury and more soluble organic forms.
Mercury tends to concentrate in living tissue once it has
been assimilated, and there is some evidence that the extent
of concentration increases with each step of the food chain;
i.e., from plankton to fish to man. If the supply is cut
off the organism tends to purge itself of mercury, but the
efficiency of recovery varies from organ to organ and
organism to organism. One study of fish after 10 days of

exposure in mercury in water with non-lethal concentrations of
ethyl mercury; i.e., less than 5 ppb, showed mercury concen-
trations ranging from 4,000 in muscle tissue to 23,000 ppb in
the blood. Almost complete elimination of mercury occurred
within 45 days except for that in the liver and kidneys.
Similar studies have shown concentration factors of 250 to
3,000 in algae; 1,000 to 10,000 in the ocean fish, and as much
as 100,000 in other forms of sea life. Birds which feed on
fish combine high intake with high concentration factors to
yield extreme residues. For example the eagle owl has been
known to have as high a content as 40,000 ppb in its feathers.

Terrestrial plants like aquatic organisms absorb minor
elements including mercury from the soils in which they grow
at rates depending on the available soil nutrients, and the
genetic characteristics of the plants. Unlike aquatic
organisms there seems to be little tendency for terrestrial
plants to concentrate mercury above environmental levels.
However, there have been claims that a few plants have a
unique capacity to concentrate mercury as droplets of pure
mercury have been found in seed capsules of members of the
chickweed family. Similar droplets of mercury occur under
moss cover of forest floors near mercury deposits. Recent
attempt to substantiate this evidence has not met with much
success (U.S. Dept. Int. 1970). In plants as in animals,
mercury tends to concentrate in fatty parts so that vegetable
fats can be relatively rich in mercury. On average, typical
soils contain from 30 to 500 ppb of mercury with an average
of about 100 ppb, and most of the plants which grow in them
are likely to contain less than 500 ppb (Warren et al. 1970,
Warren and Delavault 1970, Hamm and Stewart 1972).

Experiments have shown that when soil is contaminated
with very high levels of mercury, plants are able to absorb
and translocate it to the different plant parts. This
absorption differs greatly depending on the plant species.
A study by John et al. (1972) of the CDA Research Station,
Agassiz, B. C., has shown that both spinach and lettuce were

found to absorb and translocate the heavy metals to leafy portions whereas peas retained them at the root zone. Preliminary experiments with oats has shown that the mercury level in the leaf in ppb dry matter can be 10 to 20 times as high as the concentration in the grain (Saha et al. 1970).

Mercury as a Pollutant

Although mercury in its compounds has long been known to be toxic, it had not been generally recognized that hazards could arise from disposal of trace quantities of mercury. However, the disaster in Minimata Bay in the early 50's when 41 people died of acute poisoning after eating mercury contaminated fish and shell fish was the first incidence of industrial pollution. This was found to be caused by the direct discharge of methylmercuric chloride in sludge from factories producing vinyl chloride and acetaldehyde, where inorganic mercury compounds were used as catalysts in the production process. The muds in the bottom of Minimata Bay contained 700 ppm Hg, of which about 100 ppm was steam volatile and subsequently proved to be held as organometallics. The level of mercury in shell fish was found to drop to 10 ppm over a two year period following mercury waste treatment in the factory and has remained relatively constant since.

Another source of industrial pollution has been established as the chloralkali chemical plants and paper pulp works. These plants use mercury electrodes in the production of caustic soda and chlorine from brine, and discharge in this case consists of inorganic mercury. Paper pulp plants use phenyl mercury acetate as a slimicide and a preservative in newspaper. It has been possible to replace phenol mercury acetate by other slimicides free of mercury, and the chloralkali plants have been able to prevent the discharge of mercury from their cells.

Agricultural sources (Smart 1968) may also contribute to mercury levels in the aquatic environment as well as directly to mercury levels in the food. Mercury in agricul-

ture is usually restricted to organo mercury compounds used as fungicides for seed treatment of plant disease control. Saha et al. (1970) calculated that the level of Hg added to the soil from this source could be small (500 mg mercury per acre). In Saskatchewan, this would amount to an addition of 0.55 ppb Hg per annum. Cereal crops such as wheat, rye, barley and oats and rice have been seed dressed with methyl-mercuric fungicides. These compounds have been used in controlling pests which affect sugar beet crops, apples, pears, and other vegetable crops. In recent years, the use of these compounds has been eliminated in Canada by the withdrawal of registration by the Federal Governme

Another source of pollution of natural waters occurs within the mining industry from waste materials. It has been established (Fimriette, 1970) that base metal deposits around the Great Lakes drainage basin in Canada contain as much as several ppm of mercury within the sphalerite and galena ores. It is highly probable that lake areas overlying minerals, clay sediments or black shales may have a quite high mercury content.

