EXTRACTABLE CHROMIUM, IRON, AND MANGANESE
FROM TWO MICHIGAN SOILS AS RELATED TO
SOIL pH AND APPLIED CHROMIUM

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ABSTRACT

EXTRACTABLE CHROMIUM, IRON, AND MANGANESE

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By

John Hamman Grove

A soil incubation study was conducted on Rubicon sand (Muskegon County, Michigan) and Morley clay loam (Ionia County, Michigan) at constant temperature and moisture potential.

Chromium was applied at rates of 0, 50, 100, and 500 ppm Cr(III) and Cr(VI), and also at 700, 1400 and 2100 ppm sludge Cr. A third "soil" was generated by liming the Morley soil to a pH of 7.5 with $Ca(OH)_2$. Initial soil pH for the other two soils was 4.7 and 6.0 for the Rubicon and the unlimed Morley respectively. Pots were sampled at 24 hours, 1, 2, 4, 8, and 16 weeks of incubation.

Soil pH values were determined on 10 g subsamples. Another 5 g subsample was subjected to successive extraction with distilled water, 1 $\underline{M}$ NH_4Cl, 0.1 $\underline{M}$ $CuSO_4$, 0.3 $\underline{M}$ $(NH_4)_2C_2O_4$, and citrate-dithionite-bicarbonate. Extracts were analyzed for Cr, Fe, and Mn by atomic absorption spectrophotometry.

Trivalent chromium rapidly changed to insoluble forms, reducing soil pH and water soluble Fe and increasing water soluble Mn. Chromium precipitation occurred more rapidly on acid soils.

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Hexavalent chromium was also precipitated as a hydrous oxide of Cr(III) after reduction. After an initial reduction, soil pH was increased above control values. Similar behavior was noted for water soluble Fe. Water soluble Mn rose above that in the control initially, and decreased ultimately.

Sludge amendment resulted in little water soluble Cr. Most sludge Cr was removed by the final two extractions (oxalate, dithionite). Water soluble Fe was reduced and water soluble Mn increased as the incubation of the sludge amended soils proceeded.

Other extractions experienced complex changes during the course of the experiment.

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INTRODUCTION

In the past decade public concern has focused sharply on the issue of environmental quality. Congress enacted Public Law 92-500, The Federal Water Pollution Control Act Amendments of 1972, in response to increasing concern over discharges into surface waters. Municipalities must now comply with the federal discharge regulations for sewage treatment facilities. These cities and towns must find economical, yet effective ways of dealing with their sewage output, and all methods of treatment generate a solid component known as "sludge."

Sludge may be disposed of in three ways; incineration, landfilling, or application to the soil. The latter method recycles some sludge constituents, such as N, that are beneficial to plant growth and crop yield. But sludges contain a variety of components with a wide range in concentrations. Properly managed, land incorporation can minimize adverse environmental impact.

Heavy metals are often an important portion of sewage sludge. Deleterious effects of large quantities of these metals on plant and animal life have been well documented. And chromium (Cr), present in the effluent of plating plants, smelting plants, and tanneries, is commonly found in sludges. Until recently, little information on the soil chemistry of Cr was available. Plant uptake studies dominate the agricultural literature on Cr.

This study was designed to elucidate the soil chemistry of Cr via extraction methods. Three levels of Cr(III) (chloride salt) and Cr(VI)

(oxide anhydride), plus two levels of sludge Cr were applied to three soils of varying pH. Additional information was sought regarding the effects of added Cr on soil pH and the soil chemistry of Fe and Mn. Changes in extractable Fe and Mn were followed for a sixteen week incubation period. The knowledge gained will be important in helping treatment plant managers utilizing land incorporation of sewage sludges high in Cr content to minimize Cr induced damage to the crops grown on these soils.

CHAPTER I

LITERATURE REVIEW

General Chemistry of Chromium

The first transition series of elements in the periodic table includes Cr, element number 24, with an atomic weight of 51.996. The most common isotope is ^{52}Cr, but ^{51}Cr is a radioactive isotope suitable for tracer studies. The electronic configurations of Cr, Cr(III), and Cr(VI) are [Ar] $3d^54s^1$, [Ar] $3d^3$, and [Ar] respectively. While the 0, +2, +3, and +6 oxidation states of Cr are known, the trivalent is the most stable and important one. Lower oxidation states are strongly reducing and higher ones are moderate to strong oxidizing agents, depending upon hydrogen ion activity (Cotton and Wilkinson, 1972).

