5. Effects of selected metallic elements on vegetation.

5.1. Introduction.

The importance of certain metallic elements in plant nutrition has been recognized and clearly demonstrated. The symptoms which are produced in plants when these elements are deficient have been examined and characterized at some length. The symptoms produced in vegetation when these elements accumulate to toxic concentrations have not been examined in depth. While the deficiency symptoms produced by certain elements may be quite characteristic, the toxicity symptoms which have been examined are quite general and not distinctive.

As mentioned previously, plants require a number of elements to complete their life cycle. Some elements, the macronutrients, are needed in relatively large quantities and others, the micronutrients, only in small amounts. Although micronutrients are needed in smaller quantities, this does not mean that micronutrients are less essential to the plant for carrying on its various physiological functions. Some of the macro and micro metallic nutrients and their physiological functions are summarized in Table 5.1-1. In addition to the metallic elements listed in this table, others such as sodium, silicon, strontium, barium, cobalt, etc., may be essential micronutrients for some plant species in some areas, but are not universally essential.

Under natural conditions, elemental requirements of plants are supplied by soil solids, with some degree of supplement from atmospheric deposition and uptake. Table 5.1-2 summarizes the data on overall trace element concentrations in the earth's crust, three broad classes of rocks and soils.

Table 5.1-1. Some of the physiological functions of different macro and micro nutrients.

Nutrient	Function
Boron	Flowering, fruiting, pollen germination, cell division, photosynthesis, hormone movement, water balance
Calcium	Constituent of middle lamella, proteins and protoplasmic membranes
Copper	Constituent of several enzymes, electron transfer, chloroplasts
Iron	Chlorophyll synthesis, peroxidase and catalase enzymes
Magnesium	Constituent of chlorophyll, activator of a number of enzymes involved in trans-phosphorylation
Manganese	Catalytic, regulatory and enzymatic role, associated with chlorophyll formation
Molybdenum	Nitrate reductase and nitrogen fixation systems
Potassium	Osmotic balance, transpiration, enzyme activator
Zinc	Auxin synthesis, enzyme activator

From Chapman (1966), Hacskaylo et al. (1969), Sprague (1964) and Treshow (1970).

Table 5.1-2. Concentration (ppm) of trace elements in rocks and soils.

Element	Earth's Crust	Basic rocks	Acid rocks	Sedimentary rocks	Soils
B	3	1 - 2	3	100	10 - 20
F	700	100	1000	100 - 1000	20 - 1000
V	110	200	50	100	100
Cr	200	2000	2	100 - 500	200
Mn	1000	2000	1000	1000	1000
Fe	50,000	100,000	25,000	35,000	30,000
Co	23	50	8	20	3
Ni	80	200-1000	10		40
Cu	45	150	10	10 - 100	2 - 50
Zn	65	100	60		60
As	2	1.5	1.5	12	1.10
Se	0.09	0.1	0.1		0.01
Br	3	2.5	2.5		6
Mo	1	2	2.5	2	2.5
I	0.3	0.3	0.3	0.3	5
Ba	400	300	800		500
Pb	16				12

From Norrish (1975).

5.2. Sources of metallic elements for vegetation.

Under natural conditions, soil no doubt is the main source for the elemental requirements of plants. This aspect will be discussed in detail in a later section.

Atmospheric sources may also contribute trace elements to the soils or directly to the plant through deposition of soluble materials. Volcanoes, fugitive dust from barren soils, prairies, etc., ocean sprays, and other natural sources contribute to the total particulate load of the atmosphere. Dry particulate fallout, aerosol deposition, gas absorption and wet scavenging (rain and snow) are all contributory mechanisms to the elemental composition of soils and vegetation. In addition, the poorly understood active plant uptake mechanisms of atmospheric constituents should not be ignored.

Anthropogenic sources also contribute trace elements and others to soils and terrestrial vegetation via the atmospheric mechanisms described previously. Metallic elements from pollutant point sources have been observed to cause substantial environmental and health problems over limited areas (Linzon, 1975, Linzon - personal communication, also ref. National Academy of Sciences documents on lead, copper, etc.) and may continue to do so under certain conditions. Some of the anthropogenic sources for particulates are listed in Table 5.2-1.

As an example, Table 5.2-2 summarizes the data on some of the plume constituents which were quantified in the vicinity of a nickel smelter at Thompson, Manitoba. As a comparison, estimated rates of emission from a large coal-fired power plant, meeting all applicable air quality regulations, are provided in Table 5.2-3.

Table 5.2-1. Some of the anthropogenic sources for particulates (metals, etc.)

1. Metal smelter and recycling operations.
2. Cement mills and lime kilns.
3. Combustion of coal and oil.
4. Transportation.
5. Glass manufacture.
6. Incinerators.
7. Agricultural practices.
8. Backyard burning.
9. Mining and related operation.
10. Metal refining and processing.
11. Sewage sludge.

Table 5.2-2. Pollutant emissions from a nickel smelter at Thompson, Manitoba.

Pollutant	1971	1973
SO_2	1700 tons/day	1200 tons/day
Particulates*		
Ni	90 lbs/h	160 lbs/h
Pb	0.8 lbs/h	0.1 lbs/h
Zn	0.9 lbs/h	0.7 lbs/h
Cd	0.1 lbs/h	0.1 lbs/h
Total Particulates	30 tons/day	30 tons/day

*Other elements were not quantified. From Blanel and Hocking (1974).

Table 5.2-3. Estimated emissions from a large coal-fired power plant meeting all state air quality regulations.

Pollutant	Rate of emission lbs/hr
Ni	0.63
Pb	0.15
Zn	0.54
Cd	0.011

Source: Northern States Power Company, 1976.

To illustrate a different type of particulate addition, data on trace element concentrations in four brands of a commercial fertilizer are summarized in Table 5.2-4.

5.3 Origin and some characteristics of atmospheric particulates.

Particulates in the present context are defined as minute solid objects or liquid droplets ranging in size from 0.005 to 500 microns. The size limits are rather arbitrary but are indicated to show that atmospheric particulate matter can be as small as a cluster of several molecules or as large as a visible dust particle.

According to Fennelly (1976), "Very fine particulates behave almost like a gas or vapor: they are subject to Brownian motion, follow fluid streamlines, and are capable of coagulation and condensation. Larger particulates have more of the characteristics of solid matter: They are strongly influenced by gravity and seldom coalesce or condense. The chemical behavior of particulates is determined either by the composition of the particles themselves or by the gases absorbed by the surfaces of the particles. In some cases, the combination produces a synergistic chemical effect more powerful than that of the individual components".

Atmospheric particulates can be classified as primary and secondary particulates. Primary particulates are generally 1 - 20 micro meters in size and are introduced into the atmosphere by chemical and physical processes. Secondary particulates are formed as a result of atmospheric chemical reactions and are relatively smaller.

Table 5.2-4. Trace element concentrations (ppm) in four brands of commercial fertilizer (dried at 100° C).

Brand	Cd	Cr	Pb	Ni	Cu	Hg	Mn	Zn	Fe
				ppm					%
1	63	6000	450	75	450	16	170	1400	5.0
2	43	2900	390	60	250	8	125	900	2.9
3	1	25	10	4	45	0.4	42	30	0.15
4	2	15	20	10	50	1	45	200	0.55

From Van Loon et al. 1973.

Table 5.3-1 summarizes the size ranges of some common particles. Similarly Table 5.3-2 provides data on significant sources of man-made particulate pollution in the United States.

According to Fennelly (1976) for the most part any data based on particulate mass loading must be cautiously assessed because there is no direct correlation between the mass particulates in the air and their effect on air quality in general. Natural dust, although it constitutes almost half the total mass of particulate matter introduced into the atmosphere, has a relatively small impact.

Particles ranging from 10 to 100 micro meters in diameter tend to have characteristics in common with local soil conditions or effluents from local industries. In maritime areas, airborne sea salt is in this size range. Industries using grinding systems, such as grain elevators, feed mills, cement factories, and ore smelters also produce particles in this size range. Gartrell and Friedlander (1975) and Friedlander (1975) discussed techniques for estimating percentage contributions of various sources to the total atmospheric aerosol, using certain elements as tracers for specific pollution sources.

A detailed summary of the chemical composition and size distribution of particles from potential sources of primary particulates is not available at this time. Resolution of particle sizes smaller than several microns is not included in most of the available data and the extent of the significance of these particles has only recently gained attention (Surprenant, 1974).

Recent studies (Davison et al. 1974; Lee and von Lehmden, 1973) of the chemical composition of fly ash as a function of particle size

Table 5.3-1. Size ranges of some common particles.

Particle	Geometric diameter size range in micrometers
Sea salt nuclei	0.04 - 0.7
Fly ash	0.8 - 100
Carbon black	0.01 - 0.85
Paint pigment	0.1 - 10
Pollen	10 - 100
Tobacco smoke	0.01 - 1.0
Cement dust	0.5 - 100
Aitken nuclei	0.06 - 0.14
Milled flour	1.0 - 100
Combustion nuclei	0.01 - 0.1
Coal dust	1.0 - 100
Oil smoke	0.08 - 1.0
Metallurgical dust and fumes	0.001 - 100
Smog	0.01 - 1.2
Insecticide dusts	0.9 - 10

Adapted from Fennelly (1976) and the CRS Handbook of Chemistry and Physics (1971).

Table 5.3-2. Significant sources of man-made particulate pollution in the United States.

Source	Emissions (millions of tons/yr)
Natural dusts	63
Forest fires	11.5
Transportation	1.2
Incineration	0.931
Others	1.284

Adapted and modified from Fennelly (1976).

have found that toxic elements such as lead, manganese, cadmium, thallium, chromium, arsenic, nickel and sulfur increase markedly in concentration with decreasing particle size. It is not clear at this time whether this is a general phenomenon. However, the aforementioned studies may have an important bearing, since smaller particles have longer atmospheric residence times.

As mentioned previously, secondary particulates range in size from 0.005 micro meters to particles with diameters as large as several microns. They are a major source of ubiquitous Aitken nuclei or solid condensation centers. Secondary particulates are products of chemical reactions such as gas phase reactions or reaction between gases and already existing particles. These mechanisms will not be discussed in any further detail in the present context.

5.4 Soil as a source for the elemental requirements of plants.

In evaluating soil as a source for the elemental requirements of plants, it should be recognized that only a portion of the total elemental content of the soil is available for plant absorption. In other words there is a distinct difference between the total and the biologically available elemental composition of the soil. The actual amount of each element taken up by the plants is a function of the plant species, growth stage, environmental conditions and the edaphic environment. As uptake of elements proceeds, there may be a redistribution of nutrients in the soil, with those elements formerly present in a less available form being transferred into more readily available forms.

The concentrations and forms of trace elements in soil solutions have been examined to some degree. Greering (1969) showed that Mn in

solutions from New York soils occurred in a wide range of concentrations and indicated that the values may fluctuate by a factor of 100 during the course of a year. Similar results were obtained by Krupa and Kohut (1976) for calcium, magnesium, sodium and certain other elements in some soils in central Minnesota. The concentration of trace elements in the soil solution are generally low and a rapid replenishment from the solid phase is required to maintain concentrations adequate for plant growth.

The solid phase of most soils contains trace elements in large quantities and in a variety of forms. The rate at which an element is released to the soil solution is primarily a function of the form in which it is found. Some forms, such as the inclusion of a mineral during crystallization, release these elements very slowly, while others, such as the association of an element with a soil surface, allow for a much more rapid release.

The plant processes by which trace elements are absorbed has not been completely understood. It is known that the rate of absorption varies with plant species and the stage of growth and that it is directly related to the trace element concentration in the soil solution. The absorption is considered to be an active reductive process at the root surface which is affected by temperature, pH, aeration, etc. This is substantiated by the studies of Ambler et al. (1970), Carrol and Loneragen (1969), Choudhry and Loneragen (1972) and Robson and Loneragen (1970).

The extent and pattern of contact between soil and roots are important in determining the degree of absorption of trace elements from the soil. The physical and chemical properties of the soil influence the form and distribution of plant roots, which in turn affects absorption.

Symbiotic organisms (ecto and endomycorrhizal fungi) as well as free living organisms in the root zone influence mineral uptake by plants to a significant degree (ref. Krupa and Dommergues, 1977; Bowen, 1974; Gilmore, 1971). The plant root itself modifies the adjacent soil environment by excreting organic acids, amino acids, HCO_3^- and H^+ ions and other materials. These exudates are known to increase the availability of adjacent trace elements, as has been demonstrated by Bromfield (1958) for Mn and by Weavind and Hodgson (1971) for Fe. In addition to these direct effects, these exudates can increase the activity of soil microorganisms which in turn may affect the availability of trace elements both by competition for absorption and by increasing their release from the soil.

Trace elements may move to the root surface by mass flow in the soil solution. At the root surface, the trace element concentration will be the result of the differential of the arrival and absorption rates. If absorption is high enough, the root surface concentration will fall and a gradient will be established causing trace elements to move to the root surface by diffusion as has been shown by Oliver and Barber (1966).

The individual plant species or cultivar is an important factor in determining the quantities of trace elements which will be obtained from the soil. Species may differ significantly in foliar concentrations of particular elements and not in others.

Changes in soil pH have been observed to have pronounced influences on the absorption of trace elements by plants. The increased adsorption of certain trace elements to soil colloids as pH increases is thought to make them less available to plants. However, pH drifts in the plant rhizosphere

should not be ignored. The increased absorption by plants of Zn and Mo with decreasing soil pH has been commonly observed. The absorption of Cu, however, is relatively unaffected by changes in soil pH.

The absorption of a trace element may also be influenced by the presence of other trace elements in the soil solutions. The degree of absorption of Co was found by McKenzie (1975) to be influenced by the concentration of Mn in the soil. Similarly, Chaudhry and Loneragen (1970) found that Zn may depress the absorption of Cu.

The total quantity of a trace element absorbed by a plant is determined in part by the availability of the element in the soil and by the time and rate of absorption from the soil. Table 5.4-1 presents data on the typical concentrations of micronutrients in agricultural soils. Similarly Table 5.4-2 shows values of organic matter and macronutrients in humid and arid region soils. The quantity of the element in plant tissue on a volume or a weight basis is a function of the rate and extent of plant growth. Any factor which increases plant growth without producing a corresponding increase in the rate of trace element absorption or root surface area will decrease the trace element concentration in the plant.

Because of the complexity of the subject in question, for the sake of convenience, in the following section field assessment techniques and analytical procedures for heavy metals and terrestrial vegetation are discussed.

5.5. Field assessment techniques and analytical procedures for heavy metals and terrestrial vegetation.

The asssessment of the impact of heavy metals on terrestrial vegetation and the ecosystem is primarily dependent upon the accurate deter-

Table 5.4-1. Micronutrient concentrations in a typical analysis of agricultural soils.

Element	Normal range ppm
Fe	5,000 - 50,000
Mn	200 - 10,000
Zn	10 - 250
B	5 - 150
Cu	5 - 150
Cl	10 - 1,000
Co	1 - 50
Mo	0.2 - 5

Adopted from Brady (1974)

Table 5.4-2. Relative concentrations of organic matter and macronutrients in soils from humid and arid regions. A representative soil analysis.

Constituents	% Concentration Humid region Soil	Arid region Soil
Organic matter	4.00	3.25
N	0.15	0.12
P	0.04	0.07
K	1.70	2.00
Ca	0.40	1.00
Mg	0.30	0.60
S	0.04	0.08

All the aforementioned values fall within the ranges that may be ordinarily expected.

Adapted from Brady (1974).

mination of the biologically active concentrations of heavy metals in the ecosystem and the effect of these metals on and the accumulative capacity of the native vegetation.

Parameters such as: survey designs, choice of sampling sites, collection of plant samples, preparatory and extraction procedures of the samples, heavy metal analysis procedures and data analysis and assessment are vital for a successful study.

5.5.1. Sampling objective.

Sampling methods utilized for studying heavy metal contamination of ecosystems should attempt to generate an unbiased sampling system that effectively foresees and reduces possible confounding factors. Variables influencing the emission, dispersion, deposition, and concentrations of heavy metals should be identified and accounted for through sampling designs and proper statistical treatment of the data collected.

5.5.2. Sampling designs.

In developing sampling strategies for assessing the impact of heavy metals on an ecosystem, the pollutant source should receive primary consideration. The sampling design should be related to the type of contaminating source, with minor modifications to satisfy specific research objectives. If a different philosophical approach is taken, the sampling system becomes biased and may result in an incomplete or inaccurrate assessment.

Sources of heavy metal contamination may be grouped into three principal types: 1) point sources, 2) line sources and 3) area sources. Examples of point sources include metal smelters, fossil

fuel) power generating facilities, isolated mining operations, secondary heavy metal industrial plants, etc.; line sources consist predominantly of roadways and run-off streams from mining slag heaps; and area sources include urbanized regions and any concentration of industrialized facilities (regional sources may be considered as aggregations of area sources). Sampling designs have been developed for each source type and are grouped into the following major categories: 1) radial transects, 2) line transects, 3) grids (uniform or variable) and 4) other. In general, radial transects are used with point sources, line transects with line sources and grids with area sources.

Numerous studies have been reported concerning heavy metal emissions from isolated smelting operations, principally zinc, copper and lead complexes (Lagerwerff, Brower, and Biersdorf, 1973; DeKoning, 1973; Linzon et al. 1975). These complexes constitute point sources and the principal sampling design has been the radial transect.

DeKoning (1973), in determining Pb and Cd contamination in the immediate vicinity of a lead smelter, developed two concentric circles with 250 and 500 foot radii and sampled each circle at sixteen points of the compass. Lagerwerff et al. (1973), in determining the Cd, Cu, Pb and Zn accumulation in the proximity of a smelter, used two radial transects (SW to NE and NW to SE) and sampled at intervals of 330 to 1330 meters along the transects. The shorter sampling intervals were taken in the proximity of the smelter. Additional samples were taken between the northern arms of the transects when preliminary data indicated that this area contained the highest accumulation of heavy metals. Linzon et al. (1975), in investigating Pb contamination of an urban area by

emissions from secondary lead industries, determined Pb concentrations in the vicinity of a lead smelter by sampling radial transects along eight compass points at 100 meter intervals (up to 600 meters from the smelter). The sampling design allowed for a computer generated mapping of soil (0 - 6 cm depth) Pb and As concentrations after the survey was completed.

The advantages of sampling along radial transects from a point source are twofold. The sampling density is highest in the immediate vicinity of the point source where concentrations of heavy metals are generally highest and the impact on the ecosystem is the greatest. This high density sampling allows for accurate contour mapping of contamination zones in the vicinity of the source. Secondly, radial sampling from a point source allows for the determination of specific concentration gradients out from the source. The occurence of such gradients can be seen in the data from Linzon et al. (1975)(Table 5.5.2-1) where a highly significant correlation exists between distance from the source and concentration of Pb and As in soil.

Crecilus, Johnson and Hefer (1974) in studying soil contamination near a copper smelter, used a sampling grid based on meterological and topographical conditions rather than radial transects. Sampling sites were concentrated north of the smelter stack (26 of 38 total sites) presumably in consideration of the predominant south to southwest winds. Large areas east and west of the stack contained one or no sampling sites. The sampling efficiency of this type of design is extremely low and results in an incomplete description of metal disposition in the vicinity

Table 5.5.2-1. Lead and arsenic content of soils (0-5 cm depth) collected in vicinity of an urban secondary lead smelter - November 1973

Distance and Direction from Source (meters)	Lead (ppm, based on air-dry weight)	Arsenic (ppm, based on air-dry weight)
100 E	5380	132.0
200 E	1650	37.8
300 E	2300	61.0
400 E	4650	70.0
500 E	613	27.4
100 NE	1350	45.9
200 NE	2440	55.0
300 NE	770	24.4
400 NE	1590	43.8
500 NE	663	14.0
600 NE	318	8.7
100 N	1100	32.7
200 N	505	15.8
300 N	810	15.8
400 N	133	9.5
500 N	320	11.6
100 NW	1210	39.0
200 NW	538	18.0
300 NW	445	20.7
400 NW	415	13.5
500 NW	240	16.1
100 W	1920	36.2
200 W	3600	103.0
300 W	1140	27.5
400 W	1920	47.7
500 W	1090	34.2
200 SW	5700	170.0
300 SW	620	33.3
400 SW	378	76.1
500 SW	720	66.5
600 SW	2090	48.0
200 S	21200	533.0
300 S	9700	131.0
400 S	1990	56.0
500 S	1180	25.4
100 SE	8580	393.0
200 SE	13400	240.0
300 SE	943	36.0
400 SE	605	17.0
500 SE	378	18.8
Correlation Coefficients Between Distance and Concentration	$r = -0.48$ ($P < 0.01$	$r = -0.42$ ($P < 0.01$

From Linzon et al. (1975)

of the source. Crecilus et al. (1974) concluded that the greatest metal deposition occurred north of the stack: a possibly accurate conclusion, but with insufficient sampling data.

Lead contamination of roadways by automotive exhausts has been intensively investigated in recent years (Page et al. 1971; Smith, 1972; Dorn et al. 1975; Smith, 1975). The roadway constitutes a line source and all sampling strategies involve developing transects perpendicular to the roadway.