In soil, most information deals with the total amount of mercury in the soils, and there has been little effort to fractionate the mercury into its various forms. A considerable amount of mercury in soils may be present as elemental vapour adsorbed on soil matter. Jonasson (1970) reports that a study of mercury vapour in the Taskkent earthquake zone showed no measurable mercury in the soil, air, or atmosphere (less than 1 ppb). Samples of clay, sand and loam were collected at 1.5 meter depths down to 5 meters; these samples were degassed and the adsorbed mercury vapour collected. Highest values of about 70 ppb were collected over known faults, and compared with a background level of about 2 ppb. Warren et al. (1970) working in British Columbia found that soil samples taken from horizons with that of a high clay content or a high organic matter content carried a significantly greater quantity of mercury than did the rest of the soil profile. This meant that A horizons could be rich in mercury because of the accumulation of decayed plant materials and by the ability of the organic and clay in the A horizon to hold both

mercury ions and mercury vapour; also clay minerals, those
with a larger surface area, are probably the most efficient
scavengers for mercury. Montmorillonitic clays would be
better adsorbers than say kaolinitic clays. Anderson working
on Swedish soils (reference J. Jonasson 1970) examined 273
soil samples with a range of mercury from 4 ppb to 992 ppb.
He concluded that under normal conditions the mercury content
of soils should be below 150 ppb unless the soil has a high
humus content. Anderson also lists other factors which cause
variation in soil content, pH due to liming of cultivated
soils, varying weights that breakdown of humic matter, and
differences in hydrological and drainage conditions of the land.
Variation would be noted in cases where atmosphere pollution
from smelters, etc., could affect the soils. In general
Anderson found that mercury is distributed in the top soil
at 5 to 10 times the concentration in the subsoil. In con-
trast results (Table 3) found here in Saskatchewan, (Hamm and
Stewart 1972) show that in the majority of soils there is a
slight accumulation in the A horizon compared to the parent
material. However, the concentration in the A horizon is
much lower than that described by Anderson.

In the case of the mineral matter-water system, the
maximum fixation of mercury to solids takes place at a pH of
7.5 to 8. Adsorption of $Hg(OH)^+$ was on to ion exchange sites
of clay minerals and by hydrated oxides is the most likely
mechanism.

Nickel

Nickel toxicity for plant life was first pointed out in
1893, and since that date there have been many studies
carried out on nickel toxicity from many crops. Most of
this work was done in culture solutions. In soils, nickel
content ranges from 5 to 500 ppm with an average of about
100 ppm. Soils have been divided into two groups, viz.,
those derived from sandstones and limestones containing less
than 50 ppm and those soils derived from argillaceous sedi-
ments are basically igneous rocks containing from 5 to 500 ppm.

Also in a few areas, soils derived from serpentine could contain as much as 5000 ppm Ni.

The nickel content of plants was more related to exchangeable nickel in soils determined by neutral normal ammonium acetate solution than to total nickel content. The exchangeable nickel content of Scottish serpentine soils was found to range from 3 to 60 ppm, and in a Rhodesian serpentine soil a value of 5 to 10 ppm has been reported. These soils were found to be toxic when the exchangeable nickel value was above 10 ppm. Apart from the serpentine rocks that cause infertility due to nickel in Scotland and some in Rhodesia, the main causes of nickel impurities have been stated to be

      1) nickel contained in superphosphate as an impurity,

and   2) the fact that nickel has been added as a deposit modifying agent to certain gasolines

(Lagerwerff 1967, lagerwerff and Specht 1970).

Excess quantities of nickel may be avoided by raising the pH of the soil as an application of lime has resulted in reduction of toxic symptoms. In some plants nickel and iron are somewhat antagonistic in nutrition, and an application of iron may counteract nickel toxicity. However, where liming is used, care should be taken to prevent iron chlorosis at too high pH levels.

SUMMARY

In general, the unfavourable effects of heavy metals in plants can be alleviated by one of the following operations:

      1) increasing the pH of the soil to above 6.5 by liming,

      2) organic matter treatment of the soil (green manuring), the pH being above or near 6.5,

      3) application of iron particularly as EDTA chelate either to foliage or to the soil, and

      4) application of phosphate providing the soil pH is managed properly.

This of course is a generalization and care must be taken to examine each case separately with regard to the species of plants involved and the soil properties.

TABLE 1

MAXIMUM PERMISSIBLE LEVELS OF CONTAMINANTS IN FOOD AND WATER (ppm).

