IMPACT OF AIR POLLUTANTS ON TERRESTRIAL VEGETATION

(Sulfur dioxide, fluorides and metals)

A LITERATURE SURVEY

by

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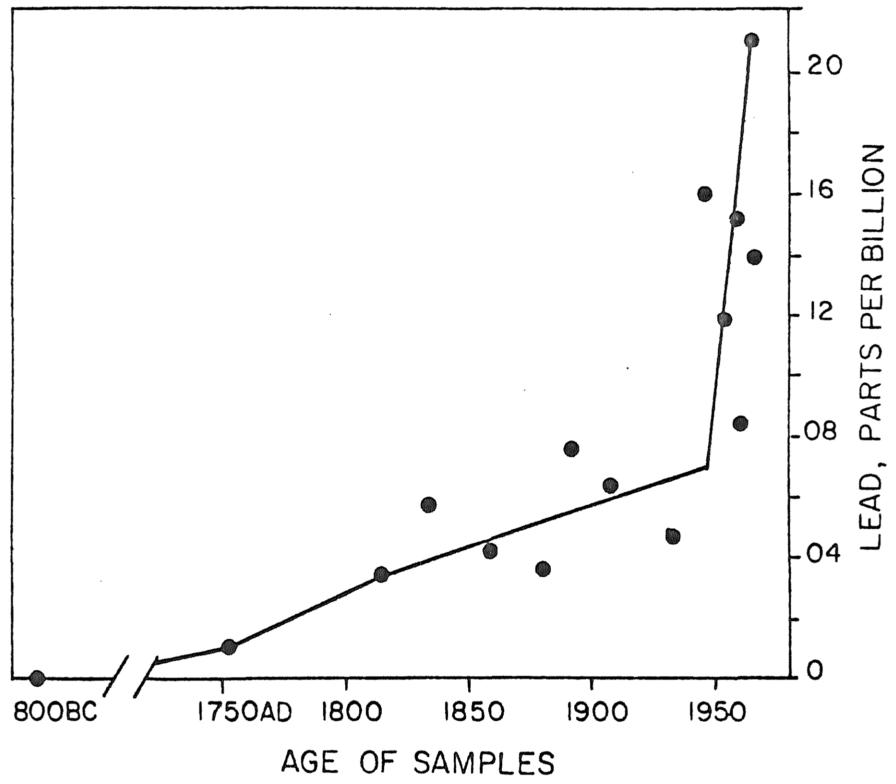
1976 Annual Report

Minnesota Environmental Quality Council

CONTENTS

Figure 5.6.8.2-1. Increase of lead in ice strata at Camp Century, Greenland, since 800 B.C. From Lead, National Academy of Science, Washington, D.C. (1972).


800BC
1750AD
1800
1850
1900
1950
AGE OF SAMPLES
0
.04
.08
.12
.16
.20
LEAD, PARTS PER BILLION

in atmospheric lead which occurred with the advent of the "industrial revolution." Figure 5.6.8.2-2 shows a similar trend, as expressed by chronologically increasing lead contents in Swedish mosses from 1860 to 1968. The principal increases were thought to be caused by increased coal combustion in 1875-1900, and increased use of leaded gasoline during 1950-1968 (NAS, 1972).

Table 5.6.8.2-1 breaks down United States atmospheric lead emissions by source for 1968. Of the activities listed, gasoline combustion contributes about 98% of the lead emissions. Emissions from metal ore smelters are the second most important source of atmospheric lead (Lagerwerff, 1967).

The residence time of lead in the atmosphere varies from 1 to 4 hours and is dependent on the size of the lead or lead contaiing particles. In a study on 59 urban and two rural sites, it was found that lead-containing aerosols had a mass median equivalent diameter of 0.25 u, with 25% of the mass in particles less than 0.16 u and 25% of the mass in particles greater than 0.43 u (Lagerwerff, 1972).

5.6.8.3. Biological availability of lead.

a. Soil solid phase.

Most of the lead in automobile exhaust gases appears as PbCL.Br. Depending on the gasoline additives, it may also appear as the borate, sulfate or phosphate (Lagerwerff, 1972). In rocks, lead usually occurs as the sulfide, and its nature is such, lead often replaces potassium, barium, strontium, and calcium in minerals (Norrish, 1975).

Whatever the source of soil lead, it apparently is easily adsorbed or complexed into mostly, unavailable forms. This is partially due to

Figure 5.6.8.2-2. Lead concentrations in the mosses *Hylocomium splendens*, *Pleurozium schreberi*, and *Hypnum cupressiforme* collected in Skane, Sweden, 1860 to 1968. The line indicates 15-year averages. From Lead, National Academy of Science, Washington, D.C. (1972).

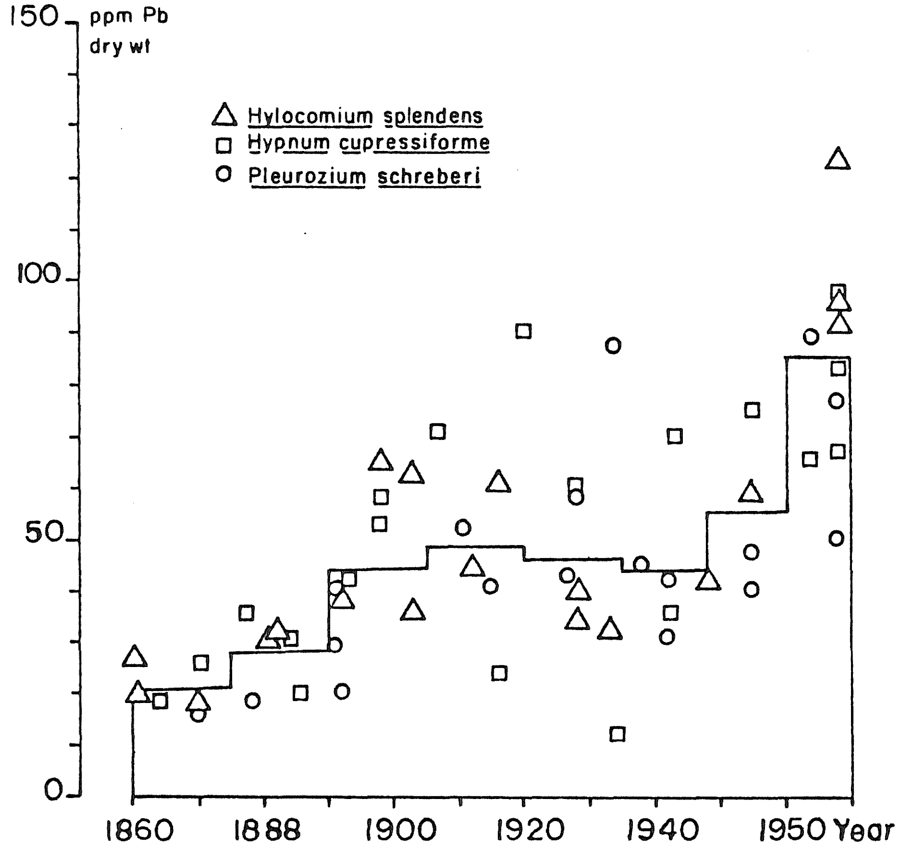

150
100
50
0
ppm Pb
dry wt
△ Hylocomium splendens
□ Hypnum cupressiforme
○ Pleurozium schreberi
1860
1888
1900
1920
1940
1950
Year

Table 5.6.8.2-1. 1968 atmospheric lead emissions in the United States by source.

Emission Source	Lead Emitted, Tons/Year
Gasoline combustion	181,000
Coal combustion	920
Fuel oil combustion	24
Lead alkyl manufacturing	810
Primary lead smelting	174
Secondary lead smelting	811
Brass manufacturing	521
Lead oxide manufacturing	20
Gasoline transfer	36
Total	184,316

Source: NAS, 1972, p. 13.

lead's divalent nature (Lagerwerff, 1972). Contaminant lead from gasoline combustion is fairly soluble, but with time the halide is stripped off and the free lead ion can be adsorbed or complexed. The efficacy of this immobilization process is made apparent by the fact that most of the lead is found in the upper soil horizons, the concentration decreasing rapidly with depth (NAS, 1972; Lagerwerff, 1972; Yopp et al., 1974).

For example, in the Charlottetown series, the lead content of the A_o horizon was 3.2 times that in the A_1 horizon and in the Armadale series, the A_o horizon contained 9.1 times that in the A_2 horizon (Lagerwerff, 1967). This lead distribution pattern is maintained to some extent and is exacerbated by the cycling from roots to leaf litter (Lagerwerff, 1972).

Manganese oxides are very good adsorbers of lead, while iron oxides are rather poor adsorbers. Aluminum oxides and phosphates are also good adsorbers of lead (Norrish, 1975) Table 5.6.8.3-1 shows the relative adsorptive capacity of several other minerals present in a lead-rich soil in Australia.

Soil organic matter is an important factor in making lead less available to plants (Lagerwerff, 1967; Lagerwerff, 1972; Yopp et al., 1974). Natural or synthetic chelates, however, may hold lead in a fairly soluble state, leading to higher leaching rate or to increased root absorption (Yopp et al., 1974).

b. Soil solution.

Lead in solution is probably in the ionic form, or as a soluble chelate. The amount in solution is usually very low (0.05 to

Table 5.6.8.3-1. Electronmicroprobe analysis of lead-rich phosphate minerals showing their relative adsorption capacity of lead.

	Sample 1 (%)	Sample 2 (%)
P_2O_5	23.8	14.64
SO_3	2.9	7.78
Al_2O_3	29.5	21.5
Fe_2O_3	3.2	10.1
PbO	1.3	35.2
BaO	11.9	2.9
La_2O_3	4.0	---
CeO_2	3.8	---
CaO	1.2	---
SrO	2.7	0.3
SiO_2	2.6	0.8

1 Average of 6 points. Laterite, Western Australia.

2 Average of 5 points. Lateritic podzolic soil, near Mt. Torrens, South Australia.

Source: Norrish, 1975, p. 78.

5 mg/g) in normal soils (NAS, 1972). Table 5.6.8.3-2 shows the reduction in soluble lead with time, and the lead uptake ability of barley.

Table 5.6.8.3-3 presents data on the soluble lead content of a number of soils.

c. Transition between soil solids and soil solution.

The availability of lead is highly dependent on pH, but no reports on the quantification of this relationship are available. As with most cation adsorption systems, lead is much more soluble and available under acidic conditions (Yopp *et al*., 1974).

The importance of lead adsorption by aerial plant parts is as yet uncertain. Most of the total lead in/on leaves is easily washed off, but some apparently remains in the leaf structure (Lagerwerff, 1972; Little, 1973; Little and Martin, 1974).

5.6.8.4. Role of lead in plant nutrition.

Lead is not a plant nutrient, however in some cases may be beneficial (Brewer, 1966).

5.6.8.5. Lead deficiency.

Lead is not a plant nutrient.

5.6.8.6. Lead toxicity.

Plants grown in uncontaminated soils usually contain less than 10 ppm lead, most of it in the roots (Yopp *et al*., 1974). Whether lead enters the plants through the leaves or by root absorption, once inside the system it is apparently retained by cell membranes, mitochondria, and chloroplasts and thus inhibits gas exchange and photosynthesis (Lagerwerff, 1972; Bazzaz *et al*., 1974a; Bazzaz and Govindjee, 1974; Bazzaz *et al*., 1974b; Overnell, 1975).

Table 5.6.8.3-2. Lead content of barley plants and readily soluble lead content of soils to which varied amounts of lead had been added.

Treatment number	Salt added	Lead added (pounds/ acre)	Dry weight: of plants (grams)	PbO content of tops (ppm.)	PbO content of roots (ppm.)	At planting time (ppm.)	At harvest (ppm.)
1	None	0	5.64	Trace	5.10	Trace	Trace
2	$Pb(NO_2)_2$	111	7.25	0.77	154.10	0.161	0.024
3	$Pb(NO_2)_2$	222	5.83	0.80	308.20	0.336	0.026
4	$Pb(NO_2)_2$	334	6.75	1.28	205.50	0.337	0.049
5	$Pb(NO_2)_2$	445	5.45	2.05	231.00	1.750	0.121
6	$Pb(NO_2)_2$	928	5.36	2.57	617.00	2.250	0.202
7	$PbCO_2$	928	6.59	1.28	154.10	2.020	0.201
8	$PbCO_2$	1,856	7.05	1.80	360.00	2.450	0.395
9	$PbCO_2$	3,712	6.88	2.57	566.00	2.890	0.471
10	$PbCO_2$	5.568	5.73	3.08	808.00	3.230	1.109

Source: Brewer, 1966, p. 214.

Table 5.6.8.3-3. Soluble lead content of soils. From Brewer (1966).

Location	Number of samples	Extracting solution	Method of analysis	Lead in Soils	
				Range (ppm.)	Average (ppm.)
Scotland:					
Northeast	3 surface soils	2.5% HAc	Spectrographic	0.30-1.60	0.80
Northeast	21 surface soils	0.5N HAc	Spectrographic	0.14-2.70	0.70
Northeast	70 subsoils	0.5N HAc	Spectrographic	0.17-6.50	0.55
Northeast	16 surface soils	Neutral 1N NH_4Ac	Spectrographic	0.05-2.60	0.45
Northeast	53 subsoils	Neutral 1N NH_4Ac	Spectrographic	0.15-0.61	0.15
Northeast	5 surface soils	1N NH_4Ac, pH 8.5	Spectrographic	0.20	...
Northeast	17 subsoils	1N NH_4Ac, pH 8.5	Spectrographic	0.15	...
Aberdeenshire	4 surface soils	2.5 % HAc	Spectrographic	0.55-5.85	2.15
United States:					
California	21 surface soils	0.05N KCl + HAc, to pH 3.2	Spectrographic	0.50-46.00	5.00
Washington	3 surface soils	0.1N NH_4NO_2	Chemical	0.07-0.24	0.18
Washington (Yakima)	1 soil	0.1N NH_4NO_2	Chemical	Trace	...

In the vicinity of major atmospheric sources of lead, the lead content is often more concentrated in the aerial parts (Tables 5.6.8.6-1 and 5.6.8.6-2). When the only source of lead is contaminated soil, however, nearly all of the lead remains in the roots or absorbed on root surfaces (Yopp et al., 1974; NAS, 1972; Lagerwerff, 1972). Lead is passively absorbed by roots (Yopp et al., 1974). Thus, barley grown in soil containing 800 ppm lead had 800 ppm lead in its roots, but only 3.0 ppm in its leaves (Yopp et al., 1974). In other experiments, the lead content of strawberries was found not to change when the extractable lead content of the soil was increased from 8 to 59 ppm and the lead content of lettuce and corn leaves was measured at 7.6 and 18 ppm when grown on a soil containing 95 ppm lead (Lagerwerff, 1972).

Many factors affect the plant uptake and, hence, toxicity of lead. Under conditions of proper plant nutrition, lead will normally not be absorbed or translocated in quantities sufficient to harm plants or to cause food chain accumulation problems, even on heavily contaminated soils (Yopp et al., 1974). However, under phosphate deficient conditions, plants have been shown to accumulate 3 to 8 times more lead in their leaves than under conditions of proper phosphate nutrition (Lagerwerff, 1972). This is apparently related to improved selectivity of uptake under healthy conditions. In radish, additions of calcium have been shown to raise the lead toxicity threshold level tenfold (Yopp et al., 1974). This involves an antidote effect of intercellular calcium, not merely an alkalyzing effect on the soil (Lagerwerff, 1972). Additions of iron as a chelate have also been shown to be beneficial under conditions of lead toxicity. This is apparently because lead interferes with normal iron metabolism (Lagerwerff, 1972).

Table 5.6.8.6-1. Concentration of lead in five crops grown at three field sites in proximity to different traffic volumes.

	Traffic Volume								
	12,500 Cars per 24 hr			47,100 Cars per 24 hr			49,000 Cars per 24 hr		
Distance from highway,ft	30	100	259	39	100	250	39	100	250
Air lead, g/m^3	1.4	1.0	1.0	4,5	2,7	2,4	5,2	3,3	2.5
Soil lead, ppm at 0-6 in.	54	38	33	134	138	300	229	130	89
Lead content, ppm, of:									
Carrot									
Tops	18	11	14	37	26	21	53	22	17
Roots	3.8	5.3	3.9	6.2	9.5	9.4	9.1	10	5.0
Corn									
Tassel	31	7.4	7.8	179	144	69	--	--	--
Leaves	19	17	14	86	47	36	88	51	40
Stalk	3.6	3.7	0.9	5.6	3.6	0.2	6.2	3.4	3.6
Husk									
Outer	11	5.0	6.8	3.0	5.0	2.6			
Inner	5.0	5.2	2.4						
Roots	6.0	3.9	5.4	19	14	19	54	19	--
Kernel	3.8	3.6	3.1	0.0	0.2	0.2	--	--	--
Cob	8.0	3.2	2.6	0.4	0.0	0.4	--	--	--
Lettuce									
Leaves	12	13	--	24	21	14	56	35	--
Roots	16	15	--	24	27	39	61	32	--
Potato									
Leaves	36	31	21	87	47	29	--	--	--
Stems	12	8.4	7.8	15	11	14	--	--	--
Roots	22	23	18	33	49	58	--	--	--
Tuber	0.5	1.5	1.0	2.6	3.0	3.0	--	--	--
Tomato									
Leaves	36	25	17	76	82	40	88	52	44
Stem	9.0	9.8	6.9	27	25	31	29	13	7.7
Root	11	15	14	27	35	50	37	12	9.6
Fruit	2.8	3.0	2.4	4.6	2.7	2.8	3.6	1.2	3.2

Source: NAS, 1972, p. 41.

TABLE 5.6.8.6-2. Concentration of lead in grass growing at sites of differing concentrations of atmospheric lead.

Distance from Highway, ft	12,800 Vehicles per 24 hr	14,700 Vehicles per 24 hr	17,700 Vehicles per 24 hr	19,700 Vehicles per 24 hr	41,000 Vehicles per 24 hr	45,600 Vehicles per 24 hr	48,600 Vehicles per 24 hr	48,600 Vehicles per 24 hr	54,700 Vehicles per 24 hr	Average
Lead Content, Not Washed, ppm										
0	-	-	-	133	141	118	-	664	219	255.0
25	63	-	-	84	66	192	154	454	139	164.6
75	76	-	-	65	103	-	66	198	83	98.5
125	-	-	31	41	-	66	45	139	78	66.7
175	-	-	-	41	60	46	66	-	61	54.8
225	-	35	-	34	56	41	48	68	59	46.3
Av.	-	-	-	66.3	85.2	92.6	75.8	304.6	106.5	112.0
Lead Content, Washed, ppm										
0	40	40	91	133	136	71	128	492	98	136.6
25	37	23	64	58	85	80	62	262	83	83.8
75	64	34	46	59	80	-	50	77	60	58.8
125	58	43	26	58	55	46	36	59	45	47.3
175	47	35	-	18	46	31	45	-	62	40.6
225	50	31	-	36	58	32	31	44	43	40.6
Av.	49.3	34.3	56.8	60.3	76.7	52.0	58.7	186.8	65.8	69.8

Source: NAS, 1972, p.44

Table 5.6.8.6-3 presents data on minimum toxicity levels for a number of plant species. No diagnostic symptoms of lead toxicity were found. A general symptom may be reduced root growth and general retardation of the plant growth (Brewer, 1966).

According to Yopp et al., (1974) acceptable limits for lead based on field studies cannot be made because of the variability of the soils studied and because of lead's great but unpredictable complexing affinity. It is apparent, however, that the soluble lead fraction will seldom exceed 0.003 to 0.005% of the total lead in the soil if the pH is in a range suitable for normal crops. Based on the work with defined nutrient cultures, the soluble form of lead in soils should not exceed 2.0 to 4.0 ppm (Yopp et al., 1974; Chapman, 1966).

Table 5.6.8.6-3. Symptoms and minimum toxicity levels of lead in several plant species.

Plants by Economic Class	Growth Medium	Minimum Phytotoxic Concentration	Plant Part Affected	Developmental Stage	Symptom
		ppm			
Corn	defined nutrient medium	2.0	roots	seedling	retardation of root growth
Corn	"	0.4	"	"	root and shoot retardation
Fescue, Sheep	"	3,0	"	"	"
Bean, dwarf French var. Carteis	"	30.0	"	"	"
Onion	"	2-4.0	"	"	"
Bean, dwarf	"	2-4.0	"	"	"
Beet, sugar	" in sand culture	51.0	"	"	interveinal chlorosis
Lettuce, var. Salad Bowl	defined soil type	1000.0	roots and	"	30% yield
Lupine	defined nutrient solution	40.0	"	"	root and shoot reduction
Pine, Loblolly	defined soil solution	207.0	"	"	smaller milky-green needles reduced root growth
Maple, Red	"	207.00	"	"	Increased anthocyanin production; increased leaf abscission

Source: Yopp <u>et al</u>., 1974.

5.6.9. Magnesium (Mg)

5.6.9.1. Introduction.

Magnesium is an essential macronutrient needed in relatively large amounts by plants and animals. It may also by phytotoxic in large concentrations.

Magnesium is the eighth most abundant element in the earth's crust. It is not found naturally in an uncombined form, but is very common in magnesite, dolomite, and other minerals. Commercially, the metal is principally obtained by electrolysis of magnesium chloride derived from brine wells and sea water. The metal is light, silvery-white, and fairly tough. It tarnishes slightly in air and when finely divided, ignites with a brilliant white flame. It is used in flash photography and in light weight alloys of aluminum in the aircrafts. It is also used in cast iron, in propellants and in the production of uranium. The hydroxide (Milk of Magnesia), the sulfate (Epsom Salt), and other compounds are used in medicine. The occupational exposure limit for magnesium oxide fumes is 15 mg/m^3. The adult daily requirement for magnesium is about 300 mg/day.

Magnesium has been known to be essential for plant growth since 1860. A great deal of information is available on magnesium deficiencies and ways to mitigate them, but little research has been done on magnesium toxicity in plants.

5.6.9.2. Sources of magnesium.

a. Natural:

Soil magnesium derives principally from minerals such as magnesite, dolomite, mica, hornblende, and serpentine and from secondary aluminum silicates such as clays, especially montmorillonite, chlorite, and vermiculite. Humid region soils average 0.30% magnesium and arid region soils 0.60% (Brady, 1974).

b. Anthropogenic:

Magnesium is probably emitted in large quantities by many industrial activities, but these are not considered significant sources from an ecological view. Magnesium deficiencies are commonly treated by applications of dolomite or dolomitic limestone, which is 12 to 18 per cent magnesium oxide (Brady, 1974). Dolomite is calcium magnesium carbonate, $CaMg(CO_3)_2$. Magnesium is also supplied by magnesium containing fertilizer (Embleton, 1966).

5.6.9.3. Biological availability.

a. Soil solid phase.

Less than 5 per cent of the total soil magnesium in typical humid-region soils is held in exchangeable forms, such as the magnesium ion (Mg^{++}) adsorbed by colloidal complexes, or simple magnesium salts, The remainder is present in such unavailable forms as mica, hornblende, dolomite, and serpentine minerals or as a constituent of secondary aluminum silicates like montmorillonite, chlorite, or vermiculite (Brady, 1974). Magnesium is released from the less available mineral forms through weathering by carbonic and other biological acids. The released magnesium ion is then readily adsorbed by the exchange complex. Some of these reactions are, however, reversible. For example, the secondary aluminum silicates can alternately release or incorporate into its structure magnesium, depending on the pH. Thus, a much lower percentage of the total soil magnesium is held in exchangeable readiness compared to calcium (e.g. Mg 0.02% vs. Ca 0.11%) (Brady, 1974).

In normal soils of the temperate region, organic matter plays only a minor role in complexing magnesium (Brady, 1974). For example, Figure 5.6.9.3-1 shows that the synthetic chelate EDTA (Ethylenediaminetetraacetic acid, $C_{10}H_{16}O_8N_2$) will complex magnesium in significant quantities only at pH values above 7.5 to 8. DPTA complexes magnesium slightly more readily, but once again, even under highly alkaline conditions, calcium is complexed much more easily (Norvell, 1972).

In peat or muck soils, the percentage by weight of magnesium is about the same as in mineral soils (0.30%), but the absolute amount is less, since the dry weight is lower. Most of the magnesium will be held in an exchangeable condition, however, since organic soils are generally acidic. This can lead to high leaching rates, which is frequent cause for magnesium deficiencies in organic soils (Brady, 1974).

b. Soil Solution:

The concentration of magnesium in the soil solution is usually similar to calcium, averaging about 10 me/l (Etherington, 1975). In solution, magnesium is usually in the ionic form Mg^{++} (Brady, 1974).

c. Transition of magnesium between solid phase and soil solution:

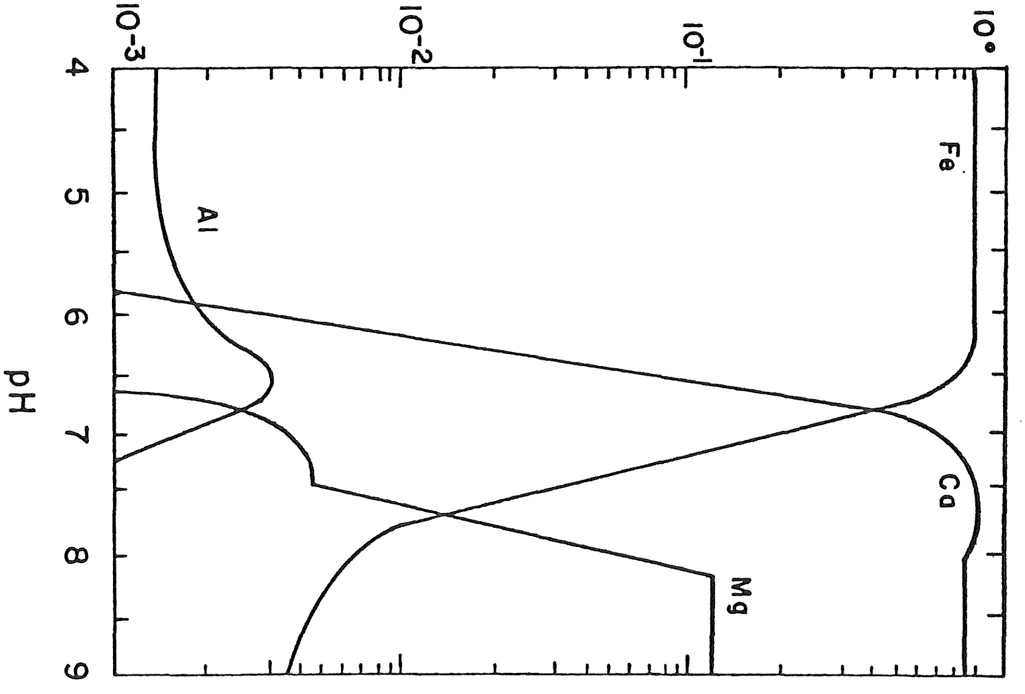
As with calcium, the transition of magnesium is controlled primarily by pH. But again, like calcium, magnesium itself influences the pH (Brady, 1972). Magnesium is most available between pH 6 and 8.5, falling off quickly above 8.5 and tapering off more gradually in the acidic end (Brady, 1974).

5.6.9.4. Role of magnesium in plant nutrition.

Magnesium is the only metallic ion which is a component of the chlorophyll molecule and is thus essential for photosynthesis

Figure 5.6.9.3-1. Stability diagram of the synthetic chelate EDTA in equilibrium with H^+, Ca^{++}, Mg^{++}, Al^{3+}, and Fe^{3+} in soil solution. From Norvell (1972).

Mole Fraction of EDTA
Associated with H, Ca, Mg, Al, Fe



(Bidwell, 1974). Magnesium is involved in the stabilization of ribosomal particles. It is also involved in numerous enzymatic reactions in various capacities, e.g., it may assist the linkage of the enzyme to the substrate; it may alter the equilibrium constant of a reaction by binding with a product, as with certain kinase reactions; and finally, it may act by complexing with an enzyme inhibitor. By these mechanisms, magnesium acts as an activator of many of the phosphate transfer reactions (of enzymes involved in the synthesis of nucleic acids) and of many of the enzymes involved in carbon dioxide transfer (carboxylation and decarboxylation reactions). Thus, magnesium is crucial for energy metabolism and for the synthesis of nuclear, chloroplast, and ribosomal constituents, as well as the chlorophyll (Bidwell, 1974).

5.6.9.5. Deficiency of magnesium.

Magnesius deficiences most commonly occur in acid, sandy soils of moderate to high rainfall. Deficiencies have also been noted in alkaline soils in Israel and British Columbia. Imperfectly drained soils and some clay soils may also be deficient in magnesium and it has been stated that alluvial soils are more likely to be deficient than glacial till soils. Peat and muck soils may also be deficient in magnesium. High soil potassium levels may cause or aggravate magnesium deficiencies, while high nitrogen levels may reduce magnesium deficiency symptoms. Phosphate additions reduce magnesium deficiencies, while high levels of calcium, sulfate, and sodium aggravate the deficiencies (Embleton, 1966).

Magnesium levels seem to be optimum when it reaches approximately 10 per cent of the exchange capacity of the soil, but this, of course, varies extensively between soils and plant species. Concentrations of 0.20 to 0.25 per cent magnesium in plants is indicative of proper soil levels (Embleton, 1966). Table 5.6.9.5-1 presents extensive tissue analysis data on healthy plants and plants suffering magnesium deficiency and toxicity.

Magnesium deficiency is easily diagnosed in plants. Characteristically there is a loss of normal green coloring between the veins, followed by chlorosis and possible appearance of brilliant red, orange, yellow, or purple pigments (Bidwell, 1974). The chlorosis may start at leaf margins or tips, and progress inward between the veins (Embleton, 1966). Under more severe deficiency conditions, whole leaves may turn yellow or brilliantly colored veinal, marginal or apical necrotic areas may develop on leaves. Leaves may curl and premature defoliation may usually occur. This may cause reduced plant growth or yield (Embleton, 1966).

Magnesium is quite soluble and readily transportable in plant systems. Consequently, old leaves are usually affected first by magnesium deficiency (Bidwell, 1974).

White oak, ground cherry, cauliflower, broccoli, gooseberry, black currant, apple, purselane, wood sorrel, horsetail, chickweed, lamb's-quarters and nasturtium are all good indicators of magnesium deficiency (Embleton, 1966).

5.6.9.6. Magnesium toxicity.

Magnesium toxicity, though rare, has been known to occur. Magnesium toxicity most often occurs in heavy clay soils or certain alkaline soils where the cation exchange capacity is dominated by magnesium

TABLE 5.6.9.5-1. Typical plant tissue analysis values for magnesium.

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
Apple (Malus spp.)	Sand	Leaves	June-July	0.063-0.094	...	0.12-0.41	...	...
	Sand	Shoot bark	December-January	0.088	...	0.16-0.29	...	...
	Sand	Shoot wood	December-January	0.042	...	0.07-0.08	...	...
	Sand	Trunk bark	December	0.065-0.067	... ...	0.16-0.19	...	...
	Sand	Trunk wood	December	0.012-0.017	...	0.03-0.04	...	...
	Sand	Stems & petioles	June-July	0.12-0.16	...	0.19-0.33	...	...
	Field	Leader tip leaves	February-March S.Hemisphere	0.17-0.38	...	0.32-0.78	...	...
	Field	Older leader leaves	February-March S.Hemisphere	0.05-0.17	...	0.22-0.45	...	...
	Field	Leaves	July-Sept. near base of terminal shoots	0.05-0.19	...	0.18-0.39	...	...
	Field	Older leaves	July, current season's shoots	0.13-0.18	...	0.14-0.19	...	...
	Field	Leaves	July, median shoots	0.02-0.33	...	0.21-0.53	...	...
	Field	Leaves	Midsummer, median shoots	0.07-0.19	...	...	...	...
	Soil	Leaves	July	0.23-0.47	...	0.64-1.13	...	...
	Field	Leaves	August, from mid-shoot	0.09-0.23	...	0.23-0.35	...	...
	Sand	Leaves	June-September	0.08-0.20	...	0.16-0.72	...	...
	Field	Leaves	July-October	0.14-0.18	...	0.19-0.20	...	...
	Field	Leaves	July-September	0.05-0.23	...	0.20-0.25	...	...
	Field	Leaves	August, from mid-shoot	0.08-0.20	...	0.11-0.27	...	...
	Field	Leaves	September	0.12-0.20	...	0.21-0.49	...	...

TABLE 5.6.9.5-1. Typical plant tissue analysis values for magnesium. (cont'd)

				Range in dry matter (ppm.)				
Plant	Type of culture	Tissue sampled	Age, stage, condition or date of sample	Showing deficiency symptoms	Low range	Intermediate range	High range	Showing toxicity symptoms
Apple (cont'd)	Field	Leaves	August, middle leaf of current season's terminal growth	<0.20	...	>0.24	...	...
	Field	Leaves	At base of new shoots	0.12	...	0.21	...	...
	Field	Leaves	With symptoms	0.01-0.05	...	...	...	...
	Field	Leaves	Healthy, from trees w/symptoms	...	...	0.09-0.10	...	...
	Field	Leaves	Healthy, from healthy trees	...	...	0.14-0.45	...	...
	Field	Leaves	Healthy, from healthy trees in Mg-deficient orchard	...	...	0.13-0.20	...	...
	Field	Leaves	With symptoms, from Mg-deficient orchard	0.130-0.135	...	...	...	...
	Field	Leaves	From twig bearing fruit, on healthy tree in Mg-deficient orchard	...	...	0.102	...	...
	Field	Leaves	...	0.05-0.18	...	0.26-0.56	...	...
Apricot (Prunus armeniaca)	Field	Leaves	Basal, from shoots of moderate vigor (May)	...	...	0.80-1.10	...	...
	Field	Leaves	Basal, from shoots of moderate vigor (May)	...	...	1.20-1.50	...	...

TABLE 5.6.9.5-1. Typical plant tissue analysis values for magnesium. (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
Avocado (Persea americana)	Field	Leaves	...	...	...	0.47-0.75	...	...
	Soil	Leaves	...	...	...	0.38-0.68	...	...
	Field	Leaves	December-January	...	...	0.50-0.83	...	...
	Field	Leaves	3 months old (June)	...	...	0.22-0.29	...	...
	Field	Leaves	11 months old (Feb.)	...	...	0.50-0.70	...	...
	Field	Leaves	Various ages and years	...	...	0.32-0.50	...	...
	Sand	Leaves	Most recently matured	<0.15	0.15-0.25	0.25-0.50	...	...
Azalea (Rhododendron spp.)	Sand	Leaves	Recently matured, from middle to terminal parts of twigs	0.06-0.08	...	0.17	...	...
Banana (Musa spp.)	Sand	Leaves	4 to 12 months old	0.04-0.09	...	0.24-0.32	0.60-0.80	...
Birch (Betula spp.)	Solution	Leaves	...	0.06	0.09	0.18-0.52	0.52	...
Blueberry (Vaccinium spp.)	Field	Leaves	Mid-section of current season's growth (July)	0.072-0.165	...	0.168-0.171	...	...
	Field	Leaves	June	0.10-0.11	...	0.11-0.16	...	...
	Field	Leaves	August	0.14-0.19	...	0.17-0.24	...	...
	Field	Leaves	October	0.18-0.19	...	0.22 0.25	...	...

TABLE 5.6.9.5-1. Typical plant tissue analysis values for magnesium. (cont'd)

				Range in dry matter (ppm.)				
Plant	Type of culture	Tissue sampled	Age, stage, condition or date of sample	Showing deficiency symptoms	Low range	Intermediate range	High range	Showing toxicity symptoms
Cabbage (Brassica oleracea capitata)	Field	Leaf bases	...	0.092	...	0.165-0.178	...	...
	Field	Leaf tips	...	0.037	...	0.076-0.119	...	...
	Field	Tops	Seedling stage	0.43	...	0.56-0.57	...	...
Cacao (Theobroma cacao)	Field	Leaves	From 3-month-old plants (June)	0.16-0.30	...	0.32	...	...
Celery (Apium graveolens	Solution	Leaves	...	0.029-0.157	...	0.172-0.340	...	...
	Field & solution	Leaflets	January-February	<0.10	...	>0.10	...	...
CITRUS FRUITS								
Grapefruit (Citrus paradisi)	Field	Leaves	October	0.013-0.017	...	0.122-0.228	...	...
	Field	Leaves	Aug. 1938	0.24-0.28	...	0.33-0.43	...	...
	Field	Leaves	July 1939	0.18-0.32	...	0.28-0.43	...	...
	Field	Leaves	April 1940	0.17-0.30	...	0.29-0.33	...	...
	Field	Leaves	Sept. 1940	0.13-0.34	...	0.34-0.47	...	...
	Field	Leaves	4 to 6	0.11-0.30	...	0.22-1.08	...	...
Lemon (Citrus limon)	Field	Leaves	Mature	0.083	...	0.233	...	...
Mandarin (Satsuma) (Citrus reticulata)	Field	Leaves	...	0.25	...	0.40	...	...

TABLE 5.6.9.5-1. Typical plant tissue analysis values for magnesium. (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 (Citrus sinensis)	Field	Leaves	Mature (Nov.) (S. Hemisphere	0.026-0.128	...	0.17-0.52	...	...
	Field	Leaves	Green, from healthy and Mg-deficient trees	0.17	...	0.31	...	...
	Field	Leaves	Chlorotic, from trees showing Mg-deficiency symptoms	Trace	...	...	...	
	Field	Leaves	Spring-cycle (May), from Mg-deficient trees	0.16 (non-chlorotic)	...	0.22 (non-chlorotic)	...	...
	Field	Leaves	Spring-cycle (October), from Mg-deficient trees	0.20 (non-chlortic)	...	0.33 (non-chlortic)	...	...
	Field	Leaves	3 to 7 months, spring-cycle	0.15-0.21	...	0.7-0.34	...	...
	Field	Leaves	All from trees with symptoms	0.025-0.47	...	0.103-0.122	...	...
	Sand	Leaves	...	0.04-0.11	...	0.21-0.28	...	...
	All types	Leaves	4 to 10 mos. spring-cycle from fruiting terminals	0.05-0.15	0.16-0.20	0.30-0.60	0.70-1.00	>1.00(?)
	All types	Leaves	3 to 7 mos. spring-cycle from fruiting terminals	<0.15	...	0.20-0.40	...	>0.60
	All types	Leaves	5 to 7 mos. bloom-cycle from non-fruiting terminals	<0.16	0.16-0.25	0.26-0.60	0.70-1.10	>1.20(?)
	All types	Leaves	4 to 7 mos. spring-cycle	<0.15	0.16-0.29	0.30-0.60	0.70-1.10	>1.20(?)

TABLE 5.6.9.5-1. Typical plant tissue analysis values for magnesium. (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	All types	Leaves	4 to 7 mos. bloom-cycle	<0.15	0.16-0.29	0.30-0.60	0.70-1.10	>1.20(?)
	Field	Leaves	...	0.30-0.33	...	...	...	...
Corn (Zea mays)	Field	Blades	...	0.07	...	0.20	...	...
	Field	Leaf sheaths	...	0.07	...	0.24	...	...
	Field	Stem nodes	...	0.06	...	0.21	...	...
	Field	Stem internodes	...	0.04	...	0.10	...	...
	Field	Leaves	...	0.13	...	0.23-0.35	...	...
Currant,black (Ribes nigrum)	Field	Leaves	July	0.11-0.43	...	0.26-0.45	...	...
Gooseberry (Ribes spp.)	Field	Leaves	Older, of current season	0.17-0.37	...	0.25-0.31	...	...
Grape (Vitis spp.)	Field	Leaves	Fully developed, mid-shoot (July)	0.07-0.22	...	0.23-0.29	...	...
	Field	Leaves	Fully developed, mid-shoot (Sept.)	0.09-0.19	...	0.26-0.50	...	...
	Field	Leaves	Fully developed, mid-shoot (October)	0.04-0.09	...	0.23-0.40	...	...
	Field	Leaves	First fully developed leaves,from tips of shoots (Aug.-Oct.)	0.09-0.26	...	0.10-0.48	...	...

TABLE 5.6.9.5-1. Typical plant tissue analysis values for magnesium. (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
Grape (cont'd)	Field	Leaves	Recently matured, on fruiting spurs (September)	0.06-0.17	...	0.12-0.22	...	...
	Field	Leaves	From fruiting spurs; harvest	0.05-0.17	...	0.18-0.30	...	...
GRASSES								
Brome grass (Bromus inermis)	Field	Foliage clipped 1 inch above ground	Blooming	...	...	0.090-0.168	...	...
Orchard grass (Dactylis glomerata)	Field	Foliage clipped 1 inch above ground	Blooming	...	...	0.11-0.21	...	...
Loquat (Eriobotryn japanica)	Sand	Leaves	...	0.05	...	...	...	...
Mango (Mangifera indica)	Sand	Leaves	August	...	...	0.26	...	...
Oats (Avena sativa)	Field	Plant (?)	April-May	0.10-0.39	...	0.18-0.52	...	...
	Soil	Plant (?)	4-6 leaf stage	0.073-0.255	...	0.13-0.39	...	...
Oil palm, African (Elaeis guincensis)	Field	Leaves	...	<0.24	...	>0.24	...	...
	Sand	Leaves	First fully opened leaf	0.14-0.27	...	0.23-0.38	...	...
	Sand	Leaflets	...	0.12	...	0.27	...	...