Chromium (III) has an ionic radius (0.69 Å) similar to other tri-valent metals of importance in natural systems. Chromium (III) forms many hexacoordinate complexes whose most important common property is a slow rate of ligand exchange in aqueous solution (Mertz, 1969). Many Cr complexes are highly colored, a property from which the element derives its name.

Soil Chromium

The abundance of Cr in the lithosphere is given by Swaine (1955) as 200 ppm Cr. The total Cr content of soils varies widely (Pratt, 1966), but Cr is nearly ubiquitous in nature (Davis, 1956). American soils contain between 1 and 1500 ppm total Cr (Lisk, 1972) with an

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average of 53 ppm (Mertz, 1974a). In a study of Vermont soils, Bartlett and Kimble (1976a) found total Cr to range between 0.1 and 18 ppm with higher values usually occurring for spodic horizons.

Soils derived from ultra-basic (serpentine) rocks may have much more Cr, with values ranging up to several percent (Swaine, 1955). Serpentine soils containing large amounts of total Cr can be found in many parts of the world, including the United States, Southern Africa, New Zealand, Australia, Japan, and Puerto Rico (Jones et al., 1977; Soane and Saunder, 1959; Lyon et al., 1970; Anderson et al., 1973; Suzuki et al., 1971; Mertz, 1969).

Hodgson (1963) has reviewed the general chemistry applicable to trace metals in soil systems. Lisk (1972) presented chemical parameters to consider in the evaluation of trace metal pollution in soils. Allaway (1968) reviewed the impact of agricultural practices on the behavior of naturally occurring and anthropogenically introduced trace elements and the cycle of these elements in the environment. Mortvedt et al. (1972) edited an extensive review on the role of trace metals (Zn, Fe, B, Mn, Cu, and Mo) in agriculture.

Hodgson (1963) presents the following schema of "pools" existing in the plant-soil system:

Primary mineral

weathering

uptake
by plants

complex with insoluble organic
MR   matter

```
 ┌ ─ ─┼+─ ─ ─ ─ ┐
 │    M      ___  MCh    │
 │ free ion    complex   │
 └_ _in solution_ _ _ _ ┘
```

incorporation
into microbial
tissue

MX------- occlusion
surface   in developing
adsorption   precipitates

oxidation
reduction

precipitation of
oxides or phosphates
for Fe and Mn

solid state
diffusion into
solid minerals
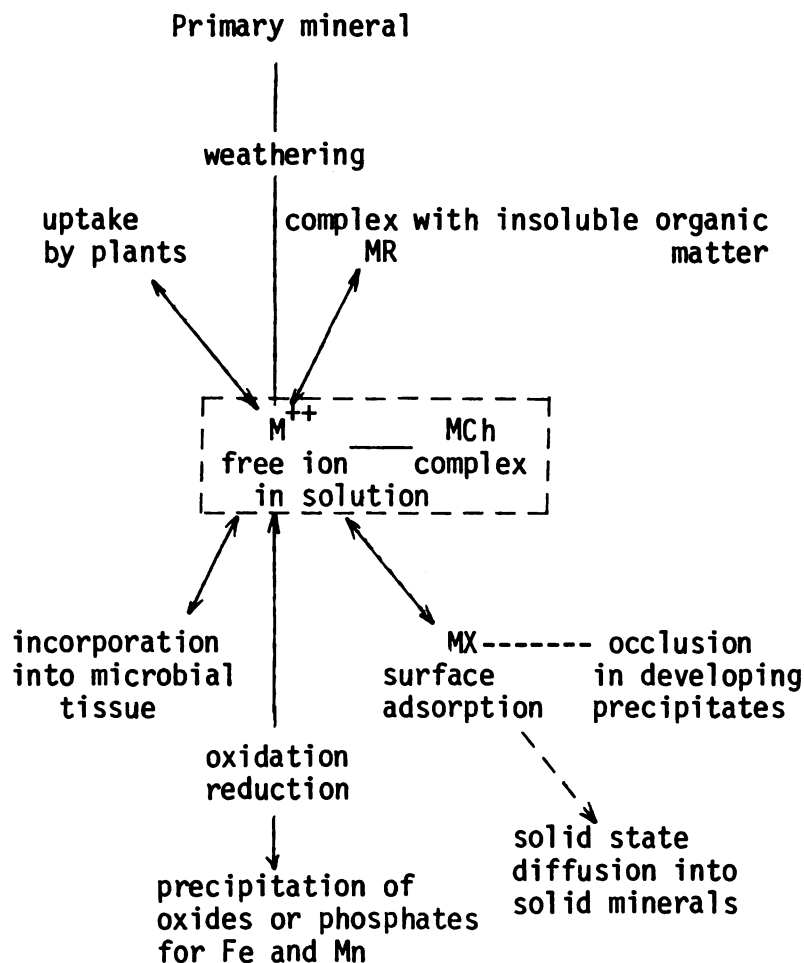
According to Viets (1962) these pools represent different chemical forms
of the element in question. The distribution of any element among its
pools determines its availability for plant uptake. The kinetics of
the various transformations required in the movement of the element
between pools are also important to consider. The schema assists one
in ascertaining the shifts in availability caused by varying soil
chemical parameters. In theory each pool can be accessed by an extrac-
ting agent, thereby providing an accurate measure of the individual
pool's relative content of a given trace metal. The soil chemistry of
the metal may be discussed relative to the absolute amount of metal in
the pools, or movement of metal between pools, or both. The soil