Page et al. (1971) sampled vegetation and soil at various distances from the roadways along line transects across the roadway. Lead content of vegetation (Table 5.5.2-2) and soil (Table 5.5.2-3) was found to decrease with increasing distance from the roadway. Lead concentrations were also influenced by wind direction. Higher concentrations were found at greater distances from the roadway on the windward side of the road. In general, Pb concentrations remained constant beyond 150 meters from the roadway. Smith (1975), in reviewing lead contamination of the roadside ecosystem, cites several investigations where lead concentrations were negatively correlated with perpendicular distances from the roadway. Several studies suggest that the major influence of the roadway is lost at approximately a distance of 50 meters. Dorn et al.(1975), in studying Pb, Cd, Zn, and Cu contamination along a main ore trucking route in the Missouri New Lead Belt region, developed a rather elaborate sampling system using a nested sampling design. However, the primary research objective was to determine heavy metal contamination of a farm located 800 meters north of a smelter. Several animals on this farm developed lead poisoning. Sampling sites were along two perpendicular transects,

Table 5.5.2-2. Lead content of cauliflower plants collected adjacent to the Santa Ana Freeway near Irvine, California (1968)

Distance from freeway meters	Pb content in cauliflower	
	Top half of flower µg/gm	Interior base of flower µg/gm
15	0.33	0.03
77	0.11	0.09
138	0.01	0.03
198	0.02	0.07
258	B.D.	B.D.
320	B.D.	B.D.
362	B.D.	B.D.

B.D. = below detectability or <0.02 µg Pb per gram fresh weight.

From Page et al. (1971).

Table 5.5.2-3. Lead content of surface soil (0 to 7.5 cm deep) at various sites adjacent to the Santa Ana Freeway near Irvine, California (1968).

Distance from freeway meters	Pb content in soil* µg/gm
15	118
77	81
138	85
198	74
258	85
320	75
362	85

*Mean of 6 samples

From Page et al. (1971)

but on only the side of the roadway where the farm was situated, at 60, 140 and 220 feet. Sampling was conducted four times during the year and duplicate composite samples were taken on each transect during every other sampling period. This resulted in a replicate sample for at least one transect at each sampling time. A significant decrease in metal concentration occurred with distance from the roadway. Criticism of this sampling design concerns the choice of sampling strategy. The presence of smelters, mines, and ore trucking routes categoriezes the pollutant source as an area source, not as a line source. Dorn et al. (1975), utilizing a 'control' farm located 45 miles from the test farm, concluded that there was an eightfold increase in the concentration of Pb on the test farm. This was the result of lead mining and processing and not due to the roadway adjacent to the farm.

Endroma (1974) in studying Cu pollution along a river and drainage channel in a copper mining region, constructed line transects along the pollution sources. Soil was sampled at 12 meter intervals along the transects and a negative correlation between Cu concentration and distance from the source was demonstrated.

Sampling designs utilized in studies of heavy metal contamination from area sources are poorly developed at present. Many investigators choose to ignore any uniform or consistent sampling design and tend to study areas in which vegetation is demonstrably affected by some type of a pollutant. Jordan (1975), in studying the effects of zinc smelter emissions on the vegetation in the Lehigh Water Gap in the Blue Mountains of Pennsylvania, chose to concentrate on the inter-

action between smelter emissions and fire on a chestnut-oak woodland. The pollution sources in the area consisted of two smelters separated by approximately 4 km. Because of the restriction of the sampling sites to burned areas (unburned areas constituted control sites), the following sampling pattern was used: unburned sites - 2 km, 16 km, 20 km, and 33 km from the east-plant smelter (compass direction not stated) and burned sites - a) 1.6 km east of highway Route 309, in Schuylkill County and b) 29 km east of the east plant. Zinc concentrations in the soil 2 km from the smelter complex was shown to be sufficiently high to inhibit germination of common tree species, resulting in the "sparsely vegetated or completely barren areas" in the vicinity of the smelter. This study is considered to be very limited in describing the impact of the area source on the ecosystem surrounding the smelting complex.

Shimwell and Laurie (1972) investigated the lead and zinc contamination of vegetation on mining spoil heaps in northern Britain. The study area encompassed 1200 km^2 and a uniform grid system based on 1 km^2 blocks was established. However, rather than sampling uniformly distributed blocks, soil analysis sites were based upon the presence of heavy metal tolerant vegetation and no samples were taken away from spoil heaps. The resulting distribution of contaminated soils mapped on the grid did not reflect the total distribution of contaminated soils in the area, since areas of several 100 km^2 were not sampled at all.

Little and Martin (1972) surveyed the Zn, PB, and Cd concentrations in soil and vegetation in the vicinity of a smelting complex in the Avonmouth area in Britain. The industrial complex contained one of

the largest zinc and lead smelting plants in the world. The entire study area was grid sampled along radial transects centered at the industrial complex. Sampling sites near the smelting complex were 200 meters apart whereas at a distance of 10 km, sites were 3 km apart. In this case the large number of sampling sites allowed accurate contour mapping of the distribution of heavy metal concentrations surrounding the industrial complex.

McGovern and Ballsillie (1974), investigating SO_2 and heavy metal contamination in the Sudbury region in Ontario, reported on the survey system used by the Phytotoxicology Section of the Ontario Air Management Branch to collect soil and vegetation samples. Twenty one sampling locations were established in a non-uniform pattern around the Sudbury complex. Remote sampling sites were located up to 55 miles from Sudbury, and sampling sites were concentrated north of the industrial complex, especially in an area of trembling aspen which showed acute SO_2 injury.

Sampling strategy for surveying heavy metal contamination from an area source can be accomplished most efficiently using a grid system. Ideally, the grid system should be composed of variable sized blocks, smaller blocks in the vicinity of the source, especially in the direction of prevailing winds, and larger blocks at increasing distances from the source. Sampling sites should be centrally located in each block. Such a grid system allows for a uniform distribution of sampling sites, yet concentrates sampling sites in the regions of expected greatest metal accumulations. Contour mapping of concentrations of heavy metals will allow for an accurate description of the dispersion of contaminants

around the source.

While it is generally impossible to fully exploit such a grid system in remote areas where access to sampling sites may be extremely limited, such as in the Copper-Nickel mining area in northern Minnesota, feasible adherence to such a survey system will yield the most efficient and accurate assessment of the effects of an area pollution source on surrounding ecosystems.

5.5.3. Sampling sites and sampling.

Establishment of specific sampling sites along transect lines or within grid blocks is at the discretion of the investigator. Few investigators give specific details on site sampling procedures. Size of sampling sites are most generally related to vegetation sampling rather than soil sampling. Endroma (1974) used 0.5 m^2 plots for vegetation samples, Dorn et al. (1975) utilized circular plots of unspecified diameter, and Page et al. (1971) used a 30 meter transect through each sampling site for vegetational sampling.

Although size and shape of the sampling sites may vary, vegetation and soil samples should be representative of the site. Establishment of circular plots marked by a central stake is one method of uniformly sampling at each site (Dorn et al. 1975). Vegetation sampling should be evenly distributed within the plot and soil samples can be collected along four radial transects at specified distances from the central stake and at the perimeter of the site.

5.5.3.1. Soil sampling.

Soil samples are most commonly collected with a 1 inch soil coring device. The vertical distribution of metals in the soil can

vary considerably (Table 5.5.3-1), with higher concentrations present in the upper soil levels. Most investigators separate soil samples into upper and lower portions or sample only the upper soil level (0-15 cm). Heavy metal concentrations in the upper soil levels affect shallow rooted plants (Endroma, 1974) and the germination of seeds (Jordan, 1975), but have less effect on deep rooted plant species.

Lagerwerff et al. (1973) reported that duplicate composite samples from the same site showed greater variation in heavy metal concentrations than subsamples of a single composite sample. Since metal concentrations in soil can vary horizontally within relatively short distances, especially in areas where mineral deposits are sufficiently concentrated for mining operations, extensive compound sampling is necessary for a representative soil sample at each site. A uniform sampling procedure, as described previously, is desirable for reducing variation if repeated samples are to be collected during the year(s).

5.5.3.2. Vegetational sampling.

Specific guidelines for the collection of vegetation at sampling sites have not been developed. Typically, vegetation samples from one or several plants (of the same species) are combined into one sample for chemical analysis. For tree species, samples may be collected at a standard height (for example, 2 meters above ground level) and duplicate samples may be taken from the same tree. Generally, only the current year growth is sampled. Broadleafed vegetation is often sampled several times during the growing season, although agricultural crops may be sampled only once, commonly at harvest time.

Table 5.5.3-1. Copper content (ppm) in soils.

Soil depth (cm)	Samples 1	2	3	4	5
0-6	7	8	14	18	80
15-20	6	7	7	10	15
30-36	<5	<5	5	7	15

From Endroma (1974).

Little (1973), in studying heavy metal contamination of leaf surfaces, found considerable variation in the concentrations of heavy metals between adjacent leaves on the same branch. Nine elm leaves collected from a twig, near a zinc smelting complex, had Zn concentrations (ppm dry weight) of 3592, 5813, 3477, 3506, 6246, 3596, 3764, 3495 and 5813. Little suggested that a minimum number of 20 leaves should be collected for each sample.

Vegetation samples representative of a specific site should include a minimum of ten specimens combined into a single, composite sample for chemical analysis to reduce sampling variation. The distribution of specimens sampled at a site should be uniform and if several samples are taken during the growing season (in the case of tree specimens), specific branches of trees should be tagged and all samples should be taken from the tagged branches. This method tends to reduce sampling variation.

5.5.4. Analytical techiques.

5.5.4.1. General preparatory procedures.

The most common analytical method currently used for determining heavy metal concentrations in soil and vegetation is atomic absorption spectrophotometry (AAS).

5.5.4.2. Soil and vegetation samples.

Composite soil samples are initially treated by thoroughly mixing the soil to obtain uniform distribution of the material. The soil is then ground in a mortar and passed through a sieve (12 to 80 mesh) to remove rocks and other debris. After the removal of large particles, the samples are dried. Various drying temperatures are commonly used;

air drying (Lagerwerff et al., 1973) and oven drying at 35°C to 105°C (Dorn et al., 1975; Little and Martin, 1972). The effect of different drying temperatures on the concentrations of metals in the soil is apparently negligible when compared to the concentration differences resulting from extracting the soil with different chemical solutions. Van Loon (1974) in studying mercury (Hg), a volatile heavy metal, in municipal sewage effluents found no appreciable loss of Hg (using National Bureau of Standards Orchard Leaves SRM No 1517) at an oven drying temperature of 75°C to 85°C (0.12 ppm $\pm$ 0.02 compared to the NBS value of 0.155 $\pm$ 0.015). After drying, samples are generally ashed at 450°C to 600°C to remove organic matter from the sample and prevent potential problems during analysis due to the organic matter in the sample solution.

Vegetation samples are initially cleaned, either by gentle shaking to remove dirt particles or washed with a variety of solutions to remove surface contaminating materials. A complete discussion of the effect of washing vegetation on heavy metal concentrations is presented in a later section. After cleaning, vegetation samples are air dried or dried in a forced air oven at temperatures ranging from 70°C to 110°C. Samples are then ground in some type of a mill, most commonly in a stainless steel-lined Wiley Mill. Care must be taken that the grinder does not contribute heavy metals to the sample. Some investigators have used Teflon-lined grinders or scintered glass grinders to reduce possible contamination from metal-lined grinders.

5.5.4.3. Sub-sampling.

Samples collected from the field are sub-sampled in the

laboratory to give replicate values for each sample. Statistical treatment of the results of duplicate analysis of samples indicates the degree of variability in the analytical technique and instrumentation involved in the analysis, assuming homogenity of the sample. To reduce variation due to heterogeniety in the composite field samples, preparatory procedures such as grinding of vegetation and grinding and sifting of soil should be conducted prior to sub-sampling.

Lagerwerff et al. (1973) studied the sampling variability of the heavy metals Cd, Cu, Pb, and Zn in soil samples. Duplicate composite samples from the same site and subsamples of the same composite sample were analyzed. The mean coefficients of variation were respectively 16% and 7% indicating that the variation of the analytical procedure is less than the variation involved in sample collection procedures. Van Loon, Lichwa, Ruttan and Kinvade (1973), in determining heavy metals in sewage sludges, found that individual grab samples from sludge tanks showed greater variation in heavy metal concentrations than composite grab samples and recommended that composite samples be taken for analysis in similar studies.

5.5.4.4. Washing vegetation samples.

Vegetation samples may become contaminated with soil particles, air borne particulates or other debris. Root or tuber samples naturally contain adherent soil particles and newly emergent vegetation or vegetation sampled near ground level (especially agricultural crops) may contain rain-splashed soil or become soil contaminated during the collection procedures. Additionally, aerial portions of vegetation collect dust particles and accumulate deposits of air borne particulates

containing heavy metals.

Consideration of the method used to reduce such contamination must take into account the effects the method will have on altering heavy metal concentrations. Root samples must be shaken, scrubbed and washed (preferably with distilled water) to remove adhering soil particles and gentle shaking of aerial portions of vegetation is usually sufficient to remove large soil particles. Rain-splashed soil contamination cannot be effectively separated from aerial deposition of dusts and particulates, however. In situations of vegetational sampling where the possibility of rain-splashed soil contamination exists, it is desirable to sample the vegetation no closer than 10 cm above ground level.

The removal of dust or particulates from leaf or stem surfaces greatly affects the concentrations of some heavy metals, particularly Pb, and the decision to use some type of washing procedure should be made based on the research objectives. If heavy metal contamination of agricultural crops used for animals or human consumption is being investigated, then total metal concentration is desired. On the other hand, if heavy metal effects on natural ecosystems is the research objective, then superficial leaf deposits are often biologically inert and may have little effect on vegetative growth or survival.

Several types of washing solutions can be used to remove varying amounts of superficial surface deposits. Page, Ganje and Joshi (1970) in their investigations on Pb in agricultural crops along major highways, used a washing process consisting of a 1-minute agitation of plant material submerged in distilled water. Lead content of unwashed, once washed and twice washed alfalfa leaves were respectively 60.9,

36.0 and 14.2 mg/g dry weight. Washing with dilute solutions of nitric acid (HNO_3) removed even more surface Pb (Table 5.5.4.4-1). Lagerwerff, Armiger and Specht (1972), using a rinsing procedure consisting of agitating fresh plant material for 5 minutes in a plastic screen in a stream of deionized water (flow rate 20 gal/hr), found a significant ($P = .95$) reduction in Pb content of alfalfa leaves. Smith (1972), in a study of Pb and Hg contamination of urban woody plants, used the following washing procedures: 1) 30 seconds vigorous agitation in metal-free water, 2) 60 second vigorous agitation in 1.0% hexadecyltrimethylammonium bromide, followed by a rinse in metal-free water, 3) 60 seconds vigorous agitation in 0.1% hexadecyltrimethylammonium bromide, followed by a rinse in metal-free water, 4) 30 seconds vigorous agitation in 0.05% hexadecyltrimethylammonium bromide and 0.05% N-(hydroxyethyl) ethylenediaminetriacetic acid, followed by a rinse in metal-free water, and 5) 30 seconds vigorous agitation in 0.05% hexadecyltrimethylammonium bromide and 0.05% diethylenetriaminepentaacetic acid followed by a rinse in metal-free water. No significant difference ($P = .95$) was found in Pb concentration between washed and unwashed samples. Smith suggested that either the washing procedures were inadequate to remove superficial deposits or that the majority of Pb was present inside the tissue.

Little (1973), in a study of heavy metal contamination of leaf surfaces to determine the proportion of heavy metal burden that might be of biological significance to the plant, used three different washing solutions to assess the proportions of Zn, Pb, and Cd remaining on the surface of elm leaves. Deionized water was used to determine the water

Table 5.5.4.4-1. Lead content of alfalfa leaves subjected to various washing procedures.

Washing treatment	Duration of washing minutes	Condition of leaves	Pb content of		
			Wash solution* µg/gm	Leaves µg/gm	Leaves plus wash solution µg/gm
Control: (unwashed)	0	Fresh	....	42.0	42.0
		Dried	....	49.0	49.0
Water	5	Fresh	28.0	28.0	56.0
		Dried		27.0	55.0
HNO_3 1.4%	5	Fresh	58.0	7.0	65.0
		Dried		7.7	66.0
1.4%	20	Fresh	58.0	4.8	63.0
		Dried		4.9	63.0
3.5%	5	Fresh	46.0	7.9	54.0
		Dried		9.4	55.0
7.0%	5	Fresh	53.0	6.3	59.0
		Dried		3.1	56.0

*Amounts of Pb removed by washing fresh leaves, oven-dry-weight (70°C), washed.

From Page et al. (1971)

soluble fraction and the proportion of heavy metals likely to be removed by heavy rainfall; a 2% detergent solution was used to determine proportions of metals physically attracted to the leaf surfaces; and two HNO_3 concentrations (0.1% and 0.01%) were used to determine the proportion of metals bound to the leaf surface by exchange phenomena. Washing with deionized water removed substantial amounts of Zn, Pb, and Cd from leaf surfaces, a larger amount of Pb being removed than Zn or Cd (Table 5.5.4.4-2). Substantial quantities of metals unaccounted for in water washings were assumed to be water insoluble fractions and acidifying the washing solution greatly reduced this insoluble fraction.

Leaves boiled after washing in deionized water left only small percentages of metal concentration in the boiling water, these metal concentrations presumably representing metals bound in the cell wall and cuticle and therefore biologically unavailable.

Additional washing procedures used by other investigators include a detergent or acid wash followed by rinsing 3 to 4 times in distilled water (Jordan, 1975; Nash, 1975; Anderson, Meyer, Mayer, 1973). In these studies no comparison was made between washed and unwashed samples and the loss of metals resulting from the washing procedure were not determined.

5.5.4.5. Extraction methods.

Metals in soil and vegetational samples must be brought into solution for analytical determination by atomic absorption spectrophotometry, emission spectrometry, or colorimetry. Several extraction solutions are used commonly for this purpose. Prior to or as a part of the extraction procedure, samples may be ashed at 450°C to 800°C, either

Table 5.5.4.4-2. The mean percentage (of 4 replicates) of total metal burden removed from elm leaves at each stage of treatment, the percentage remaining in the leaves after treatment, and the percentage of metal unaccounted for

	% In washing aliquots (soluble)	% In boilings	% Remaining after treatment	% Unaccounted for	Total % removed by washing
Zinc					
Deionized water	27.04	7.28	25.50	40.09	67.13
Detergent	34.62	5.45	34.69	25.30	59.87
5% HNO_3	90.00	N.D.	3.25	6.76	96.76
1% HNO_3	78.80	N.D.	3.81	17.39	96.19
Lead					
Deonized water	7.97	2.37	8.91	78.80	86.70
Detergent	15.52	0.995	13.60	69.90	85.40
5% HNO_3	95.55	N.D.	3.62	0.45	96.43
1% HNO_3	94.80	N.D.	4.94	0.26	95.60
Cadmium					
Deonized water	13.31	4.29	32.00	48.80	62.07
Detergent	27.72	3.32	18.64	50.33	78.05
5% HNO_3	89.90	N.D.	1.11	9.00	98.90
1% HNO_3	74.60	N.D.	1.28	24.12	98.72

(N.D. = concentration in solution below level of accurate determination.)

From Little (1973)

wet or dry, to remove organic material that could interfere with the analysis of specific heavy metals.

In the extraction of vegetation samples, the total concentration of heavy metals is most often desired. General procedures include the digestion of dried, ground vegetation with a mixture of nitric (HNO_3), sulfuric (H_2SO_4) and 60% perchloric ($HClO_4$) acids in a ratio of 10:1:4. After digestion, the samples may be either dried and then ashed, or wet ashed. After ashing, the samples are extracted with successive volumes of dilute (0.1N) HCl. The extracts are then centrifuged and the supernatant solution analyzed after suitable dilution.

The solutions used for extracting soil samples greatly effect the concentration of metals removed from the soil and the extraction procedure utilized will depend upon the research objectives of a particular study. For determination of total metal in soil samples, digestion with hydrofluoric (HF) and nitric (HNO_3) acid is used. Van Loon et al. (1973) suggests that a variety of acids such as HCl, HNO_3, HF, H_2SO_4, $HClO_4$ or a combination of two or more can be used to decompose sludge samples. Additionally, extracting solutions of H_2O (Jordan, 1975), and 2.5% HAc (Little and Martin, 1972) have been used in determining heavy metal concentrations in soil. In studying the decomposition of sludges, Van Loon et al. (1973) found that aqua regia (HCl and HNO_3) resulted in greater than 90% extraction efficiency of the elements examined. Smilde, Koukoulakis and Van Luit (1974), in studying crop response to P and lime on soils high in Zn, extracted soil for Zn using the following solutions and procedures: 1) 1:10 w/v (soil/solution) 0.025M EDTA, 15 min shaking; 2) 1:2.5 w/v 0.025M EDTA, 60 min shaking;

3) 1:2 w/v 0.01M EDTA and 1M $(NH_4)_2CO_3$, 30 min shaking; 4) 1:40 w/v 2.5% AcOH (acetic acid), 15 hr shaking; and 5) 1:10 w/v 1M $AcOHNH_4$ extraction solution (Table 5.5.4.5-1). Dudas and Pawlik (1975) in studying metal uptake by plants grown on sewage ammended soil used a solution of concentrated HNO_3, HCl and HF (total metals); 1N HCl (soil:solution ratio 1/10 w/v), and 0.5N acetic acid (soil: solution ration 1/10 w/v). Soil and sewage extracted with 0.5N acetic acid yielded the lowest metal concentrations (Table 5.5.4.5-2) yet were indicative of the biologically active metal concentrations in soil or sewage since, in general, there was agreement between metal uptake by lettuce and acetic acid solubility.