TABLE 5.6.9.5-1. Typical plant tissue analysis values for magnesium. (cont'd)

				Range in dry matter (ppm.)				
Plant	Type of culture	Tissue sampled	Age, stage, condition or date of sample	Showing deficiency symptoms	Low range	Intermediate range	High range	Showing toxicity symptoms
Olive (Olea europaea)	Sand	Leaves	Young (Jan.)	0.07	...	0.13	...	...
	Sand	Leaves	Old (Jan.)	0.14	...	0.22	...	...
	Sand	Leaves	Old (June)	0.06	...	0.15	...	...
	Sand	Leaves	July	0.10	...	0.16	...	...
	Sand	Stems	July	0.11	...	0.14	...	...
	Sand	Roots	July	0.37	...	0.41	...	...
	Sand	Leaves	...	0.09	...	...	...	...
Peach (Prunus persica)	Field	Leaves	Basal, from shoots of moderate vigor (May)	...	...	0.70-1.00	...	...
	Field	Leaves	Basal, from shoots of moderate vigor (Aug)	...	...	1.15-1.40	...	...
	Field	Leaves	From mid-shoot (Aug)	0.13-0.39	...	...	...	...
Pear (Pyrus communis)	Field	Leaves	Basal,from shoots of moderate vigor (May)	...	...	0.45-0.60	...	...
	Field	Leaves	Basal,from shoots of moderate vigor (Aug.)	...	...	0.60-0.80	...	...
	Field	Leaves	From basal part of shoots	0.051	...	...	...	...
	Field	Leaves	From terminal part of shoots	...	...	0.27	...	...
Pecan (Carya illinoensis)	Field	Leaves	September	0.04-0.12	...	0.18-0.43	...	...
Pine (Pinus spp.)	Field	Needles	...	0.078-0.095	...	0.115-0.176	...	...
	Field	Wood	...	0.059-0.133	...	0.063-	...	...
	Field	Needles	Yellowed tips; mature first-year foliage	0.07	...	...	...	...

TABLE 5.6.9.5-1. Typical plant tissue analysis values for magnesium. (cont'd)

				Range in dry matter (ppm.)				
Plant	Type of culture	Tissue sampled	Age, stage, condition or date of sample	Showing deficiency symptoms	Low range	Intermediate range	High range	Showing toxicity symptoms
Pine (cont'd)	Field	Needles	Green part deficient trees; mature, 1st-yr. foliage	0.11-	...	...	...	...
	Field	Needles	Mature; 1st yr. foliage	...	...	0.14- 0.17	...	...
Plum (Prunus domestica)	Field	Leaves	From base of terminal shoots (September)	0.14	...	0.18		
	Field	Leaves	Basal, from shoots of moderate vigor (May)	...	...	0.50- 0.95	...	...
	Field	Leaves	Basal, from shoots of moderate vigor (Aug.)	...	...	1.15- 1.40	...	...
	Sand	Leaves	...	0.11	...	...	...	...
Potato (Solanum tuberanum)	Field	Upper leaves	May-June	0.122- 0.218	...	0.231- 0.206	...	...
	Field	Lower leaves	May-June	0.043- 0.124	... ...	0.159- 0.251	...	...
	Field	Stems	May	0.135- 0.138	...	0.163- 0.166	...	...
	Soil	Leaves	...	0.124- 0.287	...	0.279- 0.662	...	...
	Soil	Plant	May	0.069- 0.133	...	0.290 0.495	...	...
	Field	Leaves	August	0.10- 0.20	...	0.37 0.40	...	...
	Field	Stems	August	0.20- 0.30	...	0.61- 0.62	...	...
	Field	Leaves	July	0.15- 0.33	...	0.40 0.86	...	...
	Field	Leaves	...	0.22- 0.24	...	0.40- 0.78	...	...
	Field	Tubers	...	0.12	...	0.13	...	...

TABLE 5.6.9.5-1. Typical plant tissue analysis values for magnesium. (cont'd)

				Range in dry matter (ppm.)				
Plant	Type of culture	Tissue sampled	Age, stage, condition or date of sample	Showing deficiency symptoms	Low range	Intermediate range	High range	Showing toxicity symptoms
Rape (Brassica napus)	Field	Leaves	...	0.066-0.126	...	0.114	...	...
	Field	Stems	...	0.054-0.078	...	0.078	...	...
Rye (Secale cereale)	Field & soil	Plant (?)	April-May	0.12-0.34	...	0.19-0.56	...	...
Soybean (Glycine soja)	Field	Plant	...	0.30	...	0.59	...	...
Spruce, Norway (Picea abies)	Solution	Needles	...	0.02	0.02-0.11	0.07-0.17	0.11-0.17	...
Sugar beet (Beta saccharifera)	Field	Leaves	...	0.08-0.20	...	0.21-1.70	...	...
Sweet potato (Ipomoea batatas)	Field	Leaves	...	0.40	...	0.71	...	...
	Field	Tubers	...	0.06	...	0.06	...	...
Timothy (Phleum	Field	Foliage clipped 1" above ground	Blooming	...	...	0.10-0.16	...	...
Tobacco (Nicotiana tobacum)	Field	Leaves	...	0.08-0.24	...	0.18-0.31	...	...
	Field	Stems	...	0.15-0.24	...	0.11-0.31	...	...
	Sand	Top leaves	...	0.41-0.47	...	0.48-0.98	...	...
	Sand	Bottom leaves	...	0.57-0.60	...	0.60-1.22	...	...
Tomato (Lycopersicon esculentum)	Field	Leaf laminae	...	0.06	...	0.25	...	...
	Soil	Whole leaves	...	<0.40	...	>0.40	...	...

TABLE 5.6.9.5-1. Typical plant tissue analysis values for magnesium. (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 (cont'd)	Soil	Whole leaves	...	0.18	...	0.30	...	...
Tung (Aleurites fordi)	Field	Leaves	October	0.05-0.16	...	0.20 0.35	...	...
	Field	Leaves	Mid-shoot	0.15-0.20	...	0.35 0.45	...	...
Wheat (Triticum spp.)	Field	Plant (?)	April-May	0.23-0.32	...	0.27-0.46	...	...
	Field	Leaves	...	0.102-0.126	...	0.156-0.168	...	...
	Field	Upper leaves	...	0.168	...	0.168	...	...
	Field	Lower leaves	...	0.00	...	0.156	...	...
	Field	Upper stems	...	0.03	...	0.072	...	...
	Field	Lower stems	...	0.00	...	0.072	...	...

Source: Embleton, 1966, pp. 242-248.

(e.g., 90 per cent). This occurs most often when magnesium amendments are applied to calcium-deficient soils. This is easily prevented with concomitant additions of calcium (Embleton, 1966). Magnesium toxicity has also been shown to be caused by insufficient levels of soil potassium (Embleton, 1966).

No naturally occurring examples of magnesium toxicity were discussed or suggested in the literature, and the only case mentioned which involved industrial emissions was associated with dust accumulations around a magnesite plant in the state of Washington (Embleton, 1966).

Very little information is available on magnesium toxicity symptoms, though when it occurs, it is usually thought to be caused by imbalances of magnesium with other elements in the plant. This, of course, could result in a widely varying degree of symptom development. In wheat, excess magnesium/calcium ratios may cause leaf rolling and spiraling and inhibition of leaf emergence. In *Stachys recta*, high magnesium levels have been reported to cause abnormally narrow leaves (Embleton, 1966).

No toxicity tolerance levels for magnesium were presented in the literature, though plant ash contents greater than 0.70 per cent may indicate an excess (Table 5.6.9.5-1).

5.6.10. Manganese (Mn)

5.6.10.1. Introduction.

Manganese is an essential micronutrient for plant growth. It may also become toxic to plants. In animals, manganese is an essential trace element and may be important for the utilization of vitamin B_1. Animals are quite tolerant to relatively high dosages of manganese (see NAS, 1973 for a review of manganese pathogenicity in animals).

Manganese occupies a position next to iron in the atomic series and was not recognized as an element separate from iron until 1788. Manganese is as widely distributed as iron, but not nearly as abundant~~;~~. ~~it~~ It is the twelfth most common element in the earth's crust, comprising about 0.1~~0~~ per cent (1,000 ppm) (NAS, 1973). Common minerals containing manganese include the oxides, silicates and carbonates. Pyrolusite (MnO_2) and rhodochrosite ($MnCO_3$) are common ores, and manganese nodules containing about 24 per cent manganese and are enticing future sources of manganese, are present on ocean floors. Metallic manganese is gray-white, resembling iron, but it is harder and very brittle. The metal is chemically reactive and is commonly used in steel and aluminum alloys to improve the rolling and forging qualities, strength, toughness, stiffness, and hardness. The metal can become ferromagnetic after special treatment. Manganese is also used in paints and in coloring glass. Manganese is responsible for the color of true amethyst. Permanganate is a powerful oxidizing agent used as a reagent and in medicine. The occupational exposure limit for manganese and its compounds is 5 mg/m^3.

Manganese was first shown clearly to be essential to plant growth in 1897 (Labanauskas, 1966). Since then, a great deal of research has been done on manganese in plants. Less is known about manganese toxicity than about deficiencies.

5.6.10.2. Sources of Manganese.

a. Natural:

Manganese is a constituent of more than 100 minerals, and perhaps 200 others contain it as an accessory element. It is very widely distributed in practically every substrate, sometimes in concentrations of parts per billion, as in many waters, but at other times in concentrations up to 50 per cent, as in some ores (NAS, 1973). In igneous rocks, it is usually present as a silicate, in the manganous form (Norrish, 1975). Like iron, manganese commonly assumes two states of valence, and, like iron, this is a fundamental reason for its wide distribution and its importance in biological systems. In reducing environments, the manganous (MN^{++}) form predominates, while in ~~the~~ oxidizing environments the manganic (Mn^{4+}) form is most important (Brady, 1974). Krauskopf (1972) lists the concentrations of manganese in granite as 400 ppm, in basalt - 1500 ppm, in limestone - 1100 ppm, in sandstone - 10-100 ppm, in shale - 850 ppm, and in soils - 20 to 30,000 ppm. According to Krauskopf (1972) the minerals most important in providing soil manganese are the following:

Silicates:	rhodonite ($MnSiO_3$)
Carbonates:	rhodochrosite ($MnCO_3$)
Simple oxides:	pyrolusite (MnO_2), hausmannite (Mn_3O_4), manganite (MnOOH)

Complex oxides: braunite $(Mn, Si)_2O_3$ and psilomelane.

Minnesota has extensive low-grade deposits of manganese on the Cuyuna Range (NAS, 1973).

Under natural conditions, the atmospher~~ic~~e ~~content of~~ contains no manganese ~~is essentially none~~, therefore, soil manganese concentrations are largely functions of the composition of the parent material (NAS, 1973).

b. Anthropogenic:

Between 1957 and 1961 the average ~~The arithmetic mean~~ concentration of manganese in 819 samples of United States urban air was 0.10 ug/m^3. ~~in 1957 - 1961.~~ Rain samples collected at 32 widespread sites in 1966 - 67 contained an average concentration of 0.012 ppm manganese. In grams per hectare deposited per month, this was equivalent to ranges of 0 to 54 gms, depending on the location. Therefore, it is apparent that anthropogenic sources will not disrupt the soil-plant systems, except possibly in localized areas near very major sources (NAS, 1973).

sources?

Significant atmospheric emitting activities include coal burning and metal smelting and processing. As part of the processing procedures, manganese is indispensible to the large scale production of steel. Ninety per cent of all manganese used commercially is consumed by the steel industry (Nas, 1973). Other potential sources of soil manganese are sewage sludge, waste waters and fertilizers, especially impure phosphate fertilizers (Lagerwerff, 1967). Manganese has also been intentionally added to soils as an ~~soil~~ amendment (Labanauskas, 1966).

5.6.10.3. Biological availability.

a. Soil solid phase:

The soil chemistry of manganese is extremely complex. In both chemical behavior and geological distribution it is remarkably similar to iron, yet it often behaves in ways totally unpredictable from this similarity. Manganese is more electropositive than iron, and its compounds, especially the sulfides, are more soluble than iron compounds. Because of this, manganese occurs more often as a silicate than does iron (Krauskopf, 1972).

In naturally occurring compounds, manganese can actually assume three states of valence (2^+, 3^+, 4^+), but the trivalent ion is unstable in solution (Krauskopf, 1972). The quadrivalent ion can be found in solutions only when pH values are below those occuring naturally.

Thus, after being released by weathering, manganese is present as a salt or as the manganous ion in the reducing environments, or as an oxide under oxidizing conditions (NAS, 1973).

In most igneous rocks, the Mn/Fe ratio is fairly constant at 1:60. Contrary to most heavy metals, limestone and dolomite contain more manganese than shale. This is because of the low solubility of $MnCO_3$ and the greater resistance to oxidation of Mn^{++} relative to Fe^{++} (Krauskopf, 1972). Under oxidizing conditions, as is usually the case in normal soils, weathering of manganese silicates and carbonates yields manganic ions which quickly undergo oxidation. However, the resulting compounds are not simple oxides and hydroxides. Rather, complex manganese oxides such as lithiophorites, birnessites, and hollandites are commonly formed. Though present in small quantities, these manganese oxides may be important suppliers of exchange sites because of their small size (0.02 to 0.1 um) and hence, their contribution to a large surface area (Norrish, 1975). Table 5.6.10.3-1 demonstrates this by comparing the trace element concentrations of manganese-rich zones with the concentrations in iron-rich zones in three different soils. In general, the table shows that the manganese oxides are responsible for holding cobalt, barium and lead, while iron oxides, because of their greater abundance, will harbor most of the nickel, copper and zinc (Norrish, 1975).

Under reducing conditions, weathering of ~~the~~ parent material~~s~~ yields Mn^{++} in solution. If the acidity is not too extreme, (extremely high or low?) a large part of this will be complexed in various forms (84% - 99%). (Krauskopf, 1972). However, the adsorption of manganese by other clay minerals has not been thoroughly studied. Comparison of the manganese content of shale with carbonate rocks indicates that manganese is adsorbed less readily than other heavy metals (Krauskopf, 1972).

Soil organic matter can complex manganese, but much less readily than it can complex copper, iron and aluminum (Loneragan, 1975). Microorganisms are also active factors in the availability of manganese. As with iron, many species of bacteria are known to be able to oxidize and reduce manganese. Catalysis of the oxidization may be especially important because of the slow rate at which this occurs under sterile conditions (Krauskopf, 1972). Also, microorganisms are very effective in releasing manganese from organic complexes, such as chelates (Lagerwerff, 1974).

b. Soil solution:

Manganese in solution is usually present as manganese ion (Mn^{++}). The total manganese content of soils averages 200 to 3,000 ppm,

Table 5.6.10.3-1. Concentrations of trace elements in iron-rich and manganese-rich zones in three soils.

Sample	1		2		3	
	Mn rich	Fe rich	Mn rich	Fe rich	Mn rich	Fe rich
	Measured concentration, %					
MnO_2	8.7	.11	21.5	1.5	9.6	2.4
Fe_2O_3	5.6	11.4	25.3	42.4	11.1	14.8
	Normalized concentration*, %					
CoO	1.22	0.1	.69	.05	3.1	.1
NiO	.15	.08	.11	.03	.62	.03
CuO	.12	.09	.04	.02	0.05	0.05
ZnO	.69	.32	.04	.09	.11	.10
BaO	2.35	0.2	.64	0.1	3.2	.2
PbO	2.2	.15	.28	.05	.37	.15

* Normalized relative to 70% MnO_2 for the mn-rich areas, and to 70% Fe_2O_3 for the Fe-rich areas.

1 Urrbrae loam. Red-brown earth developed on shale. Adelaide, South Australia

2 Wollongbar clay loam. Krasnozem developed on basalt. Lismore, New Wales

3. Black earth developed on shale. Saddleworth, South Australiz

and decreases with depth (Labanauskas, 1966). Of this, 0.2 to 2 ppm is in ~~the soil~~ solution (Bidwell, 1974).

c. Transition between soil solids and soil solution: The availability of manganese is very dependent on oxidizing conditions and pH (Norrish, 1975), since most of the reducible or readily available manganese in the solid phase is in various manganese oxides. Most of the manganese becomes less available above pH 6.5, and virtually unavailable above pH 7 - 8 (Bidwell, 1974; Norrish, 1975). However, if sufficient numbers of appropriate microorganisms are present, deficiencies may not occur at the high pH values (Etherington, 1975).

5.6.10.4. Role of manganese in plant nutrition.

Manganous ion (Mn^{++}) is actively absorbed by plant roots (Yopp et al., 1974). In fact, plants can influence the availability of manganese (and other elements) in the root zone by producing substances which speed the release of manganese from insoluble manganese oxides (Loneragan, 1975).

Within the plant, manganese plays a wide variety of catalytic activities. It is the predominant enzyme-activating metal of the Krebs cycle. Manganese is involved in other respiratory enzymes and in nitrogen metabolism and photosynthesis. It is required for nitrate reductase and for enzymes involved in the metabolism of the hormone indoleacetic acid. In photosynthesis, the chief role of manganese is in the reactions by which electrons are derived from water and oxygen is liberated. Manganese apparently has a specific role, relative to iron, in the structure of chloroplasts (Bidwell, 1974).

Plants differ markedly in their ability to absorb manganese, the dry weight concentration varying from 30 ppm (Medicago truncatula) to 500 ppm (Lupinus albus) (Loneragan, 1975). The average concentration usually amounts to 50 ppm (Yopp et al., 1974). Table 5.6.10.4-1 presents data on the manganese concentration in plants grown on identical substrates. Table 5.6.10.4-2 presents data on the manganese concentration in eight native bog plants in Wisconsin.

5.6.10-5. Manganese deficiency.

Manganese deficiencies are most common on the following soils (Labanauskas, 1966):

a. Thin, peaty soils overlying calcareous subsoils.
b. Alluvial soils and marsh soils derived from calcareous materials, such as calcareous silts and clays.
c. Poorly drained calcareous soils with a high content of organic matter.
d. Calcareous black sands and reclaimed acid heath soils.
e. Calcareous soils freshly broken up from old grassland.
f. Old black garden soils where manure and lime have been applied regularly for many years.
g. Very sandy acid mineral soils that are low in native manganese content.

Excess liming, long-term irrigation, and other practices which cause alkalinity may also cause manganese deficiency~~, so also~~ as do practices which promote growth of certain bacteria (Labanauskas, 1966). The best way to overcome manganese deficiency is to lower the pH, since manganese fertilizers by themselves are largely ineffective (Loneragan, 1975).

Manganese deficiency causes small necrotic spots on leaves. On legume seedlings, the symptom is usually necrosis of the cotyledons (Bidwell, 1974). In citrus, Mn deficiencies induce a mottled appearance between

Table 5.6.10.4-1. Manganese concentrations in the shoots of different plants grown in nutrient solutions containing manganese at 0.55 ppm.

Plant	Manganese Concentration in Tops, ppm
Tomato	242
Vetch	384
Oats	741
Buckwheat	878
Spinach	922
Peas	1,367
Lettuce	1,378
Sunflower	1,521

Source: NAS, 1973, p. 66.

Table 5.6.10.4-2. Manganese concentrations in the shoots of native plants collected from a bog soil (pH 4.0) in Wisconsin.

Plant	Common Name	Manganese Concentration, ppm
Gaultheria hispidula	Creeping snowberry	2,999
Vaccinium myrtilloides	Velvet-leafed bluberry	2,177
Vaccinium oxyococcus	Small cranberry	1,340
Smilacina trifolia	False Solomon's seal	1,288
Chamaedaphne calyculata	Leather leaf	772
Dryopteris cristata	Crested-shield fern	426
Cornus canadensis	Bunchberry	149
Kelmia polifolia	Pale laurel	116

Source: NAS, 1973, p. 67.

and along veins. These areas become dull in texture and, in severe cases, may become very chlorotic. In addition, twig growth is often reduced (Labanauska, 1966). Apple, cherry, citrus, oats, raspberry, and sugar beet are very susceptible to manganese deficiency.

5.6.10.6. Manganese toxicity.

Manganese toxicity most commonly occurs in the following soils (Labanauskas, 1966):

a. Highly acidic soils.

b. Soils with high native manganese content.

c. Soils with poor aeration.

Long-term applications of fertilizers which acidify soils may induce toxicity. Excessive use of manganese containing fertilizers will also result in Mn toxicity. In general, plants containing 400 to 500 ppm manganese may show toxicity symptoms.

Excess manganese may cause iron-deficiency symptoms in a few species (Labanauskas, 1966; Lagerwerff, 1974). In cotton, excess manganese has been found to cause increased activity of peroxidase and polyphenoloxidase, while decreasing the activity of catalase, ascorbic acid oxidase, and cytochrome c oxidase. Excess Mn can also suppress respiration and ATP production (Lagerwerff, 1974). High manganese content commonly causes necrotic spots on barley (Yopp *et al*., 1974). Necrosis of the internal bark has been reported on apple trees, and may be a good toxicity symptom on other woody plants. A more general, and hence less useful symptom, is lead chlorosis, caused by the interference with iron nutrition.

Marginal leaf yellowing may be diagnostic on some species, such as mustard and lettuce (Yopp et al., 1974). Table 5.6.10.6-1 presents specific symptoms of manganese toxicity for a number of crop species.

Table 5.6.10.6-1. Specific symptomatology of excess manganese for selected crops.

Plant	Visual Symptoms
Alfalfa (Medicago sative)	Leaves show white marginal and tip spotting, followed by scorching.
Broad bean (Vicia faba)	Yellow chlorosis of leaves appears, with white interveinal areas: leaves may show marked interveinal chlorosis, beginning near margins, followed by necrotic spotting.
Cabbage (Brassica oleracea capitata)	Chlorosis of leaf margins appears, either as a narrow rim effect or as a more diffuse mottling. There is cupping of leaves, and brown scorching and spotting of margins.
Cauliflower (Brassica oleracea botrytis)	There is marked incurling of leaf margins, with marginal browning and spotting; laminae show distortion and lateral suppression. Growing point eventually dies.
Cereals (various)	Leaves show interveinal brown spots.
Citrus (Citrus spp.)	Leaves develop marginal yellowing and necrotic spots, 1 to 4 mm. in diameter. These necrotic spots develop first on the underside of the leaves and, in many cases, the necrosis subsequently extends through them.
Clover (Trifolium spp.)	Leaves are small and cupped, and margins become scorched and distorted; tip leaves are particularly affected.
Lespedeza (Lespedeza spp.)	Severe spotting develops on the leaves.
Pineapple (Ananas comosus)	Leaves develop severe chlorosis.
Potato (Solanum tuberosum)	Plants become stunted. Upper leaves are chlorotic and the lower ones become brittle and dry. Stem-streak necrosis extends to the upper part of the stem.
Tobacco (Nicotiana tabacum)	Leaves develop severe chlorosis.
Tung (Aleurites fordi)	Leaves show necrotic spots.

Source: Labanauskas, 1966, p. 273.

Manganese toxicity is commonly alleviated by the addition of phosphate fertilizers, calcium, or potassium phosphate (Yopp et al., 1974). On the other hand, manganese excesses in soils inhibit~~s~~ the availability of cobalt (Loneragan, 1975).

Table 5.6.10.6-2 gives threshold manganese toxicity levels and symptoms for a number of economically important plants. Tables 5.6.10.6-3 and 5.6.10.6-4 contain more extensive listings of deficient, adequate and toxic manganese levels in the tissue for several plant species.

Alfalfa, cabbage, cauliflower, cereals, clover, pineapple, potato, runner bean, sugar beet, and tomato are probably especially sensitive to excess manganese (Labanauskas, 1966a).

Yopp et al., (1974) concluded their manganese discussion by recommending a 1 to 2 ppm available manganese limit in the substrate or a 200 ppm limit in plant tissue as threshold tolerance levels for most plants.

Table 5.6.10.6-2. Threshold toxicity level and symptomatology for a number of economically important plants--Manganese.

Plants	Growth Medium	Minimal Phytotoxic Concentration	Plant Part Affected	Symptomatology	Developmental Stage
Potato, var. Keswick	soil pH 4.5	100 ppm internal 12-13 ppm external	tops	chlorosis necrosis on stems	reproductive
Peanut,	clay loam	46 ppm internal 7 ppm external	"	chlorosis, interveinal	seedling
Barley, var. Herta	fine sand loam	190 ppm internal 0.25 ppm external	"	leaf chlorosis, tip burn specks reduced yield	reproductive
Cranberry, McFarlin	solution	275 ppm external	roots	growth inhibited	seedling
Birch, Yellow	solution	1300 ppm internal 15 ppm external	tops	retarded growth marginal necrosis	"
Barley, var. Atlas 46	solution	0.5 ppm external	"	older leaves	"

Source: Yopp *et al.*, 1974, p. 141.

TABLE 5.6.10.6-3. Deficient, adequate and toxic manganese concentrations in plants.

				Manganese Concentration ppm (dry wt)		
Plant	Type of Culture	Tissue Sampled	Other Information	Deficient	Adequate or Nontoxic	Toxic
HORTICULTURAL CROPS						
Almond	Field	Leaves	-	5-25	96	-
Apple	Field	Leaves	-	15	30	-
Apple	Soil	Leaves	Interveinal bark necrosis	-	-	>400
Apricot	Field	Leaves	-	10	86-94	-
Avocado	Solution	Leaves	-	-	1,300	4,300-6,000
Avocado	Field	Leaves	September	-	366-655	-
Banana	Field	Leaves	-	<10	-	-
Bean (Phaseolus vulgaris L.)	Podzol soil	Tops	-	-	-	1,000
Bean (Phaseolus vulgaris L.)	Podzol soil	Leaves	pH, 4.7	0	0	600-800
Bean (Phaseolus vulgaris L.)	Field soil	Tops	pH, 4.7	-	40-940	1,104-4,201
Brussels sprouts	Field	Leaves + petioles	Youngest fully expanded	-	78-143	760-2,035
Carrot	Solution	Tops	Bronzed leaves	-	-	>2,600
Carrot	Solution	Tops	Reduced yields	-	-	7,100-9,600
Lettuce	Steamed soil	Tops	Necrotic spots on leaves	-	-	>200

TABLE 5.6.10.6-3. (cont'd) Deficient, adequate and toxic manganese concentrations in plants.

Plant	Type of Culture	Tissue Sampled	Other Information	Manganese Concentration ppm (dry wt)		
				Deficient	Adequate or Nontoxic	Toxic
Lima beans	Field	Tops	-	32-68	207-1,340	-
Onion	Limed organic soil	Tops	Maturity	-	34	-
Orange	Field	Leaves	4-7 months	15	25-200	1,000
Orange	Field	Leaves	7-month bloom cycle; leaves from nonfruiting terminals	<19	20-90	>100
Peas (Pisum sativum)	Podzol soil	Leaves	pH, 4.7	-	-	550
Pecan	Field	Leaflets	Detergent-washed	-	141-196	-
Potato	Field	Leaves	-	7	40	-
Potato	Soil	Leaves	-	-	-	473-2,290
Spinach	Field	Plant	-	23	34-60	-
Strawberry	Sand	Plant	-	-	50	-
Tomato	Solution	Leaves	-	5-6	70-398	-
Tung	Field	Leaves	-	58-81	-	-
Turnip	Field	Leaves	-	-	75	-
CEREALS						
Barley	Solution	Old leaves	Brown spots	-	-	1,200
Barley	Solution	old leaves	Moderate to severe necrosis		-	305-410
Barley	Podzol soil	Leaves	pH, 4.7	-	-	200

TABLE 5.6.10.6-3. (cont'd) Deficient, adequate and toxic manganese concentrations in plants.

				Manganese Concentration ppm (dry wt)		
Plant	Type of Culture	Tissue Sampled	Other Information	Deficient	Adequate or Nontoxic	Toxic
Barley	Acid soil	Tops	Toxicity symptoms; yield reduced	- -	- -	80-100 700-1,000
Barley	Soil	Tops	-	-	14-76	-
Oats	Soil	Tops	-	8-12	30-43	-
Oats	Acid soil	Tops	-	-	301-370	-
Oats	Solution	Tops	-	-	774-783	-
Rice	Solution	Tops	-	<20	-	>2,500
Rice	Solution	Single leaf	-	-	-	4,000-8,000
Rice	Solution	Old leaves	-	-	-	7,000
Rye	Soil	Mature tops	-	-	10-50	-
Rye	Solution	Old leaves	-	-	-	1,400
Wheat	Soil	Tops	var. Thatcher	-	14-65	-
Wheat	Soil	Tops	var. Saunders	14	101	-
Wheat	Field	Plants	-	4-10	75	-
Wheat	Soil (pots)	Tops	Plants grown at soil pH 4.9 and 6.9	-	108-113	356-432
Wheat	Solution	Tops	Plants grown with different manganese contents	-	181-621	396-2,561

TABLE 5.6.10.6-3. Deficient, adequate and toxic manganese concentrations in plants.
(cont'd)

				Manganese Concentration ppm (dry wt)		
Plant	Type of Culture	Tissue Sampled	Other Information	Deficient	Adequate or Nontoxic	Toxic
Wheat	Solution	Roots	Plants grown with different manganese contents	-	1,094-6,183	4,096-11,761
Wheat	Solution	Tops	-	-	378-493	-
Corn	Field	Ear leaf	Single cross hybrids	-	116-214	-
Corn	Soil	Whole leaf	Moderately fertile soil	-	76-213	-
Corn	Field	Ear leaf	Several hybrids	-	19-84	-
Cotton	Sand	Leaf blade	105 days	<15	75-90	-
Cotton	Solution	Leaves	135 days	<10	10-1,200	-
Cotton	Soils	Tops	var.Pima S-2	-	27-216	1,130-2,92
Cotton	Solution	Tops	var.Pima S-2	-	196-924	1,740-8570
Cotton	Solution	Tops	var.Rex Smooth leaf	-	243-3,700	6,480
Cotton	Solution	Tops	var.Coker 100A	-	189	3,210
Cotton	Solution	Tops	var.Acala 4-42	-	216	2,810
Cotton	Solution	Tops	-	14	-	2,000
Cotton	Field	Leaves & petioles	16 varieties on 3 soils	-	58-238	-
Cowpeas	Solution	Tops	Toxicity symptoms	-	-	1,224
Cowpeas	Solution	Tops	Reduced yields	-	-	4,212
Hops	Solution	Leaves	-	-	37-88	903-1796
Peanut	Solution	Tops	Slight toxicity symptoms	-	-	1,245

TABLE 5.6.10.6-3. (cont'd) Deficient, adequate and toxic manganese concentrations in plants.

Plant	Type of Culture	Tissue Sampled	Other Information	Manganese Concentration ppm (dry wt) Deficient	Adequate or Nontoxic	Toxic
Peanut	Sand	Leaves	-	-	110-440	890-10,900
Soybean	Soil	Uppermost fully developed leaf	-	<20	-	-
Soybean	Soil	Tops	-	<15	35	-
Soybean	Solution	Leaves	30 days; var.Earlyana	2-3	14-102	173-199
Soybean	Solution	Tops	Toxicity symptoms	-	-	529
Soybean	Solution	Tops	Reduced yields	-	-	2,168
Sugarbeet	Field	Leaves	-	5-30	7-1,700	1,250-3020
Sugarbeet	Field	Leaf blade	-	4-20	-	-
Sugarbeet	Field	3rd, 4th, 5th, & 6th blades from top of plant	-	1-10	20-400	-
Tobacco	Soil	Upper leaf	var. Burley 21	10	45	-
Tobacco	Solution	Tops	Burley	-	-	3,000
Tobacco	Solution	Top leaves	-	-	-	5,250-10,670
FORAGE CROPS - TEMPERATE GROUP						
Alfalfa	Solution	Tops	-	<10	-	-
Alfalfa	Field	Tops	-	-	-	477-1083
Alfalfa	Solution	Tops	-	-	-	380
Alfalfa	Soil(pots)	Tops	Several soils of SE U.S.	-	65-240	651-1,970

TABLE 5.6.10.6-3. Deficient, adequate and toxic manganese concentrations in plants.

Plant	Type of Culture	Tissue Sampled	Other Information	Manganese Concentration ppm (dry wt)		
				Deficient	Adequate or Nontoxic	Toxic
Alfalfa	Sand	Tops	-	-	-	175-400
Alfalfa	Sand	Tops	-	-	110	140-2200
Alfalfa	Solution	Tops	-	-	71-78	184-466
Barrel medic	Soil	Top	Cultivar 173	-	-	560[a]
Lespedeza	Soil	Top	-	-	-	>570
Ryegrass	Solution	Old leaves	-	-	-	800
Sweet clover	Solution	Tops	Toxic Symptoms	-	-	321-754
Vetch	Field	Tops	-	-	-	500-1117
White clover	Soil	Tops	var. New Zealand certified	-	-	650
Medicago truncatula	Solution	Tops	Cultivar 173	-	-	560[a]
Trifolium fragiferum	Solution	Tops	Cultivar	-	-	510[a]
FORAGE CROPS - TROPICAL GROUP						
Trifolium subterraneum	Soil(pots)	Tops	-	4-25	30-300	-
Trifolium subterraneum	Solution	Tops	-	-	200	-
Centrosema pubescens	Solution	Tops	pH, 5.5	-	-	1,600[a]
Lotononis bainesii	Solution	Tops	Cultivar Miles	-	-	1,320[a]

TABLE 5.6.10.6-3. Deficient, adequate and toxic manganese concentrations in plants.

Plant	Type of Culture	Tissue Sampled	Other Information	Manganese Concentration ppm (dry wt)		
				Deficient	Adequate or Nontoxic	Toxic
Desmodium uncinatum	Solution	Tops	Cultivar Silver Leaf	-	-	1,160[a]
Stylosanthes humilis	Solution	Tops	-	-	-	1,140[a]
Phaseolus lathyroides	Solution	Tops	Cultivar Murray	-	-	840[a]
Phaseolus atropurpureus	Solution	Tops	-	-	-	810[a]
Glycine javanica	Solution	Tops	Cultivar Jineroo	-	-	560[a]
Leucaena leucocephala	Solution	Tops	-	-	-	550[a]

[a] "Toxicity threshold levels," defined as manganese concentrations found when yields were 5% below the maximum.

Source: NAS (1973).

TABLE 5.6.10.6-4. Typical plant tissue analysis values for manganese. (cont'd)

				Range in dry matter (ppm.)				
Plant	Type of culture	Tissue sampled	Age, stage, condition or date of sample	Showing deficiency symptoms	Low range	Intermediate range	High range	Showing toxicity symptoms
Almond (Prunus amyydalus)	Field	Leaves	July	5.00-25.00	...	96.00	...	...
Apple (Malus spp.)	Field	Leaves	...	15.00	...	30.00	...	...
	Field	Leaves	...	5.00	...	55.00-125.00	...	...
	Control	Leaves	...	1.00-2.00	...	33.00	...	...
	Field	Leaves	July	2.00-13.00	...	25.00-50.00	...	...
	Field	Leaves	...	11.00	...	87.00	...	...
	Field	Leaves	...	17.00	...	24.00	...	...
Apricot (Prunus armeniaca)	Field	Leaves	June-July	9.00-14.00	...	...	...	...
	Field	Leaves	...	10.00	...	86.00-94.00	...	...
Avocado (Persea americana	Field	Leaves	...	...	...	70.00	...	...
	Field	Leaves	September	...	...	56.00-66.00	...	...
	Field	Leaves	September	...	...	...	366.00-655.00	...
	Field	Leaves	September	...	...	...	295.00-568.00	
	Field	Fruit pulp	...	...	...	3.70-19.10	...	...
Barley (Hordeum vulgare)	...	Tops	...	...	...	...	...	770.00
	Solution	Tops	...	...	...	...	...	1000.00
Bean (Phaseolus spp.)	Field	Plant	...	32.00-68.00	...	207.00 1340.00	...	...
	...	Leaves	...	...	...	68.00	...	...
	Field	Tops	...	...	...	200.00-1000.00	...	1,000.00-3,000.00

TABLE 5.6.10.6-4. Typical plant tissue analysis values for manganese.
(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
Blueberry (Vaccinium spp.)	...	Jersey leaves	...	...	...	22.00-26.00	...	...
	...	Cabot leaves	...	...	...	28.00-34.00	...	...
	...	Rubel leaves	...	...	...	120.00	...	...
	Sand	Jersey leaves	...	...	25.00	253.00-357.00	...	...
	Pots	Rubel leaves	...	...	...	134.00-217.00	...	...
	Pots	Rubel leaves	...	...	...	100.00-145.00	...	...
Brussels sprouts (Brassica oleracea gemmifera)	...	leaves	...	...	...	85.00	...	...
Cauliflower (Brassica oleracea botrytis)	...	Leaves	...	10.00	...	60.00	...	...
Cherry (Prunus cerasus)	Field	Leaves	...	21.00	...	54.00-72.00	...	...
	Field	Leaves	...	7.00	...	41.00	...	...
	Field	Leaves	...	12.00	...	43.00	...	...
CITRUS FRUITS Grapefruit (Citrus paradisi)	Field	Leaves	...	9.00-10.00	...	35.00	...	...
Lemon (Citrus limon)	Field	Leaves	...	3.00-5.00	...	14.00-26.00	...	...
	Control	Leaves	...	2.00-4.00	...	14.00-75.00	...	...
	Field	Leaves	June	9.00-13.00	...	20.00	...	...
Orange (Citrus sinensis)	Field & control	Leaves	3-7 mos., spring cycle from fruiting terminals	15.00	...	20.00-80.00	...	>200.00

TABLE 5.6.10.6-4. Typical plant tissue analysis values for manganese.
(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	Control	Leaves	...	7.00-10.00	...	18.00-20.00	...	...
	Field	Leaves	...	3.00-5.00	...	14.00-26.00	...	...
	Field	Leaves	...	7.00	...	20.00	...	...
	Field	Leaves	...	4.00-11.00	...	21.00-29.00	...	...
	Field	Valencia leaves	September	...	...	21.00-50.00	...	...
	Field	Navel leaves	May	13.00	...	15.00-20.00	...	...
	Field	Navel leaves	...	...	...	16.00-18.00	...	...
	Field	Leaves	June	9.00-13.00	...	...	...	...
	Field	Valencia leaves	4-5 months old	...	20.00	...	85.00	...
	Field	Valencia leaves	3-4 months old	...	12.00	...	48.00	...
	Field	Valencia leaves	2-3 months old	...	7.00	...	34.00	...
	Field	Valencia leaves	2-3 months old	...	9.00	17.00	...	...
	Field	Valencia leaves	4-7 months old	15.00	16.00-24.00	25.00-200.00	300.00 500.00	1,000.00
	...	Leaves	3 mos. old	...	...	65.00-630.00	...	...
	...	Stems	3 mos. old	...	...	18.00-320.00	...	...
	...	Roots	3 mos. old	...	...	790.00-1800.00	...	...
	Sand	Valencia leaves	...	...	...	22.00-134.00	...	...
	Field	Leaves	...	...	...	28.00-37.00	...	...
	Field	Valencia	...	...	...	25.00-51.00	...	...
Current,black (Ribes nigrum)	...	Leaves	...	15.00	...	61.00	...	...
Flax (Linum usitatissimum)	...	Tops	...	6.00	...	50.00	...	...

TABLE 5.6.10.6-4. Typical plant tissue analysis values for manganese. (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
Lespediza (Lespediza spp.)	Field	Tops	...	...	...	...	...	400.00-500.00
Mangel (Beta vulgaris macrorhiza)	...	Leaves	...	9.00-13.00	...	20.00	...	...
Oats (Avena sativa)	Field	Tops	...	5.00	...	12.00	...	...
	Field	Tops	Flowering	10.00-14.00	...	20.00-82.00	...	...
	Control	Tops	After flowering	5.00-13.00	...	14.00-111.00	...	...
	Pots	Plants	11 weeks old	10.00	...	64.00-140.00	...	...
	Pots	Tops	Flowering	5.00-10.00	...	9.00-57.00	...	...
Pea (Pisum sativum)	Field	Seeds	Harvest	4.00-5.00	...	4.00-7.00	...	...
	Field	Seeds	Harvest	2.00-5.00	...	4.00-15.00	...	...
	Field	Seeds	Harvest	12.00-22.00	...	16.00-26.00	...	...
Peach (Prunus persica)	Field	Leaves	June-July	5.00-19.00	...	18.00-325.00	...	...
	Field	Leaves	...	...	17.00	101.00	220.00	[illegible]
	Field	Leaves	...	...	37.00	125.00	370.00	[illegible]
	Field	Leaves	...	...	...	67.09-130.00	...	[illegible]
	Field	Leaves	...	...	...	40.00-381.00	...	...
	Field	Leaves	...	9.00	...	41.00	...	...
	Field	Leaves	...	25.00	50.00	90.00	...	...
Pear (Pyrus communis)	Field	Leaves	June-July	5.00-25.00	...	32.00-96.00	...	...
	Field	Leaves	...	...	...	68.00-220.00	...	...
	...	Leaves	...	...	...	35.00	...	...