	FOOD*	WATER**
As	2	0.01
Cd	1-2	0.01
Hg	0.5	0.005
Pb	2-7	0.05
Se	5	0.01
Cu	50	1.5
Fe	-	0.3
Zn	50	5.0
Ni	-	-
Mn	-	0.05

*   From Food and Drug Regulations

**   Province of Saskatchewan regulations.

TABLE 2

TYPICAL METAL CONTENTS OF VARIOUS SOIL CONTAMINANTS
(from Lagerwerff 1967)

| | Rock phosphate mg/kg dry wt. | Limestone mg/kg dry wt | Superphosphate mg/kg dry wt | Sewage sludge mg/kg dry wt. | Spoil bank effluent mg/l | Urban aerial particulates | |
						Deposited mg/m^{2}yr	Airborne μg/m^3 of ai
Cd			110				
Cr			132				
Cu	100	5	23	758	31	95	
Mn	85	850	51	240	1800		
Ni			18		26		
Pb				7800		780	1.4
				2150			2.5
Zn	342	35	168	2411	145	336	

TABLE 3

LEVELS OF TOTAL MERCURY (ng/g)
IN SOME SASKATCHEWAN SOILS

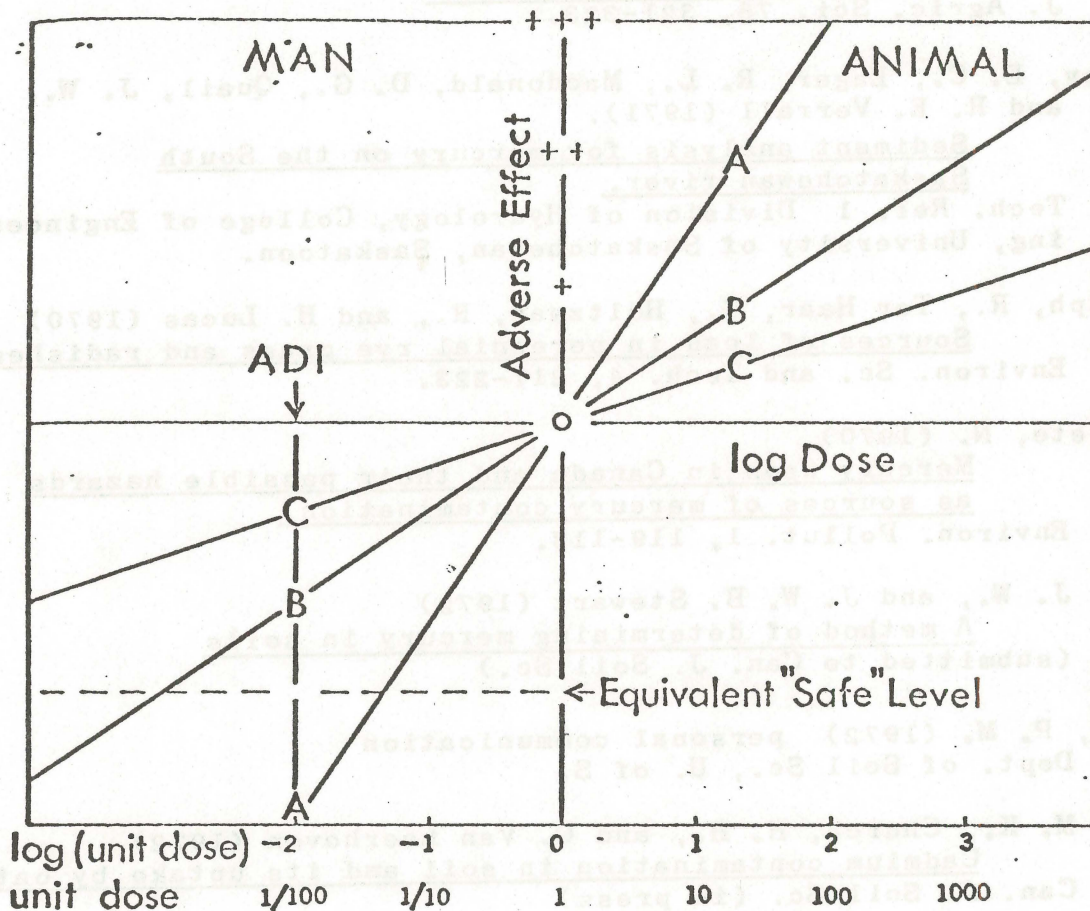| SOIL	HORIZON	Hg (ppb.)	
		Rep. I	Rep. II
Sceptre	Ap	25.0	25.0
	Ck_1	9.0	8.5
Fox Valley	Ap	43.0	42.5
	B_1	20.0	21.5
	B_2	15.5	16.5
	Ck_1	24.0	22.0
Regina	Ap	24.5	22.5
	Ck_1	23.0	25.5
Haverhill	Ap	30.0	30.0
	B_1	19.5	20.5
	Ck_1	24.5	24.0
Sceptre	Ap	23.5	24.5
	Ck_1	27.5	28.0

Fig. 1 Relation of factors used in extrapolation of safe intake levels. Ordinate represents degrees of severity, or incidence, of the effect. (from Oser 1971)

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