Table 5.5.4.5-1. Correlation coefficients for the relationship between plant Zn concentration and soil Zn concentration, as determined with various extractants in Zn polluted Neerpelt soil

	1:10 0.025 M EDTA	1:2.5 0.02M EDTA	1:2 0.01 M EDTA-1M $(NH_3)_2CO_3$	1:40 2.5% AcOH	1:10 1M $AcONH_3$
Beans (site 1)	-0.0713	0.0870	0.7253	0.3197	0.8375*
Maize (site 2)	0.1086	0.5377	0.8651*	0.3365	0.8664*

*significant at 5% level

From Smilde, Koukoulakis and Van Luit (1974).

Table 5.5.4.5-2. Trace element content of sewage sludge and cultivated soils expressed in ppm in dry sample

	Hg	Pb	Cu	Zn	Cd	Cr	Ni	Mn	Al	Sr	Li
						Total content					
Edmonton sewage		420	400	1200	23	2000	160	400	10800	102	7.0
Lethbridge sewage		220	1200	850	6.5	240	70	160	12500	129	4.2
						1 N HCl-extractable					
Edmonton sewage	5.7	360	250	1200	14	1700	48	320	2350	75	0.72
Edmonton soil†	0.028	12	5.4	26	0.26	< 1	4.5	230	2150	29	0.48
Lethbridge sewage	8.1	160	420	810	4.4	140	16	140	6700	96	0.54
Lethbridge soil††	0.025	7.1	3.6	7.2	0.34	< 1	2.0	220	1050	6.8	0.28
						0.5 N acetic acid-extractable					
Edmonton sewage		1.8	4.5	280	2.3	9.5	28	190	40	58	0.24
Edmonton soil		0.85	1.5	4.4	0.05	< 1	2.5	42	110	13	0.16
Lethbridge sewage		1.1	18	300	2.2	2.0	10	88	200	73	0.30
Lethbridge soil		0.65	0.82	2.8	0.08	< 1	1.0	75	220	4.8	0.20

† Ap horizon of an Orthic Black Chernozem.

††Ap horizon of an Orthic Dark Brown Chernozem.

From Dudas and Pawlik (1975).

5.6. Selected metals and boron: Their sources, biological availability and plant deficiency and toxicity properties.

In the following sections, the metalloid arsenic, the metals cadmium, calcium, cobalt, copper, iron, lead, magnesium, mercury, nickel, potassium, sodium and zinc and the non-metal boron are discussed on an individual basis.

In general, the discussion of each element is subdivided into:

a. Introduction

b. Sources

   Natural

   Anthropogenic

c. Biological availability

   Soil solid phase

   Soil solution

   Transition between the two phases

d. Role in plant nutrition

e. Plant deficiency symptoms and the conditions inducing such deficiency, and

f. Symptoms of toxicity on plants and the governing factors.

Our current knowledge of mineral deficiency and toxicity symptoms on a wide variety of plants and the factors governing their occurrence under field conditions is significantly limited. In the following presentation, every effort has been made to summarize the state of the art. However, this review does not represent an exhaustive coverage of all the available literature on the subject.

5.6.1. Arsenic (As)

5.6.1.1. Introduction.

Arsenic is not considered essential to plant growth, but stimulation of root growth in culture by small amounts of the element has been reported (Liebig, 1966).

As a free element, arsenic is not considered toxic. However, its compounds, such as calcium arsenate, lead arsenate, cupric arsenate, sodium arsenite, and arsenic trioxide have been used intensively as insecticides and are considered very toxic. Sodium arsenite and arsenic trioxide have also been used as herbicides. Although properties and functions of these compounds as pesticides have been studied, very little information on actual arsenic-soil-plant interactions exists at this time.

5.6.1.2. Sources of Arsenic.

a. Natural:

Arsenic is present as arsenide sulfides in igneous rocks and is capable of conversion to arsenate, AsO_4^{3-}, in an oxidizing atmosphere. In this form its crystal chemistry resembles phosphates, vanadates, silicates, or sulfates (Norrish, 1975).

The overall concentrations of arsenic in the earth's crust is approximately 2 ppm. Natural concentrations range from 0.2 ppm to 64.4 ppm (Liebig, 1966; Chisholm, 1972; Crecelius et al., 1974). Acidic and basic rocks contain only about 1.5 ppm arsenic whereas sedimentary rocks average 12 ppm. Marine iron ores contain an average of 500 ppm (Norrish, 1975).

At present, there are no published reports of the arsenic concentration in soils in the copper-nickel mining region in northern Minnesota.

b. Anthropogenic:

Anthropogenic sources of arsenic can cause serious environmental alternations, with somtimes tragic results. Two major anthropogenic sources of arsenic are:

Metal smelters.

Figure 5.6.1.2-1 illustrates the range of arsenic concentrations in soils adjacent to a large copper smelter in the vicinity of Puget Sound, Washington. Natural background levels in these soils are estimated to be 1 to 30 ppm arsenic (Crecelius et al., 1974).

Insecticides and herbicides.

Studies dealing with arsenic induced plant damage were most often concerned with insecticides and herbicides. For example, Nova Scotia soils considered to contain "normal" levels of arsenic, when treated with lead arsenate at 169 Kg/hs annually from 1949 through 1953, increased in arsenic content as follows:

	Untreated	Treated
	ppm As	(air dried)
sandy loam 1	24.5 $\pm$ 0.4	122.5
sandy loam 2	9.6 $\pm$ 0.7	

Table 5.6.1.2-1 shows marked increases in arsenic concentrations, depending on the application rate of three arsenic containing herbicides.

Potential from mining sources

(a) As atmospheric emissions

(b) Others

Could be emitted in waste water.

5.6.1.3. Biological Availability.

a. Soil solid phase:

Arsenate in soils behaves like phosphate and is fixed by iron oxides. It has been proposed that arsenate forms insoluble crystalline compounds with iron, aluminum, and other oxides, and with clay minerals. One study showed that arsenic became associated with iron (goethite) in a lateritic podzalis soil near Adelaide, Australia (Norrish, 1975).

Although other absorption experiments show that aluminum oxides and Kaolin are important in arsenate retention, evidence indicates that iron oxides hold most of the soil arsenic. This may largely be due to the relatively finer grain size of iron oxide clay minerals (Norrish, 1975).

Soils with a higher clay content are able to inactivate greater amounts of arsenate. Also soils have been found to be able to inactivate much more calcium arsenate than lead arsenate; i. e., the latter accumulates to toxic levels much sooner than calcium arsenate (Johnson and Niltbold, 1969).

Applications of methanearsenate to turf on a sandy loam soil showed that 85% of the total arsenic in the surface layer was held by the clay fraction. Little of the arsenic was found to be in the organic form. This study concluded, contrary to other hypotheses, that arsenic does not behave like phosphorus: arsenic has a greater water solubility, and a lesser tendency to be absorbed, precipitated, or occluded. Most of the soil arsenic was found associated with iron. However, most of the arsenic not readily extractable was associated with aluminum. The study also concluded that arsenic is relatively stable in soils, even though it is readily leached (Johnson and Niltbold, 1969).

One field experiment showed that in a soil (unspecified) treated with $NaAsO_2$, the arsenic gradually disappeared with a half-life of 6.5 years Creselius et al., 1974).

b. Soil solution:

No distinctions were made in the literature between arsenic in the solid phase versus that in the soil solution.

TABLE 5.6.1.2-1. Concentrations of arsenic with depth in soil after four years of surface application of monoammonium, monosodium, and disodium methanearsonate.

Depth cm	MAMA ppm As	MSMA ppm As	DiMA ppm As
	2.23 Kg/ha Application Rate		
0-5	15.6	15.1	12.2
5-15	10.9	9.2	10.7
15-30	8.9	6.9	8.5
	4.47 Kg/ha Application Rate		
0-5	18.5	20.9	13.5
5-15	12.0	14.8	10.7
15-30	9.9	10.5	5.4
	8.95 Kg/ha Application Rate		
0-5	28.3	21.5	18.1
5-15	16.2	15.6	12.0
15-30	10.9	9.9	10.5
	Untreated Check		
	ppm As	ppm As	ppm As
0-5	8.1	9.2	9.3
5-15	6.3	7.0	7.2
15-30	3.0	4.4	6.5

Source: Johnson & Hiltbold, 1969, p. 280.

c. Transition between solid phase and solution:

No discussions available.

d. Soil-plant interactions in arsenic uptake:

Arsenic enters the plant almost entirely through the roots and accumulates primarily in or on the roots (Liebig, 1966; Rosehart and Lee, 1973). The rate of arsenic absorption depends on the type of arsenic compound, the soil type, and the plant species. These factors will be discussed in more detail in the following sections.

e. Atmospheric absorption of arsenic:

No evidence is available in relation to uptake of airborne arsenic by leaves. However, arsenic sprays have been applied to the foliage of citrus trees and cotton to hasten fruit maturation. This results in premature defoliation and chemical changes in the fruit. For example, lead arsenate sprayed on grapefruit trees caused a "fruit gumming" reminescent of boron deficiency (Liebig, 1966).

f. Arsenic volatilization:

Though soil arsenic levels are reduced primarily by leaching, reducing conditions or fungi may produce arsine, which is lost to the atmosphere by volatilization (Liebig, 1966).

g. Symptoms of toxocity:

Toxic concentrations of arsenic can slow or stop the germination of seeds. Beyond this stage, the greatest toxic effects of arsenic occur at the seedling stage. Roots are affected first; experiments with arsenic in solution cultures showed either plasmolysis or rotting of the roots, the tips of fine, new roots being affected first. This leads to leaf wilting, expecially of new leaves. This is usually the first visible symptom of arsenic poisoning (Liebig, 1966).

Sand-culture experiments with rice produced arsenic toxicity symptoms of leaf curl with the dying tissue turning pink or light red. In later stages, the pink color turned to light yellow (Liebig, 1966).

On peach trees, the first symptoms of arsenic toxicity may be a brown to red discoloration along the leaf margins, followed by similar discoloration of interveinal areas throughout the leaf. These necrotic areas fall out, leaving a shot-holed appearance. In these studies, older leaves showed injury first; young leaves at the tips of terminal growth appeared unaffected even after the rest of the tree showed severe injury. The growth of the trees, overall, was stunted, and the fruit yield was reduced, with the fruit being small and astringent on severely injured trees. There was, however, a tendency for the trees to recover after a period of years (Liebig, 1966).

Studies in eastern Washington on old apple and pear orchards found no close relationship between the total arsenic in the soil, or any fraction of the total, and the degree of unproductiveness of that parcel. Studies on similar orchards in the Yakima Valley in Washington, however, showed some correlation between the concentration of readily soluble arsenic and the degree of unproductiveness of alfalfa and barley crops. The concentration of readily soluble arsenic ranged from 3.4 to 9.5 ppm in the top six inches of the soil in the contaminated orchard ground. In comparison with less contaminated sites, the study showed concentrations greater than 2 ppm caused crop damage (Liebig, 1966).

Figure 5.6.1.3-1 shows the effect of artificial soil applications of arsenic as As_2O_3 on 3 year old white spruce trees (Picea glauca). Table 5.6.1.3-1 from the same study, shows arsenic accumulation levels of various parts of the trees after the 11 month exposure. The near 50% reduction in

Figure 5.6.1.3-1. Effect of arsenic contamination on growth of three year old white spruce trees. Soil arsenic levels from 44 to 2000 ppm--11 month growth period.

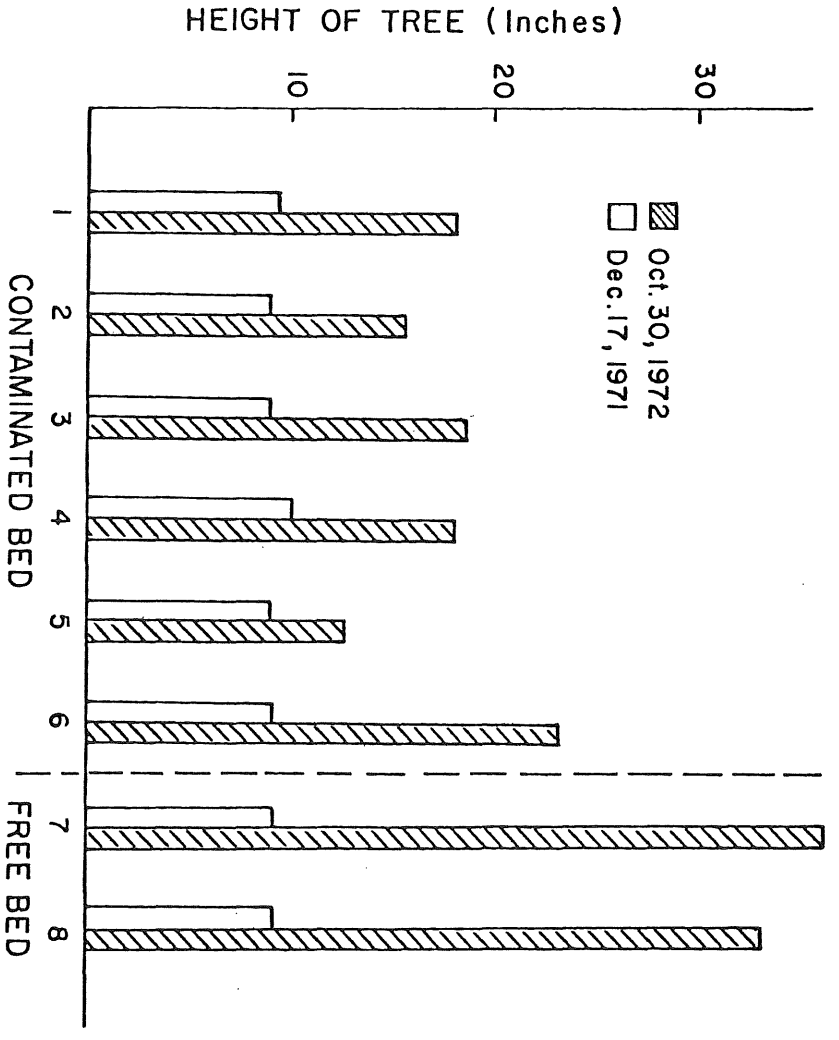

HEIGHT OF TREE (Inches)
10
20
30
Oct. 30, 1972
Dec. 17, 1971
1
2
3
4
5
6
7
8
CONTAMINATED BED
FREE BED

Table 5.6.1.3-1. Arsenic content in soil and white spruce trees.

Bed Sample	CONCENTRATION IN SOIL (PPM)		CONCENTRATION IN TREE (PPM			
	Initial As	after 11 months	Root	Trunk	Branch	Leaf
2	1000	700	59.5	0.3	14.3	2.9
3	2000	1780	130	55	3.0	2.08
5	0	44	45	6.4	2.8	9.5
7 (control)	0	0	1.0	2.4	2.1	2.1

Source: Rosehart and Lee, 1973, p. 441.

growth of the trees, even on the 44 ppm bed 5 was dramatic and indicated that arsenic is toxic at much lower dosages (Rosehart and Lee, 1973).

Liebig (1966) has suggested that arsenic does not accumulate in the upper parts of plants because its immediate effect on the roots slows or stops plant growth.

h. Influencing factors.

As previously mentioned, arsenic toxicity is dependent on plant species, soil type, and the type of arsenic compound.

(1) Plant species.

Table 5.6.1.3-2 shows the classification of vegetables, small fruits, and a few other plants according to their tolerance to water-soluble arsenic (Liebig, 1966).

Table 5.6.1.3-3 gives other indications of relative tolerance of a variety of plants to arsenic.

(2) Soil type.

In an experiment involving 80 California soils, 0 to 920 ppm of arsenic trioxide as sodium arsenite were applied Using Kanota oats as an indicator plant, the highest toxicity was found on coarse, gritty soils and sandy loams containing little colloidal material. Toxicity was moderate on loams, silt loams, and clay loams, and least on heavy soils of clay and adobe clay types. The heavy soils remained less toxic because of their ability to fix large amounts of arsenic, rending it unavailable to plants.This study also found that the arsenic toxicity was not readily altered by fertilizers (Liebig, 1966).

Applications of soil amendments to reduce arsenic toxicity of contaminated soils indicate that soil chemistry may be very important. Applications

Table 5.6.1.3-2. Comparative tolerance of certain plant species to water soluble arsenic. (Liebig, 1966).

Type	Plant Species
Very tolerant	Asparagus, potato, tomato, carrot, tobacco, dewberry, grape, red raspberry, rye and Sudan grass.
Fairly tolerant	Strawberry and sweet corn (on heavy and medium soils), beet and squash.
Low or no tolerance	Snap bean, lima bean, onion, pea, cucumber, alfalfa, other legumes, sweet corn and strawberry (on light and sandy soils.

TABLE 5.6.1.3-3. Compilation of typical arsenic concentrations in contaminated and uncontaminated plants.

Plant	Type of culture	Tissue sampled	Age, stage, condition or date of sample	Range in dry matter (ppm.) Showing deficiency symptoms	Low range	Intermediate range	High range	Showing toxicity symptoms
Alfalfa (Medicago sativa)	Field	Tops	Mature	...	...	0.05	...	...
	Field	Tops	Mature	...	...	...	14.00	...
	Field	Tops	Mature	...	...	1.96	3.38	...
	Field	Roots	Mature	...	...	0.78	3.15	...
Algae, Marine	Ocean	...	Mature	...	...	1.0-12.0	...	...
Almond (Prunus amygdalus)	Field	Edible part	Mature	...	...	0.30	...	...
Apple (Malus spp.)	Field	Fruit	Mature	...	...	0.36	...	...
	Field	Fruit	Mature	...	...	0.07-0.19	...	...
	Field	Fruit	Mature	...	...	0.3-0.7	...	...
Apricot (Prunus armeniaca)	Field	Leaves	Mature	...	...	...	6.10 injured	...
Asapargus (Asparagus officinalis)	Field	Edible part	Mature	...	...	0.75	...	...
Banana (Musa spp.)	Field	Edible part	Mature	...	...	0.33	...	...
	Field	Leaves	Mature	...	...	Trace-0.50	...	0.25-2.00
Barley (Hordeum vulgare)	Field	Grain	Mature	...	...	0.55	...	...
	Greenhouse (soil)	Tops	Mature	...	Trace	...	12.30	...
	Greenhouse (soil)	Roots	Mature	...	Trace	...	1245.00	...
	Field	Grain	Mature	...	...	0.10	...	...
Bean (Phaseolus spp.)	Field	Pods & Seeds	Mature	...	...	0.20	...	...
	Field	Pods & Seeds	Mature	...	...	0.40	...	...
	Solution	Leaves	Mature	...	0.37	...	14.00	...

TABLE 5.6.1.3-3. (cont'd) Compilation of typical arsenic concentrations in contaminated and uncontaminated plants.

Plant	Type of culture	Tissue sampled	Age, stage, condition or date of sample	Range in dry matter (ppm.) Showing deficiency symptoms	Low range	Intermediate range	High range	Showing toxicity symptoms
Bean (cont'd)	Solution	Petioles	Mature	...	0.37	...	11.00	...
	Solution	Stems	Mature	...	0.48	...	11.10	...
	Solution	Fruit	Mature	...	0.07	...	4.50	...
	Solution	Tops	Mature	...	0.32	...	12.10	...
	Solution	Tops	Killed by arsenic	...	...	...	17.99-111.00	...
	Field	Pods & Seeds	Mature	...	0.05	...	...	...
	Field	Vines	Mature	...	0.18	...	1.80	...
	Field	Roots	Mature	...	0.29	...	5.89	...
Beet (Beta vulgaris)	Field	Leaves	Mature	...	...	0.61	...	...
	Field	Tops	Mature	...	0.20	...	10.00	...
	Field	Roots	Mature	...	...	0.13	...	...
	Field	Roots	Mature	...	...	0.13-0.65	...	...
	Field	Roots	"Baby"	...	...	0.08-0.12	...	...
	Field	Tops	"Baby"	...	...	0.08-0.13	...	...
	Field	Tops	Mature	...	...	1.47	3.50	...
	Field	Roots	Mature	...	...	0.34-1.29	...	...
	Field	Roots	Mature	...	...	1.27	20.00-30.00	...
Broccoli (Brassica oleracea botrytis	Field	Edible part	Mature	...	...	Trace	...	...
Cabbage (Brassica oleracea capitata)	Field	Tops	Mature	...	...	1.30	...	...
	Field	Tops	Mature	...	...	0.28-1.66	...	...
Carrot (Daucus carota sativa)	Field	Roots	Mature	...	...	0.40	...	...
	Field	Roots	Mature	...	...	0.30	...	...
	Field	Roots	Mature	...	...	0.09-0.40	...	...
	Field	Roots	Mature	...	...	Trace	...	...
	Field	Tops	Mature	...	...	0.00-0.57	...	...
	Field	Roots	Mature	...	...	0.32-0.37	...	...

TABLE 5.6.1.3-3. Compilation of typical arsenic concentrations in contaminated and uncontaminated plants.
(cont'd)

Plant	Type of culture	Tissue sampled	Age, stage, condition or date of sample	Range in dry matter (ppm.) Showing deficiency symptoms	Low range	Intermediate range	High range	Showing toxicity symptoms
Cauliflower (Brassica oleracea botrytis)	Field	Heads	Mature	...	...	0.86	...	...
Celery (Apium graveolens dulce)	Field	Entire plant	Mature	...	...	0.86	...	...
	Field	Stalks	Mature	...	...	2.32	...	...
Cherry (Prunus cerasus)	Field	Leaves	Mature (slight injury)	...	...	...	8.60	...
Chestnut (Castanea sativa)	Field	Edible	Mature	...	...	0.11	...	...
Citrus Fruits Grapefruit (Citus paradisi)	Green-house (sand)	Leaves	Mature	...	...	3.00-5.00	48.00-116.00	...
Lemon (Citrus limon)	Green-house	Leaves	New cycle	...	0.15	0.75	1.05	...
	Solution	Stems	New cycle	...	0.05	0.45	0.80	...
	Solution	Leaves	Old cycle	...	0.10	...	6.97-11.20	...
	Solution	Stems	Old cycle	...	0.00	0.60	2.05	...
	Solution	Roots	...	...	0.15	20.00-113.00	600.00-1200.00	...
	Solution	Fruit (peel)	Immature	...	...	0.80	...	...
	Solution	Fruit (pulp)	Immature	...	...	0.35	...	...
Mandarin (Citrus reticulata)	Field	Edible part	Mature	...	...	0.85	...	...
Orange (Citrus sinensis)	Field	Edible part	Mature	...	...	0.99	...	...
	Field	Juice	Mature	...	...	0.003-0.12	...	...
	Field	Fruit (peel)	Immature	...	...	0.80	...	...