TABLE 5.6.10.6-4. Typical plant tissue analysis values for manganese.

(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
Plum (Prunus domestica)	Field	Leaves	...	15.00	...	55.00-93.00	...	...
Potato (Solanum tuberosum)	...	Leaves	...	7.00	...	40.00	...	...
Soybean (Glycine soja)	Solution	Leaves	30 days old	9.00-11.00	...	15.00-84.00	...	...
	Solution	Leaves	30 days old	2.00-3.00	...	14.00-102.00	...	173.00-999.00
	Solution	Roots	30 days old	17.00-19.00	...	24.00-43.00	...	49.00-150.00
Spinach (Spinacia oleracea)	Field	Plant	June	23.00	...	34.00-60.00	...	...
	Field	Plant	October	52.00	...	56.00-103.00	...	...
	Field	Stems & pieces	...	12.00	...	34.00	...	...
Strawberry (Fragaria spp)	Sand	Plant	February	...	...	50.00	...	...
Sugar beet (Beta sarcharifera)	Field	Leaves	...	5.00-30.00	...	7.00-1700.00	...	1250.00-3,020.00
	...	Leaves	...	17.00	...	46.00	...	...
Sugar cane (Saccharum officinarum)	Field	Leaves	...	5.00	...	30.00	...	...
Tobacco (Nicotiana tabacum)	...	Leaves	...	...	...	160.00	...	1000.00-11,000.0
	...	Roots	...	...	...	160.00	...	3,170.00
	Pots	Plants	...	...	...	334.00	...	933.00-1130.00

TABLE 5.6.10.6-4. Typical plant tissue analysis values for manganese. (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)	Solution	Leaves	October	5.00-6.00	...	70.00-308.00	...	...
	Solution	Fruit	Harvest	0.20	...	2.00	...	...
	...	Leaves	...	7.00	...	46.00	...	...
Tung (Aleurites fordi)	Field	Leaves	...	27.00-55.00	...	...	...	...
	Field	Leaves	August	25.00-122.00	...	322.00	...	...
	Field	Leaves	July-Oct.	58.00-81.00	...	638.00-3110.00	...	...
Turnip (Brassica rapa)	...	Leaves	...	...	...	75.00	...	...
Walnut (Juglans regia)	Field	Leaves	...	6.00-25.00	...	211.00-274.00	...	...
	Field	Leaves	June	5.00-8.00	...	35.00-65.00	...	...
Wheat (Triticum spp.)	Field	Plants	...	4.00-10.00	...	16.00-28.00	...	...
	...	Tops	Young plants	15.00	...	60.00	...	...

Source: Labanauskas, 1966a, pp. 274-277

5.6.11. Mercury (Hg)

5.6.11.1. Introduction.

Mercury is not essential for plant or animal growth. It is toxic to plants and animals, but the tolerance levels vary greatly between different compounds.

It is the only common metal which is a liquid at normal temperatures. Rarely it occurs free in nature. The most important ore is cinnabar (HgS). Cinnabar occurs in large quantities in the Big Bend area in the western United States. Spain and Italy produce about 50 per cent of the world's supply of mercury.

Mercury is a heavy, silver-white metal; a rather poor conductor of heat; and a fair conductor of electricity. Mercury is widely used in thermometers, barometers and other laboratory instruments. It is also used in mercury switches, mercury-vapor lamps and other electrical units. Mercury is also used in pesticides, batteries, catalysts, and anti-fouling paint. Mercury salts and organic mercury compounds are also important in a wide variety of man's activities.

Recently mercury has been brought into sharp public focus by the reports on severe cases of human toxicity caused by industrial effluents. Most of the resultant research has dealt with the cycling of Hg in aquatic systems. The meager data on the effects of Hg on terrestrial systems originate mostly from the research on long-term effects of the use of pesticides.

The occupational exposure limit for organo-mercury compounds is 0.01 mg/m^3 and for mercury 0.05 mg/m^3. Mercury, beryllium, and asbestos are the only substances for which the U. S. Environmental Protection Agency has promulgated standards for hazardous emissions. The EPA (and proposed Minnesota Pollution Control Agency's) emission standard for mercury is

2300 gms/day, but it applies only to ore processors and sewage sludge incinerators. The allowable limit of methyl-mercury in food (e.g., fish) is 0.5 ppm (Yopp *et al*, 1974).

5.6.11.2. Sources of mercury.

a. Natural:

The concentration of mercury in native soil minerals is essentially zero in most cases. Mercury in soils is found mostly in belts along major geologic faults (Lagerwerff, 1972). Therefore, the only general source of soil mercury is the atmosphere, either directly or through aquatic cycling. Mercury is highly volatile and enters the atmosphere in significant quantities from geothermal activity. An index to the importance of natural volatalization of mercury is, on a worldwide basis, an estimated 230 tons annually reaches the oceans from physical and chemical breakdown of mercury-containing rocks and minerals, while natural evaporation provides 36,000 tons (Lagerwerff, 1972).

b. Anthropogenic:

Besides geothermal activity, the principle sources of soil mercury are:

(1) Gold and other metal smelting activities

(2) Coal and other fossil fuel combustion. Coal burning is the most significant general source of environmental contamination of mercury. Coal may contain 0.02 - 2 ppm mercury, fly ash 0.1 - 18 ppm, residual fuel oil 0.002 - 0.4 ppm, and premium gasoline 0.008 - 0.02 ppm (Lagerwerff, 1974). It has been estimated that a typical 700 megawatt coal-fired power plant will emit 2.5 kilograms mercury daily (Yopp, 1974).

There are no known ways of controlling this emission because mercury is emitted as a vapor (Lagerwerff, 1974).

(3) Use of mercury as a seed dressing or as a soil pesticide (Bennett, 1971; MacLean et al., 1973). The use of these chemicals is declining and, even if continued, probably would not significantly contaminate soils (Yopp et al., 1974). It has been estimated in West Germany that contamination due to seed dressing would not contribute more than 1 to 10 per cent of the naturally occurring mercury over a long term (Lagerwerff, 1974).

(4) Use of sewage treatment plant effluents on soils (Van Loon, 1974a; Van Loon, 1974b).

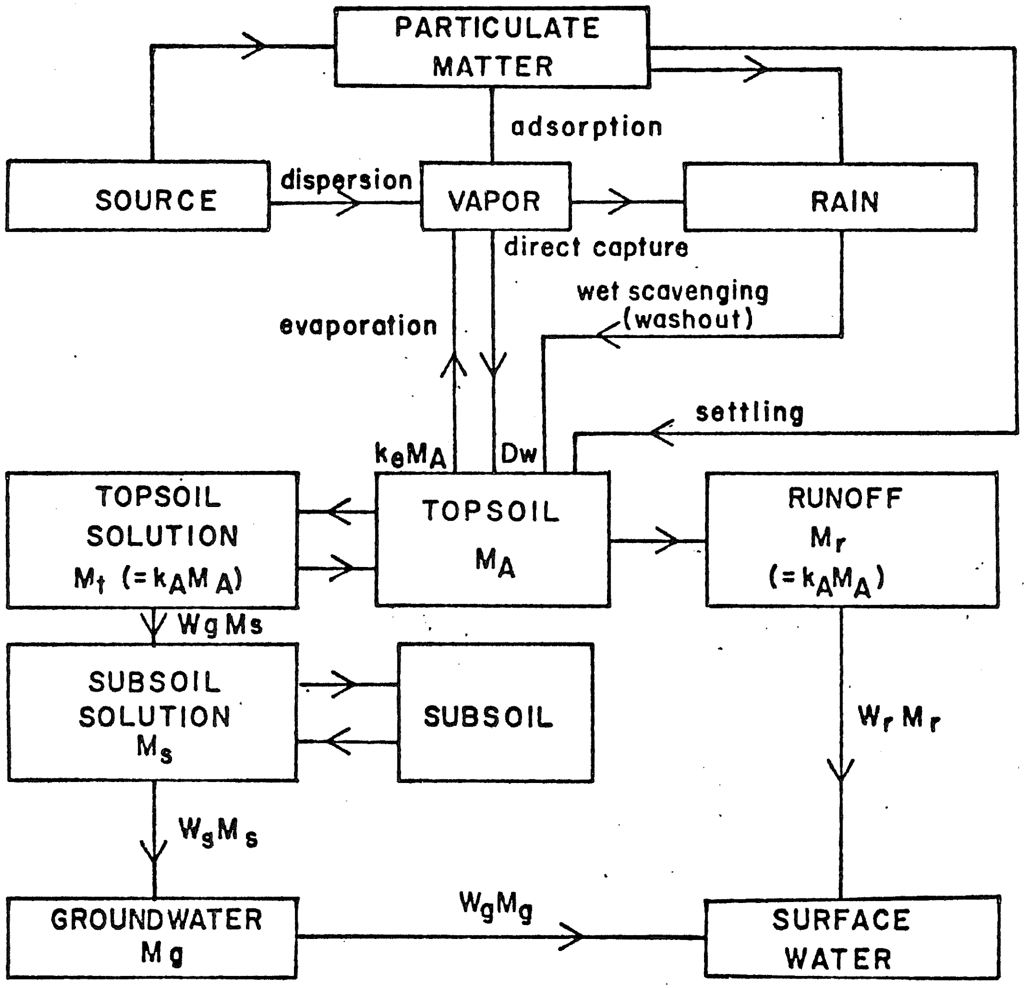
Worldwide, the annual production of mercury exceeds 7,000 tons of which 25 to 50 per cent is thought to be discharged into the environment (Lagerwerff, 1972) Phytotoxicity due these discharges, however, is seldom very significant. Most of the concern and shocking displays of mercury's virulent toxicity are associated with food chain concentration, especially in aquatic systems. Mercury is a cumulative poison, and its ability to be concentrated through the food web was amply demonstrated by the Minomata and Niigata catastrophies in Japan, where 51 people were killed and 175 seriously injured by eating shellfish contaminated with mercury from a plastic factory (Lagerwerff, 1972).

5.6.11.3. Biological availability of mercury.

a. Soil solid phase:

Figure 5.6.11.3-1 depicts a model of the deposition and subsequent fate of mercury in the environment near a large point source (e.g.,

Figure 5.6.11.3-1. A model of atmospheric mercury transport and deposition near a point source. From Lockeretz (1974).


PARTICULATE MATTER
adsorption
SOURCE
dispersion
VAPOR
RAIN
direct capture
wet scavenging (washout)
evaporation
settling
k_eM_A
Dw
TOPSOIL SOLUTION M_t (= k_AM_A)
TOPSOIL M_A
RUNOFF M_r (= k_AM_A)
W_gM_s
SUBSOIL SOLUTION M_s
SUBSOIL
W_rM_r
W_sM_s
GROUNDWATER M_g
W_gM_g
SURFACE WATER

power plant or incinerator). Table 5.6.11.3-1 lists the model's parameters and gives respective mercury concentrations which may be expected near a power plant or incinerator.

As stated previously, emissions of Hg into the air, have resulted only in a marginal impact on the soils. In a survey of urban, agricultural, and industrial soils, the urban soils contained 0.10 ppm mercury, the agricultural soils contained 0.11 ppm, and the industrial soils contained 0.14 ppm (Yopp et al., 1974). On the other hand, long-term trends of increasing mercury contamination have been detected in the enrivonment. For example, the mercury concentration in the sediments of Lake Windermere, England was related to the time course of deposition:

520 - 1269 AD (73 - 50 cm) - 122 ppb;
1400 - 1800 AD (44 - 30 cm) - 286 ppb;
1845 - 1870 AD (20 - 26 cm) - 608 ppb;
1915 - present (15 - 0 cm) - 1,026 ppb (Lagerwerff, 1974).

In a study of 912 soil samples, the mercury concentration in the eastern U. S. averaged 96 ppb, while western U. S. averaged 55 ppb. The nationwide average was 76 ppb. Another similar study estimated a nationwide average of 100 ppb (Lagerwerff, 1972).

Mercury in the soil can occur in a vast number of organic and inorganic forms. In highly oxidized soils, mercury usually attains the ionic form Hg^{++} (Lagerwerff, 1972). In this state, it is easily adsorbed by clays and other minerals. However, under conditions normally prevalent in soils, mercury is reduced to the metallic form Hg^0 (Lagerwerff, 1967). In this form it is highly volatile and will escape into the atmosphere unless complexed by organic material or by other processes. Mercury may combine with

TABLE 5.6.11.3-1. Soil mercury-model parameters and respective concentrations near a point source, St. Louis, Missouri.

Quantity	Symbol	Value	Units
Mercury concentrations			
topsoil	Ma	0.10	μg g^{-1}
topsoil solution	Mt	0.05	μg l^{-1}
subsoil solution	Ms	0.05	μg l^{-1}
groundwater	Mg	0.05	μg l^{-1}
surface runoff	Mr	0.05	μg l^{-1}
Mercury deposition rates			
wet	Dx	200	g m^{-2} yr^{-1}
dry	Dd	0	g m^{-2} yr^{-1}
		(See 2.2.3)	
Soil and hydrological parameters			
topsoil thickness times density	Ta	13.0	g cm^{-2}
surface runoff	Wr	250	l m^{-2} yr^{-1}
groundwater flow	Wg	250	l m^{-2} yr^{-1}

Source: Lockeretz (1974)

other inorganic compounds to form fairly stable compounds. Thus, it may appear as a phosphate, carbonate, or as a sulfide (Lagerwerff, 1972). All these compounds exhibit low solubility and, therefore, may be important in keeping the Hg in the soil and prevent its evaporation. Coatings on soil particles of hydrous oxides of manganese or iron adsorb mercury occurring in other forms, such as ionic (e.g., $HgCl_3^-$, $HgCl_4^{2-}$) or molecular (e.g., Hg_2Cl_2, $HgCl_2$). With regard to soil organic matter, evidence is available to indicate that mercury can be strongly chelated and thus prevented from escaping into the atmosphere (Lagerwerff, 1972). Soil sulfur plays an important role in mercury chemistry. Sulfur-containing humic substances (e.g., cysteine or thiourea) can keep mercury in a soluble form, and under alkaline conditions, HgS may be converted to soluble Hg_2S (Maclean, 1974).

The soil chemistry of organo-mercury compounds, which comprise most of the anthropogenic emissions, is too complex and is not fully understood. As such monomethyl mercury compounds are volatile, while the volatilization of ethyl and phenyl derivatives seems to be dependent upon microbial activity. Microbial activity also is important in the decomposition of mercury-containing pesticides (Lagerwerff, 1972). Besides bacteria, yeasts and fungi are able to decompose complex mercury compounds and thus release Hg^o (Lagerwerff, 1974; Stegnar et al., 1973).

In summary, the accumulation of mercury in soils is largely related to the sulfur, carbon, and possibly manganese oxide content, while the volatilization depends on the biological activity (Lagerwerff, 1972). Thus, in one soil, 44 - 56 per cent of the total mercury added as the fungicide Calocor (largely Hg_2Cl_2 and $HgCl_2$) evaporated in 57 days, while in another soil the annual application of 2.1 kg/ha of various mercury salts for 15 years led to a concentration of 455 ug Hg/Kg of soil (Lagerwerff, 1974; Estes et al., 1973). In the latter case, the growth of bentgrass was unaffected by the mercury (Estes et al., 1973).

Because of the high solubility of many of the mercury compounds and organo-mercury complexes, mercury may leach to lower soil strata or reach aquatic systems (Yopp et al., 1974).

b. Soil solution:

In soil solutions mercury is usually present as Hg^o or as a compound. Below pH 5 it may exist as Hg^{++} (lagerwerff, 1972). Solubility of mercury depends on pH and chemical form.

c. Transition between soil solids and soil solution:

The transition kinetics of mercury in soils depends on the chemical form and the environmental conditions. With sulfides, oxidation is most likely, while with Hg^{++}, volatilization either as Hg^o or as alkyl Hg is more likely. The conversion of Hg^{++} to Hg^o strongly depends on the presence of organic material and aerobic conditions (Lagerwerff, 1974).

5.6.11.4. Role of mercury in plant nutrition.

Mercury is not a plant nutrient.

5.6.11.5. Mercury deficiency.

Mercury is not a plant nutrient.

5.6.11.6. Mercury toxicity.

Mercury is biologically very active. (It is also a non-irritant and, therefore, is used commonly as an antiseptic). It is a very important agricultural pesticide. More than 40 per cent of all the currently used metal-containing pesticides contain mercury. In soil dressings or foliar sprays these compounds are used to alleviate blight, blast, blotch, bunt, scab, scurf, smut, spot, patch, rot, wilt and other seed or soil-borne fungus diseases. Mercury may enter plants through roots or through foliage, the relative importance depending on the nature of the source of contamination. Information presented in Table 5.6.11.6-1 shows that as much as 90 per cent of the total soil mercury may be available to plant roots. Most plants contain from 10 to 20 ppb mercury. Plants growing near geologic sources of mercury have been found to exhibit Hg concentrations of up to 3,500 ppb (Lagerwerff, 1972). These levels were not injurious to the plants, and indeed, no evidence was found in the literature to indicate that root uptake could lead to plant toxicity.

Direct uptake of Hg vapor by leaves has, however, been shown to cause toxicity. For example, roses grown in soils containing high concentrations of $HgCl_2$ were not affected if the chambers were well ventilated. However, in the absence of satisfactory ventilation, damage did occur (Lagerwerff, 1972). Plant roots absorb mercury primarily in the forms of monomethyl mercury or Hg^o (Lagerwerff, 1972). Stomatal absorption occurs primarily with Hg^o (Lagerwerff, 1972; Huckabee, 1973). Plants also emit Hg^o through the stomata. This mercury may have originated in the plant through root absorption of complex mercury containing pesticide, its subsequent translocation to the leaves and reduction to Hg^o in the process (Huckabee, 1973; Burkett, 1975). Plants can translocate mercury to their leaves as well as to their fruiting parts. Mercury has

Table 5.6.11.6-1. Availability of mercury in 14 soils based on the acid fractionation of total soil mercury.

Source of substrate	Hg(ppb)	After		'Available' Hg(%)
	a	b	c	
	0.1 N Hcl	HNO_3	Hf + HNO_3	$\frac{100(a + B)}{c}$
a. Iceland				
1. Krysuvik	30	50	220	36.4
2. Solheimajokull	1	32	387	8.5
3. Skogafoss	1	85	815	10.4
4. Laugurvatn	4	4	417	1.8
5. Myvatn	3	5	67	11.9
b. Hawaii				
1. Old lava, Waipio, Hawaii	1	22	35	12.4
2. Old red lava, Sulfur Banks, Hawaii	1	30	46	65.2
3. Grey soil, fumarole, Hawaii	23	31	60	90.0
4. Lava, 1971 eruption, Halemaumau	7	63	1272	5.5
5. Topsoil Hanalei, Kauai	6	21	55	49.1
6. Topsoil Manoa Valley, Oahu	10	31	130	31.5
7. Woodland soil, Hana, Maui	4	21	79	31.5
c. W. Pacific				
Japan:				
1. Mountain soil, Lake Hakone area	20	190	390	53.8
Taiwan:				
2. Garden soil, Taipei area	15	165	270	66.7

Source: Siegel *et al.*, (1975).

been shown to accumulate in the edible parts of potato, apple, pea, rice, and wheat, but not in barley (Lagerwerff, 1972).

Mercury phytotoxicity is very rare, and no general toxicity symptoms have been described, except possibly reduced growth (Lagerwerff, 1967). Being a heavy metal, mercury probably interacts with a wide variety of amino acids and proteins, rendering them inert. Mercury may affect photosynthesis, but only at unrealistic concentrations. Tissue mercury concentrations of 3000 to 5000 ppm have been produced in potatoes under laboratory conditions, without any apparent harmful phytotoxic effects (Yopp *et al.*, 1974).

In summary, phytotoxicity in the form of reduced growth may occur in sensitive plants containing concentrations greater than 1000 ppm (Yopp *et al.*, 1974). However, on the basis of food chain effects on humans and animals (the livers of bald eagles in Minnesota have been found to contain 117-130 ppm mercury according to Lagerwerff, 1972), concentrations of mercury in plant tissues should not exceed 0.5 ppm and concentrations in soils should not exceed 0.15 ppm (Yopp *et al.*, 1974).

Table 5.6.11.6-2 presents a limited amount of data on toxicity tolerance levels and symptomatology for mercury toxicity in six plant species.

Table 5.6.11.6-2. Toxicity tolerance levels and symptomatology for mercury toxicity in six plant species.

Plants	Growth Medium	Minimal Phyto-toxic Conc.	Plant Part Affected	Symptom	Developmental Stages
Rose, var. Briarcliff Collidge Madame Butterfly Templar	solution	3000 ppm internal 0.1-2 % external	root	retarded growth	seedling
Broad Bean	soil	1 % external	"	"	"
Oxalis	"	"	"	"	"
Sunflower	"	"	"	"	"
Pear, var. Conference Doyene' du Comice	spray	0.003 % external	leaves	chlorotic spots; distorted shape	"
Peanut	fungicide	0.2-0.5 % external	embryo	reduced germination	"

Yopp et al., (1974).

5.6.12. Nickel (Ni)

5.6.12.1. Introduction.

Nickel is not generally considered an essential element for plant growth, though it is present in trace amounts in nearly all plant species.

Nickel constitutes approximately 0.008% (80 ppm) of the earth's crust, mostly in igneous rocks, where its concentration averages 0.01% (NAS, 1975). The earth's core contains 8.5%, and meteorites contain 5-50% nickel. Nickel-rich nodules have been found on the ocean's floor, but currently, commercial nickel comes from ores such as pentlandite and pyrrhotite. Seventy per cent of the nickel used in the free world is produced from ores around Sudbury, Ontario, Canada. Minnesota also has significant deposits of nickel-bearing ores.

Metallic nickel is silvery white and takes on a bright polish. It is hard, malleable, ductile, somewhat ferromagnetic, and a fair conductor of heat and electricity. Nickel's chief value is in its alloys, for use in monetary coins, armor plates, burglar-proof vaults, stainless steel and other corrosion-resistant materials. Added to glass, nickel yields a green color. Nickel is used extensively as a plating for other metals, and, when finely divided, is used as a catalyst for hydrogenating vegetable oils.

Nickel may be an essential element for humans and animals, but it can also be acutely toxic. It is carcinogenic, and may be teratogenic and mutagenic. The occupational exposure limit for nickel is 1 mg/m^3 (NAS, 1975).

Information on the mechanisms and significance of nickel phytotoxicity is very limited.

5.6.12.2. Sources of nickel.

a. Natural:

Figure 5.6.12.2-1 illustrates the average concentrations of nickel in typical parent materials. Most of the nickel in igneous rocks is in ~~in~~ the ferromagnesia replacing the iron, but some may occur in sulfides (Norrish, 1975). Ultramafic rocks contain more nickel than silicic rocks: basalt, gabbro and peridotite in the fromer group range from 0.016% to 0.20% in nickel, while the members in the latter group (e.g., granites) contain only 0.0002%. Among sedimentary rocks, shales and carbonates contain an average of 0.005% nickel, while sandstone contains only 0.0001% (NAS, 1975). From ~~this~~ these figures, it is apparent that rocks low in silica are generally much higher in nickel compared to rocks with high silica content. Nickel can, however, combine with silica during weathering. The resultant minerals, garnierites, are high in nickel (10%) and are common ores. These are somehow related to clay minerals (Norrish, 1975).

Other than man's activities, atmospheric sources of nickel are insignificant. Therefore, the soil content of nickel is primarily a function of the concentration in the parent material (NAS, 1975; Yopp et al., 1974).

b. Anthropogenic:

Table 5.6.12.2-1 shows the U. S. consumption of nickel by use and form in 1972. Metal alloying consumes all ~~the nickel except approximately~~ but 4% of the total. Table 5.6.12.2-2 presents ambient air concentrations of nickel in certain urban areas of the U. S. from 1957 to 1968. In general, a downward trend in air concentrations of nickel

Figure 5.6.12.2-1. Comparison of average silica and nickel content of various sedimentary and igneous rocks. From Nickel, National Academy of Science, Washington, D.C. (1975).

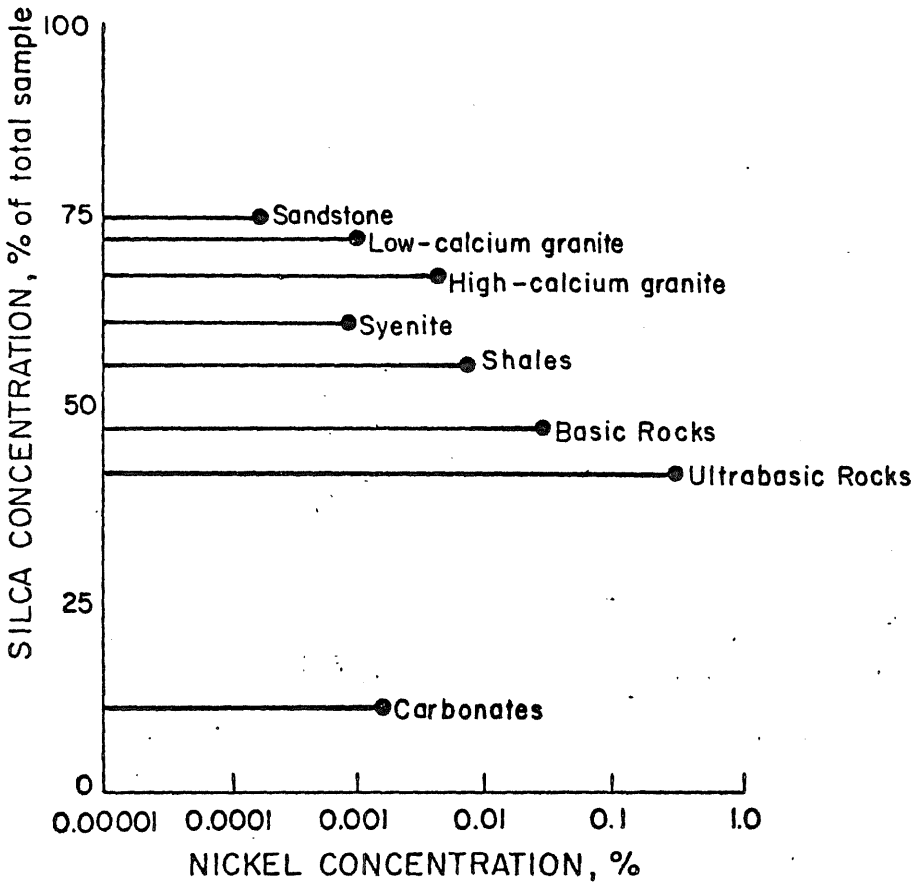

SILCA CONCENTRATION, % of total sample
100
75
50
25
0
Sandstone
Low-calcium granite
High-calcium granite
Syenite
Shales
Basic Rocks
Ultrabasic Rocks
Carbonates
0.00001
0.0001
0.001
0.01
0.1
1.0
NICKEL CONCENTRATION, %

Table 5.6.12.2-1. U. S. consumption of nickel (exclusive of scrap) by use and form, 1972

Use	Form, tons					
	Commercially Pure Unwrought Nickel	Ferronickel	Nickel (Oxide)	Nickel Sulfate	Other Forms	Total of Figures Shown
Steels						
Stainless and heat-resisting	17,155	16,788	11,196	---	227	45,366
Alloys (excludes stainless	7,930	5.004	6,408	---	213	19,555
Superalloys	11,536	251	49	---	436	12,272
Nickel-copper and copper-nickel alloys	8,307	---	36	---	199	8,542
Permanent magnet alloys	3,925	221	54	---	---	4,200
Other nickel and nickel alloys	27,873	269	698	5	49	28,894
Cast irons	2,825	272	401	---	938	4,436
Electroplating[b]	25,351	---	31	3,547	107	29,036
Chemicals and chemical uses	906	---	71	204	---	1,181
Other uses[c]	4,614	1	371	183	635	5,804
TOTAL (reported by companies canvassed and estimated)	110,422	22,806	19,315	3,939	2,804	159.286

[b] Based on monthly estimated sales to platers. Source: NAS (1975).

[c] Includes batteries, ceramics, and other products containing nickel.

Table 5.6.12.2-2. Average concentrations of suspended particles and nickel at 30 urban stations in the U. S., 1957-1968.

Station	Concentration of Particles, ug/m^3				Nickel Concentration, ug/m^3			
	1957-1960	1961-1964	1965-1968	Average	1957-1960	1961-1964	1965-1968	Average
Atlanta	125	104	105	111.3	0.021	0.012	0.007	0.013
Baltimore	141	145	129	138.3	0.057	0.071	0.051	0.060
Boise	114	90	80	94.7	0.037	0.006	0.003	0.015
Boston	156	144	98	132.7	0.171	0.076	0.090	0.112
Chattanooga	246	199	152	199.0	0.024	0.018	0.012	0.018
Charleston	217	271	226	238.0	0.058	0.040	0.015	0.038
Chicago	190	170	122	160.7	0.044	0.048	0.033	0.042
Cincinnati	145	131	131	135.7	0.024	0.018	0.013	0.018
Cleveland	165	135	122	140.7	0.035	0.027	0.015	0.026
Columbus	154	106	106	122.0	0.045	0.024	0.019	0.029
Denver	139	146	126	137.0	0.021	0.028	0.007	0.19
Des Moines	174	128	121	141.0	0.016	0.010	0.007	0.011
Detroit	139	125	155	139.7	0.037	0.020	0.033	0.030
East Chicago	206	218	181	201.7	0.202	0.123	0.070	0.031
El Paso	224	156	---	190.0	0.015	0.015	-----	0.015
Indianapolis	174	148	144	155.3	0.023	0.036	0.021	0.027
Los Angeles	186	151	119	152.0	0.055	0.041	0.031	0.042
Milwaukee	155	146	150	150.3	0.029	0.023	0.011	0.021
New Orleans	91	89	89	89.7	0.025	0.022	0.034	0.027
Newark	113	113	103	109.7	0.057	0.084	0.066	0.069
Oklahoma City	71	83	87	80.3	0.013	0.014	0.003	0.010
Omaha	139	101	128	122.7	0.018	0.013	0.005	0.012
Philadelphia	162	166	157	161.7	0.082	0.074	0.077	0.078
Phoenix	240	214	158	204.0	0.038	0.019	0.011	0.023
Pittsburgh	166	179	156	167.0	0.042	0.028	0.031	0.034
St. Louis	175	134	137	148.7	0.018	0.013	0.012	0.014
San Francisco	81	68	76	75.0	0.029	0.023	0.023	0.025
Seattle	125	68	82	91.7	0.079	0.059	0.037	0.058
Tacoma	111	96	81	96.0	0.051	0.038	-----	0.045
WashingtonDC	111	98	90	99.7	0.049	0.040	0.021	01037
AVERAGE	154.5	137.4	124.5	139.0	0.047	0.036	0.026	0.037

Source: NAS (1975).

is evident. This is due to emission control efforts, not necessarily focused on nickel, however. The average ambient air concentration of Ni in U. S. urban areas in 1966-67 was approximately 0.017 mgm/m^3 and in non-urban areas 0.002 mgm/m^3 (NAS, 1975). Significant anthropogenic sources of soil nickel include:

1. Metal smelting.

Much of the ecological research on nickel contamination has been done near Sudbury, Ontario, Canada. Atmospheric emissions can add significant levels of nickel to the soil, and similarly wastewater effluents can add significant amounts to aquatic systems.

2. Coal combustion.

Nickel during coal combustion is emitted primarily as a constituent of the fly ash, but also as nickel carbonyl vapor. The average nickel content of U. S. coal is about 0.06 lb/ton in the midwestern coal, 0.04 lb/ton in the eastern coal, and 0.01 lb/ton in the western coal. The nickel content in all the U. S. coal reserves may total 28 million tons (NAS, 1975). Domestic petroleum averages 0.00142% Ni and imported petroleum 0.0010%. Typical residual fuel oil may contain up to 0.00002% Ni (NAS, 1975).

3. Automobiles.

The recent use of nickel as a catalyst in gasoline may be a cause for concern (Lagerwerff, 1967; Yopp _et al._, 1974). Nickel is also present in tires and brake linings and attrition of these could be yet another source. In one study, grass growing along a highway was found to contain concentrations of nickel ranging from 1.3 to 3.8 ppm (dry weight). Concentrations of Ni in the vegetation were shown to decrease with increasing distance from the roadway (NAS, 1975).

4. Contaminant in superphosphate fertilizers.

This is perhaps one of the oldest sources of nickel contamination (Lagerwerff, 1967).

Nickel salts display fungicidal activities, and may be used as fungicides. However, at this time this is not common (NAS, 1975; Hardison and Anderson, 1965).

5.6.12.3. Biological availability of nickel.

a. Soil solid phase:

To summarize, the anthropogenic sources of nickel have essentially no effect on soil concentrations except in very localized areas or, in the long term, possibly along highways (Yopp _et al_., 1974).

how big an area - what about Sudbury?

Soils average 100 ppm in the nickel content (Vanselow, 1966). Soils derived from sandstone, limestone, or acid igneous rocks generally contain less than 50 ppm while those derived from argillaceous sediments or basic igneous rocks contain as much as 500 ppm nickel. Soils derived from ultrabasic igneous rocks (Serpentine) may exhibit concentrations up to 5,000 ppm total nickel (Vanselow, 1966). However, these total-nickel values are essentially meaningless from a biological viewpoint. Soils of normal nickel content seldom have more than 1 ppm in the exchangeable fraction (Vanselow, 1966; Yopp _et al_., 1974). Serpentine soils may have 10-70 ppm nickel in the readily available states (Yopp _et al_., 1974).

The extent to which nickel is incorporated into the structure of clay minerals is not known (Norrish, 1975). In certain podzolic soils, the presence of nickel is limited to the surface horizons and the availability of nickel is strongly dependent on the soil pH. Both these phenomena may be caused either by surface adsorption or by organic complexing, and it appears that these two factors control the chemistry of soil nickel (Lagerwerff, 1967). In a study of manganese oxides and iron oxides, it was found that on the soils sampled, 15% of the total nickel present was extracted with the manganese oxides, while 30% was recovered when both the iron and manganese oxides were removed. Although only a small part of the total soil nickel is held by iron and manganese oxides, that fraction may be the one most available to plants (Norrish, 1975). According to Wood (1974) the low concentration of nickel in biological systems is due to the stability of the cation in octahedra sites in silicates in the earth's crust.

Nickel is strongly chelated by soil organic matter (Vanselow, 1966; Lagerwerff, 1967; Norvell, 1972; Brady, 1974; Stevenson and Ardakani, 1972). The strength of this nickel chelation is second only to the chelation of copper (Brady, 1974). Under alkaline conditions in well aerated soils, this chelation is very important in keeping nickel in unavailable forms and can even render serpentine soils non-toxic under appropriate conditions (Vanselow, 1966).

Even though the soil chemistry of nickel is not fully understood, it can be ~~derived~~ concluded from ~~the~~ work on other heavy metals that the availability of nickel is dependent on soil pH and organic matter content. At high pH values (e.g., above approximately 6.5), nickel will be available only slowly to plants. This is specially true in oxidized soils (Brady, 1974). In these soils nickel will be adsorbed by clay minerals or chelated by organic matter. In acidic soils, more of the free ion Ni^{++} will appear in solution (Norvell, 1972).

b. Soil solution:

Nickel in solution will mostly appear as Ni^{++} or possibly as an organic complex.

c. Transition between soil solids and soil solution:

The transition of nickel to available forms or in to the solution is dependent on the soil pH (Lagerwerff, 1967).

5.6.12.4. Role of nickel in plant nutrition.

Nickel is present in minute amounts in most plants. Few reports are available on the apparent beneficial effects of nickel as a plant nutrient. In general, plants show even less tolerance to nickel ~~as compared~~ than to lead (Lagerwerff, 1967). Those cases involving apparent beneficial effects relate to foliar sprays of very dilute solutions of nickel salts. These sprays caused apparent yield improvements on potatoes and grapes (Vanselow, 1966).

See: Mishra & Kar 1974. Bot. Rev. 40:395-45

5.6.12.5. Nickel deficiency.

Nickel is not needed for plant growth.

5.6.12.6. Nickel toxicity.

Soil contamination from industrial sources of nickel is rare except near sources of mine tailings and their leachates. Most field studies of nickel contamination are of questionable value in assessing the specific toxicity of nickel, because of the concomittant influence of other elements (Yopp, 1974). The fact that nickel seldom causes phytotoxicity is not, however, a sufficient reason to disregard environmental contamination with this element. Table 5.6.12.6-1 indicates the common nickel concentrations in plant tissues (NAS, 1975).

Table 5.6.12.6-1. Common nickel concentrations in vegetables, fruits, grains, and their products.

Vegetable or Fruit	Nickel Concentration, ppm Fresh weight
Potato, raw	0.56
Peas, fresh, frozen	0.30
Peas, canned	0.46
Peas, split, dried	1.66
Beans, string, frozen	0.65
Beans, string, canned	0.17
Beans, navy, dried	1.59
Beans, yellow-eye, dried	0.69
Beans, red kidney, dried	2.59
Spinach, fresh	0.35
Celery, fresh	0.37
Beet greens	1.94
Swiss chard, organic	0.71
Escarole, fresh	0.27
Chicory, fresh	0.55
Lettuce, garden, organic	1.14
Lettuc, head	0.14
Kale, organic	1.12
Kohlrabi, leaves, organic	0.47
Cabbage, white	0.32
Cabbage, white	0.14
Cabbage, red	0.24
Cauliflower leaves	0.19
Broccoli, fresh, frozen	0.33
Tomato, fresh	0.02
Tomato juice, canned	0.05
Apple, raw	0.0
Apple, raw	0.08
Banana	0.34
Pear	0.20
Wheat, wint er, seed	0.16
Wheat, Japanese	0
Wheat, Japanese	0
Wheat flour, Japanese	0
Wheat flour, all-purpose	0.54
Wheat flour, all-purpose	0.30
Wheat, crushed, Vermont	0.75
Bread, whole-wheat, stone-ground	1.33
Wheatena	0
Wheaties	3.00
All-bran cereal	0.74
Grapenuts cereal	0.13
Buckwheat, seed	6.45
Rye, seed	2.70
Oats, seed	2.60
Oats, seed	1.71

Table 5.6.12.6-1 (continued)

Vegetable or Fruit	Nickel Concentration, ppm Fresh Weight
Oats, precooked, quick	2.35
Corn, frozen, fresh	0.70
Corn meal, New Hampshire	0
Corn oil	0
Rice, Japanese, polished	0.50
Rice, Japanese, unpolished	1.80
Rice, Japanese, polished (204 samples)	0.65
Rice, American, polished	0.47
Rice, puffed	0.30
Rye flour	0.23
Rye bread	0.21
Spinach	2.4
Squash	4.6
Tomato	0.01-0.15
Cabbage	3.30
Carrot, root	0.30
Carrot, leaves	1.80
Cress, water, tops	0.50
Cress, water, leaves	0.13
Mushroom	3.5
Pea	2.00
Potato	0.08-0.37
Onion	0.16
Lettuce	1.51
Cabbage	3.3
Lentils	1.61
Peas	2.25
Haricot beans	0.59
Tomato	0.154
Orange	0.46
Apricot	0.64
Plum	0.90
Pear	0.90
Fig	1.20
Corn, grain, mature	0.14
Oats, grain, mature	0.45
Oats, leaves, June	16-51
Oats, leaves, mature	7.00
Rice, polished	0.02
Buckwheat, seeds	1.34
Barley	1.34
Wheat, mature grain	0.35-35

Source: NAS (1975).

Under uncontaminated conditions, plants generally contain 0.005 to 5 ppm Ni with 1 ppm perhaps being the average concentration (NAS, 1975; Vanselow, 1966; Brady, 1974). The variability in plant uptake is apparent from studies on crop species, where Ni levels ranged from 0.3 ppm in carrots through 3.9 to 4.0 ppm in soybeans and wheat to 51 ppm in oats (Yopp et al., 1974). Some of these crops may have been grown in soils which were influenced by anthropogenic nickel sources such as contaminated fertilizer. Nickel levels of 56 ppm are non-toxic to certain grasses and 4,000 ppm Ni is non-toxic to Allysium (Yopp, 1974). Table 5.6.12.6-2 gives a list of nickel accumulating plants (i.e., these plants accumulate levels greater than what is found in the substrate and other co-existing plant species) commonly found on serpentine soils. These species have envolved special capacities to cope with the very high levels (e.g., 27% of ash) of nickel found in their systems. In these species, nickel usually remains in a low molecular weight, water soluble form and is not associated with any amino acids (Kelly et al., 1975).