chemistry of Cr will be discussed here using the schema as an organiza-
tional guide.

Most of the naturally occurring Cr found in soils is in the form
of chromite ($FeCr_2O_4$), chromite derivatives [(Mg, Fe)(Cr, Al, Fe)CrO_4],
or in silicate lattices. All of these compounds are relatively in-
soluble in soils and the Cr contained within them would generally be
unavailable for plant growth (Soane and Saunder, 1959; Allaway, 1968).
Suzuki et al. (1971) mentions that the infertility of serpentine soils
is due more to the presence of Ni than Cr;which is in agreement with
the findings of Anderson et al. (1973), but not with the conclusions
of Soane and Saunder (1959). Mertz (1969) and Swaine (1955) found
that most soils have little "available" Cr.

Until recently the soil chemistry of Cr was not well known
(Mertz, 1969; Lisk, 1972; Schueneman, 1974). Plant uptake studies
have generally been toxicological in intent. Pratt (1966) stated
"There have been no successful attempts to measure chromium avail-
ability, either in serpentine soils or in others."

Extractable Cr has been evaluated by many workers. Swaine
(1955) found that 0.5 $\underline{N}$ acetic acid (HOAc) extracted approximately
0.3 ppm Cr, and 1 $\underline{N}$ ammonium acetate (NH_4OAc) extracted less than
0.1 ppm Cr from most soils.

Soane and Saunder (1959) evaluated several extracting agents
for Cr and found all (NH_4OAc, HOAc, and ethylenediaminetetracetic
acid (EDTA)) to be unsuitable, settling on a cation exchange resin
instead. They removed 1.1 ppm Cr from a soil containing 4.6% Cr using
this method.

Suzuki et al. (1971) recovered no water soluble Cr, 0.2 ppm 1 $\underline{N}$ NH_4OAc soluble Cr, and 4.3 ppm 0.1 $\underline{N}$ HCl soluble Cr from a soil containing 5,200 ppm Cr. The soil pH was not given.

Anderson et al. (1973) found 0.02 ppm Cr in the soil solution of a soil with a pH of 5.3 and a total Cr content of 634 ppm. No detectable Cr could be found in 2.5% HOAc of 1 $\underline{N}$ NH_4OAc extracts of this soil.

Leep (1974) added 2.00 milliequivalents Cr(III) per 100 grams of soil as the trichloride salt to a Houghton muck soil with a pH of 6.7. He found only 2.3 ppm Cr could be extracted with 0.1 $\underline{N}$ HCl. Normal NH_4OAc and 0.005 $\underline{M}$ diethylenetriaminepentaacetic acid (DTPA) extracted no Cr. Corn plant uptake of Mn was enhanced by Cr addition and extractable Fe (0.1 $\underline{N}$ HCl, 0.005 $\underline{N}$ DTPA) was reduced. The pH of the soil after addition of the Cr was not determined.

Schueneman (1974), upon addition of 400 ppm Cr(III) as the trichloride to a catena of sandy soils that had been limed to pH's ranging from 7.01 to 7.51, found 0 to 0.3 ppm water soluble Cr, 4.9 to 9.8 ppm 1 $\underline{N}$ NH_4OAc extractable Cr, 1.3 to 1.9 ppm 0.005 $\underline{M}$ DTPA extractable Cr, and 67.4 to 90.3 ppm 0.1 $\underline{N}$ HCl soluble Cr. Soil pH's after addition of Cr(III) ranged between 6.45 and 7.31. "Available" Mn (1 $\underline{N}$ NH_4OAc and 0.005 $\underline{M}$ DTPA) increased with Cr(III) application while "available" Fe (1 $\underline{N}$ NH_4OAc and 0.005 $\underline{M}$ DTPA) decreased.