TABLE 5.6.1.3-3. Compilation of typical arsenic concentrations in contaminated and uncontaminated plants.

(cont'd)

Plant	Type of culture	Tissue sampled	Age, stage, condition or date of sample	Range in dry matter (ppm.) Showing deficiency symptoms	Low range	Intermediate range	High range	Showing toxicity symptoms
Orange (cont'd)	Field	Fruit (pulp)	Immature	...	...	0.35	...	...
Clover, Red (Trifolium pratense)	Field	Tops	Mature	...	...	0.37	...	...
	Field	Leaves	Mature	...	...	...	12.00	...
	Field	Tops	Mature	...	...	3.65	...	...
Corn (Zea mays)	Field	Grain	Mature	...	...	0.36	...	...
	Field	Grain	Mature	...	...	0.03	...	...
	Field	Edible part	Mature	...	...	0.40	...	...
	Field	Stalks	Mature	...	...	0.72-2.77	...	...
Cress, water (Rerippa nasturtium-aquaticum)	Field	Edible parts	Mature	...	...	2.10	...	...
Cucumber (Cucumis sativus)	Field	Fruit	Mature	...	...	0.09-2.40	...	...
	Field	Fruit	Mature	...	...	0.02	...	...
Eggplant (Solanum melongena)	Field	Fruit	Mature	...	...	0.18-0.77	...	...
	Field	Fruit	Mature	...	...	Trace	...	...
	Field	Fruit	Mature	...	...	...	6.16	...
	Field	Roots	Mature	...	...	0.99	...	...
Endive (Cichorium endivia)	Field	Tops	Mature	...	...	0.21	...	...
Filbert (Carylus spp)	Field	Edible part	Mature	...	...	0.11	...	...
Grape (Vitus spp.)	Field	Fruit	Mature	...	...	Trace	...	...
	Field	Leaves	Mature	...	...	2.30	...	...
Kale or collard (Bassica oleracea acephala)	Field	Leaves	Mature	...	...	0.27-0.99	...	...
	Field	Roots	Mature	...	...	0.39	17.00	...

TABLE 5.6.1.3-3. Compilation of typical arsenic concentrations in contaminated and uncontaminated plants.

(cont'd)

Plant	Type of culture	Tissue sampled	Age, stage, condition or date of sample	Range in dry matter (ppm.) Showing deficiency symptoms	Low range	Intermediate range	High range	Showing toxicity symptoms
Lettuce (Lactuca sativa)	Field	Tops	Mature	...	...	3.87	...	...
	Field	Tops	Mature	...	...	0.43	...	...
	Field	Tops	Mature	...	...	0.08-0.12	...	...
	Field	Tops	Mature	...	...	0.12-0.32	...	...
	Field	Roots	Mature	...	...	0.47	11.00	...
Macadamia (Macadamia ternifolia)	Field	Leaves	Healthy trees	...	...	4.33-5.55	...	...
	Field	Roots	Healthy trees	...	...	0.99	7.10	...
	Field	Leaves	Diseased trees	...	...	4.87	18.30	...
	Field	Roots	Diseased trees	...	...	8.75	22.20	...
Millet (Setaria or Panicum spp)	Greenhouse	Grain	Mature	...	...	...	53.00	...
Mushroom (Cantharellus cibarius)	Field	Edible part	Mature	...	...	0.45	...	...
Oats (Avena sativa)	Field	Tops	Mature	...	...	0.62	...	...
	Field	Straw	Mature	...	...	3.40	...	...
	Field	Grain	Mature	...	...	2.28	...	...
Onion (Allium cepa)	Field	Bulbs	Mature	...	...	0.12	...	...
	Field	Tops	Mature	...	...	0.30-1.71	...	...
	Field	Bulbs	Mature	...	...	0.015-0.08	...	...
	Field	Tops	Mature	...	...	3.13	8.90	...
	Field	Bulbs	Mature	...	...	0.36	...	...
Parsley (Petroselinum crispum)	Field	Leaves	Mature	...	...	0.10	...	...
Parsnip (Pastinaca sativa)	Field	Roots	Mature	...	...	0.20	...	...

TABLE 5.6.1.3-3. Compilation of typical arsenic concentrations in contaminated and uncontaminated plants.
(cont'd)

Plant	Type of culture	Tissue sampled	Age, stage, condition or date of sample	Range in dry matter (ppm.)				
				Showing deficiency symptoms	Low range	Intermediate range	High range	Showing toxicity symptoms
Pea (Pisum sativum)	Field	Seeds	Yellow	...	...	0.16	...	...
	Field	Seeds	Green	...	...	0.15	...	...
	Field	Tops	Mature	...	...	0.30	...	...
	Field	Pods	Mature	...	...	0.52	...	...
	Field	Seeds	Mature	...	...	Trace	...	...
	Field	Pods (empty)	Mature	...	...	0.12-0.37	...	...
	Field	Vines	Mature	...	...	0.23-0.50	...	...
	Field	Roots	Mature	...	...	0.14-0.23	...	...
	Field	Seeds	Mature	...	...	0.04-0.49	...	...
	Field	Vines	Mature	...	...	0.29	5.73	...
	Field	Roots	Mature	...	...	1.10	22.80	...
Peach (Prunus persica)	Field	Fruit	Mature	...	...	0.14	...	...
	Field	Leaves	Normal	...	...	1.00	...	...
	Field	Leaves	Injured	...	...	1.30	5.20	...
	Field	Leaves	No spray	...	...	1.75-2.39	...	...
	Field	Leaves	Zinc EDTA spray	...	...	1.28-2.24	...	...
Peanut (Arachis hypogaea)	Field	Edible part	Mature	...	...	0.10-0.14	...	...
Pear (Pyrus communis)	Field	Edible part	Mature	...	...	0.51	...	...
Pepper (Capsicum spp)	Field	Fruit	Mature	...	...	Trace	...	...
Plum (Prunus domestica)	Field	Leaves	Mature	...	...	...	13.00	...
Potato (Solanum tuberosum)	Field	Tops	Mature	...	...	0.31	...	...
	Field	Tubers	Mature	...	...	0.034	...	...
	Field	Tubers	Mature	...	...	0.20	...	...
	Field	Tubers	Mature	...	...	0.10-1.25	...	...
	Field	Tubers	Mature	...	...	0.019-0.033	...	...

TABLE 5.6.1.3-3. Compilation of typical arsenic concentrations in contaminated and uncontaminated plants. (cont'd)

Plant	Type of culture	Tissue sampled	Age, stage, condition or date of sample	Range in dry matter (ppm.)				
				Showing deficiency symptoms	Low range	Intermediate range	High range	Showing toxicity symptoms
Pumpkin (Cucurbita pepo)	Field	Fruit	Mature	...	...	1.95	...	...
Radish (Raphanus sativus	Field	Roots	Mature	...	...	1.80	...	...
	Field	Tops	Mature	...	...	0.17-0.61	...	...
	Field	Roots	Mature	...	...	0.17-0.27	...	...
Rice (Oryza sativa)	Green-house	Tops	Mature	...	...	0.76	12.60	...
	Green-house	Leaves	Mature	...	...	0.40	6.00	...
Rutabaga (Brassica napobrassica)	Field	Roots	Mature	...	...	0.80	...	...
Spinach (Spinacia oleracea)	Field	Edible part	Mature	...	...	0.77	...	...
Squash (Cucubita spp)	Field	Edible part	Mature	...	...	0.023-0.034	...	...
Sudan grass (Sorghum vulgare sudanense)	Green-house	Leaves	Mature	...	...	0.70	87.40	...
	Solution	Nodes	Mature	...	...	3.50	127.00	...
	Solution	Inter-nodes	Mature	...	...	3.00	31.20	...
	Solution	Tillers	Mature	...	...	2.20	52.80	...
	Solution	Tops	Mature	...	...	0.30	57.00	...
	Solution	Roots	...		...	263.00	1094.0	...
Sugar cane (Saccharum officinarum)	Field	Tops	Mature	...	...	0.00-2.00	...	...
Tomato (Lycopersicon esculentum)	Field	Fruit	Mature	...	...	1.00	...	...
	Field	Fruit	Mature	...	...	1.43-2.95	...	...
	Field	Fruit	Mature	...	...	0.08-0.10	...	...

TABLE 5.6.1.3-3. Compilation of typical arsenic concentrations in contaminated and uncontaminated plants.
(cont'd)

Plant	Type of culture	Tissue sampled	Age, stage, condition or date of sample	Range in dry matter (ppm.) Showing deficiency symptoms	Low range	Intermediate range	High range	Showing toxicity symptoms
Turnip (Brassica rapa)	...	Leaves	...	...	...	...	...	70.00
	Field	Leaves	Mature	...	...	1.54	...	...
	Field	Roots	Mature	...	...	0.83	...	...
	Field	Tops	Mature	...	...	1.00	...	...
	Field	Roots	...	...	...	0.70	...	...
Vetch (Vicia spp.)	Field	Tops	Mature	...	...	0.54	...	...
	Field	Tops	Mature	...	...	1.22-1.93	...	...
	Field	Roots	...	...	...	7.17-15.90	...	...
Wheat (Triticum spp)	Field	Grain	Mature	...	...	0.15	...	...
	Field	Grain	Mature	...	...	0.30	...	...

Source: Liebig, 1966, pp.16-22.

of calcium carbonate or calcium sulfate have very little effect while ferrous sulfate proved beneficial (Liebig, 1966).

Arsenic injury to peach trees was reduced by adding zinc sulfate or zinc chelate to the soil. Applications of aluminum sulfate plus lime improved alfalfa stands on contaminated soil and manure. Organic matter effectively reduced the soluble arsenic content of some soils. Application of sulfur or gypsum have proved ineffective (Liebig, 1966).

i. Indicator species.

No listings were found of native plants especially sensitive to arsenic alone.

j. Tolerance level of typical Minnesota species.

Sufficient information is not available at this time regarding the toxicity of arsenic alone to native Minnesota species to compile such a list.

5.6.2. Boron (B)

5.6.2.1. Introduction.

Boron is an essential micro-nutrient required in very minute amounts by most plants. Boron is also phytotoxic in relatively small amounts.

Boron is a non-metallic element found naturally only in combination with other elements. The most important world source of boron is the rasorite or borax deposits in the Mohave Desert in California. The primary uses of boron are in boric and boracic acids and borax cleaning compounds and antiseptics, in enamels for appliance coatings and in the manufacture of some types of glass.

Boron's role in plants has been studied more than that of any other trace element. (Bradford, 1966).

5.6.2.2. Sources of Boron.

a. Natural:

The total soil content of boron is usually between 2 and 100 mg/g (Etherington, 1975).

Soil boron usually originates from borosilicates, calcium and mannesium borates, iron and aluminum boron complexes and usually takes the form of ortho, meta and tetraborate anions in equilibrium in the solution. Usually less than 3 mg/g is soluble as borate, but boron toxicity may occur in arid areas where higher concentrations may occur in saline soils (Etherington, 1975).

Boron has high toxic potential and commonly forms soluble complex anions during the formation of marine sediments (Bradford, 1966). Consequently, soils derived from marine sediments usually contain the greatest

amount of available boron. Soils derived from igneous rocks, on the other hand, are much lower in boron content. Basic igneous rocks may be slightly higher in boron because of boron's affinity for alkali and alkali earth elements in the igneous rock formation process (Etherington, 1975).

There are four large areas in the United States where boron deficiency is likely to occur: the Atlantic coastal plain; the Pacific coastal area; the Pacific Northwest; and northern Michigan, Wisconsin, and Minnesota (Etherington, 1975).

b. Anthropogenic Sources

The following activities may produce boron toxicity (Bradford, 1966).

(1) Acidification of some neutral or alkaline soils.

(2) Soils that have been irrigated with high-boron water.

(3) Soils that have received drainage from packing-house wastes or sewage-effluent wastes containing high amounts of boron.

(4) High applications of readily soluble boron fertilizers.

(5) High potassium fertilization where boron tends to be high.

5.6.2.3. Biological availability.

a. Soil solid phase.

In soils derived from acid rocks and metamorphosed sediments, tourmaline (3-4%B) may be a significant source of the total boron, but this very resistant mineral cannot be a source of boron for plants (Norrish, 1975). Similarly, boron, substituting for silicon, may be present in silicates, but would be available to plants only over a long period of time (Norrish, 1975).

Calcium and magnesium borates and iron and aluminum boron complexes are the other major boron containing minerals and probably harbor most of the solid phase boron (Etherington, 1975). In studies of boron uptake by illite, other clay minerals, and oxides, it has been found that some of the retained boron is readily exchanged but some is fixed, the amount fixed increasing with time. It has been hypothesized that the exchangeable boron is held electrostatically (anion exchange) at the surface, but from there it can diffuse into the crystal lattice, occupying positions of tetrahedral coordination (Norrish, 1975).

Often much of the total boron is water soluble. This suggests that it may be linked with organic matter, but very little is known of organic complexes of boron (Norrish, 1975 and Loneragan, 1975). Compounds such as sugars and phenols containing cis-diol groups form complexes with boron and may be important in soil solutions (Loneragan, 1975).

b. Soil solution.

The dominant form of inorganic boron in soil solutions is probably undissociated boric acid (H_3BO_3). The first dissociation constant of boric acid, pk_a, is 9.2. Therefore, appreciable quantities of borate ion, $H_2BO_3^-$, will only appear with increasing alkalinity above pH 7 (Loneragan, 1975). Etherington (1975) states that meta or tetra boric acids may also be important in soil solutions.

c. Transition between solid phase and soil solution.

The reaction of the borate anions with iron oxides controls the transition of boron from the solid phase to the soil solution (Loneragan, 1975). This reaction is very sensitive to pH, being most rapid at pH

values close to the pk_a values for the dissociation of the acid. Thus, the dissociation of boric acid and the subsequent adsorption of borate ion by clays and other minerals in the solid phase is most rapid near pH 9 and decreases with decreasing pH. Conversely, lower pH values will increase the boric acid concentration of the soil solution and hence the rate of absorption by plant roots (Loneragan, 1975).

d. Soil-plant interactions in boron uptake.

The boron requirements or tolerance can be influenced markedly by the nutritional status of the plant. Thus, plants with a low supply of calcium will have a small need and low tolerance for boron, while those with an excessive supply of calcium will have a high boron requirement Similarly, nitrogen starved plants require less boron than those well supplied with nitrogen. Conversely, plants with low phosphate require more boron than plants with adequate phosphate. A balance also exists between potassium and boron in plants (Bradford, 1966).

e. Direct atmospheric absorption of boron.

There is no indication that plants can absorb boron directly from the atmosphere.

5.6.2.4. Role of boron in plant nutrition.

The biochemical role of boron is not yet well understood. Unlike other micronutrients, boron has not been shown to be part of any enzyme system. Boron is postulated to be involved in the synthesis of carbohydrates. The earliest detected physiological symptom of boron deficiency is the increased uptake of RNA percursors into root tips. These early reactions are similar to those involving plant hormones such as

auxin, gibberellic acid, and cytokinin. Thus, boron may eventually be found to play a role in plants similar to those of hormones (Jackson and Chapman, 1975).

5.6.2.5. Boron deficiency.

Microscopically, boron deficiencies in general lead to degeneration of meristematic tissue including the cambium; to breakdown of parenchyma cell walls; and/or to retarded development of vascular tissue such as the phloem and xylem. Cell disintegration is frequently preceded by hypertrophy of thin-walled cells and discoloration which may, in turn, be preceded by abnormally active cell division (Bradford, 1966). Externally, these disruptions may be expressed as:

a. Terminal growth showing rosetting, dieback, discoloration, failure to grow or elongate, and stimulation of lateral bud development, which in turn may develop well or die.
b. Leaves showing various abnormalities, such as thickening, brittleness, curling, wrinkling, wilting, and chlorotic spotting.
c. Petioles or stems may be thickened, corky, cracked, or crosshatched, or may show watersoaked, dead areas.
d. In fruit, tubers, or roots, the fleshy part may show brown flecks, necrosis, cracks, or dry rot; may be watersoaked; or may show discoloration in the vascular system.

Boron deficiency is generally associated with light, sandy, easily leached soils (Etherington, 1975). Boron deficient plants often contain less than 15 to 20 ppm boron in dry matter (Yopp et al., 1974).

5.6.2.6. Boron toxicity.

Boron concentrations in excess of 200 ppm in dry matter are often found with symptoms of boron phytotoxicity (Yopp et al., 1974). The ability to accumulate boron, however, varies significantly between toxonomic groups: monocotyledons accumulate less boron than do dicotyledons, where members of the Cruciferae and Papilionacae are especially high in boron content. Ginkgo biloba has been found to contain up to 2,976 ppm boron in its ash (Yopp et al., 1974).

The earliest symptom of boron toxicity is yellowing of the leaf-tip, but this has little diagnostic value. Further increases in boron concentrations cause a progressive necrosis of the leaf, between the lateral veins toward the midrib. The leaf tip and margins develop a scorched appearance which eventually covers the entire leaf before it drops prematurely (Bradford, 1966). Poor lobation, interveinal flecks, and downward leaf curl are possible symptoms on some plants. Boron may also inhibit flowering and cause fruit lesions (Krupa and Kohut, 1976). Table 5.6.2.6-1 presents specific symptomatology and toxicity levels for a number of crops. Yopp et al., (1974) concluded that the maximum permissible level of boron, as the borate anion in the soil solution, should not exceed 0.5 ppm.

5.6.2.7. Toxicity tolerance levels for boron.

Table 5.6.2.7-1 is a list of plants classified according to their tolerance to boron when grown in sand culture. These categories correspond approximately to the following concentrations of boron in the soil solution (Yopp et al., 1974):

boron-sensitive--injured by 0.3 to 1.0 ppm

boron-semitolerant--injured by 1.o to 2.0 ppm

boron-tolerant--injured by 2.0 to 4.0 ppm.

5.6.3. Cadmium (Cd)

5.6.3.1. Introduction.

Cadmium is not considered an essential element for either plants or animals, although it is probably a normal constituent of all plants (Yopp et al., 1974).

Cadmium is a soft, bluish-white metal similar in many respects to zinc. Cadmium and solutions of its compounds are highly toxic. The recommended maximum working area concentration is 0.1 mg/m^3 averaged over eight hours. Recent evidence shows that cadmium has the ability to be concentrated through the food chain and this has caused concern in relation to its role in plants. Research in this area is new and little is yet known on plant uptake, metabolism and tolerance levels in various plant species (Yopp et al., 1974).

5.6.3.2. Sources of Cadmium.

a. Natural.

Cadmium is found in the earth's crust at an average concentration of 0.18 ppm (Lagerwerff, 1972). Cadmium most often occurs in small quantities associated with zinc ores, such as Sphalerite (ZnS). Greenockite (CdS) is the only mineral containing cadmium in concentrations sufficient for mining. However, almost all cadmium is obtained as a by-product in the smelting of zinc, copper, and lead ores.

In areas not known to be polluted, the total cadmium concentration in soils is usually less than 1 mg/g (Friberg et al., 1974). In a 1972 study in Michigan, 70 soil samples from residential areas contained an average of 0.41 mg/g, 91 samples from agricultural areas contained an average 0.57 mg/g, and 86 samples from an industrialized area contained an average of 0.66 mg/g (Friberg et al., 1974).

b. Anthropogenic sources of cadmium.

On agricultural soils, phosphate fertilizers can be significant sources of cadmium. Concentrations range from less than 1 ppm to 63 ppm. The high cadmium content fertilizers are probably superphosphates. A second common source of soil cadmium contamination is sewage sludge, which may contain 2 to 147 ppm cadmium (Helz et al., 1974; Jorgenson, 1975; VanLoon, 1973; Dudas and Pawluk, 1975). Because of the tendency for plants to concentrate cadmium, all organic materials are potential sources of cadmium. The cadmium concentration in Illinois coal ranges from 0.3 to 28 ppm (Lagerwerff, 1974). A typical modern power plant may emit 120 grams cadmium to the atmosphere each day. Residual fuel oil and premium gasoline have been found to contain from 0.003 to 1 ppm and 0.001 to 20 ppm cadmium respectively (Lagerwerff, 1974). Automobile tire wear contributes about 6 metric tons of cadmium annually to the atmosphere in the United States (Lagerwerff, 1972).

A local, serious source of cadmium pollution is metal smelters. The effects of such contamination on vegetation is the subject of many studies (Koning, 1973; Lagerwerff et al., 1973; Little and Martin, 1972; Jordan, 1975; McCaull, 1971). Air emissions of cadmium from primary producers of zinc, lead, and copper in 1968 amounted to 1,000 metric tons nationwide (Lagerwerff, 1972). Emissions from smelting, brazing, roasting, galvanizing, and steel production added another 1,000 tons, while the manufacture of plastics, batteries, pigments, alloys, and fertilizers contributed about 20 tons.