In barley, buckwheat, and tobacco, tissue Ni levels of 0.5 to 8 ppm cause toxicity. Such tissue Ni levels may result from 2 ppm Ni in the free ion or exchangeable soil fraction (shown to be toxic to corn, oats, barley, buckwheat, dwarf green bean and pear) (Yopp et al., 1974). Table 5.6.12.6-3 presents values of plant tissue analysis for various stages of nickel toxicity.

Plant roots readily absorb nickel, but within the plant little is known about its mode of action. During translocation, nickel is believed to be carried as an anionic complex by amino acids and as a

TABLE 5.6.12.6-2. Nickel-accumulating plants and their common tissue nickel concentration.

			Nickel content (%)		
Species	Family	Locality	Plant ash	Soil	Plant/soil Ni ratio
*Alyssum bertolonii Desv.	Cruciferae	Italy	8.0	0.26	30.8
*A. murale Bieb.	Cruciferae	U.S.S.R.	10.0	0.50	20.0
*A. serpyllifolium Desf.ssp. lusitanicum	Cruciferae	Portugal	10.3	0.40	25.8
Dicoma niecolifera Wild	Compositae	Rhodesia	2.8	0.70	4.0
Homalium kanaliense Briq.	Samydaceae	New Caledonia	11.0	0.46	23.9
Hybanthus austrocaledonicus Schinz. et Guillaumin	Violaceae	New Caledonia	27.0	0.50	54.0
H. caledonicus (Turcz.)Cretz.	Violaceae	New Caledonia	10.9	0.67	16.3
H. floribundus (Lindl.) F. Muell.	Violaceae	W. Australia	10.0	0.07	143
Pimelea suteri Kirk	Thymelacaceae	New Zealand	0.59	0.33	1.8

*Closely related species variously classified in the past as A. argentea All. or A. alpestre L.

Source: Brooks, et al. (1974).

TABLE 5.6.12.6-3. Typical values of plant tissue analysis for nickel.

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	...	...	1.00-4.00	...	...
Alyssum (Alyssum bertholonii)	Field	Leaves	Mature	...	...	...	4000.00	...
	Field	Seeds	Mature	...	...	...	2500.00	...
Apricot (Prunus armeniaca)	Field	Fruit	Mature	...	...	0.65	...	...
Barley (Hordeum vulgare)	Field	Leaves	May, 1955	...	...	...	4.00-6.00	
Bean (Phaseolus spp.)	Field	Seeds	Mature	...	...	0.59	...	...
Bog asphodel (Narthecium spp.)	Field	Leaves & stems	Mature	...	...	0.40-5.30	...	...
Buckwheat (Fagopyrun spp.)	Field	Seeds	Mature	...	...	1.34	...	...
Bulrush (Scirpus cacspitosus)	Field	Leaves & stems	Mature	...	...	0.30-3.00	...	...
Cabbage (Brassica oleracea capitata)	Field	Tops	Edible	...	...	3.30	...	...

TABLE 5.6.12.6-3. Typical values of plant tissue analysis for nickel. (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
Carrot (Daucus carota sativa)	Field	Roots	Mature	...	...	0.30	...	...
	Field	Leaves	Mature	...	...	1.80	...	...
Cherry (Prunus cerasus)	Field	Fruit	Mature	...	...	0.50	...	...
CITRUS FRUITS (Citrus spp)	Greenhouse	Leaves	Young	...	...	0.40	...	55.00
	Greenhouse	Leaves	Mature	...	...	1.00	...	140.00
	Field	Leaves	Mature	...	...	2.00-4.00	...	...
	Pots	Leaves	Mature	...	...	0.70-1.80	...	...
	Field	Leaves	Mature	...	...	0.40-1.00	...	...
Clover, bur (Medicago hispida)	Field	Tops	Mature	...	...	1.00-2.00	...	...
Clover, red (Trifolium pratense)	Field	Tops	Mature	...	...	1.00	...	...
Coffee (Coffea spp.)	Field	Beans	Mature	...	...	0.40	...	...
Corn (Zea mays)	Field	Grain	Mature	...	...	0.14	...	...
Cress, water (Rorippa nasturtium-aquaticum)	Field	Tops	Mature	...	...	0.50	...	...
	Field	Leaves	Mature	...	...	0.13	...	...

TABLE 5.6.12.6-3. Typical values of plant tissue analysis for nickel.
(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
Fig (Ficus carica)	Field	Fruit	Mature	...	...	1.20	...	...
GRASSES								
Sweet vernal grass (Anthozanthum odoratum)	Field	Tops	Mature	...	...	0.70-1.70	...	...
Various grass spp.	Field	Tops	Mature	...	...	0.20-0.80	...	...
	Field	Tops	Mature	...	...	...	9.00-56.00	...
	Field	Tops	Mature	...	...	0.60-3.00	...	...
Heather and Heath (Calluna vulgaris)	Field	Tops	Mature	...	...	0.60	...	...
(Erica cinerea)	Field	Tops	Mature	...	...	1.50-1.70	...	...
(Erica tetralix)	Field	Tops	Mature	...	...	1.10-1.50	...	...
Mushroom (Cantharellus cibarius)	Field	Buttons	Edible	...	...	3.50	...	...
Oats (Avena sativa)	Field	Grain	Mature	...	...	0.45	...	...
	Field	Leaves	June	...	...	16.00-51.00	134.00	...
	Field	Leaves	Mature	...	...	7.00	32.00	...
	Pots	Tops	Mature	...	...	...	84.00-340.00	...
Onion (Allium cepa)	Field	Bulbs	Mature	...	...	0.16	...	...

TABLE 5.6.12.6-3. Typical values of plant tissue analysis for nickel.

(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	Mature	...	...	2.00	...	...
Pear (Pyrus communis)	Field	Fruit	Mature	...	...	1.30	...	...
Potato (Sulanum tuberosum)	Field	Tubers	Mature	...	...	0.25	...	...
	Field	Tubers	Mature	...	...	0.08-0.37	...	...
Rice (Oryza sativa)	Field	Grain	Polished	...	...	0.02	...	...
Sedge (Carez spp.)	Field	Tops	Mature	...	...	0.20-3.20	...	...
Soybean (Glycine soja)	Field	Seeds	Mature	...	...	3.90	...	...
Spinach (Spinacia oleracea)	Field	Tops	Mature	...	...	2.40	...	...
Squash (Cucurbita spp.)	Field	Fruit	Mature	...	...	4.60	...	...
Tea (Camellia sinensis)	Field	Leaves	Mature	...	...	3.00-5.00	...	...
Timothy (Phleum pratense)	Field	Tops	Mature	...	...	0.46	...	...

TABLE 5.6.12.6-3. Typical values of plant tissue analysis for nickel. (cont'd)

				Range in dry matter (ppm.)				
Plant	Type of culture	Tissue sampled	Age, stage, condition or date of sample	Showing deficiency symptoms	Low range	Intermediate range	High range	Showing toxicity symptoms
Tomato (Lycopersicon esculentum)	Field	Fruit	Mature	...	...	0.15	...	...
	Field	Fruit	Mature	...	...	0.01	...	...
Walnut (Juglans regia)	Field	Leaves	Mature	...	...	0.90-5.00	...	...
	Field	Meats	Mature	...	...	0.60	...	...
Wheat (Triticum SPP.)	Field	Grain	Mature	...	...	0.35	...	...
	Field	Grain	Mature	...	...	...	35.00	...
	Field	Grain	Mature	...	...	4.00	16.00	...

Source: Vanselow (1966).

chelate in the xylem systems (Tiffin, 1972; NAS, 1975). The chelate form is less stable and may be important in altering the biotoxicity of nickel within the plant (NAS, 1975).

The importance of airborne nickel may be slight in terms of phytotoxicity, but there is evidence that plants can absorb and translocate nickel salts in the airborne form (NAS, 1975). In studies with mustard, comparison of the relative efficacy of root and leaf absorption of Ni showed that roots were definitely the critical organs in nickel uptake. In this study roots contained four times the concentration of nickel accumulated in leaves and seven times that found in stems (Yopp et al., 1974).

Once inside the plant, nickel affects photosynthesis and other processes. In sunflowers, leaf tissue concentrations of 79 ppm nickel inhibited photosynthetic activity by 50%. The primary mode of action of nickel was interference with the stomatal function (Bazzaz et al., 1974b). At the molecular level, nickel acts apparently by interfering with the iron metabolism. For this reason, iron applications are often used to ameliorate nickel toxicity (Yopp et al., 1966; Lagerwerff, 1967).

Nickel toxicity most often occurs on serpentine soils and on heavily contaminated soils. It is often treated by additions of lime to raise the pH, or by additions of molybdemum, magnesius, nitrogen, and potassium, depending on the nutritional status of these elements. On the other hand, high levels of phosphorus and manganese have been shown to magnify the toxic effects of nickel (Vanselow, 1966; Yopp et al., 1974).

In cases of incipient nickel toxicity, no definite symptoms are expressed other than repression of the vegetative growth. In cases of moderate or acute nickel toxicity, chlorosis resembling iron deficiency symptoms are common. In cereals, leaf chlorosis appears in the form of white or light yellow and green striping (Vanselow, 1966; Anderson *et al.*, 1973). Table 5.6.12.6-4 presents more information on the symptomatology and toxicity tolerance levels for crop species.

Due to the lack of specific diagnostic features for nickel toxicity, indicator species are not generally recognized. However, when tissue analysis is used, nickel accumulating species are helpful in diagnosing nickel contamination. Besides the species listed in Table 5.6.12.6-2, birch, conifers, and grasses are efficient accumulators of nickel and have been used in nickel prospecting (Vanselow, 1966).

On the basis of the limited amount of data available, Yopp *et al.* (1974) concluded that the recommended maximum free or exchangeable nickel level in soils should be 2.0 ppm.

what extracting procedure

Table 5.6.12.6-4. Symptoms and threshold toxicity levels of nickel on seven crop species.

Plants by Economic Class	Growth Medium	Minimum Phyto-toxic Concen.	Plant Part Affected	Developmental Stage	Symptomology
Corn	defined nutrient medium	2.0 ppm	roots, leaves	seedling	chlorosis
Oats, var. Victory	defined nutrient med., sand cult.	2.5 ppm	leaves	"	"
Oats, var. Victory	defined soil type	9.0 ppm	"	"	"
Barley	defined nutrient	2.0 ppm	"	"	"
Alfalfa	defined soil type controlled pH	4.0 ppm	"	pre-reproductive	"
Buckwheat	defined nutrient	2.0 ppm	entire	"	"
Dwarf Bean	"	2.0 ppm	"	seedling	"
Pear	defined soil type	2.0 ppm	leaves	pre-reproductive	"

Source: Yopp et al. (1974)

5.6.13. Potassium (k)

5.6.13.1. Introduction.

Potassium is an essential macronutrient, needed in relatively large amounts, both by plants and animals. Few reports of potassium toxicity in plants or animals are available.

Potassium is a metal that is never found free in nature. It is a constituent of many insoluble minerals, but most of the metal and its salts are obtained by electrolysis of sylvite, carnallite, langbeinite, polyhalite and other minerals found in potash deposits in Germany, New Mexico, California, Utah and elsewhere. These deposits were formed in ancient lake and sea beds.

Potassium was first distinguished as an element in 1807 and as a plant nutrient in 1866. It is one of the most reactive and electropositive metals. It is also the second lightest metal known. Potassium is soft and silvery, but oxidizes very rapidly. It decomposes and ignites spontaneously in contact with water. Potassium is primarily used as a fertilizer, but it is also very important in industry and medicine as the hydroxide, nitrate, carbonate, chloride, chlorate, bromide, iodide, cyanide, sulfate, chromate, dichromate, and other forms.

The importance of potassium in soil chemistry, and plant and animal nutrition are well documented.

5.6.13.2. Sources of potassium.

a. Natural:

Potassium is the seventh most abundant element in the earth's crust, comprising up to 2.4% by weight. Soil potassium is derived principally from minerals such as feldspars and micas and from complex secondary aluminum silicates. In the latter group, clays, such as illite, are especially important (Brady, 1974). Soils high in fine-grained materials, such as clay and silt, have a higher percentage of potassium (Etherington, 1975). Overall, potassium ranges of 0.17 to 3.30 per cent can be expected, with humid region soils averaging 1.70% and arid region soils averaging 2.00%. Typical peat soils contain 0.08% (Brady, 1974).

b. Anthropogenic:

Potassium is probably emitted through many different human activities, but these are seldom of ecological significance. Potash fertilizers include potassium chloride, potassium sulfate, sulfate of potash-magnesia, manure salts, kainit, and potassium nitrate (Brady, 1974). The potassium content of commercial fertilizers can range from zero to more than half.

5.6.13.3. Biological availability of potassium.

a. Soil solid phase:

The total quantity of potassium in soils is usually relatively high, except in sandy soils. On the average, it is present in higher concentrations than any of the other macronutrients (i.e., nitrogen, phosphorous, calcium, magnesium, and sulfur). However, a very high percentage of the total soil potassium is held in unavailable form. Typically, less than 1% of the total potassium is in an exchangeable form (Brady, 1974). The remainder is present in the original feldspar and mica or, more commonly, is fixed within the lattice structure of secondary clay minerals (Brady, 1974; Bidwell, 1974).

The readily exchangeable fraction of potassium is adsorbed by clay particles or is complexed by the organic matter or is left in solution (Brady, 1974). The relationship between these three forms is illustrated by Figure

5.6.13.3-1. Only about 10% (i.e., 0.1-0.2% of total potassium) of the readily exchangeable fraction is actually in solution at any given time. Soil organic matter is generally much less important in holding potassium as compared to nitrogen, sulfur, phosphorous, and even calcium and magnesium (Brady, 1974; Etherington, 1975). Thus, most of the readily available potassium is adsorbed on clay particles, in an equilibrium with potassium in solution and potassium fixed in the lattice structure of clay particles.

b. Soil solution:

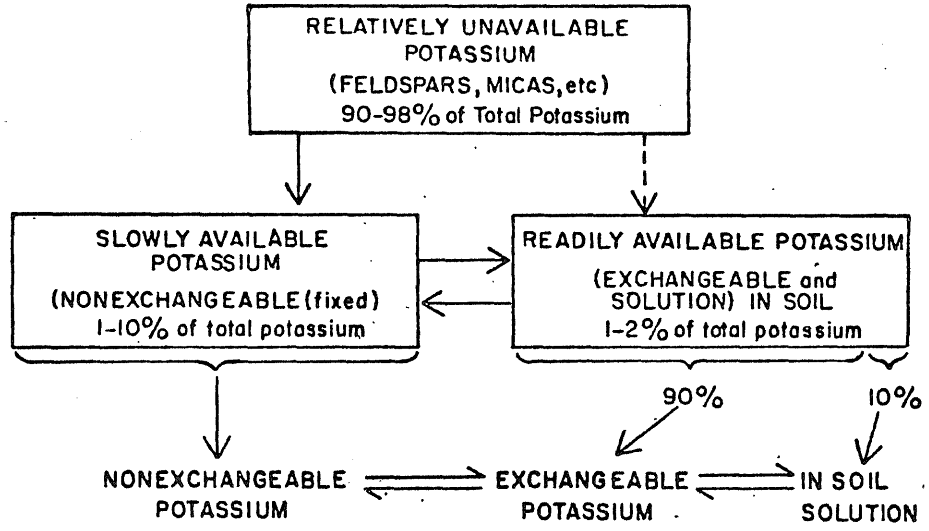
Chemically, potassium is a mobile element, its simple derivatives being very soluble in water (Etherington, 1975). However, it is also readily fixed by clay particles. This fixation safeguards the potassium from losses to leaching, but also may cause deficiencies to plants in extreme cases. Potassium in solution is usually in the cationic form K^+ (Brady, 1974).

c. Transition between solid phase and soil solution:

The potassium in solution will be in equilibrium with the exchangeable potassium. This, in turn, will be in equilibrium with the non-exchangeable potassium. These equilibria can be shifted, and hence the amount of potassium in solution modified through changes in pH. This relationship is less critical for K than is the case with other nutrients. This is mainly because of the relatively high total soil potassium. At high pH values (e.g., after lime applications) a greater proportion of the potassium will be fixed into clay lattices, and thus be less subject to losses by leaching (Brady, 1974).

357

Figure 5.6.13.3-1. Relative proportions and equilibria of soil potassium in different forms. From Brady (1974).


RELATIVELY UNAVAILABLE POTASSIUM
(FELDSPARS, MICAS, etc)
90-98% of Total Potassium
SLOWLY AVAILABLE POTASSIUM
(NONEXCHANGEABLE (fixed)
1-10% of total potassium
READILY AVAILABLE POTASSIUM
(EXCHANGEABLE and SOLUTION) IN SOIL
1-2% of total potassium
90%
10%
NONEXCHANGEABLE POTASSIUM
EXCHANGEABLE POTASSIUM
IN SOIL SOLUTION

5.6.13.4. Role of potassium in plant nutrition.

Though potassium is a very important plant nutrient, its functions in plant nutrition have not been entirely specified. It is the prevalent cation in plants and thus may be involved in maintaining the ionic balance in cells. Within the plant, potassium is highly mobile. Apparently, it does not play a structural role in plants, but is involved in a great number of reactions as a catalyst. In this role, potassium is involved in nearly every physiological function in plants. For example, in protein synthesis potassium does not seem to bind to the enzymes involved, but may act as a cofactor to create the right protein conformation, causing the exposure of active sites (Bidwell, 1974; Ulrich and Ohki, 1966). In respiration and carbohydrate metabolism, potassium is bound ionically to the enzyme pyruvate kinase (Bidwell, 1974)

The plant's need for potassium is highly specific; it is only occasionally and inefficiently replaced by sodium. Furthermore, more potassium is needed to activate enzymes dependent on its presence, as compared to other metallo-proteins (Bidwell, 1974). In photosynthesis, potassium apparently induces greater utilization of light. Conversely, respiration may at first be enhanced by potassium deficient conditions. Potassium is also involved in pigment formation, nitrogen metabolism, and carbohydrate metabolism. Putrescine, a diamine, is formed within potassium-starved plants (Ulrich and Ohki, 1966).

5.6.13.5. Potassium deficiency.

Potassium constitutes 25 per cent or more of the plant ash (Ulrich and Ohki, 1966). This is a higher concentration than any other element except silica in silica-accumulated plants. On a dry weight basis, the critical potassium level in leaves (i.e., concentration below which growth is retarded) ranges from 0.70% to 1.50% for most plants (Ulrich and Ohki, 1966). Table 5.6.13.5-1 presents data on the critical potassium levels for a number of plant species.

The types of soils in which potassium deficiencies are most likely to occur include (Ulrich and Ohki, 1966):

a. Light sandy soils which are easily leached.
b. Organic soils, such as peat and muck.
c. Acid sandy soils.
d. Soils that have been heavily cropped, leached, and eroded.
e. Soils that fix potassium into the nonreplaceable form.
f. Highly leached lateritic soils universally low in exchangeable potassium.

Also, excessive applications of calcium and magnesium may induce potassium deficiency, possibly by competition between exchange sites (Ulrich and Ohki, 1966).

Apical areas of plants have a strong priority for potassium. Thus, younger leaves and growing points will not show deficiency symptoms except in very severe cases. Potassium deficiency symptoms usually begin as a mottled chlorosis on recently matured leaves (Bidwell, 1974; Ulrich and Ohki, 1966). This characteristic symptom is usually referred to as a "scorch" and is caused by increased tyrosinase activity (Bidwell, 1974). The first stage in the symptomatology is an interveinal chlorosis near leaf margins. The chlorosis progresses from light yellow to tan, becoming necrotic and, finally, brown or scorched (Ulrich and Ohki, 1966). Leaves may curl in a characteristic manner. In trees, cases of extreme

TABLE 5.6.13.5-1. Critical potassium levels for selected crop species.*

Plant	Plant part	Age, stage, condition, or date of sample	Per cent potassium in dry matter
Alfalfa (Medicago sativa)	Middle stem	One tenth bloom	0.70
	Tops	One tenth bloom	1.00
	Tops	-	1.00
	Tops	-	1.25
	Tops	Hay stage	1.25
	Tops	-	1.00
	Tops	-	1.40
Almond (Prunus amygdalus)	Leaves	June-July	0.75
Apple (Malus spp.)	Leaves	Mature spur (June-July)	1.00
	Leaves	Shoots (Late July)	1.16
Apricot (Prunus armeniaca)	Leaves	Mature spur (June-July)	1.50
Barley (Hordeum vulgare)	Leaves	Old	0.92
	Stems	-	1.01
Clover, ladino (Trifolium repens hybrid)	Petioles	-	0.80
	Blades	-	0.90
Clover, subterranean (Trifolium subterraneum)	Tops	10 weeks old	0.80

*The critical nutrient concentration may be defined as that concentration at which growth begins to be retarded, compared with plants above the critical concentration. Plants below the critical nutrient concentrations are deficient; those above, nondeficient.

TABLE 5.6.13.5-1 (cont'd)

Plant	Plant part	Age, stage, condition, or date of sample	Per cent potassium in dry matter
Clover, white (Trifolium repens)	Tops		0.80
Corn (Zea mays)	Leaves	Sixth, at blossom stage	1.30
	Leaves	Sixth from base, at silking stage	1.00
	Leaves	Sixth	1.00
Cotton (Gassypium spp.)	Petioles	Youngest mature, 130 days old	1.00
Grape (Vitis spp.)	Petioles	Midseason	0.44
Olive (Olea europaea)	Leaves	Mature, from median position on last flush of growth (March or August)	0.50
Orange (Citrus sinensis)	Leaves	3 to 7 months old, from fruiting terminals	0.40
	Leaves	3 to 7 months old, from fruiting terminals	1.00
	Leaves	-	1.21
Pea (Pisum sativum)	Leaves	Pre-bloom, from eighth node	1.30
Peach (Prunus persica)	Leaves	Mature, from near base of current season's growth (June-July)	1.00
Peanut (Arachis hypogaea)	Leaves	First from main stem, at start of bloom	1.30

TABLE 5.6.13.5-1 (cont'd)

Plant	Plant part	Age, stage, condition, or date of sample	Per cent potassium in dry matter
Potato (Solanum tuberosum)	Petioles	-	0.50 (fresh weight)
	Petioles	Midseason	7.00
	Petioles	-	0.35 (acetic acid solution) (fresh weight)
Prune (Prunus domestica)	Leaves	-	1.00
Sugar beet (Beta saccharifera)	Blades and petioles	Mature (Na >1.50%)	1.00
	Blades	Mature (Na <1.50%)	1.00
Sugar cane (Saccharum officinarum)	Leaves	Punch samples, 4 months old	0.33
	Leaves	-	1.40
	Leaf laminae	From third fully opened leaf	1.08
	Leaf sheaths	From third to sixth leaves	2.25

Source: Ulrich and Ohki (1966).

deficiency may cause rosetting and dieback, resulting in a bushy growth habit. In cereal crops, reduced vigor often results in lodging and increased disease susceptibility. On the bio-chemical level, amino acids and sugars accumulate at the cost of proteins and polysaccharides (Bidwell, 1974). Table 5.6.13.5-2 provides specific symptomatology for potassium deficiences in a number of crop species.

Ordinarily potato, ladino clover, alfalfa, bean, tobacco, curcurbits, cotton, prune, tomato, and corn are more susceptible to potassium deficiency than are carrot, sugar beet, almond, lettuce, and cereals (Ulrich and Ohki, 1966).

5.6.13.6. Potassium toxicity.

The only case found in the literature of potassium excess involved over-application of potassium fertilizer to orange trees. When the dry weight K concentration in orange leaves exceeds about 2-2.4%, an incipient toxic reaction may occur (Ulrich and Ohki, 1966; Bidwell, 1974). In the early states, this involves fruit coarseness, while at much higher levels, leaf necrosis and other symptoms may develop (Ulrich and Ohki, 1966).

A more common result of over-application of potassium is the induction of secondary deficiencies of other nutrients in soils of low fertility. The deficiencies may occur either because of increased rate of plant growth or because of an inhibition of root absorption of these other elements. Magnesium deficiencies commonly results from this process, so also manganese, zinc, and iron deficiencies (Ulrich and Ohki, 1966).

Table 5.6.13.6-1 presents extensive tissue analysis data for plants growing under low, intermediate and high soil potassium conditions.

TABLE 5.6.13.5-2. Specific symptomatology of potassium deficiency for selected crops.

Plant	Visual symptoms
Alfalfa (Medicago sativa)	Leaflets chlorotic; small shite dots appear, later becoming necrotic and enlarging; the entire margins turn brown, tear, and produce a ragged appearance.
Apple (Malus spp.)	Leaves become bluish green; middle-aged leaves may show interveinal chlorosis, crinkling, marginal necrosis, or scorch, and remain attached to twigs for some time after they have dried up; fruit is poorly colored and small.
Barley (Hordeum vulgare)	Leaves become bluish green; older leaves turn yellow, then brown, and finally die at tips and margins; entire leaf dies eventually, resulting in scorch symptom; stalks are short and weak; grain is shriveled; plants show profuse tillering; flowering stems are few; in addition, leaves are narrow, with purplish-brown spots.
Bean (Phaseolus spp.)	Leaflets become chlorotic, with necrotic brown areas at margins between veins; leaflets curl or cup downward.
Beet (Beta vulgaris)	Leaves are bluish green around veins; surface is crinkled and margins curl downward; older leaves become yellowish to reddish brown between veins and at margins; stems of older leaves show brown spots and stripes; roots are dark and tend to rot; are poorly developed.
Begonia (Begonia semperflorens)	Lower leaves show necrotic areas at margins; leaves later turn brown and shed.
Blueberry (Vaccinium corymbosum)	Leaves show interveinal chlorosis; older leaves have necrotic spots and marginal scorch; terminal growing points abort.

TABLE 5.6.13.5-2 (cont'd)

Plant	Visual symptoms
Broad bean (Vicia faba)	Leaves become bluish green; leaf edges become black to brown, followed by marginal scorch; leaves form obtuse angle with stalk; internodes are short.
Broccoli (Brassica oleracea botrytis	Leaves become dark green, with browning of marginal and interveinal areas.
Brussels sprouts (Brassica oleracea gemmifera)	Leaves become bluish green, with browning of marginal and interveinal areas; leaves droop; sprouts are poorly developed.
Cabbage (Brassica oleracea capitata)	Leaves show yellowing; heads are soft, puffy, and small.
	Leaves become dark green, with surfaces crumpled and margins brown; older leaves show whitish-violet coloration and withering of tips.
Cabbage, red (Brassica oleracea capitata)	Leaves become pale red with bluish tinge; margins become brown and withered; surface is crinkled; heads are small, loose and of unhealthy color.
Cacao (Theobroma cacao)	Pale-yellow areas show in interveinal region near leaf margin, quickly becoming necrotic, but fusing together only after some time; marginal necrosis progresses much more rapidly between veins; yellow zone appears on inner surface of invading necrotic zone.
Calceolaria (Calceolaria integrifolia)	Young leaves become light green to yellowish green; older leaves develop necrotic areas at margins; area around petiole dries to dark brown or black; leaf centers show large spots with necrotic areas, are brittle and crinkled between veins, but are normal green except for affected areas.
Cantaloupe (Cucumis melo cantalupensis)	Leaves become light green; older leaves develop small brown and yellow necrotic spots and blister at margins; stems show longitudinal splitting; fruit splits at flower end.

TABLE 5.6.13.5-2 (cont'd)

Plant	Visual symptoms
Carnation (Dianthus caryophyllus)	Lower leaves turn brown and die; stems become limber; plants show greater susceptibility to disease.
Carrot (Daucus carota sativa)	Leaves are slightly chlorotic, followed by browning; roots are spindly; growth is short.
Cauliflower (Brassica oleracea botrytis)	Leaves become dark green; older leaves show yellowing and browning of margins and interveinal areas.
Celery (Apium graveolens dulce)	Leaves become dark green. There is curling of leaflets and brown coloration caused by necrosis; leaf stems are short, with necrotic areas.
Cherry (Prunus cerasus)	Leaves become bluish green; margins may be rolled forward, parallel with midrib; chlorosis occurs, followed by scorching or necrosis.
Chrysanthemum (Chrysanthemum vars.)	Leaves become gray-green, with slight mottling and characteristic browning of margins; leaves eventually shed.
Cineraria (Senecio cruentus)	Older leaves become mottled, with whitish-yellow markings at margins and between veins, followed by browning of margins.
CITRUS FRUITS Grapefruit (Citrus paradisi)	Topmost leaves die back; leaves are irregularly colored, pale, and bronzed; little fruit is produced.
Orange (Citrus sinensis)	Leaves show "fluting" or "tucking," as though midribs were too short; leaves curl and twist, showing a variety of chlorotic spotting patterns; fruit is thin-skinned and small, but of good color; juice content is high; acidity is a little low.

TABLE 5.6.13.5-2 (cont'd)

CLOVER	
Alsike (Trifolium hybridium)	Leaflets first show yellowish to white dots around tips and sides; entire margin become yellowish and dies as condition spreads toward the center; leaflets show cupping.
Crimson clover (Trifolium incarnatum)	Leaflets show yellowish-green to brown spots at tips and margins, followed by brown coloration and curling.
Red clover (Trifolium pratense)	Leaflets first show yellowish to white dots around tips and sides; entire margin becomes yellowish and dies as condition spreads toward the center; leaflets show cupping.
White clover (Trifolium repens)	Leaflets first show faint chlorosis, followed by development of necrotic shite dots at tips and sides, finally involving most of leaf; there is some cupping.
Coffee (Coffea spp.)	Young leaves are crowded together, becoming dark-colored between veins; leaves show irregular development.
Corn (Zea mays)	Leaves show yellow or yellowish-green streaks, and become corrugated; this is more pronounced on lower or older leaves, and is followed by tip and marginal scorch; tip ends of ears are poorly filled; stalks have short internodes; plants are weak and may blow down.
Cotton (Gassypium spp.)	Leaves show yellowish-white mottling, changing to light yellowish green; yellow spots occur between veins; the centers of these die, and numerous brown specks occur at tips and margins between veins; tips and margins curl downward; leaves finally become reddish brown, dry, and shed prematurely; bolls are improperly developed, with fiber of poor quality.
Cowpea (Vigna spp.)	Leaflets are more or less mottled, followed by necrosis and ragged appearance.

TABLE 5.6.13.5-2 (cont'd)

Plant	Visual symptoms
Cucumber (Cucumis sativus)	Leaves become bluish green near veins; leaf margins show bronzing and necrosis; young leaves are puckered or crinkled; fruit is constricted at stem end; growth is slow.
Currant, black (Ribes nigrum)	Leaves develop reddish-purple coloring, followed by marginal necrosis, finally turning brown; fruit ripens unevenly.
Currant, red (Ribes sativum)	Leaves become bluish green, followed by slight interveinal chlorosis and marginal necrosis or scorch of brown color, causing leaves to curl toward undersurfaces.
Flax (Linum usitatissimum)	Leaves show tip browning; stalks have few branches and short internodes; growth is characteristically stunted.
Fuchsia (Fuchsia hybrida)	Young leaves are slightly yellowish, and are rolled inward along margins; older leaves are dark green, with some browning in spots along margins and between veins.
Gardenia (Gardenia spp.)	Older leaves show marginal dying or necrosis.
Geranium (Pelargonium hortorum)	Young leaves become pale yellowish green with dark-green veins; older leaves become grayish yellow along margins and between veins; some yellow and brown spotting occurs between veins, with a distinct, rusty-brown ring around the center.
Gooseberry (Ribes spp.)	Leaves become bluish green with purple tints before necrosis or scorch occurs at margins; leaves finally turn brown and curl toward undersurface; defoliation is early.
Grape (Vitis spp.)	Leaves are yellow, with brown spots and necrosis; spots may fall out and leave holes; leaves then become brittle; fruit ripens unevenly.

TABLE 5.6.13.5-2 (cont'd)

Plant	Visual symptoms
GRASSES	
Canary grass (Phalaris canariensis)	Leaves show brownish coloration and withering at tips
Carpet grass (Axonopus affinis)	Leaves show browning or burning of tips.
Napier grass (Pennisetum purpureum)	Leaves show irregular brown spots, followed by firing of leaf tips and margins.
Hydrangea (Hydrangea macrophylla var.)	Lower leaves show necrotic areas, followed by browning at margins; plants fail to develop flower buds.
Kale or collard, curled (Brassica oleracea acephala)	Leaves become dark green; older leaves show yellowing and browning of margins and interveinal areas.
Lespedeza (Lespedeza spp.)	Leaflets become mottled and yellowish green; leaves die later, starting at tips.
Lettuce (Lactuca sativa)	Leaves become dark green; older leaves show marginal and interveinal necrosis.
Mangel (Beta vulgaris macrorhiza)	Leaves are bluish green around veins; surface is crinkled and margins curl downward; older leaves become yellowish to reddish brown between veins and at margins; stems of older leaves show brown spots and stripes; roots are dark and tend to rot; are poorly developed.
Oats (Avena sativa)	Leaves become bluish green; older leaves turn yellow then brown, and finally die at tips and margins; eventually, the entire leaf dies, resulting in scorch symptom; stalks are short and weak; grain is shriveled; plants show profuse tillering; flowering stems are few.

TABLE 5.6.13.5-2 (cont'd)

Plant	Visual symptoms
Onion (Allium cepa)	Older leaves first show slight yellowing, followed by wilting and death, appearing like crepe paper; dying and drying start at tips of older leaves; bulb formation is poor.
Parsnip (Pastinaca sativa)	Leaves become slightly chlorotic, followed by necrosis at margins and forward rolling of margins; growth is short.
Pea (Pisum sativum)	Leaves become dark green, with yellowing and firing of lower leaves at margins; leaflets are cupped downward; pods are poorly filled; growth is retarded.
Peach (Prunus persica)	Leaves on middle portion of current season's growth become crinkled and curled, followed by necrosis; affected leaves develop cracks, tears, and light-red or purple-red pigmentation; leaves may or may not shed; twigs are slender; fruit buds are few.
Peanut (Arachis hypogaea)	Leaves become light green, with necrotic areas around margins which may merge to produce scorched effect.
Pear (Pyrus communis)	Leaves show marginal necrosis or dark-brown scorch; twig growth is unusually poor.
Pecan (Carya illinoensis)	Leaves lose green color from margins toward veins, followed by necrosis of margins and interveinal areas, producing a rusty appearance and bronzing.
Pepper (chili; paprika) (Capsicum spp.)	Leaves show characteristic mottling at margins and between veins; leaf surface is crinkled.
Peppermint (Mentha piperita)	Leaves show yellowing, with brown spots between veins; leaves are small.

TABLE 5.6.13.5-2 (cont'd)

Plant	Visual symptoms
PINES	
Pitch pine (Pinus rigida)	Needles become bluish green; necrosis is common in needles surrounding terminal meristem, giving copper-colored effect; necrosis sometimes occurs at base of twig, starting at tips of needles.
Red pine (Pinus resinosa)	Needles become bluish green, with necrosis at tips near base of plant, turning needles tan to copper color.
Shortleaf pine (Pinus echinata)	Needles become bluish green; necrosis is common in needles surrounding terminal meristem, giving copper-colored effect; necrosis sometimes occurs at base of twig, starting at tips of needles.
White pine (Eastern) (Pinus stobus)	Needles of new growth become chlorotic, followed by necrosis with copper coloration.
Plum (Prunus domestica)	Leaves become bluish green; margins may be rolled forward parallel with midrib; chlorosis occurs, followed by scorching or necrosis.
Poinsettia (Euphorbia pulcherrima)	Yojng leaves are green; older leaves turn yellow at margins and between veins, followed by browning at margins; leaves remain attached to stem after dying; side branches appear on stems.
Potato (Solanum tuberosum)	Leaves are first bluish green; older leaves become yellowish, followed by necrosis and browning, starting from tips and margins; leaflets are cupped and crowded together; stalks (haulms) are slender, with short internodes, and may collapse prematurely; tuber flesh is bluish.
Primrose (Primula spp.)	Young leaves are the normal green; older leaves become yellow at margins and in spots elsewhere; veins remain green until leaf dies; flowers fade.

TABLE 5.6.13.5-2 (cont'd)

Plant	Visual symptoms
Radish (Raphanus sativus)	Leaves are bluish green in middle part, with margins pale yellow to brown; older leaves become deep yellow to bronze; stems may show bronze coloration; leases are thick and leathery, curling backward.
Rape (Brassica napus)	Leaves are bluish green; leaf surface is crinkled, with some chlorosis; older leaves droop, and show primature and simultaneous withering.
Raspberry (Rubus spp.)	Leaves show marginal necrosis or scorching and interveinal browning; growth may be poor.
Rice (Oryza sativa)	Leaves are bluish green when young; older leaves show irregular chlorotic and necrotic areas, turning red, with brown at tips; ears are long and thin; grain formation is poor.
Rose (Rosa spp.)	Lower leaves show marginal browning, with occasional purpling; color is poor; stems are weak.
Rutabaga (Brassica napobrassica)	Leaves are bluish green; leaf surface is crinkled, with some chlorosis; older leaves droop, and show premature and simultaneous withering.
Rye (Secale cereale)	Leaves become bluish green; older leaves turn yellow, then brown, and finally die at tips and margins; the entire leaf eventually dies, resulting in scorch symptom; stalks are short and weak; grain is shriveled; plants show profuse tillering; flowering stems are few.
Snapdragon (Antirrhinum majus)	Young leaves are yellowish green, with dark-green veins and reddish tinge along margins; older leaves are purplish green only on upper surface; necrosis occurs at margins and in spots elsewhere.

TABLE 5.6.13.5-2 (cont'd)

Plant	Visual symptoms
Soybean (Glycine soja)	Older leaves show irregular yellow mottling around margins of leaflets, merging to form yellow border at tips and margins, followed by yellowish-brown spotting of chlorotic areas and downward cupping of leaflets; dead tissue falls out, giving a ragged appearance; marginal firing may involved one-half of leaflets with centers and bases still green; roots are poor.
Spinach (Spinacia oleracea)	Leaves become slightly chlorotic, with necrosis at margins which causes curling and withering.
Strawberry (Fragaria spp.)	Leaflets show bluish-green coloration around mid-vein, with marginal scorch or necrosis; there is purpling of petioles, followed by necrosis.
Sugar beet (Beta saccharifera)	Leaves are bluish green around veins; surface is crinkled and margins curl downward; older leaves become yellowish to reddish brown between veins and at margins; stems of older leaves show brown spots and stripes; roots are dark and tend to rot; are poorly developed.
Sugar cane (Saccharum officinarum)	Young leaves are first dark green; as they grow older, leaves turn pale yellow and show definite reddish coloration on upper surface of midrib; older or lower leaves die back at tips and margins. but before they dry up, they show minute chlorotic spots between veins, followed by necrosis; stalks are short.
Sweet pea (Lathyrus odoratus)	Leaves are yellowed from bases upward, and only top leaves may show green; leaves shed early; plants are stunted.
Sweet potato (Ipomoea batatas)	Older leaves show chlorosis and necrosis at margins between veins, with downward cupping and some shedding; stems are few; growth is reduced.

TABLE 5.6.13.5-2 (cont'd)

Plant	Visual symptoms
Timothy (Phleum pratense)	Leaves become light green, with rust-brown tips; growth is stunted.
Tobacco (Nicotiana tabacum)	Lower leaves show typical mottling, beginning at tips and margins, when element has been deficient from the start; if shortage occurs during later growth, mottling may show first on upper leaves; chlorosis is closely followed by necrosis, which initially occurs as small flecks which enlarge and coalesce until most of the tissue between veins is involved; dead areas may fall out, giving a ragged appearance; leaves are bluish green, except where necrotic areas have turned brown to rusty; leaves are cupped at tips and margins; stalks are slender; roots are long, with few branches.
Tomato (Lycopersicon esculentum)	Lower leaves become yellowish or grayish green along margins and at tips, followed by necrosis, as with tobacco; dead areas turn brown, giving lower part of plant a bronzed appearance; stalks are slender, and may show necrotic areas in extreme cases; fruit ripens unevenly and lacks solidity.
Tung (Aleurites fordi)	There is partial chlorosis or necrosis of leaves in the interveinal areas. Chlorotic areas appear at margins between veins, and extend inward, followed by necrosis.
Turnip (Brassica rapa)	Leaves are bluish green; leaf surface is crinkled, with some chlorosis; older leaves droop, and show premature and simultaneous withering.
Wheat (Triticum spp.)	Leaves become bluish green; older leaves turn yellow, then brown, and finally die at tips and margins; the entire leaf eventually dies, resulting in scorch symptom; stalks are short and weak; grain is shriveled; plants show profuse tillering; flowering stems are few.

Source: Ulrich and Ohki (1966)

TABLE 5.6.13.6-1. Typical plant tissue analysis values for potassium.