5.6.3.3. Biological availability of cadmium.

Cadmium reaches the soil primarily from the atmosphere, rather than arising from a natural mineral portion of the soil solids (Lagerwerff, 1972).

The mobility of cadmium in soils is very high, and contrary to most heavy metals, is rather independent of pH (Lagerwerff, 1974).

Organic matter chelation also plays a minor role in the cadmium flow in soils (Lagerwerff, 1974).

In a strictly inorganic system, the cadmium-calcium exchange coefficients for aqueous suspensions of clay saturated with these cations was found to be 1.04, 1.01, and 0.89 for montmorillonite, illite, and aolinite.

The proportion of total soil cadmium in the soil solution is apparently reduced by, in decreasing order of efficacy, calcium-silicate, calcium-phosphate, and lime, as indicated by rates of cadmium uptake by rice (Lagerwerff, 1974).

Increased levels of nitrogen also slows cadmium uptake. In the presence of an iron chelate, such as FeDTPA, cadmium uptake was much higher at pH 4.6 than at pH 6.5 (Lagerwerff, 1974).

5.6.3.4. Role in plant nutrition.

Cadmium is not a necessary plant nutrient.

5.6.3.5. Deficiency.

Cadmium is not a necessary plant nutrient.

5.6.3.6. Cadmium toxicity.

a. Microscopic effects.

Cadmium is one of the most mobile and readily accumulated heavy metals (Lagerwerff, 1974). The concentration in plant parts is, therefore, a function primarily of the total concentration in the substrate (Yopp et al., 1974). However, little is known about the mode of operation of this element in plant systems.

In animals, zinc, chemically very similar to cadmium and an essential micro-nutrient in plants, is an effective counter-actant to cadmium toxicity. In plants, however, the reactions vary (Lagerwerff, 1974). In radish, the presence of zinc inhibited the uptake of cadmium when the cadmium concentration was 2 ppb, but enhanced the uptake at higher cadmium concentrations. The same enhancement has been observed in other species (Yopp et al., 1974).

Cadmium is a potent inhibitor of photosynthesis in plants (Bazzaz and Govindjee, 1974; Overnell, 1975; Bazzaz et al., 1974).

In studies on Quercus rubra, Betula populifolia, and Populus tremuloides seedlings, radicle elongation was significantly reduced by 5 ppm cadmium in solution culture (Jordan, 1975).

Most of the biologically active cadmium enters plants through root uptake (Jordan, 1975). Small metal oxide particles (0.01 to 0.03 μm) may enter leaves through the stomates, but it is thought that this portion remains largely inert for most metals. Work with cadmium, however, has shown that the metal accumulated in apple leaves was translocated and incorporated in the fruit as it developed (Yopp et al., 1974). Table 5.6.3.6-1 compares the heavy metal concentration in unwashed and washed elm leaves. The results indicate that washing with dionized water or with a strong detergent removed an average of 28.1% of the zinc, 64.0% of the lead, and 20.4% of the cadmium.

b. Symptoms of cadmium toxicity.

Figure 5.6.3.6-1 illustrates the wide variability in the cadmium accumulating ability of different food crops. It also illustrates the difference in plant tolerance levels, though there was little information

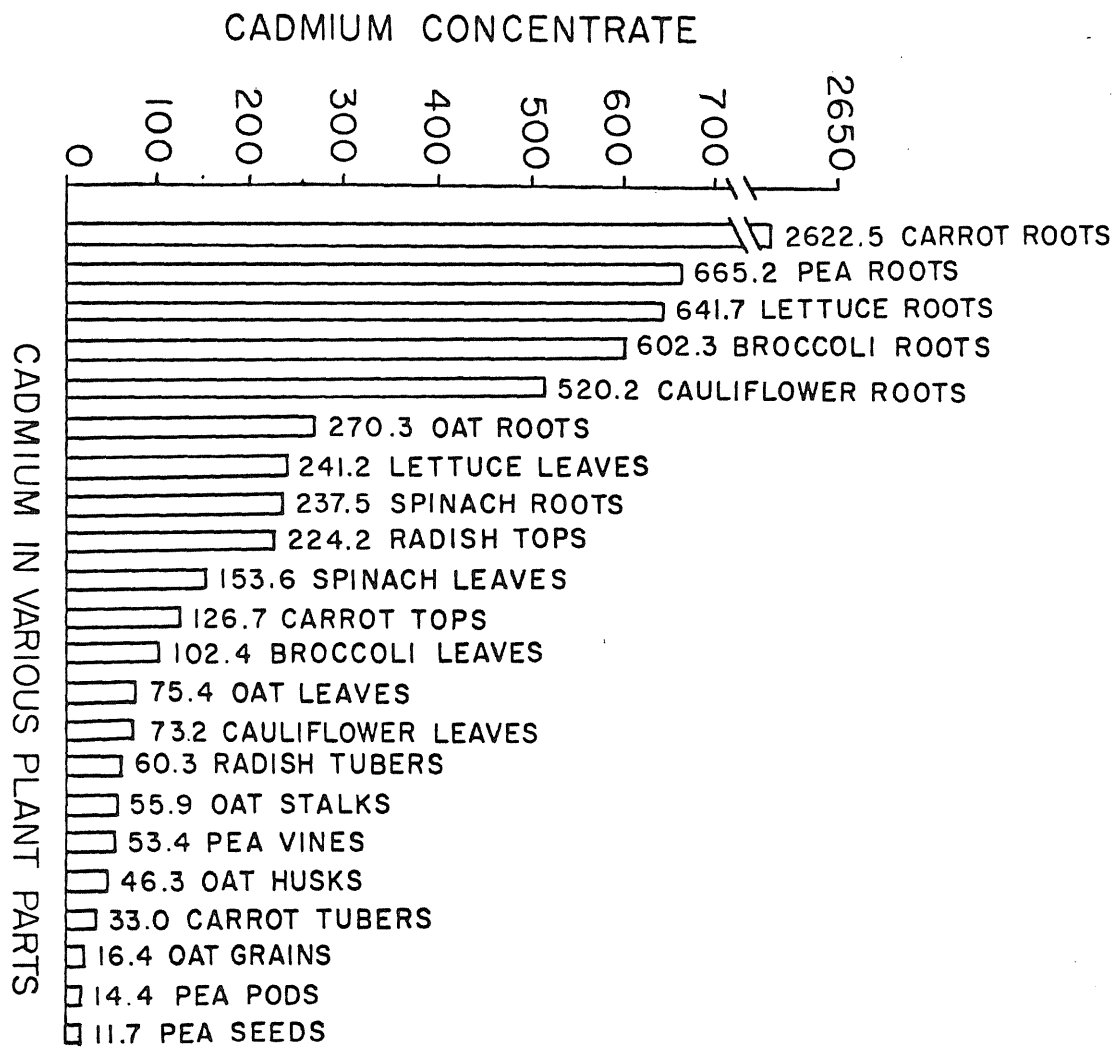
Table 5.6.3.6-1. Comparison of heavy metal concentration on or in washed and unwashed elm leaves.

Unwashed leaves ppm dry wt			Washed leaves ppm dry wt			% removed by washing		
Zn	Pb	Cd	Zn	Pb	Cd	Zn	Pb	Cd
6950	6200	50	5050	1130	40	27	32	20
5400	4200	35	3600	950	27.5	33	77	21
5350	4800	35	3600*	870*	25*	33*	82*	28*
4950	5200	35	3700*	800*	25*	25*	85*	28*
4700	3600	42.5	4000	1700	37.5	15	53	12
2900	1020	15	1600	690	12.5	45	33	17
2100	1190	15	1700	760	12.5	19	36	17
				Mean Values		28.1	64.0	20.4

*Denotes detergent washed.

Source: Little and Martin, 1972, p. 252.

Figure 5.6.3.6-1. Concentration of cadmium (ppm) in various parts of food species grown on highly contaminated (40-200 mg Cd/kg soil) soil. From John (1973).


CADMIUM CONCENTRATE
0
100
200
300
400
500
600
700
2650
CADMIUM IN VARIOUS PLANT PARTS
2622.5 CARROT ROOTS
665.2 PEA ROOTS
641.7 LETTUCE ROOTS
602.3 BROCCOLI ROOTS
520.2 CAULIFLOWER ROOTS
270.3 OAT ROOTS
241.2 LETTUCE LEAVES
237.5 SPINACH ROOTS
224.2 RADISH TOPS
153.6 SPINACH LEAVES
126.7 CARROT TOPS
102.4 BROCCOLI LEAVES
75.4 OAT LEAVES
73.2 CAULIFLOWER LEAVES
60.3 RADISH TUBERS
55.9 OAT STALKS
53.4 PEA VINES
46.3 OAT HUSKS
33.0 CARROT TUBERS
16.4 OAT GRAINS
14.4 PEA PODS
11.7 PEA SEEDS

given regarding degrees of toxic reactions. Natural cadmium content of vegetation is 0.2-0.8 ppm on a dry weight basis. Generally, accumulation of cadmium above 3 ppm may cause toxicity, but this is highly variable (Yopp et al., 1974).

Most plants studied expressed cadmium toxicity, only as stunted growth and decreased yield. However, in soybeans containing 7 ppm cadium the veins at the lower part of the first primary leaves became reddish brown. As the cadmium level was increased, the discoloration spread throughout the leaves until a chlorosis resembling that of iron deficiency resulted (Yopp et al., 1974). Table 5.6.3.6-2 presents additional information on cadmium symptomatology and dosages.

Yopp et al., (1974) concluded their evaluation recommending a maximum permissible level of cadmium of 0.1 ppm in soil water and 2.5 ppm by total dry weight in soil.

c. Indicator species.

According to Yopp et al., (1974) tomato is the most sensitive species to cadmium pollution, being injured by as little as 0.1 ppm cadmium in the nutrient medium. This concentration caused accumulation levels of about 21.5 ppm (dry weight basis) and severe growth reduction.

5.6.3.7. Toxicity tolerance level.

Table 5.6.3.6-2 presents limited data on the tolerance levels of some food crops.

Table 5.6.3.6-2. Phytotoxic effects of cadmium in soil solution on selected plants.

Plants by Economic Class	Growth Medium	Minimum Phytotoxic Concentration	Plant Part Affected	Developmental Stage	Symptomatology
Soybean	defined soil type	2.5 ppm	entire	seedling	Reddish brown veins in youngest trifoliate leaves; growth reduction
Winter wheat	defined soil type	2.5 ppm	entire	seedling	general growth retardation
Lettuce	defined soil type	2.5 ppm	entire	seedling	general growth reduction
Radish	defined soil type	2.5 ppm	entire	seedling	general growth reduction
Celery	defined soil type	2.5 ppm	entire	seedling	general growth reduction
Green Pepper	defined soil type	2.5 ppm	entire	seedling	general growth reduction
Beet (root)	defined nutrient medium	1.0 ppm	entire	seedling	general growth reduction
Swiss Chard	defined nutrient medium	0.1 ppm	entire	seedling	general growth retardation
Tomato	defined nutrient medium	0.1 ppm	entire	seedling	general growth retardation
Carrot	defined nutrient medium	1.0 ppm	entire	seedling	general growth retardation

Source: Yopp et al., 1974, p. 74.

5.6.4. Calcium (Ca)

5.6.4.1. Introduction.

Calcium is an essential macronutrient needed in relatively large amounts by plants.

Calcium, a silvery, hard metal, is the fifth most abundant element in the earth's crust, of which it forms more than three per cent.

Because of the importance of calcium in plants and animals, it has been studied well, especially in relation to agriculture.

5.6.4.2. Sources.

a. Natural.

Most of the calcium needs of the plants are provided by natural calcium in soil solids. Calcium is never found naturally in an uncombined form. It occurs abundantly as limestone ($CaCO_3$), gypsum ($CaSO_4 \cdot 2H_20$), fluoriet (CaF_2), and apatite, a fluoro- or chloro-phosphate of calcium.

Normal ranges of total soil calcium are from 0.07% to 3.60%, with soils in the humid region averaging 0.40% and arid region soils averaging 1.00%.

b. Anthropogenic sources.

Though calcium, as quicklime (CaO) or as the metal, is used in large quantities as a deoxidizer, desulfurizer, decarbonizer, or alloying agent in many chemical and metalurgical processes, the only anthropogenic sources of significance to vegetation are intentional soil amendments, such as lime or gypsum.

5.6.4.3. Biological availability of calcium.

a. Soil solid phase.

The more complex, less active forms of calcium in mineral soils are such minerals as feldspars, hornblende, calcite, and dolomite. The simpler, more active forms include calcium ions (Ca^{++}) adsorbed by colloidal complexes and a variety of simple calcium salts (Brady, 1974).

Under normal soil conditions, calcium is the dominant base in the base-exchange system (Chapman, 1966). Under this condition, calcium occupies 60 to 85 per cent of the total exchange capacity. Such soils have approximately a neutral pH. Under acidic conditions, as in coniferous forests or in soils with a large organic component, calcium and other bases are replaced by hydrogen ions. The free calcium is then often leached away. Under alkaline or saline conditions, the calcium is also replaced, but usually by sodium (Chapman, 1966).

The proportion of calcium in an available form greatly exceeds that of any of the other macronutrients (Brady, 1974). Thus, in soils such as those existing over most of the study area, where the rainfall is relatively high but native calcareous minerals are scarce, the soil becomes acidic and most of the calcium present is leached away. The remaining calcium is tightly held by soil minerals, making calcium deficiencies possible (Chapman, 1966). Furthermore, the acidity caused by the replacement of calcium (and magnesium) by hydrogen ions upsets the balance of other soil minerals. For example, if the acidity becomes high enough, manganese, aluminum, copper, nickel, and other elements become more mobile--go into soil solution--and thus may become toxic to plants and other soil organisms (Chapman, 1966). Also, in soils containing high boron levels,

enough boron may be solubilized to injure plants or be forever leached away. Phosphorus becomes less available with increasing acidity, and low pH may cause montmorillonic clay minerals to break down to kaolinic forms which have a lower exchange capacity. High acidity may also cause magnesium, potassium, and molybdenum to become deficient (Chapman, 1966).

Calcium is the primary regulator of soil pH, and, in agricultural lands, the profound effects of its loss by leaching are avoided through the addition of calcium in the form of lime, calcite, dolomite, or gypsum (Brady, 1974).

Table 5.6.4.3-1 illustrates the relation between soil pH and calcium content, as well as the high variability betweeen individual soils (Chapman, 1966).

Most of the calcium-containing minerals in soils are readily weathered or broken down by carbonic and other biological acids in rainfall. The mobilized calcium ion released by this reaction is then usually adsorbed by clay minerals. Very little of the calcium is held by organic compounds (Brady, 1974). Thus, if little or no clay minerals are available, such as in sandy soils, the calcium is leached away. In a 1920 study of the composition of all the world's lakes and rivers, it was found that of the total dissolved constituents, calcium constituted 20.39%, magnesium 3.41%, sodium 5.79%, potassium 2.12%; carbonate (CO_3) 35.15%, sulfate (SO_4) 12.14%, chloride 5.68%, and nitrate (NO_3) 0.90% (Chapman, 1966).

b. Soil solution.

Most of the soluble calcium in soils occurs as nitrate, bicarbonate, chloride, or sulfate, depending on the respective dominance

of these elements. Much of the calcium remains in these forms adsorbed to soil colloids, but when it is in solution or is absorbed plants, it is primarily in the ionic form Ca^{++} (Chapman, 1966).

c. Transition between solid phase and soil solution.

This occurs very rapidly and depends on the pH and amount of precipitation..

5.6.4.4. Role of calcium in plant nutrition.

The primary importance of calcium is in the formation of cell walls: the synthesis of pectin in the middle lamella of the cell wall. It is also involved in the formation or metabolism of the nucleus and mitochondria, performs a minor catalytic role as the activator of a few enzymes such as phospholipase, and may be important in detoxifying oxalic acid (Bidwell, 1974).

Calcium enters plants primarily by diffusion of Ca^{++} into plant roots, but once deposited in the plant, it is immobile (Brady, 1974; Bidwell, 1974).

Typical calcium contents of health plants range from 1.5% to 6% of the plant ash (Bidwell, 1974).

5.6.4.5. Deficiency of calcium.

a. According to Chapman (1966) calcium deficiencies most often occur in:

(1) Acid soils.

(2) Sandy soils, particularly those found in humid regions with rainfall of 30 or more inches per year.

(3) Soils derived from serpentine rock.

(4) Strongly acid peat soils.

(5) Soils in which the dominant clay is montmorillonitic rather than kaolinitic.

(6) Alkali or sodic soils where exchangeable sodium and pH are high.

(7) Soils subjected to long-continued use of sulfur as an insecticide or ammonium sulfate or high sodium fertilizers.

b. Symptoms.

Microscopically, multinucleate cells are characteristic of calcium deficiencies (Bidwell, 1974). Visual symptoms of moderate to acute deficiency stages include impaired root growth or rotted and distorted roots, small leaves with irregular margins and spotted or necrotic areas. Dieback of terminal buds may also occur. Roots are normally affected before tops, and in the aerial portion, young leaves are affected first because of the aforementioned immobility of in-place calcium (Chapman, 1966).

5.6.4.6. Toxicity of calcium.

Calcium toxicity occurs only rarely, and then is usually caused by the anion with which the calcium is associated (Chapman, 1966).

Calcium toxicity is most often associated with saline soils in which excessive amounts of gypsum, calcium chloride, or other soluble calcium salts have accumulated or with soils high in calcium carbonate. Overhead irrigation with waters high in calcium, poor drainage, excessive lime, gypsum, or sulfur applications, or over-application of calcium containing fertilizers can also lead to caclium toxicity (Chapman, 1966).

No descriptions of calcium toxicity symptoms were found in the literature.

5.6.4.7. Toxicity tolerance levels for calcium.

In plants, an ash content of calcium of greater than 7% may indicate an excess (Bidwell, 1974).

5.6.5. Cobalt (Co).

5.6.5.1. Introduction.

Cobalt is not essential per se to the normal development of higher plants but is essential to the nodulation of legumes (Brady, 1974; Vanselow, 1966). Also, it is essential to animals, especially ruminants, because it is a constituent of vitamin B_{12} (Kubota and Allaway, 1972).

Cobalt is a brittle, hard metal, closely resembling iron and nickel in appearance. Cobalt occurs in the minerals cobaltite, smaltite, and erythrite and is often associated with nickel, silver, lead, and copper ores. It is commonly used as an alloying agent in magnets and high strength alloys and as a radioactive tracer and therapeutic agent.

The importance of cobalt in animal nutrition and legume nodulation is well documented, though its mode of operation is not yet known with complete certainty.

5.6.5.2. Sources of cobalt.

a. Natural.

Nearly all soil cobalt is supplied by minerals in the parent materials (Brady, 1974). Cobalt is present in concentrations of about 23 ppm in the earth's crust and about 3 ppm in typical soils.

In igneous rocks, there are no cobalt metals. Rather, the cobalt is tightly bound in ferromagnesian minerals where it replaces iron (Norrish, 1975).

b. Anthropogenic.

Cobalt is not considered an environmental contaminant and no indication was found of significant emissions from any human activities. Cobalt is added as a soil amendment, in quantities of grams per acre, to alleviate cobalt deficiencies in alfalfa and grazing ruminants (McKenzie, 1975).

5.6.5.3. Biological availability of cobalt.

a. Soil solid phase.

Once released from soil minerals, cobalt is usually adsorbed by secondary silicates (Brady, 1974), but does not enter the layer lattice silicate structure (Norrish, 1975).

b. Soil solution.

In a study of New York and Colorado soils, it was found that cobalt was present in the soil solution in concentrations of 0.007 to 0.2 micromoles (um) and 8 to 50 per cent of this cobalt was present as a complex with other elements (Loneragan, 1975). According to Norrish (1975) evaluation, active soil cobalt is primarily associated with manganese oxides. He found that clays and iron oxides can fix cobalt. In many normal soils, however, the manganese oxides hold most of the cobalt, even though they are present in lower concentrations.

When released by the adsorbing silicates and manganese oxides into the soil solution, cobalt is usually in the form of Co^{++} in acidic soils, and possibly in the monovalent hydroxy cation form $Co(OH)^{+}$ in neutral or alkaline soils (Loneragan, 1975). These are probably the forms which are absorbed by plant roots.

c. Transition between solid phase and soil solution.

Cobalt availability is increased in waterlogged soils (Norrish, 1975).

Cobalt availability is markedly affected by pH in most soils. Soil acidification increases the transition of cobalt to the soil solution. Conversely, liming of soils reduces plant absorption of water soluble cobalt (Vanselow, 1966).

Table 5.6.5.3-1 illustrates the relations between total and available Co and manganese oxide content, clay content, and pH of 24 North American soils.

5.6.5.4. Role of cobalt in plant nutrition.

Cobalt is essential to nodulation of legumes, but there is no definitive evidence of such needs in non-nodulating plants (Vanselow, 1966; Nicholas, 1975). Deficiencies in tomatoes, rubber plants, and non-nodulated subterranean clover have been reported, but no symptoms other than reduced growth were observed, and the results have not been verified (Nicholas, 1975).

In root nodules on legumes, cobalt is needed in the production by the rhizobia of cobamide compounds. The cobamide compounds--coenzymes--are required for the metabolic processes of the bacteroids which fix atmospheric nitrogen (Nicholas, 1975).