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	Plant	August	0.44-1.02	...	1.26-2.30	...	...
	Field	Stems	One-tenth in bloom	0.48-0.94	...	1.50	...	...
	Field	Leaves	...	0.14	...	0.83	...	...
	Field	stems	...	0.83	...	0.91	...	...
Almond (Prunus amygdalus)	Field	Leaves	Mature, from spurs (June-July)	0.50	...	0.75	...	...
Apple (Malus spp.)	Field	Leaves	...	0.23-0.52	...	0.42-1.65	...	...
	Sand	Leaves	October	0.33-0.68	...	0.83-2.31	...	...
	Field	Leaves	July-Aug.	0.28-0.90	...	0.74-1.49	...	...
	Sand	Leaves	...	0.37-0.59	...	1.70-2.90	...	...
	Field	Leaves	September	0.25-0.45	...	0.51-1.28	...	...
	Field	Leaves	From middle of terminal shoots (July-August)	0.28-0.95	...	0.73-1.56	...	...
	Field	Leaves	Shoots (late July)	0.56-0.58	...	1.16-2.18	...	...
	Sand	Leaves	June	0.60-0.75	...	1.30-3.10	...	...
	Field	Leaves	July	0.60-0.75	...	1.01-1.83	...	...
	Field	Leaves	July-Oct.	0.45-0.93	...	1.53-2.04	...	...
	Field	Leaves	July-Sept.	0.79-1.10	...	1.00-2.08	...	...
	Sand	Delicious leaves	From shoots (May)	0.34-0.90	...	1.81-3.35	...	...
	Sand	McIntosh leaves	From shoots (May)	0.24-0.63	...	1.66-3.70	...	...
	Sand	Leaves	...	0.37	...	1.19-3.63	...	...
	Field	Leaves	March-April	0.41-1.25	...	1.31-2.21	...	...
	Field	Leaves	From mature spurs (June-July)	<0.50	...	>1.00	...	...

TABLE 5.6.13.6-1. Typical plant tissue analysis values for potassium. (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
Apricot (Prunus armeniaca)	Field	Leaves	From mature spurs (June-July)	1.00	...	1.50-2.00	...	...
Bean, lima (Phaseolus limensis)	Solution	Second petiole	Early-bloom stage	0.29-0.44	...	1.11-4.45	...	...
	Solution	Second petiole	Early-bloom stage	0.24-0.86	...	1.24-6.50	...	...
Blueberry (Vaccinium virgatum)	Sand	Rabbit-eye leaves	September	0.04-0.05	...	0.10-0.18	...	...
	Sand	Rabbit-eye stems	September	0.05-0.06	...	0.10-0.15	...	...
Broad bean (Vicia faba)	Field	Upper	May-June	0.58-1.19	...	1.05-1.75	...	...
Cacao (Theobroma cacao)	Sand	Leaves	...	1.67	...	2.81-3.27	...	...
	Field	Leaves	...	0.55-1.94	...	1.43-2.33 (some plants showed deficiency symptoms)	...	...
Carpet grass (Axonopus affinis)	Field	Clippings	Summer	0.37-1.40	...	0.43-1.56	...	...
Carrot (Daucus carota sativa)	Sand	Petioles	...	0.054-0.32 (sol. in 2% HAc) (fr.wt)	...	0.49-0.65 (sol. in 2% HAc) (fr.wt)	...	...

TABLE 5.6.13.6-1. Typical plant tissue analysis values for potassium.
(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
Cherry (Prunus cerasus)	Field	Montmorency leaves	July	0.39-1.82	...	2.06-2.13	...	...
	Field	Leaves	July-August	...	...	0.41-	...	...
	Field	Montmorency leaves	August	0.38-0.91	...	0.76-1.98	...	...
	Field	Leaves	From mid-shoot (July-August)	0.46-0.51	...	...	...	...
	Field	Montmorency leaves	...	0.62	...	0.93	...	...
CITRUS FRUITS								
Grapefruit (Citrus paradisi)	Field	Leaves	From fruiting terminals	0.16-1.10	...	1.10-2.16	...	...
Lemon (Citrus limon)	Sand	Leaves	October	0.05-0.30	...	1.55-2.62	...	...
Lime (Citrus aurantifolia)	Sand	...	...	0.42	...	...	...	...
Mandarin (Citrus reticulata)	Field	Satsuma leaves	From nonfruiting terminals	0.30-0.47	...	0.90-1.08	...	...
Orange (Citrus sinensis)	Field	Valencia & Navel leaves	10 months, spring-cycle from fruiting terminals	<0.30	0.30-0.70	0.70-1.50	1.50-2.00	>2.100
	Field	Valencia & Navel	10 months, spring-cycle, from fruiting terminals	<0.30	0.30-0.50	0.50-1.00	1.00-1.50	>1.50

TABLE 5.6.13.6-1. Typical plant tissue analysis values for potassium. (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	Valencia leaves	10 months, spring-cycle from fruiting terminals	<0.40	0.40-0.50	0.50-1.50	1.50-2.20	>2.20
	Field	Leaves	10 months, spring cycle from fruiting terminals	<0.25	...	>0.40	...	...
	Field	Valencia & Navel leaves	10 months, spring-cycle from fruiting terminals	...	...	>0.60	...	...
	Field	Valencia & Navel leaves	10 months, spring-cycle from fruiting terminals	...	...	0.50-1.20	...	...
	Field	Leaves	4-7 months, spring-cycle from nonfruiting terminals	<0.60	0.70-1.10	1.20-1.70	1.80-2.30	>2.40
	Field	Valencia leaves	4-7 months, spring-cycle from nonfruiting terminals	<0.60	0.70-1.10	1.20-1.70	1.80-2.30	>2.40
	Solution	Navel leaves	3-7 months, spring-cycle from fruiting terminals	<0.35	...	0.38-1.12	...	>2.00
	Sand; solution field	Valencia leaves	3-7 months, spring-cycle from fruiting terminals	<0.30	0.30-0.40	0.40-1.50	1.50-2.00	>2.00
	Field	Navel leaves	...	0.19	0.20-0.25	...	...	...
	Field	Shamouti leaves	3-10 months	0.25	...	...	...	...

TABLE 5.6.13.6-1. Typical plant tissue analysis values for potassium. (cont'd)

				Range in dry matter (ppm.)				
Plant	Type of culture	Tissue sampled	Age, stage, condition or date of sample	Showing deficiency symptoms	Low range	Intermediate range	High range	Showing toxicity symptoms
Corn (Zea mays)	Field	Leaves	...	0.58-0.78	...	0.74-1.49	...	...
	Field	Leaves	3rd from base, at tasseling	0.39-1.30	...	1.46-5.80	...	...
	Field	Lower stems	August	0.029-0.10 (% in sap	...	0.33-0.59 (% in sap)	...	...
	Field	Plant	Early	0.88-1.37	...	1.99-4.54	...	...
Cotton (Gossypium spp.)	Field	Petioles	...	0.60	...	>0.60	...	...
Cowpea (Vigna spp.)	Field	Petioles	...	0.0041 (2% HAc sol.) (fr.wt)	...	0.498 (2% HAc sol.) (fr.wt)	...	...
Currant, black (Ribes nigrum)	Field	Leaves	September	0.78	...	0.91-1.06	...	...
Currant, red (Ribes sativum)	Field	Blades	June	0.24-0.99	...	0.99-1.59	...	...
	Pots	Blades	...	0.35-1.45	...	0.89-3.16	...	...
Gooseberry (Ribes spp.)	Field	Leaves	From terminal shoots (June)	0.53-0.88	...	1.48-1.67	...	...
	Field	Leaves	Older, from current season's shoots (July)	0.77-0.91	...	1.93-4.24	...	...

TABLE 5.6.13.6-1. Typical plant tissue analysis values for potassium.

(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
Grape (Vitis spp.)	Field	Leaves	...	0.27-0.59	...	0.45-0.78	...	...
	Field	Leaves	September	0.23-0.61	...	...	...	...
	Field	Blades	September	0.22-0.41	...	0.41-1.27	...	...
	Field	Petioles	September	0.15-0.28	...	0.44-3.85	...	...
	Field	Concord petioles	July	0.22-0.55	...	0.85-1.62	...	...
	Field	Concord blades	Youngest mature (June-Sept)	0.42-0.55	...	0.83-1.30	...	...
	Field	Concord petioles	Youngest mature (June-Sept)	0.16-0.27	...	0.82-3.30	...	...
Oats (Avena sativa)	Field	Leaves	Before maturity	0.30-0.41	...	1.15	...	...
	Field	Leaves	...	1.12	...	2.33	...	...
Olive (Olea europaea)	Field	Leaves	Mature; from median position on last flush of growth (Mar. or Aug)	<0.30	...	>0.75	...	...
Pea (Pisum sativum)	Field	Leaves	...	0.21-0.25	...	0.50	...	...
	Field	Lower stems	...	0.004-0.033 (2% HAc sol.) (fr. wt)	...	0.50 (2% HAc sol.) (fr. wt)	...	...
	Sand	Stems	Flowering	0.22-0.38 (fr. wt)	...	0.76 (fr. wt)	...	...
Peach (Prunus persica)	Field	Leaves	From mid-terminal shoot (August)	0.55-1.16	...	2.36-3.41	...	...

TABLE 5.6.13.6-1. Typical plant tissue analysis values for potassium. (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
Peach (cont'd)	Field	Leaves	Mature; from near base of current growth (June-July)	<0.75	...	>1.50	...	...
	Field	Leaves	From 5-year old tree	0.59-1.35	...	1.58-2.65	...	...
	Field	Leaves	Current season (summer)	0.50-0.84	...	1.26-2.78	...	...
	Field	Leaves	Current season (lt.summer)	0.64-0.93	...	2.05-2.82	...	...
	Sand	Leaves	October	0.46-0.55	...	1.71-2.72	...	...
	Field	Leaves	...	0.56-0.93	...	1.50-2.41	...	...
	Field	Leaves	Median;from terminal shoot (September)	0.26-0.33	...	0.97-2.58	...	...
	Field	Leaves	Median;from terminal shoot (June-Aug.)	0.39-0.83	...	1.18-2.28	...	...
	Field	Elberta leaves	From median shoot (July)	0.51-0.55	...	1.95-2.22	...	...
	Sand	Leaves	From median part of shoot (June)	0.27-0.28	...	0.69-2.51	...	...
	Sand	Shoots	June	0.19-0.22	...	0.32-0.62	...	...
Peanut (Arachis hypognea)	Sand	Leaves	...	0.01 (water-soluble K) (fr.wt)	...	0.21- (water-soluble K) (fr.wt)	...	...

TABLE 5.6.13.6-1. Typical plant tissue analysis values for potassium. (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 (Pyrus communis)	Field	Leaves	Mature, on spurs (June-July)	<0.50	...	>1.00	...	...
	Field	Leaves	From middle of terminal shoots (August)	0.28-0.43	...	1.07-1.13	...	...
	Field	Leaves	Mature, on spurs (July-August)	0.35-	...	0.60- (Some showed deficiency symptoms)	...	...
Plum and prune (Prunus domestica)	Field	Plum leaves	From spurs (July)	0.22-0.66	...	0.77-2.57	...	...
	Field	Plum leaves	...	0.22-1.11	...	1.47-2.00	...	...
	Field	Plum leaves	From middle of terminal shoots (August-September)	0.32-1.82	...	1.58-3.30	...	...
	Field	Plum leaves	...	0.46	...	1.86	...	...
	Field	Plum	From mature spurs (June-July)	<0.75	...	>1.50	...	...
	Field	Prune leaves	...	...	...	>1.00	...	...
Potato (Solanum tuberosum)	Field	Leaves	Mid-stem (July)	3.00-3.51	...	5.85-6.79	...	...
	Field	Upper leaves	July-August	1.20-2.10	...	2.10-3.80	...	...
	Field	Leaves	Mid-stem (August)	1.55-3.19	...	5.19-6.34	...	...
	Field	Leaves	...	0.38-0.44	...	1.00	...	...
	Sand	Leaves	old, mid-stem	0.30-0.68	...	4.17-6.72	...	...
Raspberry, black (Rubus occidentalis)	Field	Leaves	Recently matured (August)	0.50-0.77	...	1.00-1.15	...	...

TABLE 5.6.13.6-1. Typical plant tissue analysis values for potassium. (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
Raspberry, red (Rubus idaeus)	Solution	Leaves	First 6, mature	0.57-1.02	...	1.47	...	...
	Solution	Petioles	...	0.31-0.74	...	2.97	...	...
Rhubarb (Rheum rhaponticum)	Field	Petioles	...	0.108 (sol. in 2% HAc) (fr.wt)	...	0.308 (so.in 2% HAc) (fr.wt)	...	...
Rose (Rosa spp.)	Sand	Leaflets	First 5 from terminal (May)	0.33-0.63	...	0.70 1.63	...	...
Rubber (Hevea brasiliensis)	Sand	Leaf laminae	Top whorl, 4-10 months old	0.40-0.50	...	1.10-1.60	...	...
	Sand	Leaf laminae	Second whorl 4-10 months old	0.30-0.40	...	1.00-1.40	...	...
Strawberry (Fragaria spp.)	Sand	Temple plant	...	0.25-0.81	... ...	1.29-1.80	...	...
	Sand	Leaves	February	0.10 (H_2O sol) (fr.wt.	...	0.32- (H_2O sol) (fr.wt)	...	...
	Sand	Fruit	February	0.027-0.051 (H_2O sol) (fr.wt)	...	0.107-0.210 (H_2O sol) (Fr.wt)	...	...
	Field	Climax leaves	May-July	0.45-0.99	...	1.10-1.95	...	...
Sugar beet (Beta saccharifera)	Field	Petioles	...	0.18	...	...	...	...
	Field	Leaves	...	0.43-0.93	...	0.94-8.00	...	...
	Field and solution	Petioles	Recently matured, with NA>1.50%	0.20-0.60	...	1.00-11.00	...	...

TABLE 5.6.13.6-1. Typical plant tissue analysis values for potassium. (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
Sugar beet (cont'd)	Field and solution	Blades	Recently matured, with Na>1.50%	0.30-0.60	...	1.00-6.00	...	...
	Field and solution	Petioles	Recently matured, with Na<1.50%	0.50-2.00	...	2.50-9.00	...	...
	Field and solution	Blades	Recently matured with Na<1.50%	0.40-0.50	...	1.00-6.00	...	...
Sugar cane (Saccharum officinarum)	Sand	Blades	Nov.-April	0.36-0.72	...	0.96-2.48	...	...
	Sand	Stems	Nov.-April	0.28-0.34	...	0.44-1.50	...	...
	Solution	Blades	Leaves 3,4, 5, and 6 with mid-ribs removed	1.00	...	1.90	...	...
	Solution	Leaf sheaths	...	0.90	...	2.40	...	...
	Solution	Stalks	Immature	2.40	...	4.45	...	...
	Solution	Stalks	Mature	0.14	...	1.30	...	...
Tea (Camellia sinensis)	Field	Leaves	New(7 months old)	0.61	...	0.91-1.12	...	...
	Field	Leaves	Old	0.48	...	0.95-1.25	...	...
Tobacco (Nicotiana tabacum)	Field	Leaves	September	2.79-3.70	...	4.37-5.29	...	...
	Sand	Top leaves	...	0.55-1.08	...	2.64-3.17	...	...
	Sand	Bottom leaves	...	0.42-0.51	...	2.44-2.83	...	..

TABLE 5.6.13.6-1. Typical plant tissue analysis values for potassium.
(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)	Sand	Leaves	April-May	0.96-1.23	...	1.55-3.76	...	...
	Sand	Stems	April-May	0.36-1.06	...	1.55-5.30	...	...
	Sand	Lower	April-May	0.30-1.00	...	1.40-2.40	...	...
	Sand	Upper stems	April-May	0.20-3.20	...	1.90-6.00	...	...
	Solution	Blades	From middle third (Feb.-June)	0.46-0.95 (+ Na)	...	...	...	...
	Solution	Blades	From middle third (Feb.-June)	0.30-0.70 (minus Na)	...	...	...	...
Tung (Aleurites fordi)	Field	Leaves	Median, from nonfruiting terminals (Sept.)	0.24-0.64	...	0.61-1.01	...	...
	Field	Leaves	...	0.41-0.74	...	0.70-0.92	...	...
	Field	Leaves	Mid-shoot (June-Oct.)	0.46-0.67	...	0.81-1.12	...	...
	Field	Leaves	August	0.40-0.60	...	0.80-1.00	...	2.50
Vanilla (Vanilla planifolia)	Gravel	Leaves	May	0.79	...	3.00	...	...
Walnut (Juglans regia)	Field	Leaf-	Terminal,	<0.50	...	>1.00	...	...

Source: Ulrich and Ohki (1966)

5.6.14. Sodium (Na)

5.6.14.1. Introduction.

Sodium is very important in animal nutrition, but only a few plant species require it for growth. It may be toxic to plants and animals in very high concentrations. Sodium plays a major role in soil-plant relationships in saline or alkaline soils.

Sodium is the most abundant element in the alkali metal group and is the sixth most abundant element overall in the earth's crust, comprising about 2.6%. It is never found in a free form in nature. The most common form of Na is sodium chloride (NaCl). Other sodium-containing minerals include soda niter, cryolite, amphibole, zeolite, and sodalite. Sodium is a soft, bright, silvery metal which is very reactive. It floats on water, and may ignite spontaneously with water. Products of Na are important to the paper, glass, soap, textile, petroleum, and chemical industries. The metal is used as an alloying agent and as a purifier in the metal industry and as a heat transfer agent in, for example, certain nuclear power plants. Compounds of sodium which are of the greatest industrial importance include common salt, soda ash (Na_2CO_3), baking soda ($NaHCO_3$), caustic soda (NaOH), Chile saltpeter ($NaNO_3$), di- and tri-sodium phosphates, sodium thisulfate (hypo, $Na_2S_2O_3 \cdot 5H_2O$), and borax ($Na_2B_4O_7 \cdot 10H_2O$).

The occupational exposure limit for sodium hydroxide is 2 mg/m^3.

The physical effects of excess sodium in the soil have been extensively studied, but the nutritional needs and chemical toxicity of sodium in plants are not understood completely.

Although this review will deal primarily with the biochemical effects of sodium, comments must be made about its importance in the so-called saline and alkaline soils. These soil types occur in arid regions where the rainfall is seldom more than 20 inches per year. With this low rainfall, little or no leaching occurs, thus leaving the base status high (Brady, 1974). In certain of these soils, drainage is impeded and surface evaporation becomes excessive, leading to soluble salt accumulation in the surface horizon. When the soluble salt content of the soil reaches or exceeds 0.2 per cent on the dry weight basis, and the pH is below 8.5, the soil is classified as saline. The primary salts involved are chlorides and sulfates of sodium, calcium and magnesium (Yopp et al., 1974). Alkali soils are usually defined as those soils with a pH of 8.5 or more, or with an exchangeable sodium content of 15% or more of the exchange capacity, or both (Brady, 1974).

The saline soils are sometimes called "white alkali" soils because of the white crust left by water evaporation. Such soils are unproductive because of the high salt concentration in the soil solution. Under certain conditions the salt concentration may reach 10,000 ppm. These concentrations affect plant growth by disrupting the normal osmotic mechanisms of water absorption by plant roots. In general, salt solutions in excess of 2,000 ppm are too concentrated to allow for the normal osmotic movement of water (and dissolved nutrients) from the soil solution into the plant roots (Yopp et al., 1974).

The low productivity of alkali soils may be caused by the same osmotic factors, or by the effect which high pH values have on nutrient availability. The availability of nitrogen, phosphorus, calcium, magnesium, iron, manganese, boron, copper, and zinc are all suboptimal at pH values above approximately 7.5 (Bidwell, 1974).

Thus, excess soil salt concentrations can severely impede plant growth on saline and alkaline soils. These effects are caused by extreme physical relations in the soil. However, these physical effects are not specific to sodium and often occur in soils without appreciable concentrations of sodium.

5.6.14.2. Sources of sodium.

a. Natural:

Since sodium is the sixth most abundant element in the earth's crust, it is generally ubiquitous in the environment. The sodium concentration in soil exchange complexes, normally range from 3 to 5 ppm, and in soil solutions it ranges from 10-500 ppm. Geologic sources of sodium would include common salt, soda niter, cryolite, amphibole, zeolite, sodalite, and other native minerals. Atmospheric sources of sodium, such as airborne sea salt, may contribute significantly to the naturally occurring sodium concentrations of some soils (Edwards, 1969).

b. Anthropogenic:

Many human activities may add sodium to the environment, but seldom in amounts directly toxic to plants. Soda ash, a critical ingredient in glass production and other industries, has been mentioned as being a possible concern. High levels of sodium may also be found along highways, where salt is commonly used as a deicing agent. Levels of 360-2900 ppm sodium have been found in urban plant tissue, whereas the rural controls contained only 10-22 ppm. However, the salt burn frequently seen on vegetation along highways is more often caused by osmotic and other physical effects rather than direct sodium toxicity (Yopp et al., 1974)

Since sodium is present in all plants, it is also present in fossil fuels, and therefore may be emitted by industries utilizing fossil fuels (e.g., coal-fired power plants). Also, water contains salts of sodium and other elements. Therefore, when water is used in cooling towers, the resultant plume may contain sodium in an aerosol form (McCune et al., 1974).

5.6.14.3. Biological availability of sodium.

a. Soil solid phase:

Sodium is very soluble, easily leached, and readily available. Clay particle adsorption of sodium in humid-region soils is weak compared to hydrogen, aluminum, calcium, magnesium, and potassium. Also, the ionic radius of Na is such that it is seldom fixed within the lattice structure of clay particles (Brady, 1974).

Sodium is readily complexed by soil organic matter (Brady, 1974; Tiffin, 1972). Frequently, in arid region soils, the humus fraction is saturated with sodium (Yopp et al., 1974). Such soils are referred to as "black alkali" soils.

b. Soil solution:

The overall concentration of sodium in the organic and inorganic exchange complex usually ranges from 3 to 50 ppm. In these normal, non-saline soils, the sodium concentration in the soil solution ranges from 10-500 ppm. The sodium in solution is in the cationic form Na^+ (Bidwell, 1974).

c. Transition of sodium between solid phase and soil solution:

Since sodium is highly soluble, its transition from mineral solids or colloid adsorption occurs very readily and is independent of pH.

5.6.14.4. Role of sodium in plant nutrition.

A few plant species require sodium for normal development, while other species have developed tolerance mechanisms to allow them to grow under saline or alkaline conditions. Together, these two groups of plants are referred to as halophytes or salt-loving (all other species may be termed mesophytes).

The plant species in which sodium is essential belong to the genera Atriplex and Halogeton (Yopp et al., 1974). Both these genera live in deserts. Atriplex (salt-bush) is an important forage plant, while Halogeton is a noxious and sometimes toxic weed. Atriplex apparently requires sodium for effective glycolysis. This plant absorbs large amounts of sodium, but actively translocates the excess Na to specialized gland cells on the leaf surfaces (Bidwell, 1974).

In the halophytes and certain other plants, sodium may partially replace potassium in potassium-dependent functions. Thus, significant responses to sodium on potassium-deficient soils, have been found with turnip, radish, rutabaga, table beet, cucumber, buckwheat, sugar beet, mangel, oats, carrot, cabbage, rape, barley, rye, wheat, millet, lettuce, and chicory. Similar responses were not found for corn, soybean, squash, onion, and potato. Some crops, for example, table beet, sugar beet, and mangel, show significant responses to sodium even when the potassium level is adequate (Lunt, 1966). Table 5.6.14.4-1 summarizes these sodium-potassium relationships for a number of plants.

5.6.14.5. Sodium deficiency.

In Atriplex vesicaria, tissue concentrations below about 350 ppm causes deficiency symptoms of cessation of growth, yellowing, smaller and fewer leaves, and development of necrotic areas along the tips and margins of cotyledons and older leaves. Potassium additions do not alleviate these symptoms. In Halogeton, sodium deficiency causes a reduction in turgidity (Lunt, 1966).

5.6.14.6. Sodium toxicity.

The plant toxicity properties of various alkali metals differ markedly: lithium is toxic to most plants; cesium is commonly toxic, but less so than lithium; rubidium is toxic at moderate concentrations, but may also replace potassium; sodium commonly replaces potassium, and is toxic only in relatively high concentrations; and potassium is essential to all plants and is generally non-toxic (Lunt, 1966).

The toxicity of sodium varies considerably between plant species. As with other elements,plants vary considerably in their ability to accumulate sodium and in their sites of accumulations. Some plants, such as Atriplex, accumulate relatively large amounts of sodium in their shoots, while others, such as mangrove trees which also inhabit saline environments, do not absorb sodium (Bidwell, 1974). Still other plants exclude sodium from their shoots, but accumulate considerable quantities in their roots. The exclusion process operative in, e.g., mangrove, is apparently metabolic, while the differences between root and shoot accumulation in the other plant species suggest two parallel but differing accumulation mechanisms (Lunt, 1966).

Table 5.6.14.4-1. Yield, quality, or growth response of some higher plants to sodium as related to potassium status.

Sodium essential	Response with ample potassium supply		Response with insufficient potassium supply	
	Large	Slight to moderate	Moderate to large	None to moderate
Bladder saltbush	Beet	Cabbage	African violet	Bean,white
(*Atriplex vesicaria*)	chard	Celeriac	Alfalfa	Buckwheat
	fodder	Coconut	Asparagus	Clover, red
	mangel	Kale	Barley	Corn
Halogeton glomeratus	sugar	Kale,	Broccoli	Cucumber
	table	marrowstem	Brussel sprouts	Grass
	Celery	Kohlrabi	Carrot	Bahia
	Spinach	Lupine	Chicory	Bermuda
	Turnip	Oats	Clover, ladino	carpet
		Pea	Cotton	Pensacola
		Radish	Flax	Bahia
		Rape	Grass	weeping love
		Rubber	pangola	*Lespedeza*
		Rutabaga	Sudan	*sericea*
		Salicornia	Horseradish	Lettuce
		herbacea	Millet	Onion
			Mustard	Parsley
			Rape	Parsnip
			Salsify	Peppermint
			Stock	Potato
			Tomato	Rutabaga
			Vetch	Rye
			Wheat	Soybean
				Spearmint
				Squash
				Strawberry
				Sunflower

Source: Lunt (1966)

The detrimental effects on plants of saline soils, though not specific to sodium, consist of reduced growth and other moisture stress problems. Table 5.6.14.6-1 presents information on the relative tolerance of a number of plants to salty soils. Culture experiments with some species show a specific-ion effect of sodium which is greater than the expected osmotic effect. Many of the species most sensitive to sodium, exclude the element from their tops, but accumulate it in the roots. In these species, root injury or disease may bring on a sudden rise in the sodium levels in the tops. Similarly, sodium in tree trunks may be released when the wood becomes senescent. Avocado, citrus, and some of the stone fruits are examples of plants which are relatively intolerant to moderate leaf tissue concentrations of sodium (Lunt, 1966).

The mechanisms of sodium toxicity are not well known. Excess sodium can displace other nutrients from exchange sites, and it may directly inhibit the absorption of essential calcium and potassium (Lunt, 1966; Yopp et al., 1974). Leaf injury caused by sodium excesses usually appears as necrotic areas on the tips, margins, or interveinal areas. Mottled or chlorotic conditions may be indicative of incipient sodium injury. Alfalfa often displays a reddish coloration and a collapse of petioles on soils with high exchangeable sodium levels. In other plants, depressed vigor, especially of the roots, may be the only symptom of excess sodium (Lunt, 1966).

Sprinkler irrigation with water high in sodium may lead to sodium toxicity by direct leaf absorption. In such cases, the symptomatology is the same as for root absorption (Lunt, 1966).

Table 5.6.14.6-1. Relative tolerance of selected plants to saline soils.

High Tolerance	Medium Tolerance	Low Tolerance
Alkali sacation	Alfalfa	Alsike clover
Bermuda grass	Barley	Apples
Canadian wild rye	Birdsfoot trefoil	Cabbage
Cotton	Carrots	Celery
Date palm	Figs	Ladino clover
Garden pea	Grapes	Lemon
Kale	Lettuce	Orange
Milo	Oats	Peach
Rape	Olives	Pear
Rescue grass	Onions	Peas
Rhodes grass	Rye	Plum
Salt grass	Sweet clover	Potatoes
Sugar beets	Sudan grass	Red clover
Western wheat grass	Tomatoes	White clover

Source: Brady (1974).

The only effective means of dealing with excess soil sodium is by flushing or deep leaching of the soil with large quantities of low-salt water.

Yopp et al., (1974) cite one author who suggested a general threshold toxicity level of 5,000 ppm sodium in plant tissue. In view of this very high level, and of the naturally occurring, variable but relatively high levels in soils and plants, no maximum recommended level for soil sodium can be specified.

5.6.15. Zinc (Zn)

5.6.15.1. Introduction.

Zinc is an essential micronutrient for plants, but it may also become phytotoxic in relatively large concentrations. In animals, zinc plays many critical nutritional roles, such as in the enzymes carbonic anhydrase and lactic dehydrogenase and possibly in RNA biosynthesis. In humans, zinc may be important in preventing schizophrenia and other neurological disorders (England, personal communication, 1976). In large quantities, zinc can cause respiratory problems from the inhalation of zinc fumes, dermatitis from skin contact with zinc salts, and acute poisoning from ingestion. In nearly all cases, these illnesses are reversible and non-fatal. Probably, the most common ailment associated with zinc is "metal-fume fever," a non-fatal self-limiting disease caused by zinc oxide fumes and consisting of fever, nausea, and aches. Zinc oxide fumes were the principal agents responsible for the Donora air pollution incident of 1948 in Pennsylvania (Athanassiadis, 1969). The occupational exposure limit for zinc oxide fumes if 5 mg/m^3 and for zinc chloride fumes 1 mg/m^3, both averaged over an eight-hour period. The normal dietary consumption of zinc is 10-15 mg/day for most people (Athanassiadis, 1969).

The zinc alloy, brass, is mentioned in the Bible, but metallic zinc was not produced until the 13th century, in India. In Europe, the element was not rediscovered until 1746. The common ores of zinc are sphalerite or blende (a sulfide), smithsonite (a carbonate), calamine (a silicate), and franklinite (a zinc, manganese, and iron oxide). Zinc is a bluish-white, lustrous metal. It is brittle at room temperature and is a fair conductor of electricity. At high temperatures, zinc burns in air with the evolution of white clouds of the oxide. Some of the more important alloys of zinc include brass, nickel silver, typewriter metal, commercial bronze, spring brass, German silver, soft solder, and aluminum solder. Zinc is also used extensively to galvanize iron to prevent corrosion. Zinc oxide, a unique and very important compound to civilization, is used in paints, rubber products, cosmetics, floor coverings, plastics, printing inks, soaps, storage batteries, textiles, electrical equipment, and other products. In medicine, zinc oxide is important in pharmaceuticals and as zinc oxide ointment, an insoluble, astringent, and antiseptic wound dressing. Zinc sulfide, chloride, and chromate are also important compounds.

Zinc's essentiality to plants and animals is well documented, as are plant deficiency symptoms and cures. The role of Zn in the physiological processes of plants is fairly well known, but plant toxicity has not received the same thoroughness of research.

5.6.15.2. Sources of zinc.

a. Natural:

Zinc has an ionic radius similar to Fe^{++} and Mn^{++} and, like copper, forms strong covalent bonds with sulfur. Therefore, zinc is most commonly associated with basic and sulfur-containing minerals in igneous formations. In the earth's crust, zinc is present at a concentration of 70 ppm. In basaltic rocks, zinc levels average 100 ppm, while in granite rocks the average is only 40 ppm. In sedimentary formations, shales hold most of the zinc, containing about 95 ppm. Limestone and sandstones contain only 20 ppm and 16 ppm zinc respectively (Krauskopf, 1972).

The most common zinc containing minerals are sphalerite, a sulfide (ZnS); smithsonite, a carbonate ($ZnCO_3$); and hemimorphite, a silicate ($Zn_4(OH)_2Si_2O_7{}^{\circ}H_2O$) (Krauskopf, 1972; Athanassiadis, 1969; Brady, 1974). Of these, the sulfide sphalerite (or zinc blende) is the most common and widespread, often appearing in combination with lead and iron sulfides (Athanassiadis, 1969; Krauskopf, 1972). Most ore-grade deposits of sphalerite have cadmium associated with them, as a coating or solid solution (Athanassiadis, 1969). In the silicates, such as hemimorphite, zinc usually replaces manganese or iron, though zinc may form silicate minerals on its own (Krauskopf, 1972). Zinc may also be high in such minerals as ilmenite and magnetite, which resist weathering in the soil (Norrish, 1975). Zinc is much more electropositive than copper and hence is more difficult to reduce. Consequently, natural occurrences of the native metal are very rare (Krauskopf, 1975).

Sphalerite and other zinc minerals are highly soluble. Therefore, compared to copper, zinc commonly migrates farther from its source and becomes widely distributed in soils and waters. Atmospheric distribution is not, however, thought to be a significant factor in determining the natural levels of soil zinc, though zinc chloride is one of the more volatile (Krauskopf, 1972) compounds.

b. Anthropogenic:

In 1967, a total of 1,591,997 tons of zinc was used in the United States (Athanassiadis, 1969). Table 5.6.15.2-1 shows that the leading domestic producers of zinc are located in Tennessee, New York, Idaho, and Colorado. As discussed previously, most of this zinc is used

Table 5.6.15.2-1. Mine production of recoverable zinc in the United States, 1967 (in tons).

State	1963	1964	1965	1966	1967
Tennessee	95,847	115,943	122,387	103,117	113.065
New York	53,495	60,754	69,880	73,454	70,555
Idaho	63,267	59,298	58,034	60,997	56,528
Colorado	48,109	53,682	53,870	54,822	52,442
Pennsylvania	27,389	30,754	27,635	28,080	35,067
Utah	36,179	31,428	27,747	37,323	34,251
Wisconsin	15,114	26,278	26,993	24,775	28,953
New Jersey	32,738	32,926	38,297	25,237	26,041
Washington	22,270	24,296	22,230	24,772	21,540
New Mexico	12,938	29,833	36,460	29,296	21,380
Illinois	20,337	13,800	18,314	15,192	20,416
Virginia	23,988	21,004	20,491	17,666	18,846
Arizona	25,419	24,690	21,757	15,985	14,330
Oklahoma	13,245	12,159	12,715	11,237	10,670
Missouri	321	1,501	4,312	3,968	7,430
Kentucky	1,461	2,063	5,654	6,586	6,317
Kansas	3,508	4,665	6,508	4,769	4,765
Montana	32,941	29,059	33,786	29,120	3,341
Nevada	571	582	3,858	5,827	3,035
California	101	143	225	335	441
North Carolina	13				
Oregon	3	*	*		
Total	529,254	574,858	611,153	572,558	549,412

* Withheld to avoid disclosing confidential data of individual companies; excluded from total.

Source: Athanassiadis (1969).

in the metal industry either as an alloy or as a protective plating. It is in these settings, and in the reduction of zinc ores, most of the human toxicity occurs. However, given the nearly universal presence of zinc in soils, and the widely varying soil and plant adaptability to zinc, the chances of significant soil contamination from anthropogenic sources are slight.

While surface mining of zinc and other elements may produce zinc dusts and zinc fumes, no instances of human illnesses have been reported associated with these sources. In addition, no reports have been found on soil or plant damage from these sources (Athanassiadis, 1969). Leachates from spoil heaps can, however, contaminate soils and injure vegetation (Lagerwerff, 1967).

Smelting of copper, nickel, lead, and other metals can result in very high emissions of zinc, but the resultant soil and vegetation damage cannot be attributed solely to zinc (Nash, 1975; Shimwell and Laurie, 1972; Little and Martin, 1972). Similarly, zinc emissions from zinc smelters are nearly always accompanied by cadmium and, to a lesser extent, lead (Jordan, 1975; Lagerwerff and Specht, 1971). In a study of the Palmerton Pennsylvania area, where zinc ores have been smelted since 1898, Jordan found surface soil concentrations of 8% zinc, 1500 ppm cadmium, 1200 ppm copper, and 1100 ppm lead. Tree foliage in this area was found to contain as much as 4500 ppm zinc and 70 ppm cadmium (washed, oven-dried, and by weight). From a series of culture experiments and tests for soil availability of the metals, Jordan concluded that only zinc was present in concentrations sufficient to cause the massive vegetation damage occurring in the area (Jordan, 1975).

Besides metal extraction and processing, other anthropogenic sources of zinc include:

1. Sewage sludge and effluents (Lagerwerff, 1967). Municipal sludge may contain as much as 19,000 ppm zinc.
2. Fossil fuel burning activities (Lagerwerff and Specht, 1971).
3. Fertilizers.

   Zinc is a common contaminant in fertilizers, especially superphosphate fertilizers (Lagerwerff, 1967). In the past, this helped to prevent zinc deficiency in crops on which the fertilizers were used. The highly refined commercial fertilizers being currently used, however, contain very little zinc, raising the question in some people's minds of impending wide-scale zinc deficiencies in crops in this country (Viets, 1972).

   Fertilizers in which the primary active ingredient is zinc are also commonly used, especially on rice, sorghum, corn, and pecans (Cunningham, 1972). Table 5.6.15.2-2 lists data on the U. S. consumption of zinc fertilizers by region for the period 1967 to 1970.
4. Pesticides.

   Zinc represents the metal component of several successful fungicides used as foliar applications to prevent, for example, early blight on tomato and similar diseases on potato (Yopp et al., 1974; Chapman, 1966a; Lagerwerff, 1967).

Table 5.6.15.2-2. Consumption of zinc fertilizers in the United States.

Region of application	Quantity sold, metric tons on elemental basis		
	1967-68	1968-69	1969-70
New England	178.7	79.9	93.0
Mid-Atlantic	287.4	1,455.8	847.4
South Atlantic	3,465.5	5,859.7	4,373.4
East North Central	1,540.5	1,848.6	1,397.3
West North Central	4,462.7	3,777.7	3,754.7
East South Central	256.3	681.6	894.1
West South Central	734.0	725.3	1,307.9
Mountain	768.9	1,501.2	1,152.9
Pacific	1,346.5	2,246.4	1,618.4
Alaska, Hawaii, Puerto Rico	5.0	1.7	0.8
United States	13,045.5	18,177.9	15,439.9

Source: Cunningham (1972).

5. Other agricultural practices.

Zinc deficiencies in trees are sometimes corrected by driving galvanized nails into their trunks. Researchers have found that plants grown in the vicinity of galvanized iron may suffer from zinc toxicity (Chapman, 1966). Milbocker (1974) reports zinc toxicity in corn grown on an artificial substrate of sphagnum peat and ground rubber tires. In this case, the growth of corn was severely retarded by excessive amounts of zinc leached from the rubber.

5.6.15.3. Biological availability of zinc.

a. Soil solid phase:

Zinc is a very widespread metal. It is present in nearly all igneous rocks, and, because of human activities, is also present in trace amounts in the atmosphere. The national 24-hour average atmospheric concentration of zinc was 0.67 ug during 1960-64. The peak during that period occurred in 1963 in East St. Louis, Illinois, when a 24-hour average concentration of 58.00 ug/m^3 was recorded (Athanassiadis, 1969).

Total zinc in soils varies from 10 to 300 ppm, with values of 60-100 ppm being most common. Zinc is usually more concentrated in the surface than in the subsurface horizons (Chapman, 1966a).

The soil chemistry of zinc is relatively straightforward. In soils, zinc may be a component of resistant ilmenite, magnetite, etc., or more soluble sulfides or silicates (Norrish, 1975). Once released from the parent minerals, zinc will be in solution as Zn^{++} or $Zn(OH)^+$ (Quirk and

Posner, 1975). Zinc is readily adsorbed by clay minerals and this mechanism accounts for the generally small concentration of Zn^{++} solution. Secondary minerals, such as Zn $(OH)_2$, Zn $(OH)_4^{2-}$, ZnO (zincite), $ZnCO_3$ (smithsonite), $Zn_4(OH_2)Si_2O_7.H_2O$ (hemimorphite), Zn_2SiO_4 (willemite), and sphalerite, are quite soluble at normal pH values and hence are inaffective at binding the available Zn^{++}. To the extent that secondary zinc minerals are formed in the soil, the process occurring only at unusually high zinc concentrations, the most likely Zn sources are smithsonite, hemimorphite, and the clay mineral sauconite (Krauskopf, 1972).

In an extensive study of New York and Colorado soils, zinc was found to be complexed 28% to 99% with only 0.03 - 3 uM remaining in solution (Loneragan, 1975). Zinc is complexed by clay minerals or by fine-grained constitutent adsorption, or by organic complexing or chelation. Analysis of a Tennessee soil showed that 30% to 60% of the zinc was associated with fine grained Fe_2O_3 minerals and 20% to 45% was associated with clay minerals (Krauskopf, 1972). Norrish (1975) reports a similar study where 45% of the zinc was associated with the free iron oxides, and 35% with clay minerals. In a third study, 15% of the zinc was associated with manganese oxide particles. According to Norrish (1975) the zinc fraction associated with iron and manganese oxides may be the soil component most available to plants.