5.6.5.5. Deficiency of cobalt.

The cobalt needs of even nodulated plants are extremely low; field cases of cobalt deficiencies have not been reported in the United States, though they have been observed in Australia (Kubota and Allaway, 1972). Thus, were it not for the dietary needs of ruminants, cobalt deficiencies would be of academic interest only.

The total cobalt content of soils is usually 1 to 40 ppm (Vanselow, 1966). To provide cobalt in quantities sufficient to meet livestock needs, the total concentration should be from 3 to 40 ppm, depending on the biological availability in the individual soils (Vanselow, 1966). Soils most likely to fall below these levels include: (Vanselow, 1966)

Table 5.6.5.3-1. Comparison of cobalt uptake by clover and soil pH and clay, manganese oxide, and total cobalt content for 24 North American soils.

Great Soil Group	Site	Clay %	C %	MnO ppm	Co ppm	pH	Recovery of applied Co, ug per pot	
							Actual	Predicted+
Prairie	3	41.4	4.1	5800	97	7.1	0.4	- 0.3
	4	25.9	4.3	2100	51	6.3	0.6	0.6
	5	41.6	3.0	1570	49	7.1	0.01	0.1
	6	39.2	8.3	3500	78	6.3	0.05	0.3
	7	36.2	4.8	1100	46	6.5	-0.2	0.8
Gleyed podzolic	8	26.4	3.1	1200	16	5.6	-	-
	9	18.4	3.5	495	3.7	6.0	2.7	2.2
	10	9.2	2.4	500	5.2	6.2	2.9	1.8
	11	18.6	2.6	2700	33	5.8	2.1	0.9
	12	10.9	2.7	990	8.5	5.2	4.0	2.7
Rumus podzolic	13	4.4	2.9	30	0.22	5.8	6.2	8.8
	14	4.9	3.5	40	0.45	5.5	9.9	9.4
	15	4.6	2.9	125	0.18	7.5	1.1	1.3
	16	5.2	3.5	40	0.35	5.2	7.1	11.3
	17	4.7	3.7	49	0.48	5.1	7.1	11.0
Yellow podzolic	18	16.2	3.8	350	1.3	5.5	5.3	3.7
	19	29.4	2.8	4100	8.3	5.4	0.9	1.0
	20	33.2	3.7	166	2.4	5.1	10.6	6.7
	21	28.9	4.5	3600	5.6	6.0	0.2	0.5
	22	25.2	3.9	100	0.9	5.2	15.5	7.8
Krasnozem	23	29.2	10.9	560	4.9	5.2	4.4	3.6
	24	42.9	9.1	3800	10.4	5.4	0.2	1.0
	25	38.4	8.3	6700	26.2	5.8	0.3	0.3
	26	36.4	5.7	21000	89	5.8	-0.2	- 0.1
	27	25.9	5.8	4600	29.9	5.5	0.3	0.8

+ log (Co +1) = 2.9023 - 0.369 (log MnO ppm) - 0.235 pH.

Actual recovery of Co : S.D. between duplicates = 2 ug.

S.D. between actual and predicted recovery = 1.6 ug.

Source: Norrish, 1975, p. 68.

a. Acid, highly leached, sandy soils with low total cobalt.

b. Soils derived from granites.

c. Some highly calcareous soils.

d. Some peaty soils.

Soils with insufficient cobalt can be amended with additions of cobalt compounds such as cobalt chloride or limonite. Usually, however, cobalt deficiencies are corrected by administering cobalt directly to the animals in their food or salt licks (Vanselow, 1966).

5.6.5.6. Cobalt toxicity.

No reports were found on the field illustrations of cobalt phytotoxicity (Anderson et al., 1973) However, laboratory culture experiments have shown that cobalt toxicity is possible in many species. Corn and beans have been injured by cobalt concentrations of 1 ppm in the culture solution and a number of other crop plants have been injured by concentrations as low as 0.1 ppm. The symptoms produced in these experiments included depressed growth, chlorosis, necrosis and, sometimes, death of the plant (Vanselow, 1966). The chlorosis described is similar to that caused by iron deficiency (Vanselow, 1966). Cobalt toxicity can be effectively counteracted by the addition of 2 to 25 ppm of molybdenum to the soil solution or by painting the leaves with solutions of iron salts (Vanselow, 1966).

5.6.5.7. Toxicity tolerance levels for cobalt.

Plants under field conditions, even if subjected to environmental contamination, are unlikely to be harmed by cobalt. Consequently, there has been no need for recommended tolerance levels.

Table 5.6.5.7-1 presents tissue analysis data on typical cobalt levels found in plants.

TABLE 5.6.5.7-1. Typical plant tissue analysis values for cobalt.

Plant	Type of culture	Tissue sampled	Age, stage, condition or date of sample	Range in dry matter (ppm.)				
				Showing deficiency symptoms	Low range	Intermediate range	High range	Showing toxicity symptoms
Alfalfa (Medicago sativa)	Field	Tops	Mature	...	...	0.02-0.24	...	...
	Field	Tops	Early bloom	...	...	0.04-0.29	...	...
Algaroba (mesquite) (Prosopis chilensis)	Field	Leaves	...	...	...	0.75-2.20	...	...
Apricot (Prunus armeniaca)	Field	Fruit	Mature	...	...	0.03	...	...
Banana (Musa spp.)	Field	Tops	Mature	...	...	0.50	...	...
Barley (Hordeum vulgare)	Field	Leaves	Immature	...	...	0.20-0.30	...	...
	Plots	Tops	Forage	...	...	0.24	...	...
Bean (Phaseolus spp.)	Field	Seeds	Mature	...	...	0.10	...	...
	Field	Pods	Edible	...	...	0.02-0.26	...	...
	Field	Tops	...	...	...	1.12	...	...
Beet (Beta vulgaris)	Field	Tops	Mature	...	...	0.40	...	...
	Field	Roots	Edible part	...	...	0.07	...	...
	Field	Tops	Mature	...	...	0.19	...	...
	Field	Roots	Edible part	...	...	0.03	...	...
Bitter melon (Momordica charantia)	Field	Tops	Mature	...	...	1.00	...	...
Black gum (Nyssa sylvatica)	Field	Leaves	Mature	...	...	1.00	216.00	...
	Field	Leaves	Mature	...	...	6.00	845.00	
Bog asphodel (Narthecium spp.)	Field	Leaves & Stems	Mature	...	...	0.04-0.50	...	...

TABLE 5.6.5.7-1. Typical plant tissue analysis values for cobalt. (cont'd)

Plant	Type of culture	Tissue sampled	Age, stage, condition or date of sample	Range in dry matter (ppm.)				
				Showing deficiency symptoms	Low range	Intermediate range	High range	Showing toxicity symptoms
Buckwheat (Fagopyrum spp.)	Field	Grain	Ripe	...	...	0.36	...	...
Bulrush (Scirpus caespitosus)	Field	Stems	Mature	...	...	0.02-0.60	...	...
Cabbage (Brassica oleracea capitata)	Field	Tops	Edible part	...	...	0.07	...	...
	Field	Tops	Edible part	...	...	0.00-0.15	...	...
	Field	Tops	Mature	...	...	2.25	...	...
	Field	Tops	Edible part	...	...	0.19	...	...
	Field	Heads	Mature	...	...	0.11	...	...
Carrot, garden (Daucus carota sativa)	Field	Tops	Mature	...	...	0.30	...	...
	Field	Roots	Edible	...	...	0.02	...	...
	Field	Roots	Mature	...	...	0.80	...	...
	Field	Tops	Mature	...	...	0.11	...	...
	Field	Roots	Edible	...	...	0.03	...	...
Carrot, wild (Daucus sativa)	Plots	Tops	Mature	...	...	0.08	...	...
Cauliflower (Brassica oleracea botrytis)	Field	Heads	Mature	...	...	0.07	...	...
Celery (Apium graveolens dulce)	Field	Tops	Mature	...	...	7.50	...	...
Cherry (Prunus cerasus)	Field	Fruit	Mature	...	...	0.005	...	...
Clover, alsike (Trifolium hybridum)	Plots	Tops	Blooming	...	...	0.20-0.27	...	...
Clover, red (Trifolium pratense)	Field	Tops	Mature	...	...	0.19	...	...
	Plots	Tops	Blooming	...	...	0.13-0.21	...	...

TABLE 5.6.5.7-1. Typical plant tissue analysis values for cobalt. (cont'd)

Plant	Type of culture	Tissue sampled	Age, stage, condition or date of sample	Range in dry matter (ppm.)				
				Showing deficiency symptoms	Low range	Intermediate range	High range	Showing toxicity symptoms
Clover, white (Trifolium repens)	Field	Tops	Mature	...	...	4.60	...	...
	Plots	Tops	Blooming	...	...	0.17-0.20	...	...
Coffee (Coffea spp.)	Field	Beans	Mature	...	...	0.002	...	...
Corn (Zea mays)	Field	Grain	Mature	...	...	0.01	...	...
	Field	Ears	Edible part	...	...	0.01	...	...
	Field	Tops	Silage	...	...	0.04	...	...
	Field	Grain	Mature	...	...	0.01	...	...
Cress, water (Rorippa nasturtium aquaticum)	Field	Tops	Mature	...	...	0.15	...	...
Crotalaria, Striped (Crotalaria mucronata)	Field	Tops	Mature	...	...	2.25	...	...
Fig (Ficus carica)	Field	Fruit	Mature	...	...	0.20	...	...
GRASSES Bermuda grass (Cynodon dactylon)	Field	tops	Mature	...	...	0.26-3.75	...	...
Bluegrass Kentucky (Poa pratensis)	Field	Tops	Mature	...	...	3.25	...	...
	Field	Tops	Early bloom	...	...	0.24	...	...
	Plots	Tops	Forage	...	...	0.20	...	...
Bluestem or broom sedge (Andropogon spp.)	Field	Tops	Mature	...	...	0.01-0.14	...	...
	Field	Tops	Mature	...	...	0.06-0.61	...	...
	Field	Tops	Mature	...	...	0.00-0.38	...	...

TABLE 5.6.5.7-1. Typical plant tissue analysis values for cobalt.

(cont'd)

Plant	Type of culture	Tissue sampled	Age, stage, condition or date of sample	Range in dry matter (ppm.)				
				Showing deficiency symptoms	Low range	Intermediate range	High range	Showing toxicity symptoms
Brone grass (Bromus spp.)	Field	Tops	Early blobm	...	...	0.08	...	...
Carpet grass (Aronopus affinis)	Field	Tops	Mature	...	...	0.12	...	...
Crab grass hairy (Digitaria sanguinalis)	Plots	Tops	Mature	...	...	0.12	...	...
Fescue, meadow (Fescuta elatior)	Field	Tops	Early bloom	...	...	0.09	...	...
Foxtail (Setaria glauca)	Plots	Tops	Mature	...	...	0.08	...	...
Foxtail, bristly (Setaria verticullata)	Field	Tops	Mature	...	...	0.26-2.50	...	...
Guinea grass (Panicum maximum)	Field	Tops	Mature	...	...	0.26-0.48	...	...
Hilo grass (Paspalum conjatum)	Field	Tops	Mature	...	...	2.60	...	...
Kikuyu grass (Penniselum claudestinum)	Field	Tops	Mature	...	...	3.00	...	...
Moor grass (Molinia caerulea)	Field	Tops	Mature	...	...	0.03-0.16	...	...
Orchard grass (Dactulis glomerata)	Field	Tops	Mature	...	...	0.08	...	...
	Field	Tops	Early bloom	...	...	0.03-0.07	...	...
	Plots	Tops	Forage	...	...	0.09	...	...

TABLE 5.6.5.7-1. Typical plant tissue analysis values for cobalt.

(cont'd)

Plant	Type of culture	Tissue sampled	Age, stage, condition or date of sample	Range in dry matter (ppm.)				
				Showing deficiency symptoms	Low range	Intermediate range	High range	Showing toxicity symptoms
Para grass (Panicum purpurascens)	Field	Tops	Mature	...	...	0.35-3.20	...	...
Pili or tanglehead grass (Heterapogon contortus)	Field	Tops	Mature	...	...	0.50	...	...
Rattail or dropseed grass (Sporobolus capensis)	Field	Tops	Mature	...	...	2.25	...	...
"Rice" grass (Paspalum orbiculare)	Field	Tops	Mature	...	...	0.75	...	...
Rye grass, Italian (Lolium multiflora)	Field	Tops	Mature	...	...	0.07	...	...
	Field	Tops	Early Bloom	...	...	0.03-0.07	...	...
Sour grass (Trichachae insularis)	Field	Tops	Mature	...	...	0.26	...	...
Sweet vernal grass (Anthosanthum odoratum)	Field	Tops	Mature	...	...	0.13-	...	...
Switchcane grass (Arundinaria teeta)	Field	Reeds	Mature	...	...	0.01-0.11	...	...
Witch grass (Panicum capillare)	Plots	Tops	Mature	...	...	0.15	...	...
Various grass spp.	Field	Tops	Mature	...	...	0.20-1.00	...	...
	plots	Tops	Mature	...	...	0.05-0.14	...	...
Guava (Psidium guajava)	Field	Leaves	Mature	...	...	4.35	...	...

TABLE 5.6.5.7-1. Typical plant tissue analysis values for cobalt. (cont'd)

Plant	Type of culture	Tissue sampled	Age, stage, condition or date of sample	Range in dry matter (ppm.) Showing deficiency symptoms	Low range	Intermediate range	High range	Showing toxicity symptoms
Heather or Heath (Calluna culgaris)	Field	Leaves & stems	Mature	...	...	0.10-0.20	...	...
(Erica cinerea)	Field	Leaves & stems	Mature	...	...	0.10-0.15	...	...
(Erica tetralix)	Field	Leaves & stems	Mature	...	...	0.15-0.19	...	...
Illima weed (Sida fallax)	Field	Tops	Mature	...	...	0.40-2.40	...	...
"Japanese tea" (Cassia lescheraultiana)	Field	Leaves	Mature	...	...	0.50	...	...
Koa, Formosan (Acacia confusa)	Field	Leaves	Mature	...	...	0.43	...	...
Lambsquarter (Chenopodium album)	Plots	Tops	Mature	...	...	0.08	...	...
Lead Tree (Leucaena glauca)	Field	Leaves	Mature	...	...	0.40-1.25	...	...
Lespedeza (Lespedeza spp.)	Field	Tops	Mature	...	...	0.03-0.73	...	...
Lettuce (Lactuca sativa)	Field	Tops	Edible part	...	...	0.00-0.20	...	...
	Field	Tops	Mature	...	...	6.25	...	...

TABLE 5.6.5.7-1. Typical plant tissue analysis values for cobalt.

(cont'd)

Plant	Type of culture	Tissue sampled	Age, stage, condition or date of sample	Range in dry matter (ppm.) Showing deficiency symptoms	Low range	Intermediate range	High range	Showing toxicity symptoms
Lettuce (cont'd)	Field	Tops	Edible part	...	...	0.21	...	...
	Plots	Heads	Mature	...	...	0.07	...	...
Mushroom (Cantharellus cibarius)	Field	Buttons	Edible	...	...	2.10	...	...
Oats (Avena sativa)	Field	Tops	Early bloom	...	...	0.03	...	...
	Plots	Straw	Ripe	...	...	0.05	...	...
	Plots	Grain	Ripe	...	...	0.02	...	...
	Plots	Tops	Early maturity	...	...	0.04-0.45	...	...
Onion (Allium cepa)	Field	Bulbs	Mature	...	...	0.13	...	...
	Plots	Bulbs	Mature	...	...	0.02	...	...
Papaya (Carica papaya)	Field	Leaves	Mature	...	...	0.70	...	...
Pear (Pyrus communis)	Field	Fruit	Mature	...	...	0.13	...	...
Pepper (Capsicum spp.)	Plots	Plant	Mature	...	...	0.31	...	...
	Plots	Fruit	Mature	...	...	0.12	...	...
Pigweed (Amaranthus retroflexus)	Plots	Tops	Mature	...	...	0.20	...	...
Potato (Solanum tuberosum)	Field	Tubers	Mature	...	...	0.06	...	...
Purslane (Portulaca oleracea)	Plots	Tops	Mature	...	...	0.32	...	...
Ragweed (Ambrosia artemisifolia)	Plots	Tops	Mature	...	...	0.20	...	...

TABLE 5.6.5.7-1. Typical plant tissue analysis values for cobalt.

(cont'd)

Plant	Type of culture	Tissue sampled	Age, stage, condition or date of sample	Range in dry matter (ppm.)				
				Showing deficiency symptoms	Low range	Intermediate range	High range	Showing toxicity symptoms
Rice (Oryza sativa)	Field	Grain	Tipe	...	...	0.006	...	...
Rye (Secale cereale)	Plots	Tops	Forage	...	...	0.70	...	...
Sedge (Carex spp.)	Field	Tops	Mature	...	...	0.03-0.50	...	...
Silk oak (Grevillea robusta)	Field	Leaves	Mature	...	...	0.50	...	...
Smartweed (Polygonum pennsylvanicum)	Plots	Tops	Mature	...	...	0.31	...	...
Soybean (Glycine soja)	Plots	Tops	Pods forming	...	...	0.12	...	...
	Plot	Seeds	Mature	...	...	0.20	...	...
Spinach (Spinacia oleracea)	Field	Tops	Edible	...	...	0.07	...	...
	Field	Tops	Mature	...	...	0.20-0.25		...
	Field	Tops	Edible	...	...	0.67	...	...
	Plots	Greens	Edible	...	...	0.27	...	...
Sudan grass (Sorghum vulgare sudanense)	Plots	Tops	Early bloom	...	...	0.05	...	...
Sugar cane (Saccharum officinarum)	Field	Leaves	...	...	...	0.50-1.75	...	...
Sweet potato (Ipomoea batatas)	Field	Tubers	Edible	...	...	0.03	...	...

TABLE 5.6.5.7-1. Typical plant tissue analysis values for cobalt.

(cont'd)

Plant	Type of culture	Tissue sampled	Age, stage, condition or date of sample	Range in dry matter (ppm.)				
				Showing deficiency symptoms	Low range	Intermediate range	High range	Showing toxicity symptoms
Timothy (Phleum pratense)	Field	Tops	Mature	...	...	0.03	...	...
	Field	Tops	Early-bloom stage	...	...	0.01-0.03	...	...
	Plots	Tops	Early-bloom stage	...	...	0.05	...	...
	Plots	Tops	"Boot" stage	...	...	0.01-0.20	...	...
	Field	Tops	Mature	...	...	0.05-0.15	...	...
Tomato (Lycopersicon esculentum)	Field	Fruit	Mature	...	...	0.10	...	...
	Field	Fruit	Mature	...	...	0.005	...	...
	Field	Fruit	Mature	...	...	0.06-0.25	...	...
	Field	Tops	Mature	...	...	4.00	...	...
Turnip (Brassica rapa)	Field	Greens	Edible	...	...	0.34	...	...
Vetch (vicia spp.)	Plots	Tops	Full bloom	...	...	0.13	...	...
Walnut (Juglans regia)	Field	Meats	Mature	...	...	0.05	...	...
Wheat (Triticum spp.)	Field	Grain	Ripe	...	...	0.01	...	...
	Field	Grain	Ripe	...	...	0.01	...	...
	Field	Tops	Early bloom	...	...	0.03	...	...
	Field	Leaves	Immature	...	...	0.13-1.40		..
	Plots	Tops	Forage	...	...	0.14	...	...

Source: Vanselow, 1966, pp. 144-150.

5.6.6. Copper (Cu)

5.6.6.1. Introduction.

Copper is unquestionably an essential micronutrient for plant and animal growth, but in concentrations greater than normal, it can be toxic. The recommended level of occupational exposure for copper fumes is 0.1 mg/m^3 and for copper dust and mist is 1 mg/m^3.

Copper is a malleable, ductile reddish-colored metal with heat and electrical conductance properties second only to silver. Copper occasionally occurs native and is found in many minerals.

The copper-nickel ores in Minnesota are primarily pyrrhotite, chalcopyrite, cubanite, and pentlandite (Bonnichsen, 1974). The two elements occur as sulfides in these minerals and in a ratio of three parts copper to one part nickel (Bonnichsen, 1974). Copper is present in a concentration of about 55 ppm in the earth's crust (Krauskopf, 1972).

Copper is used primarily in electrical conductors and as an alloy in brass, bronze, and other metals.

5.6.6.2. Sources of copper.

a. Natural.

Copper is a naturally occuring element in many minerals, and is present in most soils in concentrations of 10-80 ppm (Krauskopf, 1972). Because of its mobility, copper also commonly occurs in sedementary formations.

Gaseous copper compounds have been reported only from high temperature volcanic emissions (Krauskopf, 1972; Goldberg, 1976).

b. Anthropogenic.

There are four prevailing sources of copper contamination: industrial particulate emissions, mine effluents, sewage treatment water and sludge, and copper containing fungicides (Lagerwerff, 1976).

The phytotoxic properties of copper was known as early as the 1800's. Bordeaux mixture, the first widely used fungicide, is prepared by dissolving copper sulfate and lime or sodium carbonate in water (Reuther and Labanauskas, 1966). This and other copper mixtures are still used as fungicides or algacides and as aquatic herbicides.

A five per cent solution of copper sulfide was also used as one of the first chemicals for the control of weeds (Reuther and Labanauskas, 1966). The use of these pesticides led to the discovery of the stimulatory effects of copper on some plants, and eventually to its essentiality in plants and animals (Chisholm, 1972 and Bennett, 1971).