Zinc holds its double ionic charge up to pH values higher than that exhibited by Cu^{++}, but the covalent bonding of zinc to clay minerals is weaker than the covalent bonding of copper. Together, these two factors result in zinc being slightly less strongly adsorbed by clay minerals than copper (Krauskopf, 1972). Using the isotope Zn^{65}, the relative adsorption capacity of three common clay minerals was found to be the following: vermiculate > montmorillonite > kaolinite (Lagerwerff, 1974).

Zinc can also enter the lattice structure of clay minerals, thus becoming relatively unavailable to plants. For example, sauconite is a montmorillonitic clay in which zinc is the primary constituent (approximately 30% ZnO) (Norrish, 1975). In other montmorillonites, zinc replaces aluminum. In magnesium-containing clay minerals, zinc often replaces magnesium and in Ca-montmorillonite zinc can replace calcium (Ellis and Knezek, 1972).

Soil organic matter forms very stable complexes and chelates with Zn^{++} (Loneragan, 1975; Ellis and Knezek, 1972). At high pH values, this process of making zinc unavailable may result in zinc deficiencies (Lagerwerff, 1967; Yopp et al., 1974).

b. Soil solution:

The predominant zinc ion in the soil solution is Zn^{++}, though under certain circumstances $ZnOH^+$ and $ZnCl^-$ may also be present (Bidwell, 1974). The total zinc in solution usually ranges from 0.1 to 0.3 ppm where the exchange complex harbors 3 to 20 ppm (Bidwell, 1974). Total soil zinc may range from 10 to 250 ppm (Brady, 1974).

c. Transition of zinc between solid phase and soil solution:

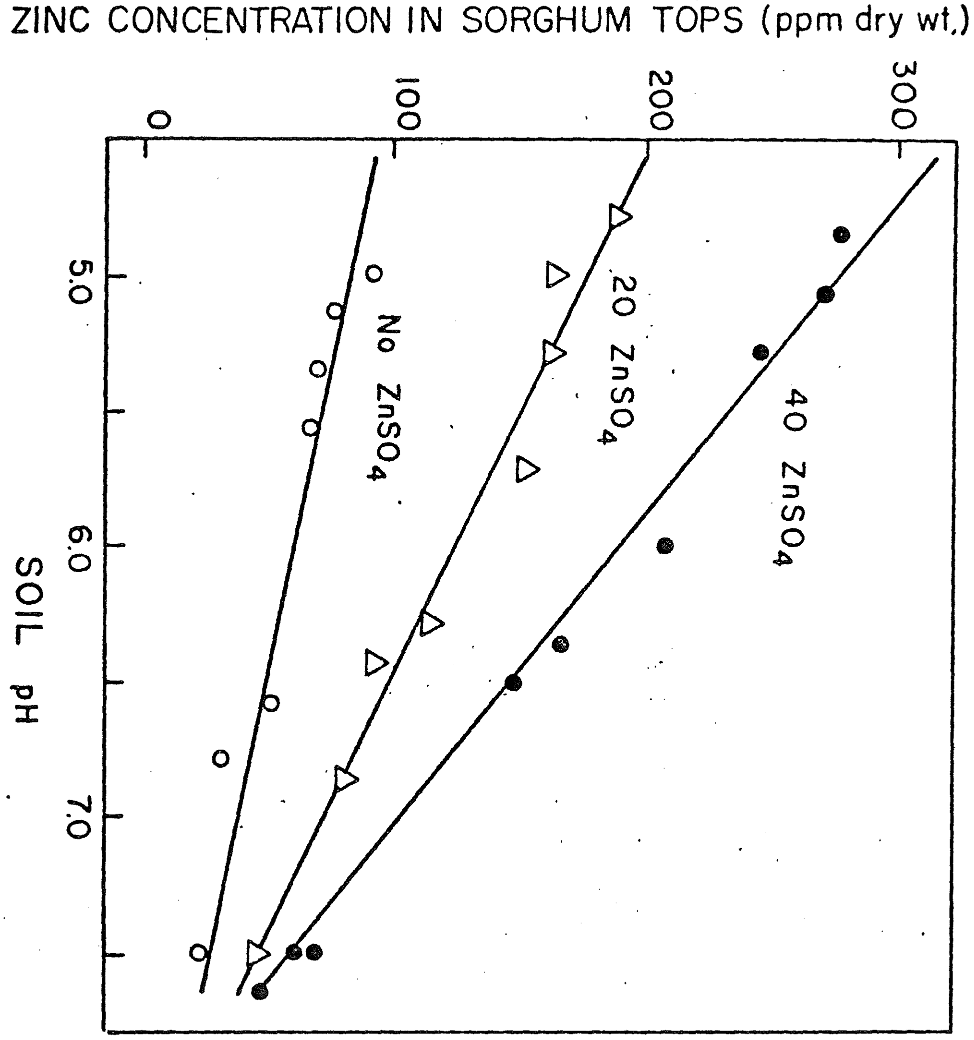
The transition of zinc between the soil solution and the various solid states is primarily dependent on the pH. Like copper and manganese, zinc is most available under acidic conditions, becoming relatively unavailable at pH values above 7.5 to 8 (Brady, 1974; Bidwell, 1974). This positive correlation in bonding strength with pH is true not only with clay minerals and fine-grained oxide particles, but also with organic complexes and chelates (Loneragan, 1975). The relationship between soil pH and zinc availability as indicated by plant tissue analysis values is shown in Figure 5.6.15.3-1. In this study it was found that the availability of Zn depended primarily on the effect of pH on soil colloids (Loneragan, 1975).

As with iron, manganese, and other essential elements, biological activity of soil microorganisms as well as plant roots enhances the availability of zinc in localized areas. Dilute acids, chelates, pectin, and other organic compounds present in the mucilaginous slime and other secretions from young plant roots reduce or otherwise release zinc from the surrounding soil. In addition, some of these excretions have been shown to stimulate the activity of microorganisms, which in turn affect the supply of zinc and other trace elements. Some of these microorganisms can even accelerate the release of zinc from otherwise insoluble silicates (Loneragan, 1975).

5.6.15.4. Role of zinc in plant nutrition.

The absorption of zinc by plant roots is metabolically controlled, i.e., zinc is actively absorbed (Loneragan, 1975). The chemical species absorbed is Zn^{++} (Brady, 1974). Once within the roots, zinc is readily moved throughout the plant. Once fixed at a site Zn has only limited mobility, being controlled by the zinc status of the plant. For example, subterranean clover plants growing under conditions of luxurious Zn levels, may translocate up to 25% of the zinc in old leaves and petioles to developing fruit, while plants growing under moderate or deficient zinc conditions may translocate very little or no zinc to the fruit. Oats behave similarly (Loneragan, 1975).

Figure 5.6.15.3-1. Relationship between zinc concentration in sorghum tops and pH of Norfolk sandy loam soil. From Loneragan (1975).


ZINC CONCENTRATION IN SORGHUM TOPS (ppm dry wt.)
0
100
200
300
SOIL pH
5.0
6.0
7.0
No ZnSO4
20 ZnSO4
40 ZnSO4

Once within the plant, zinc plays many important functions. Zinc is an essential element of several key enzymes. For example, in carbonic anhydrase, zinc constitutes approximately 0.2-0.3% (Nicholas, 1975). This enzyme is present in animal erythrocytes, and in plants it catalyzes the reversible reaction of CO_2 and water (Boardman, 1975). Carbonic anhydrase may also be important in certain of the dark phase reactions in photosynthesis, such as facilitating the diffusion of CO_2 to the chloroplasts, and catalyzing the dehydration of carbonic acid at the site of carboxylation (Boardman, 1975; Dwivedi and Randhawa, 1973). Zinc is also an essential constituent of NAD-linked alcohol dehydrogenase and glutamic dehydrogenase. Lactic dehydrogenase is another enzyme in which zinc is an essential component (Nicholas, 1975).

Zinc appears to be important in the synthesis of DNA in plants, since it is a constituent of the enzyme deoxyribonucleic acid polymerase I (Nicholas, 1975). Zinc is also somehow involved in RNA synthesis and is a constituent of the enzymes carbonic anhydrolase and carboxypeptidase (Dwivedi and Takkar, 1974; Yopp et al., 1974; Nicholas, 1975).

5.6.15.5. Zinc deficiency.

Zinc deficiencies are most likely in the following soils (Chapman, 1966a):

a. Acid, leached, sandy soils where total zinc is low.
b. Alkaline soils where zinc availability is decreased.
c. Soils derived from granites, gneisses, etc.
d. Old corral sites and Indian burial grounds.
e. Some organic soils where zinc is tied up in forms that are not easily available to plants.

f. Soils containing clays with low Si/Mg ratios. In these soils, zinc may be fixed in unavailable forms.

g. High-phosphate soils caused by excessive use of phosphate fertilizers.

h. Other soils subjected to farming practices which enhance the adsorption or complexing of zinc, such as liming, prolonged nitrogen fertilization, and excessive additions or build-ups of organic matter.

Zinc deficiency may also be caused by high nematode populations in the soil, and by the concentrations of certain other metals (Sharma et al., 1971). For example, when zinc concentrations in solution are low, additions of phosphorus may greatly reduce zinc uptake, causing deficiencies, while phosphorus additions to zinc-rich soils may greatly increase zinc uptake causing toxicity (Wallace at al., 1974; Yopp, et al., 1974). Some of this zinc-phosphorus interaction may be explained by changes in the soil chemistry, but it is thought at high zinc levels. the antagonism is mainly due to physiological processes within the plant (Smilde et al., 1974; Loneragan, 1974).

Copper in the soil can also markedly suppress zinc absorption and cause a deficiency, but the mechanism of this interaction is unknown (Yopp et al., 1974; Loneragan, 1974; Petit, 1974). Cadmium is still another metal which affects zinc metabolism. As mentioned earlier, cadmium is frequently associated with zinc ore deposits and with zinc emissions from various sources. Cadmium is known to readily replace zinc in many important animal and plant enzymes, causing zinc deficiency or cadmium toxicity, depending on how it is viewed (Lagerwerff and Specht, 1971).

The zinc content in tissue from healthy plants varies greatly, from less than 20 ppm to 10,200 ppm. In general, however, deficiency is usually exhibited by tissues with zinc concentrations lower than 20 to 25 ppm on a dry weight basis. Ample tissue zinc levels are characterized by ranges from 25 to 150 ppm. The meager data on excess Zn levels suggest that tissue concentrations greater than 400 ppm may cause toxicity symptoms (Chapman, 1966a). Table 5.6.15.5-1 presents more specific data on tissue analysis values for zinc.

In the early states, zinc deficiency is often expressed as "leaf mottle" "frenching" and other types of interveinal symptoms (Bidwell, 1974; Chapman, 1966a). In most plants, terminal growth is affected first. In corn chlorosis is expressed as white striping or banding on the lower half of the leaves. In cases of moderate or acute zinc deficiency, the characteristic symptoms are small leaves and rosette-type growth (Chapman 1966a). These symptoms are especially common in citrus trees and other tropical fruits (Chapman, 1966a; Lefebvre, 1973). Premature fruit drop may also occur under zinc deficient conditions (Hoda et al., 1969). The specific symptomatology of zinc deficiency in several crops is presented in Table 5.6.15.5-2.

Fruit trees, especially citrus and peaches, and other plant species such as corn, bean, cotton, onion, sorghum, and tomato are particularly sensitive to zinc deficiency. Barley, oats, rye, and wheat are relatively insensitive to zinc supply (Chapman, 1966a).

5.6.15.6. Zinc toxicity.

Zinc toxicity is relatively uncommon, but is most likely to occur in the following soils (Chapman, 1966a):

TABLE 5.6.15.5-1. Typical plant tissue analysis values for zinc.

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	Top half of shoots	In Bloom	8.00	...	13.80	...	...
	Control	Tops	12 wks.old	13.00	...	39.00-48.00	...	...
Apple (Malus spp.)	Field	Leaves	Apical 6-8 inches (Sept.-Oct.)	4.00-54.00	...	4.00-80.00	...	...
	Field	Stems	Apical 6-8 inches (Sept.-Oct.)	4.00-28.00	...	16.00-80.00	...	...
	Field	Leaves	...	5.00-10.00	...	...	...	...
	Field	Leaves	...	1.20-2.30	...	9.60 10.30	...	...
	Field	Leaves	August	<14.00	...	...	...	...
	Field	Leaves	...	3.00-22.00	...	6.00-	...	...
Apricot (Prunus armeniaca)	Field	Leaves	Apical 6-8 inches (Sept.-Oct.)	24.00-30.00	...	19.00-31.00	...	...
	Field	Stems	Apical 6-8 inches (Sept.-Oct.)	7.00-9.00	...	11.00-34.00	...	...
Avocado (Persea americana)	Field	Leaves	Mature	4.00-15.00	...	50.00	...	...
Clover, subterranean (Trifolium subterraneum)	Solution	Tops	12 weeks old	24.00-25.00	...	76.00-90.00	...	...
	Field	Leaves	Blooming	<15.00	...	...	...	...
Corn (Zea mays)	Field	Lower leaves	Tasseling	9.00-9.30	...	31.10-36.60	...	...
	Field	Leaves	6th node from base, at silking	14.00-15.10	...	>15.00	...	...

TABLE 5.6.15.5-1. Typical plant tissue analysis values for zinc. (cont'd)

				Range in dry matter (ppm.)				
Plant	Type of culture	Tissue sampled	Age, stage, condition or date of sample	Showing deficiency symptoms	Low range	Intermediate range	High range	Showing toxicity symptoms
Flax (Linum usitatissimum)	pots	Tops	71 days old	18.00	...	32.00-83.00	...	...
Oats (Avena sativa)	Sand	Leaves	Mature	...	...	...	...	1,700.00-7,500.00
	Sand	Whole plant	Before inflorescence	<20.00	...	...	...	...
	...	Plant (?)	6-8 weeks old	...	...	20.00	...	...
Orange (Citrus sinensis)	Field	Leaves	...	3.80-11.70	...	7.80-47.30	...	...
	Field	Leaves	3-12 months old	4.00-15.00	...	20.00-80.00	...	...
	Field	Leaves	...	4.00-6.00	...	8.00-10.00	...	...
	Field	Leaves	...	10.00-26.00	...	14.00-34.00	...	...
	Field	Leaves	4-7 months old	<15.00	16.00-24.00	25.00-100.00 (?)	110.00-200.00 (?)	300.00(?)
	Field	Leaves	4-7 months, spring cycle from fruiting terminals	15.00	...	20.00-80.00	...	...
	Field	Leaves	4-10 months from fruiting terminals	4.00-15.00	15.00-24.00	25.00-100.00	110.00-200.00	>200.00 (?)
	Field	Leaves	...	7.10	...	...	...	...
Peach (Prunus persica)	Field	Leaves	Apical 6-8 inches (Sept.-Oct.)	6.00-15.00	...	6.00-43.00	...	...
	Field	Stems	Apical 6-8 (Sept.-Oct.)	5.00-12.00	...	11.00-50.00	...	...
	Field	Leaves	From median shoot position (Aug.-Sept)	3.50-25.40	...	6.00-140.00	...	...

TABLE 5.6.15.5-1. Typical plant tissue analysis values for zinc. (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 (Pyrus communis)	Field	Leaves	Lower; current season	9.90	...	16.00	...	...
Pecan (Carya illinoensis)	Field	Leaves	Top of tree	Trace-7.00	...	66.00-202.00	...	...
	Field	Leaflets	August	3.70	...	3.90-16.70	...	...
	Field	Petioles	August	Trace	...	Trace-10.00	...	...
	Field	Shoots	August	Trace	...	7.90-15.30	...	...
Pineapple (Ananas comosus)	Field	Leaves	Base	4.00-26.00	...	16.00-41.00	...	...
	Field	Leaves	Distal end	4.00-26.00	...	4.00-22.00	...	...
	Field	Stems	Growing point	6.00-96.00	...	144.00-158.00	...	...
Potato (Solanum tuberosum)	Field	Leaves	Mature; from mid-section	...	<30.00	30.00-87.00	...	...
Tomato (Lycopersicon esculentum)	Field	Leaves	Mid-season	6.00-8.70	...	13.00	...	...
	Sand	Leaves	From middle third of plant	14.40	...	26.90	...	...
	Solution	Leaves	Basal and median, at fruit-setting stage	9.00-15.00	...	65.00-198.00	...	526.00-1,480.00
Tung (Aleurites fordi)	Field	Leaves	...	3.60 6.20	...	15.70-35.30	...	...
	Field	Petioles	...	3.70-4.00	...	9.10-28.40	...	...
	Field	Leaves	Mid-shoot	10.00-25.00	...	30.00-229.00	...	...

TABLE 5.6.15.5-1. Typical plant tissue analysis values for zinc.

(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
Tung (cont'd)	Sand	Leaves	Mid-shoot (August)	...	...	...	...	485.00
Walnut (Juglans regia)	Field	Leaves	Apical 6-8 inches	11.00-22.00	...	16.00-30.00	...	...
	Field	Stems	Apical 6-8 inches	8.00-17.00	...	24.00-34.00	...	...

Source: Chapman (1966a)

Table 5.6.15.5-2. Specific symptomatology of zinc excess in several crop species.

Plant	Visual Symptoms
Apple (*Malus* spp.)	Leaves developing in spring are characterized by whorls of small, stiff, and sometimes mottled leaves near the tips of current season's growth; except for terminal rosetts, twigs are bare for for some time; later, branches may arise below twigs and produce almost normal leaves early; which later become mottled and misshapen; fruit bud formation is reduced; many of the developing fruits are small and malformed; twigs may die back after the first year.
Barley (*Hordeum vulgare*)	Leaves show uniform chlorosis and drying up; tip growth ceases.
Bean (*Phaseolus* spp.)	Leaves and flower buds shed.
Broad bean (*Vicia faba*)	Leaves and flower buds shed; seed pods fail to develop.
CITRUS FRUITS Grapefruit (*Citrus paradisi*) Lemon (*Citrus limon*) Mandarin (*Citrus reticulata*) Orange (*Citrus sinensis*)	Leaves become chlorotic; this is known as "mottle-leaf" in California and "frenching" in Florida. Irregular green bands develop along midribs and lateral veins; leaves become small and narrowed; small green dots often appear in chlorotic areas; twigs tend to die back; fruit quality and quantity vary with severity of deficiency.
Coffee (*Coffea* spp.)	One or more branches have short internodes; there is reduction in leaf and fruit size, along with chlorosis; the latter may resemble the pattern of citrus "mottle-leaf"; dieback occurs.
Corn (*Zea mays*)	Older leaves have light-yellow streaks of chlorotic striping between veins, this may show as a broad band of white or yellow tissue between the midrib and edge of the leaf, occurring mainly in the lower half of the leaf, and is visible when the young leaf is coming out of the whorl. Silking and tasseling are delayed. Severely deficient plants are also stunted, and have short internodes.

415

Table 5.6.15.5-2 (continued)

Plant	Visual Symptoms
Cotton (Gossypium spp.)	There is general bronzing of the first true leaves, and often a pronounced interveinal chlorosis. The leaves become thick and brittle, with their margins turned upward. Elongation practically ceases; the shortened internodes tend to give the plant a small, bushy appearance. Growth and fruiting are delayed.
Flax (Linum usitatissimum)	Grayish-brown collapsed spots appear on the younger leaves, followed by drying and color changes to brown or white. Internodes between leaves are shortened, with rosetted appearance. Later, the top of the main stem becomes necrotic.
Oats (Avena sativa)	Leaves become pale green; older leaves show collapsed areas at margins and tips, and are grayish in color; necrosis extends down leaf; remainder of leaf is gray to bronze-green.
Pea (Pisum sativum)	Lower leaves become necrotic at margins and tips; stems are stiff and erect; flowers are absent.
Peach (Prunus persica)	Leaves become chlorotic, the mottling progressing upward from lowermost leaves. Leaves are narrow and more or less crinkled; twigs are short, the internodes near tips producing rosettes of leaves; defoliation progresses upward; formation of fruit buds is drastically curtailed; peaches are few, misshapen, and worthless.
Pecan (Carya illinoensis)	Leaves become chlorotic, with a yellow mottling between veins; regions along margins and veins may remain green; sometimes only one or two branches are affected; later the leaves may show bunching owing to shortened axes at twig ends, producing "pecan rosette."
Potato (Solanum tuberosum)	Leaves show grayish brown to bronze irregular spots, usually on leaves halfway up plant, but sometimes on older or younger leaves and finally on almost all leaves; with severe deficiency, the stems and leaf petioles develop brown spots, plants are short.

Table 5.6.15.5-2 (continued)

Plant	Visual Symptoms
Squash (<u>Cucurbita</u> spp.)	Leaves become mottled, with necrotic areas.
Sugar beet (<u>Beta saccharifera</u>)	Leaves become necrotic, and develop brown to grayish spots; tops of the leaves wither; only the petioles retain green color.
Tobacco (<u>Nicotiana tabacum</u>)	Lower leaves show slight chlorosis at tips and margins, followed by necrosis of chlorotic tissue; small areas are affected at first, sometimes surrounded by a halo; these areas enlarge rapidly and become water-soaked in appearance; small veins are at first involved in breakdown, but later veins as well as interveinal tissue dry up; internodes are short; leaves are apparently thickened.
Tomato (<u>Lycopersicon esculentum</u>)	Early growth is very slow; leaves become very thick, soon developing a faint interveinal chlorosis; they also have a tendency to curl downward. In transplants, there is extreme relaxing of leaflets, followed by downward curling of petioles; in severe cases, these curl like a corkscrew. This is followed by a brownish-orange chlorosis of the older leaves, which often show necrotic spots.
Tung (<u>Aleurites fordi</u>)	Leaf bronzing, necrosis, and spotting produce a ragged appearance, followed by defoliation and rosetting (bunching) of new leaves.

Source: Chapman (1966a)

a. Some kinds of acid peats.
b. Soils in the vicinity of lead and other mine dumps where the soils have been contaminated by seepage.
c. Soils contaminated by zinc from other mining operations.
d. Soils derived from rocks and materials which are high in zinc.
e. Soils acidified by agricultural activities.
f. Soils subjected to excessive accumulations of zinc fertilizers.

Another influencing factor, as discussed previously, is the presence of other elements such as phosphorus (Smilde et al., 1974).

The mechanisms of zinc toxicity are largely unknown. The most common symptom of zinc toxicity is an iron chlorosis. This may indicate that excess zinc inhibits iron metabolism, and zinc's antagonistic interactions with phosphorus may indicate that excess zinc can inhibit the metabolism of other essential nutrients (Chapman, 1966a)

As mentioned earlier, field cases of zinc toxicity are rare. Tissue values in excess of 400 ppm on a dry weight basis, are generally required for toxicity to occur, but this number is highly variable between species (Jones, 1972). A number of plant species have been described as zinc tolerant or zinc loving, including ragweed, false Solomon's seal, horsetail, and several marine phytoplankton (Chapman, 1966a; Jensen and Rystad, 1974). Intra-specific differences in zinc tolerance have also been noted for some species (Walley et al., 1974; Gartside and McNeilly, 1974b). A number of mechanisms for the evolution of this tolerance have been proposed, and the tolerance itself appears to be related to changes in enzyme activity which channel among other things, a greater concentration of zinc to the cell walls and vacuoles in zinc-tolerant plants (Turner and Marshall, 1972; Mathys, 1975; Antonovics et al., 1972).

Table 5.6.15.5-1 includes tissue analysis values for a few crops growing under conditions of zinc toxicity. It should be recalled that leaf tissue values from plants growing in the vicinity of sources of airborne pollutants should be corrected for surface accumulations of zinc (or other metals) which have not entered the leaf and hence may not have affected the plant (Little, 1973). Table 5.6.15.6-1 gives additional tissue analysis values and symptomatology for excess zinc in six crops, and Table 5.6.15.6-2 gives symptomatology for five additional crop species.

Soil analyses which may cause toxicity are hard to generalize for zinc. Available Zn at 400 ppm is toxic to corn. In pot culture tests with corn, 0.688 to 1.376 meq. of zinc per 100 g. of soil was found toxic in Norfolk sand; 0.758 to 1.137 meq. in Orangeburg fine sandy loam; and 1.615 to 2.153 meq. in Greenville clay loam. In Norfolk sand, 0.275 to 0.482 meq was found to be toxic to cowpeas. New York peat soils toxic to spinach, lettuce, and carrots were found to contain 0.43 to 10.16% zinc, mostly in available forms. Soil toxicity due to zinc availability or absorption. Molybdenum salts have also been shown to correct zinc toxicity, but this is generally an unacceptable remedial procedure because of molybenum toxicity to animals (Chapman, 1966a).

Table 5.6.15.6-1. Symptomatology and threshold toxicity levels of zinc in several crop species.

Plants	Growth Medium	Minimum Phyto-toxic Conc.	Plant Part Affected	Symptom	Developmental Stage
Corn, var. Whatley's Prolific	sandy loam	13.7 ppm internal	tops	reduced yield chlorosis	seedling
Cowpeas, var Suwannee	clay loam	43 ppm external	"	"	"
Corn, var. Ida Hybrid 330	soil pH 7	484 ppm internal 300 ppm external	"	reduced yield	"
Barley, var. Trail	soil pH 7	530 ppm internal 200 ppm external	"	"	"
Wheat, var. Gaines	soil pH 7	522 ppm internal 300 ppm external	"	"	"
Oats, var. Victory	solution	25 pm external	"	reduced yield chlorosis	"

Source: Yopp et al., (1974)

Table 5.6.15.6-2. Symptomatology of zinc toxicity in some crops.

Plant	Visual Symptoms
Barley and various grasses	Rusty-brown flecks on leaves, followed by death.
Citrus fruits (*Citrus* spp.)	Leaves show iron chlorosis.
Oats (*Avena sativa*)	Leaves show iron chlorosis.
Sugar beet (*Beta saccharifera*)	Leaves show iron chlorosis.

Source: Chapman (1966a)

APPENDIX

2.7.f Procedure for Foliar Chemical Analyses

All plant tissue are dried under forced air at 65°C for 24 - 48 hours and ground in a stainless steel Wiley Mill through a 20-mesh sieve.

In quantification of all metals except Pb and Ni, samples of plant tissue (500 mg) are ashed in 20 ml fused quartz crucibles with covers for eight hours at 485°C. The ashed material is dissolved in 5 ml of LiHCl (0.5 per cent Li; 1.5 per cent ~~HCL~~ HCl). This solution is analyzed on a Jarrell-Ash Emission Spectrograph.

In quantification of Pb and Ni, samples of plant tissue (500 mg) are ashed at 450°C and dissolved in 2.5 ml of 1.2 per cent HCl. This is analyzed on a Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer against standards prepared in the same solution. A deuterium arc background corrector is used in all analyses. Pb is analyzed at 283.5 nm and Ni at 232.5 nm.

In quantification of total sulfur, samples of plant tissue (250 mg) are digested in Folin - Wu tubes with 3 ml of nitric acid and 2 ml of perchloric acid for two hours at 235°C on a block digester. After adding 1 ml of 4N HCl and diluting to 50 ml with deionized double glass distilled water, the digest is allowed to stand overnight to clear. Sulfur analysis is done turbidimetrically on a Klett-Summerson Colorimeter using $\mathrm{B}\overset{a}{\cancel{\mathrm{S}}}\mathrm{Cl}_2$.

In quantification of flouride, samples of plant tissue (500 mg) are weighed into 50 ml polyethylene tubes and one drop of Brij-30 wetting solution and 20 ml of 0.05 N H_2SO_4 added. Tubes are then shaken for 15 minutes and centrifuged, and then 20 ml of 0.01 N NaOH are added and tubes shaken for an additional 15 minutes. The liquid is then neutralized by the addition of 20 ml of 0.05 N H_2SO_4 and buffered with 5 ml of 3 M sodium acetate (pH 7.0). Finally, a 10-ml aliquot of 0.5 M sodium citrate, previously adjusted to pH 7.0 with 0.5 M citric acid, is added.

Fluoride concentration is then measured using a fluoride specific-ion electrode with the help of a standard curve.

2.7.g Procedure for the Chemical Analysis of the Soil

All the soil samples are dried under forced air at 36° - 38°C for at least 48 hours and then passed through a 2-mm sieve.

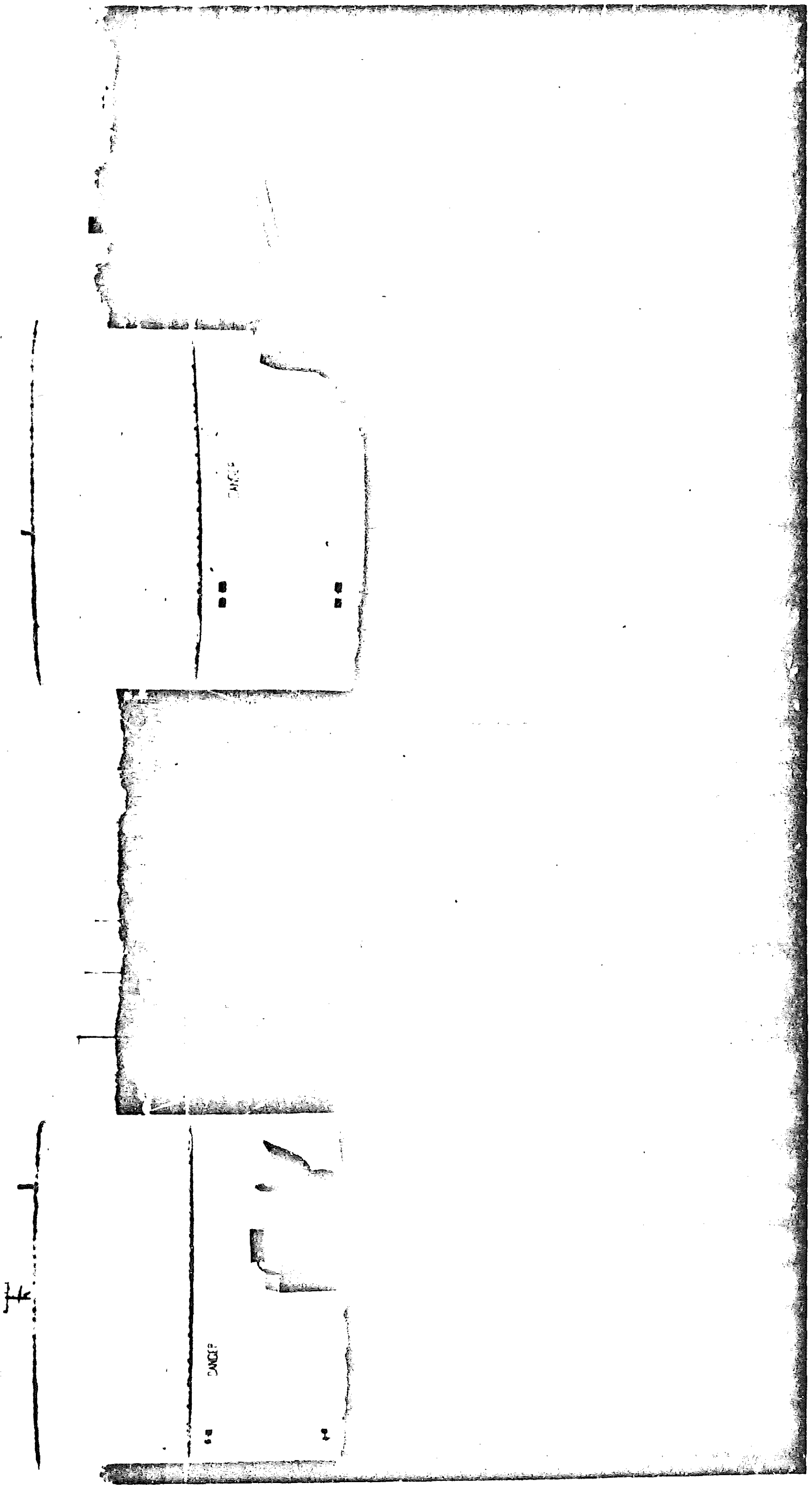
In quantification of available Ca, Mg, Na, and K, weighed air-dried soil samples (3 g) are dispersed into 50-ml polyethylene centrifuge tubes and 30 ml of neutral 1N ammonium acetate are added. The tubes are shaken for 30 minutes and centrifuged. The extracts are analyzed on a Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer against standards prepared in 1N ammonium acetate. Lanthanum is added in the analysis of Ca and Mg to prevent interference from phosphate. Calcium is analyzed at 212.1 nm; Mg at 285.5 nm; Na at 294.8 nm; and K at 383.2 nm. Lithium is added in the analysis of K as an ionization buffer.

In quantification of available Mn, Fe, Cu, Zn, Pb, and Ni, 30 ml of DTPA extracting solution is added to 15 g of air dried soil samples in 50-ml polyethylene centrifuge tubes. The tubes are shaken for two hours and centrifuged. The extracts are analyzed on an Atomic Absorption Spectrophotometer against standards prepared in DTPA solution. A deuterium arc background corrector is used in the analysis of Zn, Pb, and Ni. The metals are analyzed at the following wave lengths: Mn - 280.3 nm, Fe - 302.3 nm, Cu - 324.9 nm, Zn - 214.5 nm, Pb - 283.5 nm, and Ni - 232.2 nm.

In quantification of extractable sulfate, air-dried soil samples (12 g) are weighed into 180-ml Dispo bottles and 30 ml of 0.008 M calcium phosphate added. The samples are shaken for 30 minutes and the suspension filtered through Whatman No. 40 filter paper. The filtrates are analyzed turbidimetrically using $BaCl_2$.

In quantification of extractable fluoride, air-dried soil samples (500 mg) are dispersed into 50-ml polyethylene tubes and 25 ml of 0.01 N HCl added. The tubes are shaken for 30 minutes. To these tubes 25 ml of citric acid-phosphate buffer (8.47 g/l sodium phosphate diabasic heptahydrate) is added and the fluoride concentration measured using a fluoride specific-ion electrode with the help of a standard curve.

2.7.i. Open-top chambers - model developed by Boyce Thompson Institute for Plant Research. (After Mandl _et al_., 1973).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2.7.i. A brief description of the open-top chambers - Boyce Thompson model.

EVALUATION OF AIR POLLUTANT EFFECTS ON PLANTS UNDER FIELD CONDITIONS: OPEN - TOP EXPOSURE CHAMBER.

(Exhibitors: Dr. Sagar V. Krupa and Dr. F. A. Wood, Department of Plant Pathology, University of Minnesota, St. Paul, Minnesota 55101, U.S.A.)

In the recent years extensive effort has been directed towards investigating the effects of air pollutants on plant life. Much of the knowledge we have in this area relates to studies performed under controlled-environment or greenhouse conditions. These studies, however, do not simulate the ambient atmosphere. Portable and fixed fumigation chambers have been developed in the past. Though these come closest to providing the ambient environment, the usual closed designs alter the normal field conditions.

Very recently Heagle *et al.*(1) and Mandl *et al.*(2) developed chambers with open tops for the exposure of plants to air pollutants in the field. The model on exhibition has been slightly modified from the design of Mandl *et al.*

The chamber is 8' in height and 9' in diameter. The walls are fabricated from corrugated fiberglass panels (Type 550 Filon panels, Filon Corporation, Division of Vistron, U.S.A.) fastened to aluminum hoops. The base of the chamber in addition to a hinged door, posesses an orifice through which the stem portion (10" OD) of a galvanized metal tee has been inserted for the introduction of air into the chamber. The ends of the metal tee top (8" OD) are connected to a plenum (approx. 28' long) forming a ring around the inner wall of the chamber. The plenum is composed of 8" diameter lay-flat polyethylene tubing with 1" diameter holes through one layer, at 3" intervals. The holes are oriented so that the air stream is directed horizontally towards the center of the well.

A non-overloading blower (Type BI 12 of Cincinatti Fan and Ventilator Co., U.S.A.) circulates the air (1000 scfm of air at 1.5" swg). A sheet metal housing is connected to the blower inlet and air from the blower passes through two pre-filters and a standard 1000 scfm charcoal filter. The companion unit does not have filters and ambient air is moved into the chamber from the blower. The blower is connected to the plenum tee by a 10" ID flexible duct.

The top of the chamber is covered with a mesh netting which reduces the effect of wind on air movement within the chamber, but does not impede the entrance of precipitation, insects etc.

This chamber can be used to study;

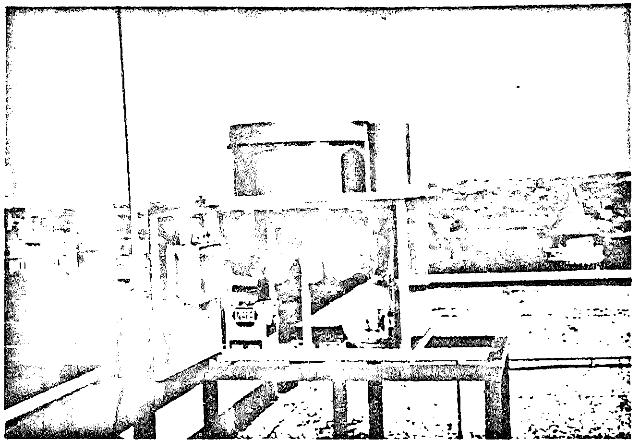
1) The effects of air pollutants in ambient air on plant life.
2) The effect of controlled levels of air pollutant/s on plant life under field conditions.
3) The interactions between plant diseases and pollutants either in ambient air or artifically introduced, under field conditions.

References

1) Heagle, A.S., D.E. Body, and W.W. Heck. An open-top field chamber to assess the impact of air pollution on plants. In press.

2) R.H. Mandl., L.H. Weinstein., D.E. McCune, and Monic Keveny. A cylindrical, open-top, chamber for the exposure of plants to air pollutants in the field. In press.

3.1.2 Automatic, sequential precipitation sampler for studies on acidic rain. (After Krupa and Coscio, Ann. Amer. Phytopath. Soc. 1976).



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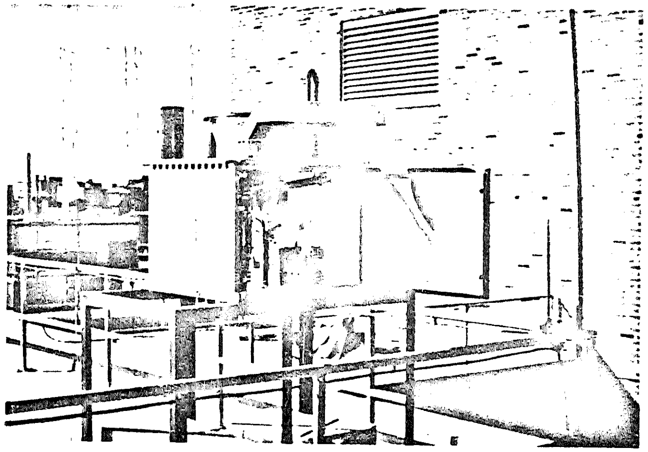

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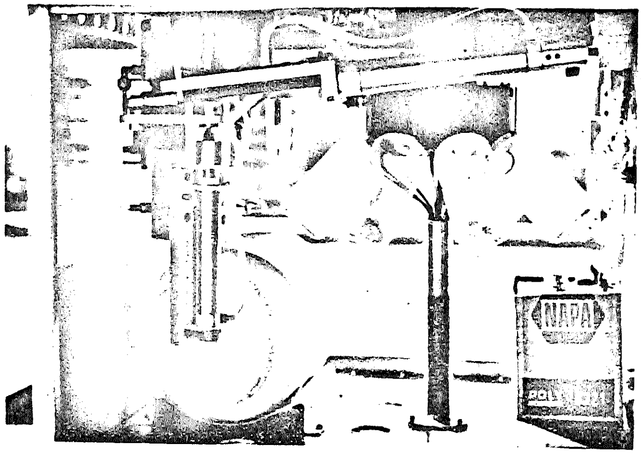

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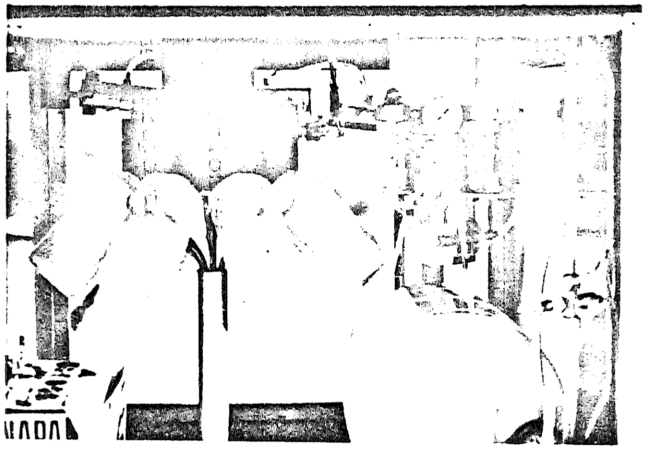

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(See announced deadline for submission date)

ANNUAL PROCEEDINGS of
THE AMERICAN PHYTOPATHOLOGICAL SOCIETY
3340 Pilot Knob Road
St. Paul, Minnesota 55121

433

I. **GENERAL INFORMATION** (see reverse side Section I for instructions for completion).

A— SUBJECT MATTER AREA: 1. Air Pollution Damage to Plants 2. Pollution Damage to Plants
(select from listing on reverse side I-A)

B— TITLE OF PAPER: Automatic, sequential, precipitation sampler for studies on acidic rain.

C— AUTHORS (underline name of speaker): S. V. Krupa and M. R. Coscio, Jr.

D— COMPLETE BUSINESS MAIL ADDRESS:
Department of Plant Pathology
University of Minnesota
St. Paul, MN 55113

E— WORK DONE AT: University of Minnesota, St. Paul, MN 55108.

F— ABSTRACT REVIEWED BY: 1. Thor Kommedahl 2. Carl J Eide
Thor Kommedahl Carl J. Eide

II. **ABSTRACT** (see reverse side instructions within "SAMPLE" and Section II for completion.

AUTOMATIC, SEQUENTIAL, PRECIPITATION SAMPLER FOR STUDIES ON ACIDIC RAIN. S. V. Krupa and M. R. Coscio Jr., Department of Plant Pathology, Univ. of Minnesota, St. Paul, MN 55108.

Acidic rain (pH 2.1-6.18) may be a threat to the environment regionally and around point sources. Much of the current information on precipitation chemistry is based on poor sampling techniques: bulk samples, questionable collection surfaces etc. Many rain samples, in addition to being contaminated with dry fallout, are subject to physico-chemical and biological changes in the field, when left standing for prolonged periods. We have designed a battery operated, automatic, electronically controlled, sequential precipitation sampler. The unit remains open only during rain. The rain-sensing mechanism involves a balanced thermistor bridge that can be adjusted to collect drizzles and downpours. The sampler lid is operated by a pneumatic piston. Rain is collected in Teflon containers attached to an 8-position rotating turret controlled by another pneumatic piston. Samples can be collected as whole rain events or as sequential fractions during the same rain. The turret will rotate only with either the onset of each new rainfall, or when the individual sample container is full during sequential sampling. When a sample container is rotated out of the collection position, it is sealed against the turret. Turret rotation is also controlled by a balanced thermistor bridge. A quartz crystal clock with a memory bank records all events for subsequent retrieval. No service is required up to 90 days.

REV 1/75 6M

3.1.2. An integrated approach for the study of rain water chemistry with emphasis on acidity.

435

Ministerium für Forst- und Wasserwirtschaft der ČSR

Forschungsanstalt für Forstwirtschaft und Jagdwesen
Zbraslav - Strnady

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IX. INTERNATIONALE TAGUNG ÜBER DIE LUFTVERUNREINIGUNG UND FORSTWIRTSCHAFT

Tagungsbericht

SEPARATUM

Mariánské Lázně, Tschechoslowakei

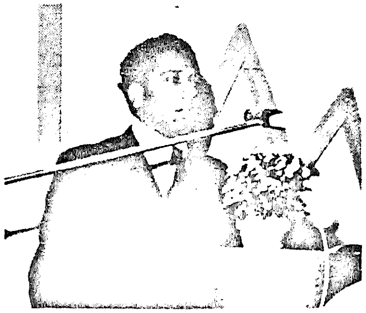
den 15. bis 18. Oktober 1974

IX. International Conference on Air Pollution
and Forestry, October 15. - 18. 1974
Mariánské Lázně, Czechoslovakia

AN INTEGRATED APPROACH TO THE STUDY OF RAIN WATER CHEMISTRY WITH EMPHASIS ON ACIDITY

S. KRUPA [1](Speaker), M.R. COSCIO, Jr.[2] and F.A.WOOD[1]

[1]Assistant Professor and Professor respectively, Department of Plant Pathology, University of Minnesota, St. Paul, Minnesota, USA.
[2]Scientist. Department of Geology & Geophysics, University of Minnesota, Minneapolis, Minnesota, U.S.A.



INTRODUCTION

Fall out of acid rain is a threat to the regional environment. Rainfall with a pH as low as 2.8 and 2.1 has been reported from Sweden (ODEN, 1968) and the United States (LIKENS and BORMANN, 1974) respectively. Effects of acid rain on vegetation and ecosystems have been classified as : 1) Direct injury to the foliage, 2) deleterious effects on the soil, 3) deleterious effects on aquatic systems, and 4) indirect injury to the foliage through deposition of other harmful substances. According to reports (see ENGSTRÖM, 1971), 10 % of the raw material base for Sweden's forest and pulp industry would disappear by the year 2000.

BARRETT and BRODIN (1955) stated that since SO_2 is a major constituent of atmospheric pollution, H_2SO_4 is the most likely cause for the acidity of rain water. Since then, almost all of the published reports are based on correlations between total SO_4 and pH. Measurement of total sulfates does not differentiate the levels and extent to which SO_4 is present in the particulate fraction, soluble fraction, as salts and as acid per se. Similarly, pH measurements do not indicate the parent species for the hydrogen ion.

The objective of the present investigation was to develop a comprehensive analytical system to understand the origin of acidity in rain water as a prelude to the study and interpretation of acid rain effects on vegetation.

MATERIALS AND METHODS

Approximately 250 ml of rain water was collected each time, from the same rain fall at several locations in the Minneapolis - St. Paul area in the U.S.A. Sampling was performed manually at approximately 5-6 ft. from the ground, away from trees, buildings etc.

Sampling was started from the time the first rain droplets fell on the ground and was terminated after approximately 30 minutes. Samples were collected in FEP-TEP (DuPont Co. U.S.A.) trays and was immediately transferred to screw capped bottles made of TEP teflon. Precaution was taken to prevent any dead space between the sample and the cap of the bottle. Samples were frozen immediately at -20 C. At the time of analysis, samples were allowed to thaw and equilibrate to the room temperature (20 C) without opening the bottle. Samples were processed according to the scheme shown in Figure 1.

The analytical techniques used, along with their application, are summarized in Table 1. For determining the morphology and gross composition of the inorganic particulate matter in each sample, 10 ml of the rain water was filteres through 0,22 u Millipore (Millipore Corp. U.S.A.) or Nuclepore (General Electric, U.S.A.) filter. After drying the filter in a vacuum, discs were punched at random, mounted on scanning electron microscope (SEM) stubs, carbon coated and viewed under a Cambridge SEM at

different magnifications. Whenever the gross inorganic composition was to be determined, the particle was bombarded for approximately 2 min with an energy beam from the internal electron source and the qualitative relative composition was identified by a precalibrated, non-dispersive x-ray analyzer.

The coulometric procedure used was a modified from that of LIBERTI et al. (1972). The unit (Figure 2) consists of a constant current source (A), a measuring cell located on a magnetic stirrer (B) and a potentiameter (modified pH meter) with a four digit visual read out (C). Based on the relationship between ψ (a function of the electromotive force) and time in seconds (t) in two portions of the same rain sample, with and without volatiles, the molarities of non-volatile strong, and non-volatile and volatile weak acids were calculated (KRUPA et. al. 1974). When a sample was to be freed of volatiles, the solution was bubbled vigorously with N_2 for 30 minutes with simultaneous stirring and kept under a blanket of N_2 throughout the analysis.

Quantification of the cations and NH_4^+ & anions were perfromed according to the conventional procedures using a Perkin-Elmer (U.S.A.) model 330 atomic absorption unit and Technikon (U.S.A.) model II autoanalyzer respectively.

RESULTS AND DISCUSSION

In the analysis of randomly selected particles from various rain water samples (ref. Table 2.), the following elements were found, based on the frequency of their occurrence:

Al, Si > Fe > K > Ca > Ti > S > P > F > Cl.

Gross morphology and elemental composition of some representative anorganic particles are shown in Figure 3. Based on frequency of occurrence x relative amount (comparative peak height), elemental composition of the particulate matter in the rain samples was as follows:

Si > Al > Fe > K > S,> Ca > Ti > P > Cl, F

Coulometric data on the rain samples are presented in Table 2. There was an increase in the strong acid component with a decrease in pH. At the same time, there was also an increase in the concentration of the total weak acid component. No direct correlation existed between the magnitude of changes in the concentration of the strong acid and differences in pH between the various rain samples. The concentration of total weak acid, as well as the volatile weak acid, exceeded the strong acid component in the rain water collected at "Golden Valley". This sample had the lowest pH value - 4.45 (Table 2). Similarly, the sample collected at "Jonathan" contained the second largest concentration of SO_4-S (Table 3). However, it was completely devoid of a strong acid component. The quantity of alkali-alkaline earth metals found in that particular sample may account for the absence of a strong acid component. (Table 4). The concentration of volatile weak acids present (Table 2) can satisfy the pH value (5.65) observed in that case. On the contrary, in the other samples, no clear relationship was found between pH, SO_4-S, and levels of alkali-alkaline earth metals.

The aforementioned results indicate the complexity of rain water chemistry and questions concerning the parent sources of hydrogen ion. If it is assumed that the total available SO_4^{2-}, NO_3^- and Cl^- contribute the hydrogen ions found in the strong acid component, then the coulometric data for strong acid concentrations in the different rain samples used in this study may be satisfied by the measured values for the three aforementioned anions. Howerer, the simultaneous presence of weak acid components, NH_4^+ and cations (metals) should be considered in this context. Furthermore, common ion effects can not be ignored.

Thus the acidity of rain water down to a pH of 4.0 may be contributed to by at least five different hydrogen donors: H_2SO_4, HNO_3, HCl, weak acids such as H_2CO_3 and HF, etc. and hydrolysable salts. This is particularly meaningful, since the average pH values of rain water reported for the United States during 1972 range between 6.59 and 4.39 (MILLER, 1974). It should be pointed out that the extent of contribution by the individual hydrogen donors will vary between different rain falls, and between the same reinfall at differer locations, depending on the physicochemical parameters of the environment. The proportions between

TABLE 1

Some Techniques and Their Application in Rainwater Analysis

Technique	Description of its Use
Coulometry	Quantification in molarities (M) of: 1) non-volatile strong acid, 2) non-volatile weak acid, and 3) volatile weak acid.
Scanning E.M. + x-ray analysis	Morphology and gross qualitative inorganic composition of particulate matter
Atomic Absorption	Quantification of metallic components Eg: Ca, Mg, Na, K, Fe, Zn, Cu, Mn, Pb, Cd etc.
Colorimetry + Specific ion electrode	Quantification of SO_4, Cl, NO_3, NO_2, NH_4, PO_4, F, etc.

TABLE 2

ACID COMPONENTS IN THE SAME RAIN COLLECTED AT DIFFERENT LOCATIONS IN THE TWIN CITIES AREA

Date of Collection: June 6, 1974

		Concentration 10^{-5}M			
Location	pH	SA	TWA	NWA	VWA
Golden Valley	4.45	5.89	8.01	1.85	6.16
Mound	4.52	3.62	3.38	1.16	2.22
Delaware Avenue	4.70	3.39	1.73	1.64	0.09
N.E. University Avenue	4.80	2.64	1.78	1.40	0.38
Jonathan	5.65	0.00	0.22	0.00	0.22

SA = Strong Acid
TWA = Total Weak Acid
NWA = Non-volatile Weak Acid
VWA = Volatile Weak Acid

TABLE 3

Non-metallic components in the same rain collected at different locations in the Twin Cities area*

Date of collection: June 6, 1974

Sampling Location	Concentration in ppm					
	NH_4-N	NO_3-N	PO_4-P	Cl	SO_4-S	Total salts** (Approx.)
Golden Valley	0.21	0.129	<0.002	<0.10	0.5	9.35
Mound	0.82	0.450	0.005	<0.10	0.8	11.10
Delaware Ave.	0.10	0.147	<0.002	<0.10	0.4	7.48
N.E. University Ave.	0.07	0.063	<0.005	<0.10	0.4	3.47
Jonathan	0.48	0.292	0.009	0.60	0.7	9.63

---

* Quantitative elemental differences between the filtered and unfiltered samples were not significant.

** ppm total salts were calculated on an approximate basis as follows: Electrical Conductivity in μmohs/cm at 25 C x 0.55.

TABLE 4

Metallic components in the same rain collected at different locations in the Twin Cities area*

Date of collection: June 6, 1974

Sampling Location	Concentration in ppm										
	Cu	Fe	Mn	Zn	Cd	Cr	Pb	Mg	Ca	Na	K
Golden Valley	<0.01	<0.1	<0.01	0.02	<0.02	<0.02	<0.2	0.016	0.055	0.03	0.03
Mound	<0.01	<0.1	<0.01	<0.02	<0.02	<0.02	<0.2	0.053	0.529	0.04	0.11
Delaware Ave.	<0.01	<0.1	<0.01	0.02	<0.02	<0.02	<0.2	0.011	0.115	0.10	0.06
N.E. University Ave.	<0.01	<0.1	<0.01	<0.02	<0.02	<0.02	<0.2	0.012	0.020	0.05	0.07
Jonathan	<0.01	<0.1	<0.01	<0.02	<0.02	<0.02	<0.2	0.203	1.23	0.38	0.23

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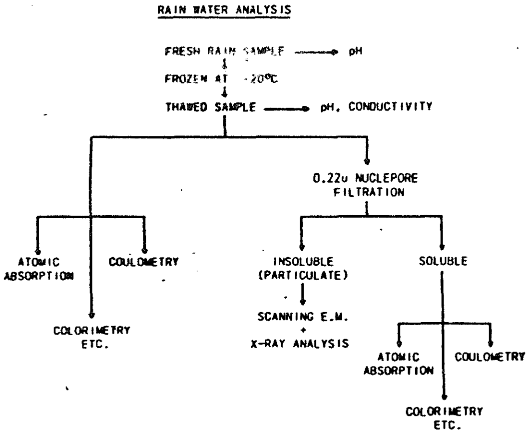
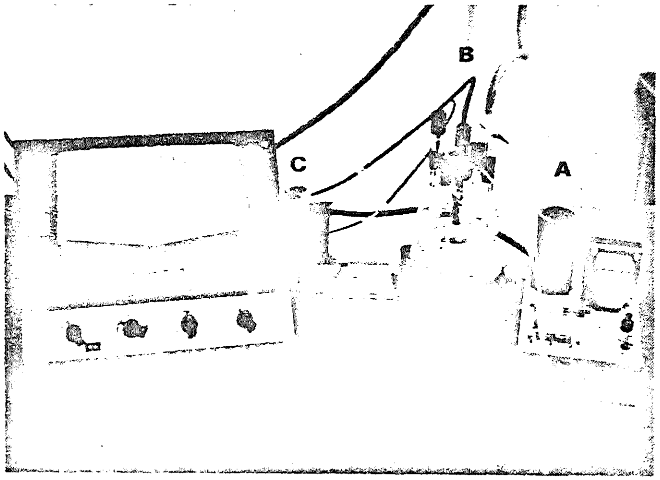
* Quantitative elemental differences between the filtered and unfiltered samples were not significant.



Legend for Figure 1

Flow chart showing the procedure for the integrated analysis of rain water.



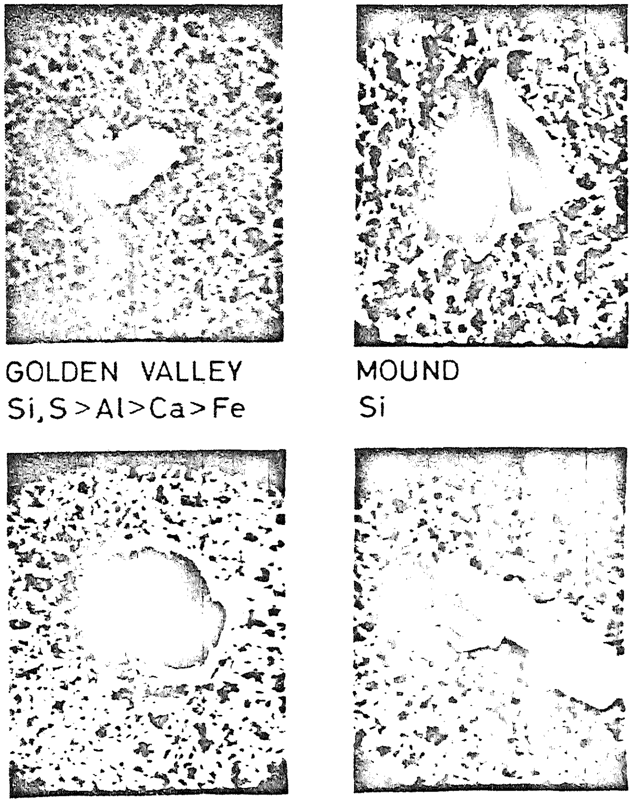
Legend for Figure 2

Coulometric unit for determining the strong and weak acid components in rain water.

(A) = Constant current source

(B) = Titration cell

(C) = Converted pH meter and four digit readout.



Legend for Figure 3

Scanning electron micrographs of inorganic particulate matter in different rain samples. Golden Valley, Mound, etc. are locations of sampling.

these variables may largely dictate the basis for the pH in a given rain water sample.

ACKNOWLEDGEMENT

We acknowledge the U.S. National Park Service for providing us with a research grant for this study. We express our gratitude to Mr. R.C. Munter, University of Minnesota, St. Paul, for generous help and advice during the course of this study.

ABSTRACT

An integrated analytical system to study the chemistry of rain water is reported. The procedure consists of the following techniques: Scanning electron microscopy & x-ray analysis, coulometry, atomic absorption and colorimetry. Preliminary data obtained using the aforementioned methods, show that rain water samples collected from the same rainfall at different sampling sites within a metropolitan area vary in their pH, molarities of strong non-volatile, weak non-volatile and volatile acids and total salts. In addition, the results indicate the coexistence of roughly comparable concentrations of strong and weak acids down to a pH of 4.0.

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3.1.2. A coulometric procedure for the determination in molarities of strong, non-volatile and volatile weak acids in rain and acqueous solutions.

Evaluation of a Coulometric Procedure For the Detection of Strong and Weak Acid Components in Rainwater

Sagar Krupa, M. R. Coscio, Jr., and F. A. Wood
University of Minnesota

A rapid coulometric procedure is described for the determination of non-volatile strong and non-volatile and volatile weak acids in rain samples. A constant current with known amperage is passed into a measured volume of the sample, with and without volatiles, and the changes in the electromotive force monitored with a potentiometer. Molarities of the different acids are calculated by plotting the function of the electromotive force against time in seconds according to Gran's theory. The method is useful at acid concentrations of 10^{-6} to 10^{-4} M.

Fall out of acidic rain with a pH ranging from 2.1 to 6.82 has been reported from the U. S.[1,2] and with a pH as low as 2.8 from other parts of the world.[3] Barrett and Brodin[4] concluded that, because SO_2 is one of the major constituents of pollution, it is likely that sulfuric acid is the contributing factor of acidic pH. Since then, almost all studies on the origin of acidity in rainwater have been based on correlations between pH maps and sulfur depositions.

Measurement of pH does not differentiate the individual contributions of strong acids (e.g., H_2SO_4), weak acids (e.g., RCOOH), hydrolysable salts (e.g., $Fe(H_2O_6)^{3+}$), etc. Similarly the sulfur content in rainwater is generally measured as sulfate sulfur. This does not identify the extent to which sulfur is present as acid *per se* in a given sample and as other constituents. Sulfur in the atmosphere can be present as $(NH_4)_2SO_4$, acids, metallic salts, S_2O_5, dithionate, mercaptan, and thionyl derivatives, etc.

Liberti *et al.*[5] reported on the specific determination of the non-volatile strong acid component in rainwater by a coulometric procedure.

Dr. Krupa is Assistant Professor and Environmental Pathologist and Dr. Wood is Professor and Head, Department of Plant Pathology, University of Minnesota, St. Paul, MN 55108. Mr. Coscio is a scientist at the Department of Geology and Geophysics, University of Minnesota, Minneapolis, MN 55455.

This report concerns an expanded study of the coulometric procedure for the determination in *M* of not only the strong but also the non-volatile and volatile weak acid components in rainwater.

Materials and Methods

The coulometry unit, which is essentially the same as that of Liberti *et al.*[5] (Figure 1), consists of a titration cell (B), a constant current source (A) and a potentiometer with an accuracy to the third decimal (C). The titration unit consists of an anode and a cathode generator, a calomel and a glass electrode and one glass inlet for bubbling nitrogen. The constant current source is capable of delivering 0–7 mA.

Reprinted from APCA JOURNAL, *Vol. 26, No. 3, March 1976*

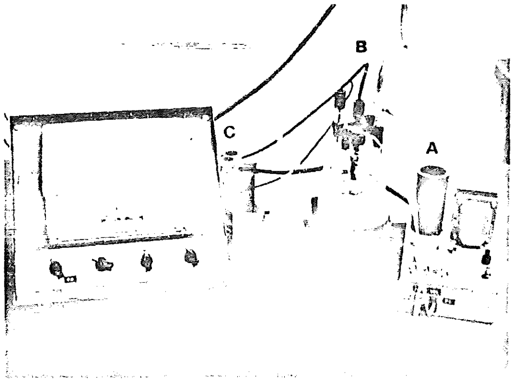

Figure 1. Coulometric unit for determining the strong and weak acid components in rainwater. (A) Constant current source. (B) Titration cell. (C) Converted pH meter and four digit readout (Potentiometer).

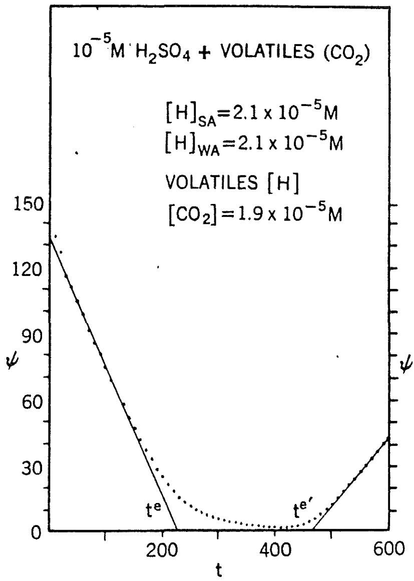

Figure 2. Graphic representation of the coulometric data on a H_2SO_4 standard with volatiles. ψ = function of the electromotive force, t = time in seconds, *SA* = Strong acids, and *WA* = Weak acids.

The procedure is as follows: One hundred ml of the rainwater sample is transferred to the titration cell and 0.02 M KBr is added as a constant current carrier. The solution is continuously stirred by a magnetic stirrer and a constant current of 0.89 to 4.9 mA is applied. The electromotive force (emf) is measured with the potentiometer every 5–10 sec up to a point beyond the generation of excess hydroxyl ions. When a sample is to be freed of volatiles, it is bubbled with a fast stream of N_2 for 30 min with simultaneous vigorous stirring and subsequently maintained in an atmosphere of N_2. Using data obtained from parallel samples with and without volatiles, one can calculate all three types of acid components in a rainwater sample as follows:

Rainwater with volatiles = Total acids (strong acids[a] + non-volatile and volatile weak acids).

Rainwater without volatiles = Strong acids + non-volatile weak acids.[b] (Total acid component* in 1) − (Total acid component* in 2) = Volatile weak acid.

Theory of Coulometry

1. At the cathode (platinum electrode)

   $$H_2O + e^- \rightarrow \tfrac{1}{2}H_2 + OH^-$$

   At the anode (silver — silver bromide electrode)

   $$Ag^{0} + Br^{-} \rightarrow AgBr + e^-$$

2. The electromotive force E is determined with a potentiometer against time in seconds (t).
3. The function

   $$\psi = 10^{-E}\frac{F}{2.3RT},$$

   is plotted versus t.
   F = Faraday's constant
   T = Temperature in Kelvin
   R = Gas constant
   By extrapolating the slope, a straight lined intercept is obtained on the abscissa at a value t_e (Figure 2).
4. The hydrogen ion concentration for the strong acid is then calculated as follows:

   $$[H] = \frac{it_e}{FV_0}$$

   i = Current used in mA
   V_0 = Volume of sample used in ml
5. Continued OH^- ion generation beyond this point will yield a new intercept t_e' (Figure 2) if the function

   $$\psi' = 10^{E}\frac{F}{2.3RT}$$

   is plotted versus generation time. From this, the non-volatile and volatile weak acid components are calculated.

Results and Discussion

Extensive testing of the coulometric method showed its usefulness for strong (H_2SO_4, HCl, and HNO_3) as well as weak (HF and CH_3COOH) acids, but only at molarities ranging from 10^{-4} to 10^{-6} (Krupa *et al.*[6]).

Figure 2 shows the relationships between ψ and ψ^1 and time (t) for 10^{-5} M H_2SO_4. The curved portion of the graph is due to the presence of weak acids. The $t_e{}^1$ intersect represents the generation of excess hydroxyl ions.

Figure 3 shows coulometric data on the same concentration of H_2SO_4, but after the removal of volatiles by N_2 bubbling. By extrapolating the slope of ψ vs. t in this figure, the strength of the strong acid component is calculated to be 1.9×10^{-5} M. The difference between the $t_e{}^1$ and t_e in Figure 3 is due to the presence of non-volatile weak acids. In the absence of a weak acid component t_e and $t_e{}^1$ would intersect at the same point. Value of the volatile weak acid derived by subtracting $t_e{}^1$ in Figure 3 from $t_e{}^1$ in Figure 2 is 1.9×10^{-5} M.

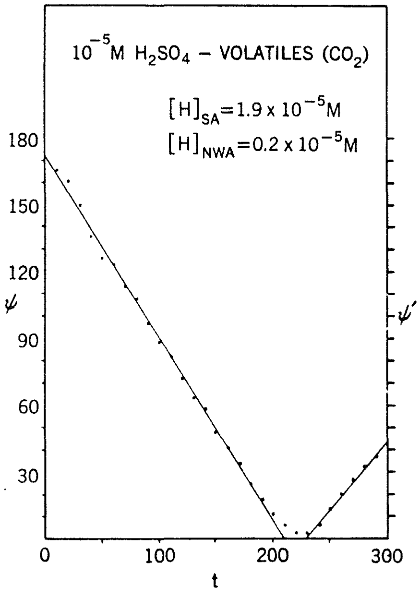

Figure 3. Graphic representation of the coulometric data on a H_2SO_4 standard freed of volatiles. ψ = function of the electromotive force, t = time in seconds, *SA* = Strong acids, and *NWA* = Non-volatile weak acids.

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[a] Strong acid is directly determined from t_e in 2.

[b] Non-volatile weak acid is also determined from 2, by subtracting t_e from t_e'.

* Total acid component is calculated from t_e' in a given sample.

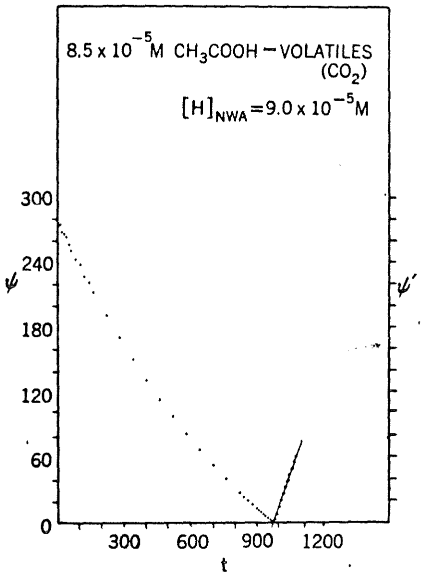

Figure 4. Graphic illustration of the coulometric data on a CH_3COOH standard freed of volatiles. ψ = function of the electromotive force, t = time in seconds, *NWA* = Non-volatile weak acids.

Figure 4 represents the coulometric data for a weak acid, 8.5×10^{-5} M CH_3COOH. Removal of any volatile components by N_2 bubbling results in the intersection of t_e and $t_e{}^1$ at the same point. In this case, as opposed to a strong acid, there is no slope *per se*. According to the original coulometric theory of Gran,[7] in instances where there is no slope, the intersect of a true curve, as illustrated here, should be accepted as real. The $t_e{}^1$ in this case is 5 times in excess of the value obtained for the corresponding concentration of a strong acid. The correct strength of CH_3COOH in this case is 9.0×10^{-5} M.

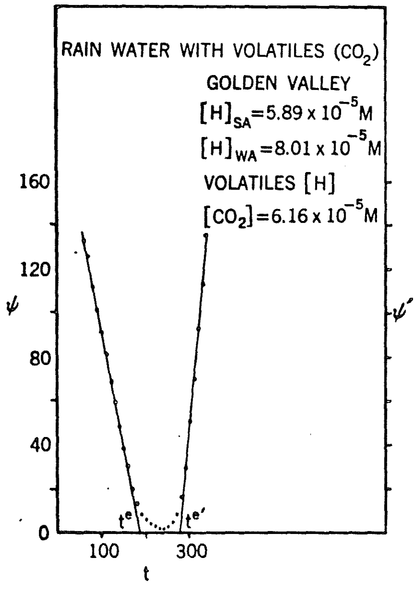

Figure 5. Graphic illustration of the coulometric data on a rain sample with volatiles. Collection site: Golden Valley, Minn. ψ = function of the electromotive force, t = time in seconds, *SA* = Strong acids, and *WA* = Weak acids.

Figure 5 illustrates the results obtained from a rainwater sample collected in the Twin Cities area. The pH of this sample is 4.45. Both strong and weak acid components are present in this rainwater. Total acid concentration ($t_e{}^1$) is 13.90×10^{-5} M.

Figure 6 shows the analytical results of a parallel sample of the same rain freed of volatiles. Based on the data obtained from this and Figure 5, the strengths of the strong and non-volatile and volative weak acid components are 5.89×10^{-5} M, 1.85×10^{-5} M, and 6.16×10^{-5} M, respectively.

Data on rain samples collected approximately during the same time in different localities of the Twin Cities area are presented in Table I. In these samples, strength of the strong acid generally increases with decreasing pH. However, a similar pattern is also observed with the volatile weak acid component.

Sulfuric[1,3] and nitric[8] acids have been implicated in acidic rain. For example, to obtain a pH of 2.80, if H_2SO_4 is the sole cause of acidity, a $SO_4{}^=$ concentration of 70 ppm is required. Similarly, if HNO_3 is the sole H^+ donor, 100 ppm $NO_3{}^-$ is required. To our knowledge, values of this magnitude are far in excess of the reported levels of $SO_4{}^=$ and $NO_3{}^-$ in rain.[9] According to Frohliger and Kane[10] rain is a weak acid.

The coulometric procedure described in this paper can be used to quantify acids *per se* in rain collected around point sources or on a regional basis. This information coupled with the measurements of pH, electrical conductivity, anion and cation concentrations, etc., may help to resolve some of the existing controversies on acidic rain.

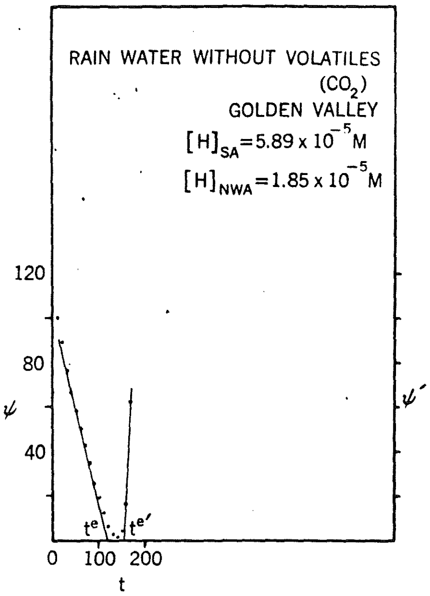

Figure 6. Graphic representation of the coulometric data on a rain sample freed of volatiles. Collection site: Golden Valley, Minn. This rain water was one half of the same sample represented in Figure 5. ψ = function of the electromotive force, t = time in seconds, *SA* = Strong acids, *NWA* = Non-volatile weak acids.

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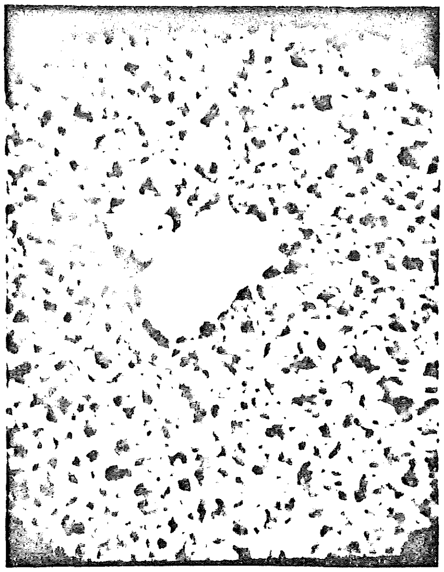
Table I. Acid components in the same rain collected at different locations in the Twin Cities area. Date of collection: June 6, 1974.

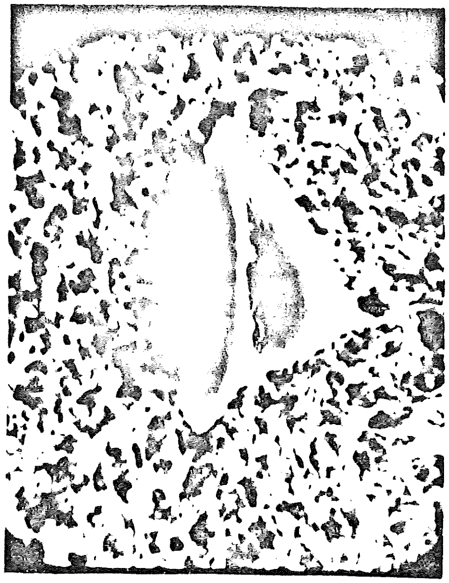
		Concentration 10^{-5} M			
Location	pH	SA	TWA	NWA	VWA
Golden Valley	4.45	5.89	8.01	1.85	6.16
Mound	4.52	3.62	3.38	1.16	2.22
Delaware Avenue	4.70	3.39	1.73	1.64	0.09
N.E. University Avenue	4.80	2.64	1.78	1.40	0.38
Jonathan	5.65	0.00	0.22	0.00	0.22

SA = Strong acid.
TWA = Total weak acid.
NWA = Non-volatile weak acid.
VWA = Volatile weak acid.

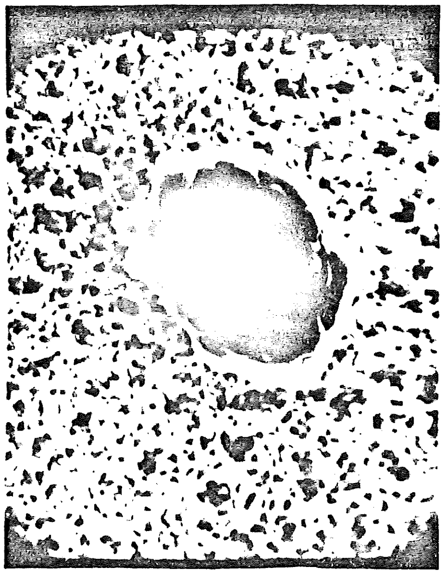
3.1.3. Scanning electron micrographs of inorganic particulate matter collected at different sampling sites during an individual rain event. Golden Valley, Mound, etc., are sampling locations.



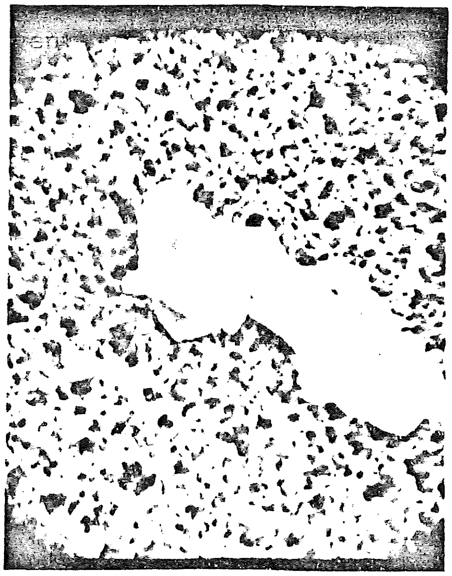
GOLDEN VALLEY
Si, S > Al > Ca > Fe



MOUND
Si



JONATHAN
Al, Si > K > F

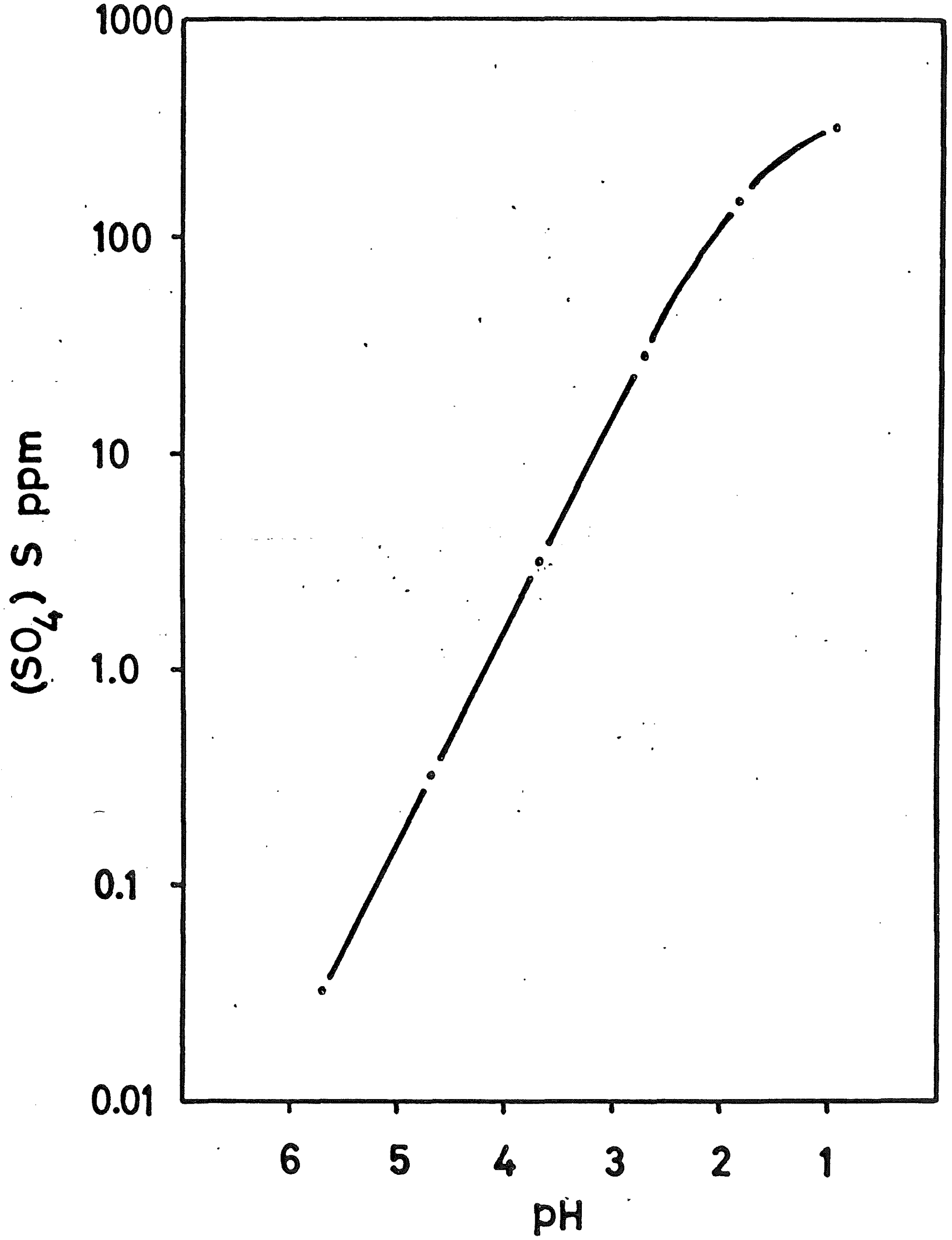


DELAWARE AVE.
Al, Si > Fe

x 5,000

1cm = 1μ

3.1.3.e. Relationship between pH and (SO_4)-S in aqueous systems. This is based on the kinetics of the two step dissociation of H_2SO_4.