Municipal sewage sludge may contain up to 3000 ppm copper. This copper, together with the other metals present, may make sewage sludge unacceptable for long term use as a soil amendment (Dudas and Pawluk, 1975). Metal smelters, particularly copper and nickel ore smelters, are major sources of copper pollution. The literature is replete with examples of the ecological impacts of copper and other metallic particulate emissions (McGovern and Balsillie, 1975; Edroma, 1974; Day and Ludeke, 1973; Stokes, 1973; Whitby and Hutchinson, 1974; Lagerwerff et al., 1973; Hutchinson and Whitby, 1974).

Other anthropogenic sources of copper contamination include large coal-fired power plants and inadvertent overapplication of copper supplements (Gladstones et al., 1975).

5.6.6.3. Biological availability of copper.

a. Soil solid phase.

Copper is a transition element. As such, it is present in naturally occurring compounds with two valences: Cu^{+} and Cu^{++} (Krauskopf,

1972). The igneous copper sulfide minerals, primarily chalcopyrite ($CuFeS_2$), are more common in basaltic rock than in granitic rock. In sedementary rocks, chalcopyrite once again dominates with other sulfide and oxide minerals such as the basic carbonates malachite, azurite, and the silicate chrysocolla playing lesser, but more colorful roles. In shales, copper may also be present as adsorbed ions on fine-grained particles (Krauskopf, 1972).

Nearly all of these mineral forms of copper weather easily, making copper one of the most mobile of the trace elements. Whatever the form in the native rock, copper almost invariably weathers out as the cation Cu^{++}. If the amount of copper in solution exceeds the adsorption capacity of the soil, and where conditions are acid and oxidizing, some copper will remain in solution. If this solution then becomes alkaline, oxides, basic carbonates, or hydrated silicate minerals may be formed. If the solution is reduced, Cu_2O or native Cu may be formed. One of the sulfides (CuS or Cu_2S) may be formed if the solution encounters a more soluble mineral or a source of hydrogen sulfide (H_2S), such as in swamp soils (Krauskopf, 1972). However, under normal conditions, such as in agricultural soils, nearly all of the copper is adsorbed by clay minerals or complexed by organic matter (Krauskopf, 1972). Less than 1 mg/g is likely to be in solution (Etherington, 1975).

According to Krauskopf (1972), of the six micronutrient elements, copper is the one most strongly adsorbed by soil solids. Copper is strongly adsorbed because of its tendency to form covalent bonds. The adsorption capacity for copper of the different clay minerals increases in the usual order from kaolin to illite to montmorillonite. Copper can

be adsorbed in appreciable amounts by quartz. Ferric hydroxide is also an effective adsorbant of Cu so long as the pH is above the isoelectric point of the hydroxide. Adsorption of copper by these soil minerals is strongly controlled by pH.

Copper is also readily adsorbed by soil organic matter, a process which may lead to copper deficiencies in peat soils (Krauskopf, 1972).

b. Soil solution.

As discussed previously, copper is present in the soil solution usually in the form of Cu^{+} or Cu^{++}. Because of its active bonding abilities, however, the copper concentration in solution is usually less than 1 ug/g (Etherington, 1975). If some of the total copper is chelated by soluble organic matter, than this portion may also appear in the solution as an organic copper complex (Lagerwerff, 1967).

c. Transition between solid phase and soil solution.

The adsorption of copper by clay minerals and the chelation of copper by organic matter are both highly dependent on soil acidity. Copper is most mobile and available below about pH 5.5, while becoming virtually unavailable, especially in organic soils, above pH 7 (Brady, 1974; Lagerwerff, 1967).

Two other influencing factors not yet mentioned are the presence of iron and manganese oxides in soils. These soil minerals apparently have a high affinity for copper and may play important roles in some soils in complexing copper into unavailable forms (Norrish, 1975).

5.6.6.4 Role of copper in plant nutrition.

Copper is actively absorbed by the roots; i.e., copper absorption is metabolically controlled. There is also some evidence that leaf

surfaces actively absorb airborne copper (Moore, 1972). The normal range of copper concentrations in plant tissues is from 5 to 20 ppm. Copper concentrations below 4 ppm dry weight will likely result in deficiencies, while concentrations above 20 ppm in mature leaves may cause toxicity (Jones, 1972).

Copper plays exclusively a catalytic role in plants (Bidwell, 1974). Tyrosinase, laccase, cytochrome oxidase, ascorbic acid oxidase, phenol oxidase, and some other enzymes are known to contain copper. Cytochrome C oxidase, ascorbate oxidase, and laccase all contain copper and are responsible for catalyzing the reactions which reduce molecular oxygen to water (Nicholas, 1975). Plastocyanin, a copper containing substance, is a necessary component in the electron transfer chain of photosynthesis (Nicholas, 1975; Boardman, 1975). Besides these roles in respiration and photosynthesis, copper is also involved in the synthesis of chlorophyll and in carbohydrate and protein metabolism (Brady, 1974).

Experiments with some plants (e.g., corn, soybeans, and sugar beets) show that copper is usually present in greater concentrations in leaves and fruits than in stems and other supporting structures (Jones, 1972).

5.6.6.5. Copper deficiency.

Plants slightly lacking in copper will exhibit symptoms no more diagnostic than reduced vigor and yield. As copper becomes less available and the activity of its enzymes become critically reduced, terminal dieback and rosetting (shortening of internodes) may occur (Reuther and Labanauskas, 1966). Terminal leaves may show such

pathological symptoms as necrosis, chlorosis, or spotting, or become rolled or withered (Bidwell, 1974). More specific symptoms depend on the plant and are not as characteristic as those caused by deficiences of iron, magnesium, manganese, or zinc (Reuther and Labanauskas, 1966). Table 5.6.6.5-1 presents specific symptomotology of copper deficience in a number of crop species.

Copper deficiencies are most likely to occur on the following soil types (Reuther and Labanauskas, 1966):

a. peat and muck soils

b. alkaline and calcareous soils, especially sandy types

c. leached sandy soils

d. old corrals and sites of Indian burial grounds

e. soils heavily fertilized with nitrogen

f. leached acid soils

5.6.6.6. Copper toxicity.

Copper toxicity may occur naturally, especially on metalliferous soils, where copper (and other metals) are present in very high amounts. Research at these sites and in laboratory cultures has shown that some plants can evolve a tolerance for excess copper over several generations (Antonovics et al, 1972; Wally et al., 1974; Gartside and McNeilly, 1974). Cases of such high, naturally occurring concentrations of copper are, however, rare, and the applicability of tolerance evolution to anthropogenic contamination of natural communities is uncertain.

Because of the strong adsorption and chelating properties of copper, a significant effect of its excess is the displacement of other trace elements from these sites. This causes leaching or other

Table 5.6.6.5-1. Specific symptomatology of copper deficiency in selected crop species.

Plant	Visual Symptoms
Alfalfa (Medicago sativa)	Terminal leaf petioles show epinastic curvature; there is backward folding of leaflets along petioles, followed by withering and death of leaflets; no chlorosis develops.
Apple (Malus spp.)	Terminal shoots which have been making vigorous growth die back. Terminal leaves develop necrotic spots and brown areas, followed by withering and death of shoot tips; the following season, growth is resumed by buds below the point of death. Repetition of the dieback over a period of years causes affected trees to have a bushy, stunted appearance.
Apricot (Prunus armeniaca)	Terminal branches die back from tips, preceded by cessation of terminal growth; there is rosette formation and multiple bud growth on terminals.
Avocado (Persea americana)	Older leaves have a dull appearance with the veins becoming a reddish-brown color which gradually spreads into the leaf blades; there is multiple bud formation at tips of twigs. Abortive new leaves form, which almost immediately begin drying up and dying back until the entire twig dies. Cultures deprived of copper develop dark-green foliage and S-shaped shoots.
Barley (Hordeum vulgare)	There is withering and graying of the leaf tips; also bending, loss of turgor, turning backward of leaves, and dying of tips of newly emerging leaves.
Beet (Beta vulgaris)	Young leaves appear blue-green; older leaves become chlorotic, with marked characteristic patterns beginning at the tip and spreading over the entire leaf; veins remain green.
Cabbage (Brassica oleracea capitata)	Leaves become chlorotic; heads fail to form; growth is stunted.
Canary grass (Phalaris canariensis)	Newly emerging leaf tips die before unrolling; older leaves appear limp, turn gray, and wither.

Table 5.6.6.5-1. Specific symptomatology of copper deficiency in selected crop species. (continued)

Plant	Visual Symptoms
Carrot (Daucus carota sative)	Top growth is stunted; root development is poor; no chlorosis appears on the tops.
Celery (Apium graveolens dulce)	Leaves become chlorotic and unhealthy in appearance; growth is stunted.
CITRUS FRUITS	
Grapefruit (Citrus paradisi)	Usually, the first evidence of incipient copper deficiency is the development of large, dark-green leaves on long, soft, angular shoots; the leaves usually show a "bowing-up" of the midrib. When the copper deficiency is more acute, very small leaves may develop, which quickly abort on twigs that are going to die back; on the older wood, the leaves will be large, dark green, and somewhat twisted or malformed. Gummy excrescences are commonly seen on fruit rind and in axes of fruit segments.
Lemon (Citrus limon)	Affected twigs usually show multiple bud development. These produce a dense, somewhat bushy growth in trees of moderate vigor. Gum pockets occasionally develop between the bark and the wood. In acute cases, twigs with multiple buds send out a profusion of young, soft shoots with small leaves; these quickly die back from the tips.
Orange (Citrus sinensis)	Terminal growth dies back; the first symptoms are often large, dark-green leaves on long, soft angular shoots. Leaves are commonly irregular in contour, usually with a "bowing up" of the midrib; in acute cases, twigs with multiple buds put out a profusion of young, soft shoots with small leaves; these die back from the tips. There are sometimes reddish excrescences over large portions of twig bark. Fruits may be bumpy, and have the rind covered with reddish-brown excrescences; there are gum pockets around core, and fruit may split; juice is low in acid and pulp dries out early in the season.

Table 5.6.6.5-1. Specific symptomatology of copper deficiency in selected crop species. (continued)

Plant	Visual Symptoms
CLOVER	
Red clover (Trifolium pratense)	Leaves become light green, wither, and die suddenly; growth is poor.
Subterranean clover (Trifolium subterraneum)	Leaves become light green without center markings; they wither and die suddenly; growth is poor.
Corn (Zea mays)	Leaves become chlorotic; there is withering and graying of the tips, bending, and loss of turgor; turning backward of leaves; tips of newly emerging leaves die.
Currant (Ribes spp.)	Leaves become pale green and mottled; dieback of the young, growing tips occurs; also, bushy growth and rosetting.
Eggplant (Solanum melongena)	Leaves become pale green and mottled with yellow; there is dieback of the young, growing tips.
Flax (Linum usitatissimum)	Terminal leaves turn yellow and die; there is rosetting of leaves at the top of the plant; growth is stunted, and plants fail to produce seed or capsules.
Lettuce (Lactuca sativa)	Leaves become chlorotic and bleached; this starts at the stem ends and margins; leaves become cupped; heads lack firmness; growth is stunted.
Oats (Avena sativa)	Terminal or new leaves roll at the tips, become chlorotic, and yellow-gray spots appear which turn yellow-white; leaves may be striped with green and yellow; seed is light or shriveled.
Olive (Olea europaea)	There is death of the young, growing tips, after which the axillary buds below the dead part are often stimulated and produce a bushy growth.
Onion (Allium cepa)	The scales are thin and pale yellow; bulbs lack solidity; leaves are chlorotic.

Table 5.6.6.5-1. Specific symptomatology of copper deficiency in selected crop species. (continued)

Plant	Visual Symptoms
Pea (Pisum sativum)	Terminal stem tips become wilted; basal buds are green, with weak lateral growth, flowers abort and no pods form.
Peach (Prunus persica)	The first symptom of copper deficiency is the occurrence of unusually dark-green foliage. As the deficiency becomes more acute, the leaves turn yellowish green between the small veins, giving the appearance of a green network on a whitish-green background; malformed leaves develop at the tips; these leaves are long and narrow, with irregular margins. Terminal branches die back, starting at the tips. This is preceded by cessation of terminal growth; there is rosette formation and multiple bud growth on terminals.
Pear (Pyrus communis)	There is death and withering of the terminal leaves and current shoot growth, from tips toward points of origin. The following year, one or more shoots may develop from buds below the dead part of the previous year's growth; these may grow normally for a time, until the dieback is repeated. In severely affected trees, terminal growth is stunted, leaves are small, the trees are not fruitful, and the recurrent dieback and renewal of growth may cause a brushy, "witches'-broom" appearance. The bark of the twigs and trunk is rough.
Pepper (Capsicum spp.)	Leaves become dark bluish green; there is no chlorosis. Growth of both roots and tops is stunted, and there is failure to produce flowers.
Plum (Prunus domestica)	Early growth in the spring is normal, but about two months following full bloom, the terminal buds die and the terminal leaves turn a yellowish color. Eruptions and gumming of the bark occur.
Potato (Solanum tuberosum)	Young leaves show loss of turgor and remain permanently wilted. Terminal buds tend to drop when the flower buds are developing, especially if the shortage of copper is marked. Drying of leaflet tips occurs in advanced stages. No pronounced chlorosis of foliage develops.

Table 5.6.6.5-1. Specific symptomatology of copper deficiency in selected crop species. (continued)

Plant	Visual Sumptoms
Prune (Prunus domestica)	Terminal branches die back at the tips about two months following full bloom; there is rosette formation and multiple bud growth on the terminals.
Sugar beet (Beta saccharifera)	Young leaves are bluish green; older leaves become chlorotic, with a marked pattern beginning at the tip and spreading over the entire leaf; veins retain their green color; the leaves are thin, and chlorotic areas become white to gray, then brown; they may also become wavy along the margins. Roots show long, white laterals.
Sunflower (Helianthus annuus)	There is withering and graying of the leaf tips; also bending, loss of turgor, and turning backward of leaves; newly emerging leaves often die at the tips. There is no chlorosis, but the growth of both roots and tops is stunted. The foliage becomes dark bluish green, and there is failure to produce flowers.
Tobacco (Nicotiana tabacum)	The upper leaves are unable to retain their turgor, and wilt badly. Such plants are permanently wilted; they do not recover at night or during cloudy periods. When copper deficiency becomes evident during the flowering stage, the seed stalk does not stand erect and the amount of seed is reduced.
Tomato (Lycopersicon esculentum)	There is a very stunted growth of shoots, and exceedingly poor root development, the foliage becomes dark bluish green in color. There is curling of leaves and lack of flower formation. Chlorosis develops, and leaves and stems lack firmness.
Tung (Aleurites fordi)	The foliage is chlorotic and dwarfed, and there is "cupping-up," usually with marginal burn and premature abscission of terminal leaves.
Wheat (Triticum spp.)	Terminal or new leaves are pale green, lack turgor, and become rolled and yellowed; older leaves become limp and bent at the ligule. The leaves die, and dry to a bleached gray.

Source: Reuther and Labanauskas, 1966, pp. 159-162.

losses of these elements, leading to plant deficiencies. This chain of events is most apparent with zinc and iron (Yopp et al., 1974).

Copper may also cause zinc and iron deficiencies by directly suppressing root absorption of these elements (Yopp et al., 1974). Within the plant, copper is also known to obstruct iron translocation by promoting the oxidation of ferrous to ferric ions (Lagerwerff, 1967). This, of course, may lead to iron chlorosis, a common symptom of excess copper.

Besides iron chlorosis and related manifestations if iron deficiencies, excess copper may cause reduced growth, stunting, reduced branching and thickening and abnormally dark coloration of rootlets (Reuther and Labanauskas, 1966).

Applications of iron to the foliage in the form of Fe EDTA may relieve these symptoms, and addition of zinc and manganese to the soil may also help (Lagerwerff, 1967).

Tables 5.6.6.6-1 and 5.6.6.6-2 present data on symptomatology and tolerance levels for a number of plants.

Fruit trees are good indicators of copper deficiencies, as are oats, barley, and corn. Clover, alfalfa, and poppy are highly sensitive to excess copper, as are spinach and gladiolus Copper indicators (those species universally or locally restricted to soils high in copper) may be useful in locating soils high in copper. These species belong mainly to three families: the Caryophyllaceae (pink family), the Labiatae (mint family), and mosses (Reuther and Labanauskas, 1966).

Yopp et al. (1974) recommended that maximum soil concentrations, as determined by EDTA extraction, should not exceed about 15 ppm and that

tissue concentrations should not exceed 10 ppm in immature, growing foliage. Table 5.6.6.6-3 presents further data on typical tissue analysis for reference.

Table 5.6.6.6-1. Specific symptomatology of copper excess on selected crop species.

Plant	Visual Symptoms
Bean (*Phaseolus* spp.)	Root development is stunted. Leaves are chlorotic, and there is reduced vegetative growth.
Citrus fruits (*Citrus* spp.)	Plants are stunted because of chlorosis of the foliage. Roots are stubby, stunted, and dark colored. Foliage is sometimes yellowed, as in nitrogen deficiency.
Corn (*Zea mays*)	There is reduced growth, chlorosis of the foliage, and stunted root development.
Mustard (*Brassica* spp.)	The main symptoms are reduced growth, purple stems, small, chlorotic leaves and stunted roots.

Source: Reuther and Labanauskas, 1966, p. 162.

Table 5.6.6.6-2. Copper toxicity levels for selected crop species.

Plants	Growth Medium	Minimal Phyto-toxic Conc.	Plant Part Affected	Symptom	Developmental Stage
Pine *P. pinaster*	solution	1 ppm external	tops	reduced	seedling
Lupine	solution	3.2 ppm external	tops	reduced	seedling
Sugar beet	solution	3.2 ppm external	tops	chlorosis	seedling
Tomato, var. Market King	solution	0.06 ppm external	tops	chlorosis reduced growth	seedling
Potato, var. Majestic	solution	0.06 ppm external	tops	chlorosis reduced growth	seedling
Oat, var. Star	sand	0.06 ppm external	tops	reduced growth	seedling
Barley	solution	480 ppm external	tops	reduced growth	seedling
Broad Bean	solution	960 ppm external	tops	reduced growth	reproductive
Lettuce	solution	10 ppm external	tops	no growth	seedling
Carrot	solution	5 ppm external	tops	no growth	seedling
Cauliflower	solution	0.5 ppm external	tops	no growth	seedling
Potato	solution	10 ppm external	tops	no growth	seedling

Source: Yopp *et al.*, 1974.

TABLE 5.6.6.6-3. Typical plant tissue analysis values for copper.

Plant	Type of culture	Tissue sampled	Age, stage, condition or date of sample	Range in dry matter (ppm.)				
				Showing deficiency symptoms	Low range	Intermediate range	High range	Showing toxicity symptoms
Alfalfa (Medicago sativa)	Field	Stems & leaves	...	...	...	11.50	...	...
	Field	Tops	...	...	...	5.10-9.60	...	...
	Control	Tops	...	...	6.00	16.40	...	...
Apple (Malus spp.)	Field	Leaves	Uppermost four	1.00-4.00	...	3.20-12.00	...	...
	Field	...	...	2.00-2.50	...	5.10-6.00	...	...
	Field	Leaves	...	...	...	23.00	...	...
	Field	Leaves	...	<5.00	...	...	...	...
	Field	Leaves	...	1.00-3.00	...	5.50-12.00	...	...
Avocado (Persca americana)	Field	Leaves	Fully expanded 6 months old	...	...	4.00-7.00	...	...
	Field	Leaves	Fully expanded 7 months old	...	...	4.00-6.00	...	...
	Field	Leaves	Fully expanded 7 months old	...	...	6.00-8.00	...	...
	Field	Leaves	Fully expanded 6 months old	...	...	4.00-7.00	...	...
	Field	Leaves	1 to 12 months old	...	...	4.00 11.00	...	...
	Field	Leaves	6 months old	...	...	6.00-10.00	...	...
Barley (Hordeum vulgare)	Field	Grain	Harvest	...	...	6.20-11.90	...	...
Cacao (Theobroma cacao)	Field	Leaves	...	...	...	11.00-15.00	...	...
Cauliflower (Brassica oleracea botrytis)	Field	Leaves	...	...	...	5.40	...	...
	Field	Leaves	...	...	...	4.30	...	...
Cherry (Prunus cerasus)	Field	Leaves	July-August	...	...	5.00-200.00	...	...
	Field	Leaves	...	...	...	57.00	...	...

TABLE 5.6.6.6-3. Typical plant tissue analysis values for copper.