1000
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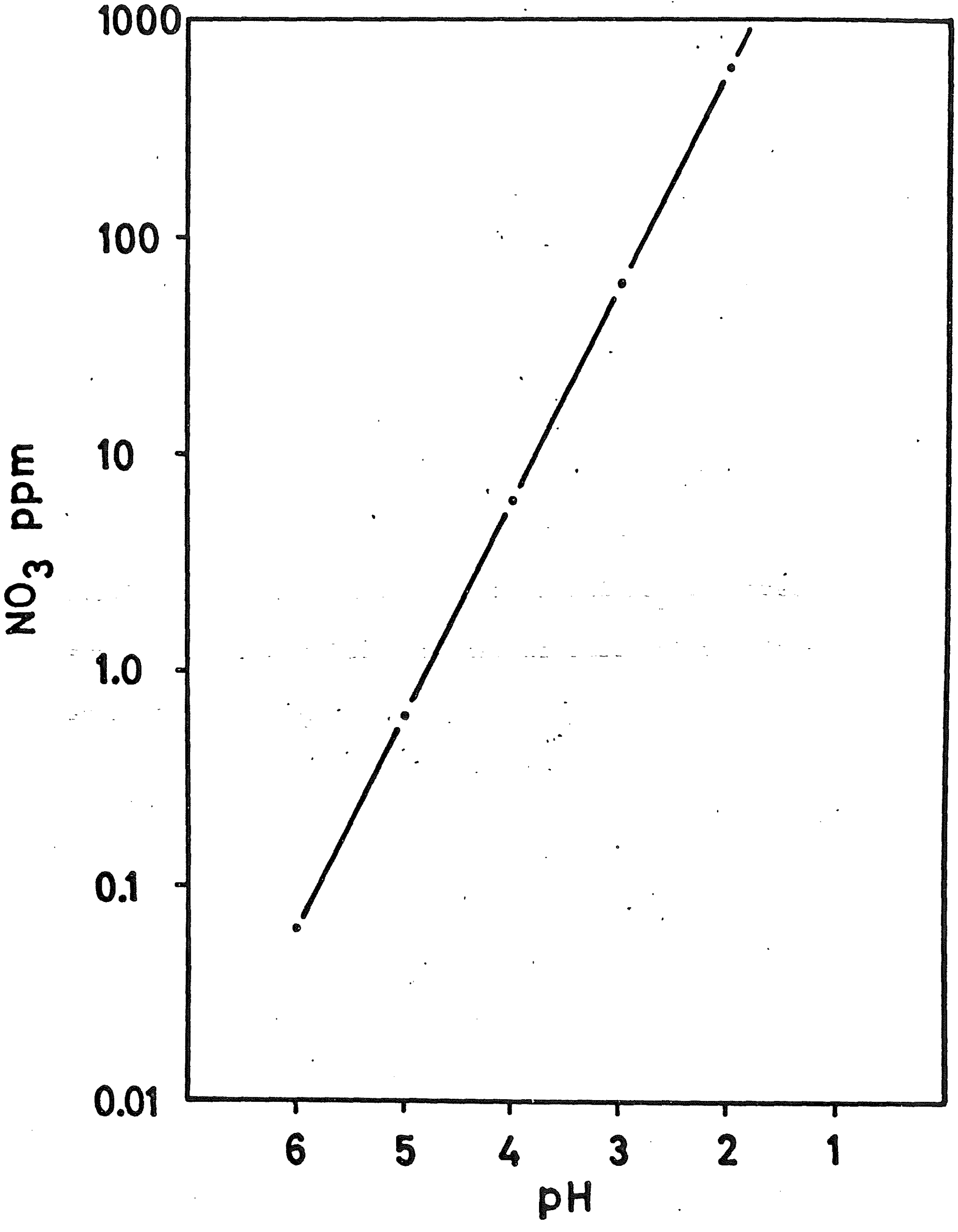
10
1.0
0.1
0.01
(SO4) S ppm
6
5
4
3
2
1
pH

3.1.3.e. Relationship between pH and NO_3 in aqueous systems. This is based on the kinetics of the dissociation of HNO_3.


1000
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0.01
NO_3 ppm
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pH

3.1.3.e. Relationship between pH and Cl in aqueous systems. This is based on the kinetics of the dissociiation of HCl.

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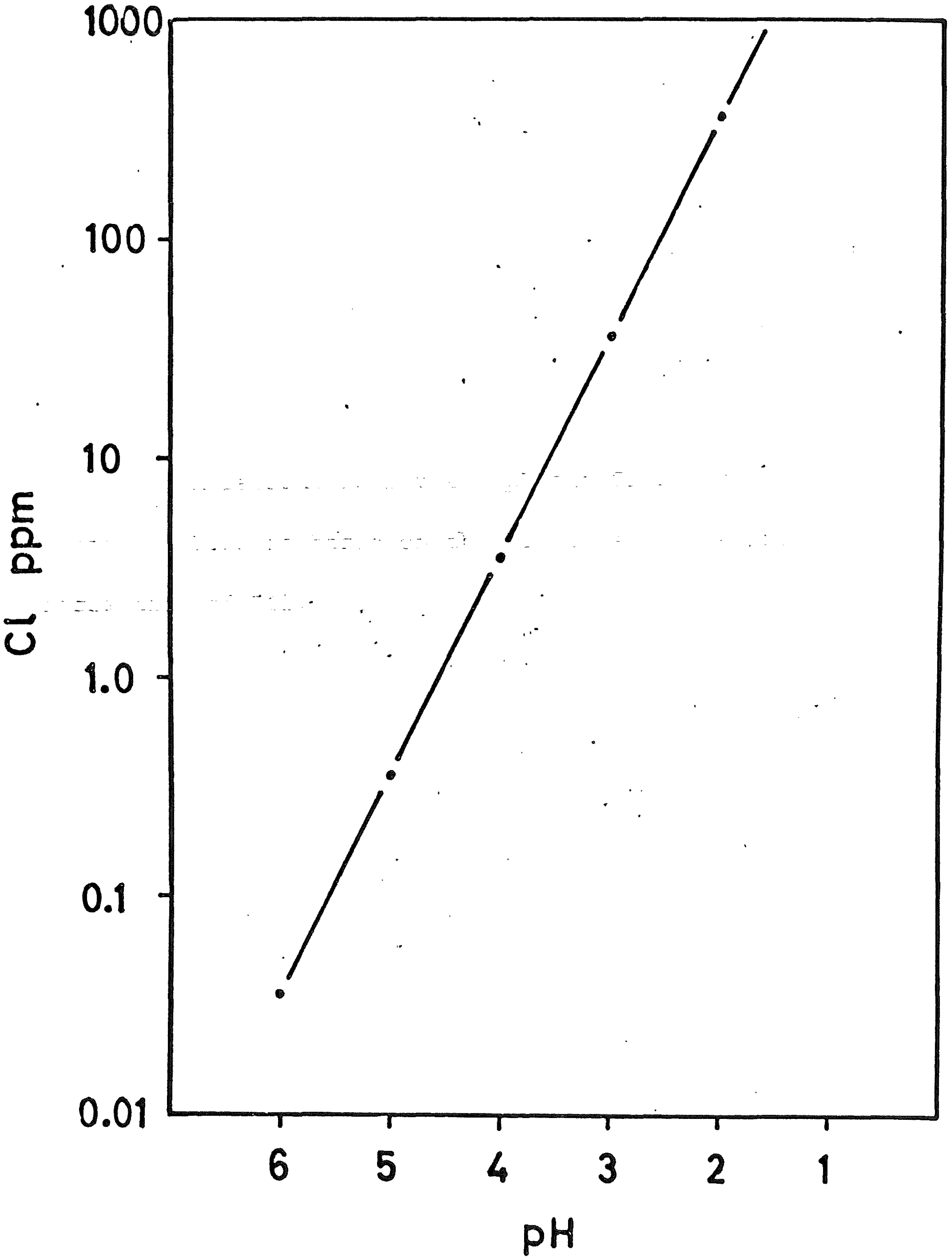

3.1.3.e. Evidence for multiple hydrogen-ion donor systems in rain.

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PROCEEDINGS OF THE FIRST INTERNATIONAL SYMPOSIUM
ON ACID PRECIPITATION AND THE FOREST ECOSYSTEM
USDA Forest Service General Technical Report NE-23
1976

EVIDENCE FOR MULTIPLE HYDROGEN-ION DONOR SYSTEMS IN RAIN[1]

SAGAR V. KRUPA, M. R. COSCIO, JR., AND F. A. WOOD, Assistant Professor, Scientist and Head respectively, Department of Plant Pathology, University of Minnesota, St. Paul, Minnesota 55108.

ABSTRACT

An integrated analytical system consisting of combined scanning electron microscopy and x-ray analysis, atomic absorption, colorimetry and coulometry was used to study rain water chemistry. The coulometry facilitated the determination in molarities of strong and non-volatile and volatile weak acids. The pH of individual rains in St. Paul - Minneapolis, Minnesota ranged from 4.0 to 5.65 during the summer of 1974. Samples of a given rain from different sites had different qualitative and quantitative bases for the measured pH. Increase in strong acid concentrations with a decrease in pH was not an exclusive phenomenon. Molarities of weak acids (volatile and/or non-volatile) also increased with an increase in the acidity. Studies conducted on Twin Cities rain samples indicated that the total salt content expressed from the electrical conductivity could not be accounted for by the total concentrations of individual metals quantified (Fe, Pb, Zn, Mn, Cu, Cr, Cd, Ca, Mg, Na, and K). In addition, no correlation could be shown between the contents of $SO_4^=$, NO_3^-, Cl_2^- & PO_4^- and the observed changes in pH.

INTRODUCTION

Fall out of acidic rain may be a threat to the regional environment. Rainfall with a pH as low as 2.8 and 2.1 has been reported from Sweden (Odén, 1968) and the United States (Likens and Bormann, 1974) respectively.

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[1] This investigation was supported by grants, in part from the National Park Service, U.S. Department of Interior and in part from the Northern States Power Company, Minneapolis, Minnesota. Paper No. 1570 of the University of Minnesota Agricultural Experiment Station.

Barrett and Brodin (1955) stated that since SO_2 is a major constituent of atmospheric pollution, H_2SO_4 is the most likely cause for the acidity of rain water. Since then, almost all of the published reports are based on correlations between total sulfate and pH (Pearson and Fisher, 1971). Measurements of total sulfates do not differentiate the levels and extent to which sulfate is present in the particulate fraction, soluble fraction, as salts and as acid *per se*. Similar considerations are also important in the case of nitrate (Pearson and Fisher, 1971) and chloride (ref. Junge, 1963) and their status as HNO_3 and HCl respectively. Furthermore, pH measurements do not indicate the parent species for the hydrogen ions. In general, our current knowledge of the chemistry of rain water is inadequate.

In this paper we report the results of some of our efforts to understand the chemistry of rain water in the St. Paul - Minneapolis, Minnesota area and the origin of its acidity, as a prelude to the study and interpretation of acidic rain effects on Minnesota vegetation.

MATERIALS AND METHODS

Approximately 250 ml of rain water were sampled from individual rainfalls at several locations in the St. Paul-Minneapolis area in the U.S.A. Sampling was performed manually at approximately 5-6 ft. from the ground, away from trees, buildings, etc. Sampling was started from the time the first rain droplets fell on the ground and was terminated after approximately 30 minutes. Samples were collected in FEP-TEP teflon (DuPont Co. U.S.A.) trays and were immediately transferred to screw cap bottles made of TEP teflon. Precaution was taken to prevent any dead space between the sample and the cap of the bottle. Samples were frozen as quickly as possible in a conventional freezer. At the time of analysis, samples were allowed to thaw and equilibrate to the room temperature (20 C) without opening the bottle.

The analytical techniques used, along with their application, are summarized in Table I. For determining the morphology and gross composition of the inorganic particulate matter in each sample, 10 ml of the rain water were filtered through 0.22μ Millipore (Millipore Corp. U.S.A.) or Nuclepore (Sargent Welch & Co., U.S.A.) filter. After drying the filter in a vacuum, discs were punched at random, mounted on scanning electron microscope (SEM) stubs, carbon coated and viewed under a Cambridge SEM at different magnifications. Whenever the gross inorganic composition was to be determined, the particle was bombarded for approximately 2 min with an energy beam from the internal electron source and the qualitative, relative composition was identified by a precalibrated x-ray analyzer.

TABLE 1

Some Techniques and Their Application in Rainwater Analysis

Technique	Description of its use
Coulometry	Quantification in molarities (M) of: 1) non-volatile strong acid, 2) non-volatile weak acid, and 3) volatile weak acid.
Scanning E.M. + x-ray analysis	Morphology and gross qualitative inorganic composition of particulate matter.
Atomic Absorption	Quantification of metallic components Eg: Ca, Mg, Na, K, Fe, Zn, Cu, Mn, Pb, Cd etc.
Colorimetry + Specific ion electrode	Quantification of SO_4, Cl, NO_3, NO_2, NH_4, PO_4, F, etc.

Concentrations in molarities of different acids in the rain samples were determined by coulometry. The coulometric unit consists of a constant current source, a measuring cell located on a magnetic stirrer and a potentiometer (modified pH meter) with a four digit visual read out. Based on the relationship between Ψ (a function of the electromotive force) and time in seconds (t) in two portions of the same rain sample, with and without volatiles, the molarities of non-volatile strong, and non-volatile and volatile weak acids were calculated (Krupa et al. 1974). When a sample was to be freed of volatiles, the solution was bubbled vigorously with N_2 for 30 minutes with simultaneous stirring and kept under a blanket of N_2 throughout the analysis.

Quantification of the cations and NH_4^+ & anions were performed according to the conventional procedures using a Perkin-Elmer (U.S.A.) Model 330 atomic absorption unit and Technicon (U.S.A.) model II Autoanalyzer respectively.

RESULTS AND DISCUSSION

The pH of individual rains varied from 4.00 to 5.65 during the summer of 1974. Inorganic and organic particulate matter ranged in the samples at approximate ratios of 8 : 2 to 5 : 5. In the analysis of randomly selected inorganic particles from various samples, the following elements were found, based on the order of frequency of their occurrence:

Al, Si > Fe > K > Ca > Ti > S > P > F > Cl

Gross morphology and elemental composition of some representative inorganic particles are shown in Figure 1. Based on frequency of occurrence X relative amount (comparative peak height), elemental composition of these particles in the rain samples was as follows:

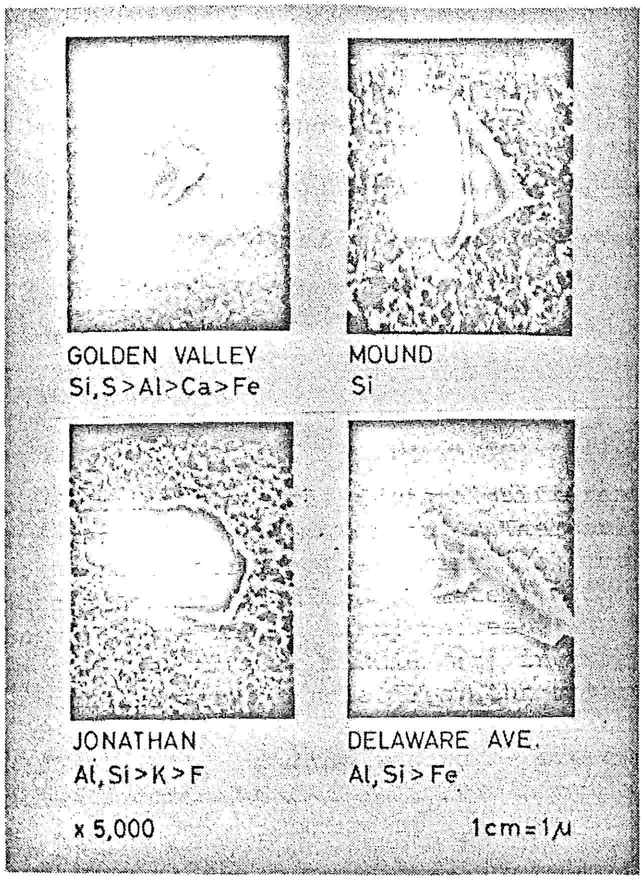

Figure 1. Scanning electron micrographs of inorganic particulate matter collected at different sampling sites during an individual rain event. Golden Valley, Mound, etc. are locations of sampling.

Si > Al > Fe > K > S,Ca > Ti > P > Cl,F

Coulometric data on samples collected at five different sites during a representative rain event are shown in Figure 2. Strong acid(s) concentration in the rain samples ranged from 0.0 to 5.89 × 10^{-5}M. There was an increase in the concentration of the strong acid component with a decrease in pH. However, this was not an exclusive phenomenon. Molarities of weak acids (volatile and/or non-volatile) also increased (0.22 to 8.01 × 10^{-5}M) with an increase in the acidity.

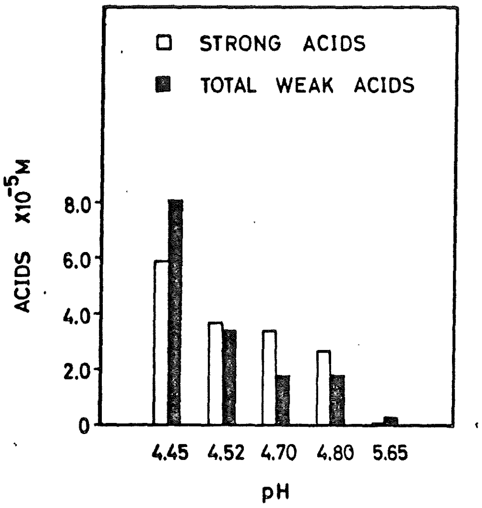

Figure 2. Relationships between pH and strong and weak acids in rain. Acid concentrations expressed as molarities.

The strong acid component may consist of different combinations of H_2SO_4, HNO_3, HCl and possibly dithionate. Figures 3, 4, and 5 illustrate the relationships between pH and SO_4-S, NO_3 and Cl when they exist as their corresponding acids and when each acts as the sole hydrogen ion donor. These values are based on known dissociation rates in aqueous systems. Barium chloride precipitable sulfur content (expressed as sulfate units) ranged in the rain samples from 1.2 mg/l to 2.4 mg/l. There was no correlation between the changes in the strong acid concentration and $SO_4^=$ levels (Figure 6). Patterns of change in NO_3^- concentration paralleled the $SO_4^=$ change in relation to pH. One of the most effective methods of SO_2 oxidation and neutralization is considered to be the "SO_2-NH_3-H_2O" system (Scott and Hobbs, 1967; ref. Krupa and Wood, 1974). NH_4-N content in our samples ranged from 0.7 mg/l to 0.82 mg/l. No definite correlations could be found when ratios between ($SO_4^=$ + NO_3^- + Cl^-) and NH_4^+ or ratios between $SO_4^=$ and NH_4^+ were plotted against pH (Figure 7). pH of rain samples varied irrespective of the calculated levels of NH_3 neutralization. Inorganic acid forming groups other than $SO_4^=$ varied in their concentration as

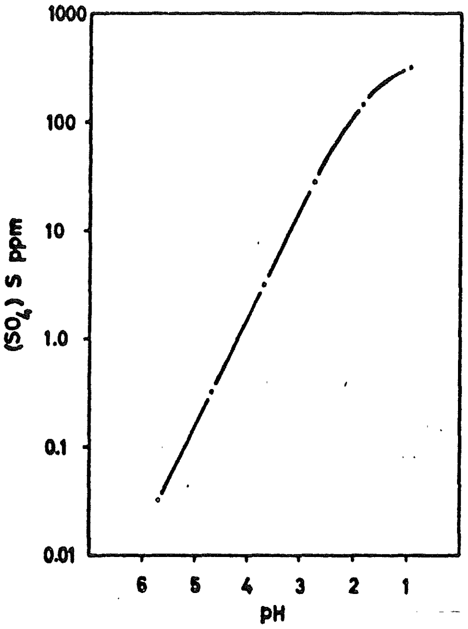

Figure 3. Relationship between pH and SO_4-S based on the values for the two step dissociation of H_2SO_4. SO_4-S should be multiplied by 3 to obtain SO_4 values.

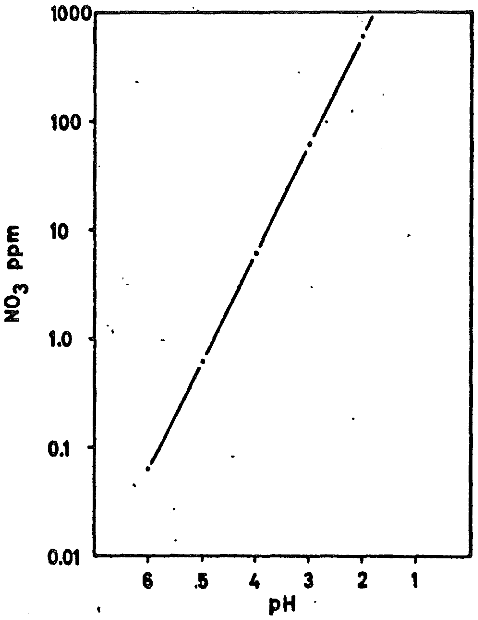

Figure 4. Relationship between pH and NO_3 based on the single step dissociation of HNO_3.

follows: NO_3-N - 0.063 mg/l to 0.450 mg/l; Cl - 0.10 mg/l to 0.60 mg/l; and PO_4-P - 0.002 mg/l to 0.009 mg/l.

Approximate total salt concentration expressed from electrical conductivity measurements (3.47 mg/l to 11.10 mg/l) could not be accounted by the total concentration of the individual cations quantified by atomic absorption (Table 2).

As mentioned previously the weak acid component also increased with a decrease in pH. Figure 8 illustrates the relationship between non-volatile and volatile weak acids and pH of our rain samples. It is not clear at this time as to what extent the volatile acid component is constituted by CO_2-H_2O-H_2CO_3-HCO_3 system. The CO_2-H_2O system can be influenced by the SO_2 dissolved species, HSO_3^-.

The aforementioned results demonstrate a multiple hydrogen-ion donor system in rain. These includes: 1) a strong acid component (H_2SO_4, HNO_3, HCl, and possibly dithionate); 2, a non-volatile weak acid component (HF, organic acids, hydrolysable salts etc.); and 3) a

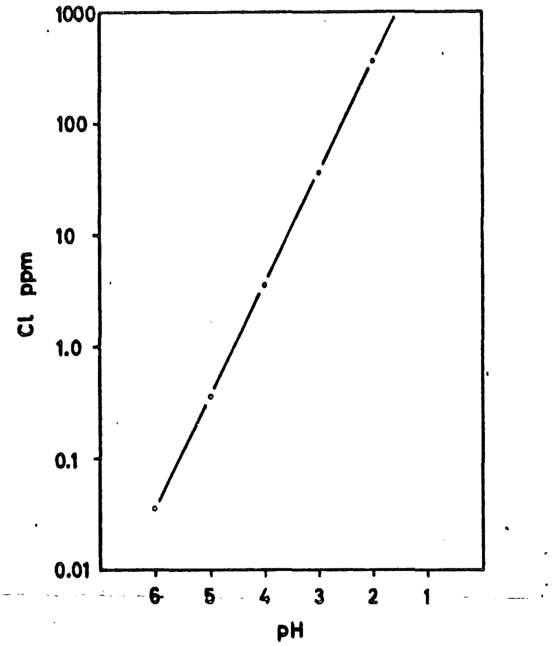

Figure 5. Relationship between pH and Cl based on the single step dissociation of HCl.

volatile weak acid component (CO_2-H_2O system and unknowns). Sulfur in the atmosphere may exist in several different forms: SO_2, SO_3, SO_4,

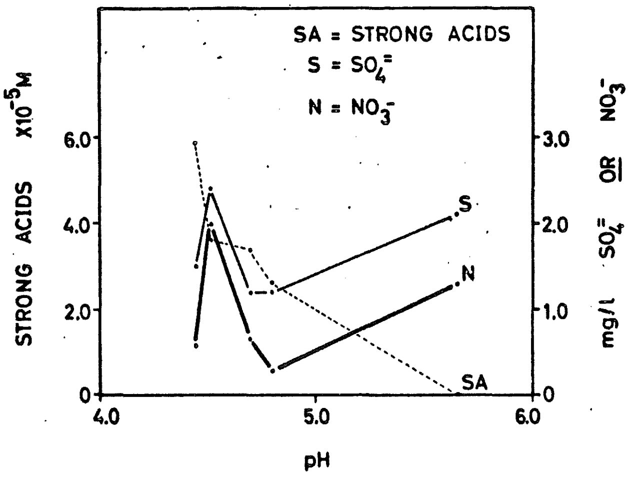

Figure 6. Relationship between pH and 1) molarities of strong acids, 2) $SO_4^=$ concentrations, and 3) NO_3^- concentrations in rain samples.

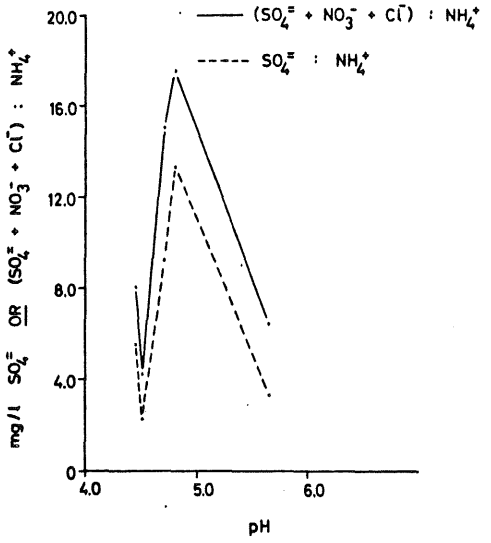

Figure 7. Relationship between pH and ratios of $(SO_4^= + NO_3^- + Cl^-)$ and NH_4^+ or ratios of $SO_4^=$ and NH_4^+. Ratios calculated on the basis of mg/l of different components in rain.

TABLE 2

Metallic components in the same rain collected at different locations in the Twin Cities area

Date of collection: June 6, 1974

Sampling Locaion	Concentration in ppm										
	Cu	Fe	MN	Zn	Cd	Cr	Pb	Mg	Ca	Na	K
Golden Valley	<0.01	<0.1	<0.01	0.02	<0.02	<0.02	<0.2	0.016	0.055	0.03	0.03
Mound	<0.01	<0.1	<0.01	<0.02	<0.02	<0.02	<0.2	0.053	0.529	0.04	0.11
Delaware Ave.	<0.01	<0.1	<0.01	0.02	<0.02	<0.02	<0.2	0.011	0.115	0.10	0.06
N.E. University Ave.	<0.01	<0.1	<0.01	<0.02	<0.02	<0.02	<0.2	0.012	0.020	0.05	0.07
Jonathan	<0.01	<0.1	<0.01	<0.02	<0.02	<0.02	<0.2	0.203	1.23	0.38	0.23

S_2O_5, S_2O_6, H_2S, dithionates, mercaptans, thionyls, $(NH_4)_2SO_4$, metallic salts, H_2SO_4 etc. Components such as organic acids form weak acids and may be part of the non-volatile weak acid component. Our results also show that samples of a given rain from different sites have different qualitative and quantitative bases for the measured pH. Semonin (1973) was unable to find correlations between point sources and pH of rain in the St. Louis, Missouri area and found that pH varied widely during the same rain at different sampling sites.

These considerations are important with reference to any direct vegetational effects. Shriner (1974) was able to demonstrate adverse effects on terrestrial vegetation by subjecting plants to pH 3.2 H_2SO_4 simulated to fall as rain. While acidity can have influence on plants through nutrient leaching etc., more recent evidence by Wood and

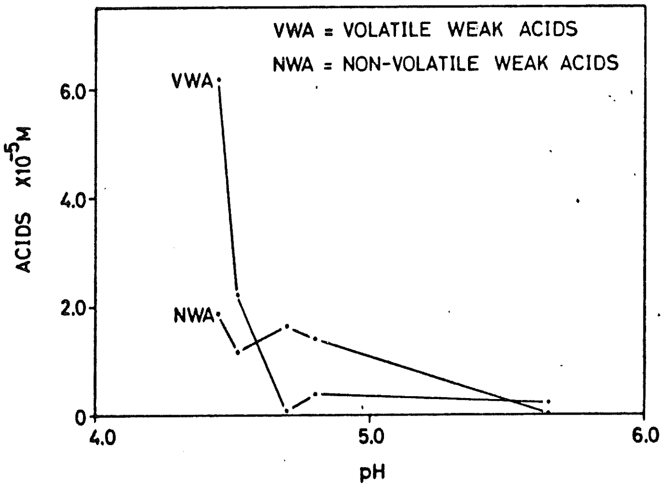

Figure 8. Relationship between pH and molarities of non-volatile and volatile weak acids in rain.

Pennypacker (1975) indicates that anions may play an important role in direct effects on foliage. The chemistry of rain in a given geographic region should be evaluated on per rain basis as a prelude to vegetational studies.

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Pennypacker [illegible] indicated that aerosols may play an important role in direct effects on foliage. The chemistry of rain in a given geographic region should be evaluated on per rain basis as a prelude to vegetational studies.

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cause for the acidity of rain water. Since then, almost all of the published reports are based on correlations between total SO_4 and pH. Measurement of total sulfates does not differentiate the levels and extent to which SO_4 is present in the particulate fraction, soluble fraction, as salts and as acid *per se*. Similarly, pH measurements do not indicate the parent species for the hydrogen ion.

The objective of the present investigation was to develop a comprehensive analytical system to understand the origin of acidity in rain water as a prelude to the study and interpretation of acid rain effects on vegetation.

MATERIALS AND METHODS

Approximately 250 ml of rain water was collected each time, from the same rain fall at several locations in the Minneapolis - St. Paul area in the U.S.A. Sampling was performed manually at approximately 5-6 ft. from the ground, away from trees, buildings etc.

Sampling was started from the time the first rain droplets fell on the ground and was terminated after approximately 30 minutes. Samples were collected in FEP-TEP (DuPont Co. U.S.A.) trays and was immediately transferred to screw capped bottles made of TEP teflon. Precaution was taken to prevent any dead space between the sample and the cap of the bottle. Samples were frozen immediately at -20 C. At the time of analysis, samples were allowed to thaw and equilibrate to the room temperature (20 C) without opening the bottle. Samples were processed according to the scheme shown in Figure 1.

The analytical techniques used, along with their application, are summarized in Table 1. For determining the morphology and gross composition of the inorganic particulate matter in each sample, 10 ml of the rain water was filtered through 0,22 u Millipore (Millipore Corp. U.S.A.) or Nuclepore (General Electric, U.S.A.) filter. After drying the filter in a vacuum, discs were punched at random, mounted on scanning electron microscope (SEM) stubs, carbon coated and viewed under a Cambridge SEM at

different magnifications. Whenever the gross inorganic composition was to be determined, the particle was bombarded for approximately 2 min with an energy beam from the internal electron source and the qualitative relative composition was identified by a precalibrated, non-dispersive x-ray analyzer.

The coulometric procedure used was a modified from that of LIBERTI *et al.* (1972). The unit (Figure 2) consists of a constant current source (A), a measuring cell located on a magnetic stirrer (B) and a potentiometer (modified pH meter) with a four digit visual read out (C). Based on the relationship between Ψ (a function of the electromotive force) and time in seconds (t) in two portions of the same rain sample, with and without volatiles, the molarities of non-volatile strong, and non-volatile and volatile weak acids were calculated (KRUPA *et. al.* 1974). When a sample was to be freed of volatiles, the solution was bubbled vigorously with N_2 for 30 minutes with simultaneous stirring and kept under a blanket of N_2 throughout the analysis.

Quantification of the cations and NH_4^+ & anions were performed according to the conventional procedures using a Perkin-Elmer (U.S.A.) model 330 atomic absorption unit and Technikon (U.S.A.) model II autoanalyzer respectively.

RESULTS AND DISCUSSION

In the analysis of randomly selected particles from various rain water samples (ref. Table 2.), the following elements were found, based on the frequency of their occurrence:

Al, Si > Fe > K > Ca > Ti > S > P > F > Cl.

Gross morphology and elemental composition of some representative anorganic particles are shown in Figure 3. Based on frequency of occurrence x relative amount (comparative peak height), elemental composition of the particulate matter in the rain samples was as follows:

Si > Al > Fe > K > S, > Ca > Ti > P > Cl, F

Coulometric data on the rain samples are presented in Table 2. There was an increase in the strong acid component with a decrease in pH. At the same time, there was also an increase in the concentration of the total weak acid component. No direct correlation existed between the magnitude of changes in the concentration of the strong acid and differences in pH between the various rain samples. The concentration of total weak acid, as well as the volatile weak acid, exceeded the strong acid component in the rain water collected at "Golden Valley". This sample had the lowest pH value - 4.45 (Table 2). Similarly, the sample collected at "Jonathan" contained the second largest concentration of SO_4-S (Table 3). However, it was completely devoid of a strong acid component. The quantity of alkali-alkaline earth metals found in that particular sample may account for the absence of a strong acid component. (Table 4). The concentration of volatile weak acids present (Table 2) can satisfy the pH value (5.65) observed in that case. On the contrary, in the other samples, no clear relationship was found between pH, SO_4-S, and levels of alkali-alkaline earth metals.

The aforementioned results indicate the complexity of rain water chemistry and questions concerning the parent sources of hydrogen ion. If it is assumed that the total available SO_4^{2-}, NO_3^- and Cl^- contribute the hydrogen ions found in the strong acid component, then the coulometric data for strong acid concentrations in the different rain samples used in this study may be satisfied by the measured values for the three aforementioned anions. However, the simultaneous presence of weak acid components, NH_4^+ and cations (metals) should be considered in this contex . Furthermore, common ion effects can not be ignored.

Thus the acidity of rain water down to a pH of 4.0 may be contributed to by at least five different hydrogen donors: H_2SO_4, HNO_3, HCl, weak acids such as H_2CO_3 and HF, etc. and hydrolysable salts. This is particularly meaningful, since the average pH values of rain water reported for the United States during 1972 range between 6.59 and 4.39 (MILLER, 1974). It should be pointed out that the extent of contribution by the individual hydrogen donors will vary between different rain falls, and between the same rainfall at different locations, depending on the physicochemical parameters of the environment. The proportions between

TABLE 1

Some Techniques and Their Application in

Rainwater Analysis

Technique	Description of its Use
Coulometry	Quantification in molarities (M) of: non-volatile strong acid, 2) non-volatile weak acid, and 3) volatile weak acid.
Scanning E.M. + x-ray analysis	Morphology and gross qualitative inorganic composition of particulate matter
Atomic Absorption	Quantification of metallic components Eg: Ca, Mg, Na, K, Fe, Zn, Cu, Mn, Pb, Cd etc.
Colorimetry + Specific ion electrode	Quantification of SO_4, Cl, NO_3, NO_2, NH_4, PO_4, F, etc.

TABLE 2

ACID COMPONENTS IN THE SAME RAIN

COLLECTED AT DIFFERENT LOCATIONS IN THE TWIN CITIES AREA

Date of Collection: June 6, 1974

Location	pH	Concentration 10^{-5}M			
		SA	TWA	NWA	VWA
Golden Valley	4.45	5.89	8.01	1.85	6.18
Mound	4.52	3.62	3.38	1.18	2.22
Delaware Avenue	4.70	3.39	1.73	1.64	0.09
N.E. University Avenue	4.80	2.64	1.78	1.40	0.35
Jonathan	5.65	0.00	0.22	0.00	0.22

SA = Strong Acid
TWA = Total Weak Acid
NWA = Non-volatile Weak Acid
VWA = Volatile Weak Acid

TABLE 3

Non-metallic components in the same rain collected at different locations in the Twin Cities area*

Date of collection: June 6, 1974

Sampling Location	Concentration in ppm					
	NH_4-N	NO_3-N	PO_4-P	Cl	SO_4-S	Total salts** (Approx.)
Golden Valley	0.21	0.129	<0.002	<0.10	0.5	8.35
Mound	0.82	0.450	0.005	<0.10	0.8	11.10
Delaware Ave.	0.10	0.147	<0.002	<0.10	0.4	7.48
N.E. University Ave.	0.07	0.083	<0.005	<0.10	0.4	3.47
Jonathan	0.48	0.292	0.009	0.60	0.7	9.63

- * Quantitative elemental differences between the filtered and unfiltered samples were not significant.

** ppm total salts were calculated on an approximate basis as follows: Electrical Conductivity in μmohs/cm at 25 C x 0.55.

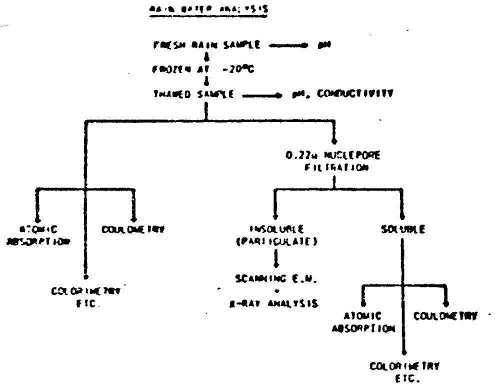
TABLE 4

Metallic components in the same rain collected at different locations in the Twin Cities area*

Date of collection: June 6, 1974

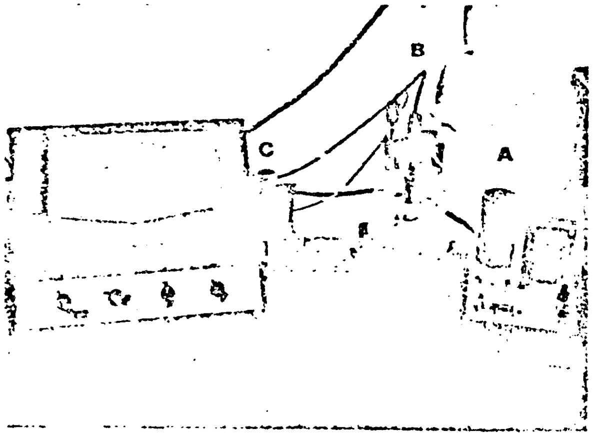
ampling ocation	Concentration in ppm										
	Cu	Fe	Mn	Zn	Cd	Cr	Pb	Mg	Ca	Na	K
olden Valley	<0.01	<0.1	<0.01	0.02	<0.02	<0.02	<0.2	0.018	0.055	0.03	0.03
ound	<0.01	<0.1	<0.01	<0.02	<0.02	<0.02	<0.2	0.053	0.529	0.04	0.11
elaware Ave.	<0.01	<0.1	<0.01	0.02	<0.02	<0.02	<0.2	0.011	0.115	0.10	0.08
.E. University Ave.	<0.01	<0.1	<0.01	<0.02	<0.02	<0.02	<0.2	0.012	0.020	0.05	0.07
onathan	<0.01	<0.1	<0.01	<0.02	<0.02	<0.02	<0.2	0.203	1.23	0.38	0.23

- * Quantitative elemental differences between the filtered and unfiltered samples were not significant.



Legend for Figure 1

Flow chart showing the procedure for the integrated analysis of rain water.



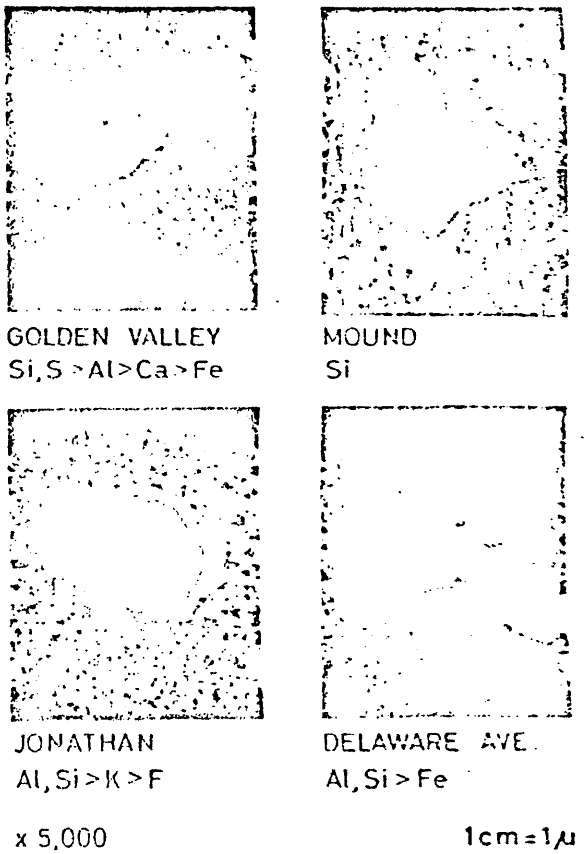
Legend for Figure 2

Coulometric unit for determining the strong and weak acid components in rain water.

(A) = Constant current source

(B) = Titration cell

(C) = Converted pH meter and four digit readout.



Legend for Figure 3

Scanning electron micrographs of inorganic particulate matter in different rain samples. Golden Valley, Mound, etc. are locations of sampling.

these variables may largely dictate the basis for the pH in a given rain water sample.

ACKNOWLEDGEMENT

We acknowledge the U.S. National Park Service for providing us with a research grant for this study.We express our gratitude to Mr. R.C. Munter, University of Minnesota, St. Paul, for generous help and advice during the course of this study.

ABSTRACT

An integrated analytical system to study the chemistry of rain water is reported. The procedure consists of the following techniques: Scanning electron microscopy & x-ray analysis, coulometry, atomic absorption and colorimetry. Preliminary data obtained using the aforementioned methods, show that rain water samples collected from the same rainfall at different sampling sites within a metropolitan area vary in their pH, molarities of strong non-volatile, weak non-volatile and volatile acids and total salts. In addition, the results indicate the coexistance of roughly comparable concentrations of strong and weak acids down to a pH of 4.0.

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