(Cont'd)

Plant	Type of culture	Tissue sampled	Age, stage, condition or date of sample	Range in dry matter (ppm.) Showing deficiency symptoms	Low range	Intermediate range	High range	Showing toxicity symptoms
CITRUS FRUITS Lemon (Citrus limon)	Field	Leaves	3 months old from non-fruiting terminals	...	...	8.40-8.60	...	...
	Field	Leaves	...	3.90	...	...	...	>20.00 (injured by HCN fumigation)
Orange (Citrus sinensis)	Field	Leaves	5 months old from non-fruiting terminals	...	...	8.60-9.60	...	...
	Field	Valencia leaves	1-16 months old	...	...	9.90-14.00	...	...
	Field	Leaves	...	...	...	5.00-8.30	...	...
	Field	Leaves	3 to 7 months old, from nonfruiting terminals	...	...	5.00-11.40	...	...
	Field	Leaves	4 to 7 mos. old, from nonfruiting terminals	<4.00	4.10-5.90	6.00-16.0(?)	17.00-22.00 (?)	23.00 (?)
	Culture	Leaves	3 mos. old	...	...	19.00-20.00	...	...
	Culture	Stems	3 mos. old	...	...	13.00-20.00	...	...
	Culture	Roots	3 mos. old	...	...	120.00-630.00	...	...
	Culture	Leaves	4-7 mos.old spring-cycle from fruiting terminals	4.00	...	4.00-10.00	15.00	...
	Field	Leaves	3-7 mos. spring cycle from fruiting terminals	1.00-4.00	...	4.00-10.00	...	...
	Field	Leaves	...	3.90	...	4.00-	...	>20.00 (injured by HCN fumigation
	...	Leaves (?)	...	...	...	...	...	>20.00
	Field	Valencia leaves	Bloom-cycle from non-fruiting terminals	<3.50	3.60-4.90	5.00-16.00 (?)	17.00-22.00 (?)	>23.00

TABLE 5.6.6.6-3. Typical plant tissue analysis values for copper. (cont'd)

Plant	Type of culture	Tissue sampled	Age, stage, condition or date of sample	Range in dry matter (ppm.) Showing deficiency symptoms	Low range	Intermediate range	High range	Showing toxicity symptoms
Orange (cont'd)	Field	Navel leaves	...	...	...	3.50-3.10	...	...
	Field	Leaves	10 mos., from fruiting terminals	...	...	8.00-20.00	...	...
	Field	Leaves	Spring cycle from fruiting terminals	<3.00	3.00-	5.00-25.00	...	...
	Control	Leaves	...	...	...	3.20-15.00	...	...
	Control	Leaves	...	0.70-1.60	...	4.80-7.20	...	...
	Field	Valencia leaves	7 mos. old, from non-fruiting terminals	...	...	5.10-8.90	...	...
	Field	Navel leaves	7 mos. old, from non-fruiting terminals	...	...	4.00-8.00	...	...
	Field	Navel leaves	7 mos. old, from non-fruiting terminals	...	...	4.40-6.90	...	...
	Field	Leaves	3 mos. old, from non-fruiting terminals	...	...	5.30-6.20	...	...
	Culture	Valencia leaves	...	...	...	7.50-14.40	...	...
	Culture	Valencia leaves	...	...	...	135.00-614.00	...	...
Clover, red (Trifolium pratense)	Field	Tops	...	...	...	7.00-16.40	...	...
Clover, subterraneun (Trifolium subterraneum)	Field	Leaves	Blooming	<3.00	...	7.00-12.00	...	...
	Field	Tops	...	<3.00	...	3.00-32.00	...	...
Coffee (Coffea spp.)	...	Raw beans	...	...	...	8.00-20.00	...	...
	...	Roasted beans	...	...	...	10.00-22.00	...	...

TABLE 5.6.6.6-3. Typical plant tissue analysis values for copper. (cont'd)

Plant	Type of culture	Tissue sampled	Age, stage, condition or date of sample	Range in dry matter (ppm.) Showing deficiency symptoms	Low range	Intermediate range	High range	Showing toxicity symptoms
Coffee (cont'd)	...	Liquid coffee	...	...	...	2.00-13.00	...	...
Currant, black (Ribes nigrum)	Field	Leaves	December	2.00-4.00	...	7.50-10.00	...	...
Grape (Vitis spp.)	Field	Leaves	Mature (April)(fall)	1.00-1.80	...	2.60-3.90	...	...
	Field	Leaves	Young	2.10-5.40	...	7.50-9.90	...	...
	Field	Leaves	Second from base	...	...	20.00-30.00	...	...
Oats (Avena sativa)	Field	Straw	Harvest	3.10-5.10	...	5.20-7.00	...	...
	Solution	Tops	Harvest	1.00-2.50	...	1.10-3.30	...	...
	Field	Plants	Harvest	2.00	...	2.00-4.00	...	...
	Field	Leaves	6-9 wks old	<3.00	...	7.00-12.00	...	...
	Field	Grain	Harvest	...	...	6.40-9.80	...	...
	Field	Tops	Flowering	...	...	2.50	...	...
	Field	Tops	Harvest	...	...	11.60-16.30	...	...
	Field	Grain	Harvest	...	...	8.30-12.10	...	...
	Field	Grain	Harvest	...	...	1.80-3.50	...	...
Peach (Prunus persica)	Field	Leaves	...	...	4.00	7.00-16.00	20.00-30.00	...
	Field	Leaves	...	...	...	13.00	...	...
Pear (Pyrus communis)	Field	Leaves	June-Oct.	3.10-5.10	...	5.00-20.00	...	...
	Field	Leaves	...	3.20-6.70	...	4.90-41.00	...	...
	Field	Wood	June-July	1.20-4.60	...	1.30-11.60	...	...
	Field	Bark	June-July	3.00-4.00	...	3.70-16.60	...	...

TABLE 5.6.6.6-3. Typical plant tissue analysis values for copper. (cont'd)

Plant	Type of culture	Tissue sampled	Age, stage, condition or date of sample	Range in dry matter (ppm.) Showing deficiency symptoms	Low range	Intermediate range	High range	Showing toxicity symptoms
Pear (cont'd)	Field	Leaves	...	<4.00	...	...	...	...
	Field	Leaves	...	<5.00	...	...	...	...
	Field	Leaves	...	...	...	5.00-100.00	...	...
	Field	Leaves	...	3.10-5.10	...	11.20	...	...
Pecan (Carya illinoensis)	Field	Leaves	...	...	...	21.00-28.00	...	...
Pineapple (Ananas comosus)	Field	Leaves	White basal portion (22 mos.old)	...	...	8.60-11.50	...	...
Plum (Prunus domestica)	Field	Apical leaves	...	3.00-4.00	...	7.00-9.00	...	...
Potato (Solanum	Field	Tubers	Harvest	...	...	2.50-5.50	...	...
Rye (Secale cereale)	Field	Grain	...	<0.50	...	<2.00	...	...
Timothy (Phelum pratense)	Field	Tops	...	...	...	6.40	...	...
Tomato (Lycopersicon esculentum)	Green-house	Leaves	...	...	...	3.10-12.30	...	...
	Control	Fruit	Harvest	...	...	13.00-37.00	...	...
	Field	Fruit	Harvest	...	...	15.00-25.00	...	...
Tung (Aleurites	Field	Leaves	August	2.60-3.10	...	4.30-5.70	...	...

TABLE 5.6.6.6-3. Typical plant tissue analysis values for copper. (cont'd)

Plant	Type of culture	Tissue sampled	Age, stage, condition or date of sample	Range in dry matter (ppm.)				
				Showing deficiency symptoms	Low range	Intermediate range	High range	Showing toxicity symptoms
Wheat (Triticum spp.)	Field	Straw	...	8.50	...	9.00-18.00	...	...
	Field	Grain	...	1.50	...	3.00-4.50	...	...
	Field	Grain	Harvest	...	...	5.00-16.70	...	...
	Field	Wheat germ	Harvest	...	...	46.00	...	...

Source: Reuther and Labanauskas, 1966, pp. 166-169.

5.6.7. Iron (Fe)

5.6.7.1 Introduction.

Iron has been known to be essential to plants and animals since the mid-nineteenth century. Iron is not commonly considered to be an environmental contaminant. The few isolated examples of iron toxicity have been caused by excessive additions of iron-containing soil amendments (Wallihan, 1966).

Of all metals iron is the cheapest, most abundant, and important element. In the pure form, which is rarely seen in commerce, iron is silvery. However, it reacts very quickly with air to become dark or rust colored.

The occupational exposure limit to iron oxide fumes is 10 mg/m^3 and to soluble iron salts 1 mg/m^3.

5.6.7.2 Sources of iron.

a. Natural.

Iron is the most abundant element in the planetary system as a whole and fourth most abundant element in the earth's crust (Krauskopf, 1966). The earth's core is thought to be primarily iron. The concentration of iron in the earth's crust is approximately 50,000 ppm. In soils it averages 30,000 ppm.

Iron can occur naturally as the native metal or in two common states of valence, ferrous (Fe^{++}) and ferric (Fe^{3+}). The form in which it appears is dependent on the oxidizing potential of its environment (Krauskopf, 1966). In the deep layers of the earth's crust, iron is present mainly as silicates, mostly in the ferrous state. Nearer to the surface, ferric minerals predominate. The ferric/ferrous ratio is higher in granite

than in basalt, and lower in volcanic minerals than in plutonic minerals (Krauskopf, 1966). The three commercial iron minerals, hematite, magnetite, and taconite, are all present in Minnesota.

At ordinary temperature, the volatility of iron minerals is far too low to be significant sources of atmospheric iron (Krauskopf, 1966).

Igneous rocks, then, contain iron primarily in the ferrous state. When this rock is exposed, the iron is released by weathering and occurs in solution chiefly as the ferrous ion Fe^{++}. The ferrous ion is oxidized rapidly, however, and precipitates in the ferric form as a hydrated ferric oxide, such as $Fe(OH)_3$. This is usually oxidized further to Fe_2O_3, which is by far the most abundant form of iron in surface environments. In the ferric form, Fe_2O_3 is extremely insoluble and has a high thermodynamic stability. Goethite (FeOOH) and hematite (Fe_2O_3) are crystalline ferric oxides and are even more insoluble. The inorganic geochemistry of soil iron involves primarily the transformations between insoluble ferrous compounds, ferrous ion in solution or adsorbed on surfaces, and ferric oxides. Other soil minerals containing iron include hydrous silicates, (e.g., glauconite and chamosite), which are common and more stable than $Fe(OH_2)$. Iron sulfides such as mackinawite (FeS), greigite (F_3S_4) and the commonest, pyrite (FeS_2) are formed in sulfide rich environments. Iron carbonates, such as siderite ($FeCO_3$), are uncommon (Krauskopf, 1966).

b. Anthropogenic.

Possible anthropogenic sources of iron include:

(1) Sewage sludge.

(2) Fertilizer and intentional use of iron supplements.

(3) Metal mining and reduction activities.

(4) Fossil fuel burning.

While the number of possible human activities which may locally enrich the environment with iron is great, the significance of this enrichment in relation to naturally occurring amounts of iron is very slight.

5.6.7.3. Biological availability of iron.

a. Soil solid phase.

The iron content of soils, in general, reflects the composition of the parent material (Krauskopf, 1966). Ferric oxide is the commonest form of iron in oxidized soils, while in reducing soils, such as those containing abundant organic matter, iron is commonly in the ferrous form, in solution or adsorbed on surfaces. In young oxidized soils, the ferric oxide is commonly hydrated, but in older soils, much of it is hematite. Besides the oxide, iron may also be present as the crystalline magnetite, which weathers very slowly. Locally, ferric sulfates and phosphates may be important constituents of oxidized soils. (Krauskopf, 1966).

Besides amorphous ferric oxide, soil iron may be present as fine-grained hematite or goethite crystals. Hematite gives reddish soils their color, and goethite is yellowish. Soil goethites are often sufficiently fine-grained (0.02 um) to contribute to the surface activity of soils (Norrish, 1975).

While iron may enter the structure of certain clay minerals, surface adsorption by clay minerals seems to play only a minor role in biological availability of iron. The availability of iron is controlled primarily by the pH and redox potential of the soil, as discussed previously. Two other factors which may play significant roles in iron

availability are microbial activity and organic complexing capability of the soil.

The role soil microbes play in iron availability is not yet completely understood. Though Fe^{++} is oxidized to Fe_2O_3 spontaneously in well aerated soils, it is known that several species of bacteria (e.g., Gallionella sp.) can also perform this reaction under more anaerobic conditions (Krauskopf, 1966; Etherington, 1975). The reverse reaction, the reduction of ferric oxides to Fe^{++}, occurs much more slowly, even where organic matter is present to act as a reducer. Fortunately, however, this reduction is catalyzed by a great variety of different bacterial species (Krauskopf, 1966).

If it were not for organic matter, the iron in many soils would largely be transformed to various insoluble compounds. Organic matter protects iron from precipitating in insoluble forms by combining it with proteins, amino acids, humic acids, and organic complex. These compounds can later release the iron to the soil solution (Brady, 1974).

b. Soil solution.

The predominant form of iron in the soil solution is the ferrous ion Fe^{++}. However, this ion is so readily oxidized or complexed, it is usually present in very low concentrations.

c. Transition between soil solids and soil solution.

The transition of iron from soil solids to the solution is primarily dependent on the pH and redox potential of the soil, and on the amount of organic matter present.

In well aerated soils, iron is readily oxidized. In this state, most of the iron is insoluble and unavailable in soils of normal pH. If the

soil becomes more acidic, more iron will go into solution. Under alkaline conditions the opposite is true; the iron becomes even more insoluble and unavailable (Brady, 1974).

In poorly aerated, waterlogged or peaty soils, much of the iron will be in the reduced form Fe^{++}. Under these conditions, the iron will not precipitate, but will remain available to plants (Brady, 1974). So, much of the iron may be in solution under these conditions and may reach toxic levels (Etherington, 1975).

The pH, redox potential, and the organic content of soils are, of course, interrelated. Organic matter tends to make soils more acidic. This makes iron more available by reducing pH and also by reducing the aeration (i.e., the oxidizing potential) of the soil. On the other hand, the organic matter itself will complex the iron. This may, in rare cases, cause slight iron deficiencies (Brady, 1974).

5.6.7.4. Role of iron in plant nutrition.

Plants absorb iron exclusively in the form Fe^{++}. Roots themselves have the ability to reduce Fe^{3+} to Fe^{++}, for example when iron is present as a ferrous-chelate complex (Longeragan, 1975). The absorption of iron by the roots is metabolically controlled (Moore, 1972).

Because of iron's ability to assume two state of valence, like copper and molybdenum, it plays an important role as an electron carrier in enzyme systems (Brady, 1974). This enzymatic role is mediated through the heme proteins (cytochromes and cytochrome oxidase) of the electron transport chain. In this context, iron's ability to be alternatively oxidized or reduced is essential to plant respiration(Bidwell, 1974). Non-heme enzymes of which iron is a part include flavoproteins, and

the extremely important electron transfer agent ferredoxin. Iron is also a constituent of the oxidizing enzymes catalase and peroxidase and may be structurally involved in the nucleus, chloroplasts, and mitochondria. The common chlorosis symptom of iron deficiency is considered to be due to its role in chlorophyll synthesis (Bidwell, 1974).

In plants, as in soils, iron has a tendency to form insoluble compounds which, once formed, prevent iron from moving to plant structures most needing it and this may partially explain the requirement of iron in near-macronutrient amounts (Bidwell, 1974).

5.6.7.5. Deficiency of iron.

The nearly universal and diagnostic symptom of iron deficiency is a reduction in the concentration of chlorophyll (Wallihan, 1966). This symptom is expressed as chlorosis or yellowing of leaves. In mild cases, leaves may express a green color paler than normal. In intermediate cases, interveinal chlorosis appears and is very characteristic of iron deficiency. More severe chlorosis is expressed first by the absence of green color in the finest veins, then larger veins, and finally, the whole leaf (Wallihan, 1966). In growing plants, the chlorosis is sharply confined to the younger leaves (Bidwell, 1974). Severe chlorosis in trees and shrubs may cause necrotic areas on some leaves, which may lead to leaf drop (Wallihan, 1966).

Iron deficiencies are most common under the following soil conditions (Wallihan, 1966):

a. Calcareous soils.

b. Poorly drained soils.

c. Manganiferous soils.

d. Acidic soils with high concentrations of zinc, copper, managese, nickel, or other heavy metals.

e. Soils with excessively high or low temperatures.

f. Soils with certain organisms, such as fungi or nematodes.

g. Soils with an oxygen deficit.

These and other management problems are discussed more completely by Wallihan (1966); Kashirad and Marschner (1974); Raju and Marschner (1972); Nelson and Selby (1974); Wallace et al. (1974); and Woolhouse (1966).

Iron deficiencies are commonly treated with soil amendments or foliar sprays containing iron chelates (Norvell, 1972).

Table 5.6.7.5-1. shows typical tissue analysis values for iron.

Cauliflower, broccoli, kale, mallow, and morning glory are good indicators of iron deficiencies (Wallihan, 1966).

5.6.7.6. Iron toxicity.

Iron toxicity is vary rare and occurs, apparently, only in waterlogged soils with very high content of organic matter, and with low redox potentials. The only discussion found of iron toxicity was with regard to "bronzing" and other diseases of rice, apparently somewhat common in the orient (Etherington, 1975). These diseases may be partially or completely caused by high sulfide levels in the waterlogged soils. Iron toxicity may also be caused by excess application of iron salts. This causes necrotic spots, but the pathological condition may not be caused solely by excess iron (Wallihan, 1966).

TABLE 5.6.7.5-1. Typical plant tissue analysis values for iron.

Plant	Type of culture	Tissue sampled	Age, stage, condition or date of sample	Range in dry matter (ppm.) Showing deficiency symptoms	Low range	Intermediate range	High range	Showing toxicity symptoms
Avocado (Persea americana)	Field	Leaves	Recently matured	26.00-40.00	...	50.00-80.00	...	...
CITRUS FRUITS Lemon (Citrus limon)	Field	Leaves	4-7 months old	20.00	...	77.00	...	...
Orange (Citrus sinensis)	Field & control	Leaves	Recently matured	16.00-63.00	...	42.00-137.00	...	...
	Field	Hamlin lvs.	Recently matured	11.00-34.00	...	40.00-47.00	...	...
Corn (Zea mays)	Control	Golden Bantam leaves	Recently matured	24.00-56.00	...	56.00-176.00	...	...
Pear (Pyrus communis)	Field	Leaves	April 28	19.00-36.00	...	40.00-47.00	...	...
	Field	Leaves	June 3	21.00-23.00	...	28.00-39.00	...	...
	Field	Leaves	July 21	21.00-30.00	...	36.00-45.00	...	...
	Field	Leaves	September 22	31.00-36.00	...	38.00-47.00	...	...
Rice (Oryza sativa)	Control	Leaves	...	<63.00	...	>80.00	...	...
Soybean (Glycine soja)	Control	Shoots	34 days old	28.00-38.00	...	41.00-60.00	...	...
Sunflower (Helianthus annuus)	Control	Leaves	Recently matured	24.00-79.00	...	...	...	...
	Control	Leaves	Recently matured	30.00	...	113.00		
Tobacco (Nicotiana tabacum)	Control	Leaves	Recently matured	63.00-70.00	...	63.00-110.00	...	...
	Control	Tops	45 days old	33.00-36.00	...	91.00-130.00	...	...

TABLE 5.6.7.5-1. Typical plant tissue analysis values for iron.
(cont'd)

Plant	Type of culture	Tissue sampled	Age, stage, condition or date of sample	Range in dry matter (ppm.)				
				Showing deficiency symptoms	Low range	Intermediate range	High range	Showing toxicity symptoms
Tomato (Lycopersicon esculentum)	Control	Upper leaves	...	93.00-115.00	...	107.00-250.00	...	...
Tung (Aleurites fordi)	Field	Leaves	August	35.00	...	51.00 92.00	...	...

Source: Wallihan, 1966, p. 206.

5.6.8. Lead (Pb)

5.6.8.1 Introduction.

Lead is not considered an essential element for plant growth, even though a few reports are available regarding the benefits from lead additions through fertilizers (Brewer, 1966). Lead is phytotoxic, but only in very large dosages. However, it is toxic to animals at much lower dosages. Lead is a bluish-white metal with a bright luster. It is soft, highly malleable, and ductile, but a poor conductor of electricity. Lead is very resistant to corrosion.

Natural lead is a mixture of four isotopes, Pb^{204}, Pb^{206}, Pb^{207}, and Pb^{208}, all end products of radioactive decay. Native lead occurs rarely in nature. Commercial lead is obtained mostly from the mineral galena (PbS). Anglesite ($PbSO_4$), cerrusite ($PbCO_3$), and minim (Pb_3O_4) are other common lead minerals.

Great quantities of lead are used in storage batteries, cable covering, plumbing, and as an anti-knock compound (tetraethyl lead) in gasoline. Lead is also used as a sound barrier and for radiation shielding. Carbonates, sulfates, chromates, and oxides of lead are used extensively in paints, and lead salts, such as lead arsenate, have been used as insecticides.

The long-term use of lead arsenate as an insecticide has led to considerable amounts of research on lead phytotoxicity. The microscopic aspects of that toxicity are not completely known. Work on the effects of lead from automobile exhausts is fairly recent and largely incomplete.

The occupational exposure limit for lead arsenate is 0.15 mg/m^3 and for lead and other inorganic compounds 0.2 mg/m^3, 8 hour weighted average.

5.6.8.2 Sources of lead.

a. Natural.

Lead is present in the earth's crust at a concentration of about 16 ppm, while soils average 12 ppm. The amount of lead naturally occurring in any given soil probably reflects the amount present in the parent material. Natural concentrations of lead in the atmosphere have been estimated to be about 0.0005 mg/m^3 (NAS, 1972). This airborne lead results from natural dust containing an average of 10-15 ppm lead and from gases diffusing from the earth's crust (NAS, 1972).

b. Anthropogenic.

Anthropogenic sources of lead include:

(1) Lead arsenate pesticides (Chisholm, 1972). The use of these pesticides decreased from 16 X 10^6 kg in 1950 to 1.5 X 10^6 kg in 1968, but has recently increased considerably because of the ban on DDT (Lagerwerff, 1972).

(2) Metal smelter emissions (Little and Martin, 1972; Shimwell and Laurie, 1972; Crecelius et al., 1974; JAPCA, 1976).

(3) Combustion products from leaded gasoline (Smith, 1972; Smith, 1971; Page et al., 1971).

(4) Coal combustion.

(5) Fertilizers.

The amount of lead in quiescent ice sheets provides a very useful index to the changes in atmospheric lead content. Figure 5.6.8.2-1 presents such data graphically, illustrating the very marked increase