The low solubility of naturally occurring and added Cr(III) to soils has been explained variously by several authors. Davis (1956) stated that little "available" Cr would be present at soil pH's above 4.0. Soluble Cr would form insoluble oxides and addition of Cr chelates would result in the formation of the correspondingly more

stable Fe chelates (Allaway, 1968). Murrman and Koutz (1972) give the solubility product of $Cr(OH)_3$ as 7×10^{-31} in neutral solutions. Mertz (1969) pointed out that the aquo complexes of Cr tend to hydrolyze, olate, and precipitate rapidly. Udy (1956) points out that $Cr(OH)_3$ does not exist and that the indeterminate hydrous oxide, $Cr_2O_3 \cdot xH_2O$, is produced upon precipitation of Cr(III) solutions by alkali hydroxides.

Murrman and Koutz (1972) list Cr(III) as an ion that could coprecipitate with Fe and aluminum (Al) hydroxides. Schueneman (1974) and Leep (1974) felt that a Cr-Fe complex could account for the lowered levels of available Fe in solution. Schueneman (1974) suggested the possibility of Cr adsorption to the surface of the hydrous oxides of Mn, Fe, and Al. Lisk (1972), noting the irretrievability (except by dry ashing) of Cr(III) from certain synthetic exchange resins, speculated on the specific adsorption of Cr(III) by negative sites on soil particles.

Whether these insoluble particles be organic or inorganic in nature is also unclear. Pavel (1959) found that Cr formed four types of chelates with fulvic acids. Schueneman (1974) and Leep (1974) accounted for the increased level of "available" Mn to a Cr-Mn exchange on soil organic matter. Schueneman (1974) noted that Cr bound or chelated by organic matter seems to be stable and unavailable for plant uptake.

Chromium (VI) additions to soil should result in reduction to Cr(III), followed by precipitation (Mertz, 1969; Lindsay, 1973; Council for Agricultural Science and Technology, 1976). Chromium (VI) would only be expected to persist under alkaline, oxidizing conditions

(Allaway, 1968).

Bartlett and Kimble (1976a, 1976b) and Cary et al. (1977b) have now published more definitive data on the soil chemistry of added Cr(III) and Cr(VI). Bartlett and Kimble (1976a, 1976b) concluded that:

a) Sodium pyrophosphate ($Na_4P_2O_7$), acidified (pH 4.8) NH_4OAc, and 0.1 N sodium flouride (NaF) extracted organically bound Cr, while 1 $\underline{N}$ HCl extracted inorganic Cr.

b) Pyrophosphate and HCl extracts represented Cr "quantity parameters" in soils while NaF and NH_4OAc extracted the small "intensity" quantities of Cr in soils.

c) Organic complexes of Cr(III) formed at low pH and remained stable and soluble as the pH was raised to levels where Cr(III) normally precipitates.

d) Chromium (III) and Al(III) exhibited similar behavior in adsorption and solubility as pH and phosphorous (P) were varied.

e) The oxidation of Cr(III) to Cr(VI) was not brought about under any of the systems studied.

f) Organic matter stimulated the reduction of Cr(VI) to Cr(III), even at pH values above neutrality, and soils low in organic matter inhibited the reduction.

g) Chromium (VI) solubility and adsorption character was similar to that of orthophosphate in soils.

h) Organically complexed and bound Cr(III) would be appreciable where Cr compounds are added to soils and that the chemistry of these organo-Cr complexes will be significant.

Cary et al. (1977b) came to some different conclusions regarding the chemistry of Cr:

a) Soluble Cr was rapidly converted to insoluble forms of Cr in soils of widely varying pH (4.7 to 7.4).

b) Chromium (VI) will be reduced to Cr(III) in a process which occurs more rapidly in acid than alkaline soils.

c) The insoluble forms of Cr have the properties of the mixed hydrous oxides of Cr(III) and Fe(III).

d) There are similarities in the chemical properties of Cr(III) and Fe(III) in soils.

e) The ease of reduction in the Fe(III)-Fe(II) couple as contrasted to the Cr(III)-Cr(II) couple explains the greater uptake of Fe than Cr by plants; the Fe(II) ion being quite mobile in soils.

Chromium chemistry is important when trying to predict the fate of Cr compounds added to soils via disposal of chrome smelter and plating wastes, spillage of Cr chemicals, application of sewage effluent water, and incorporation of sewage sludges. Purves (1972), Leeper (1972), and Page (1974), have reviewed the literature on trace metal additions to soils and the consequences of these additions.

Gemmell (1973a, 1973b) found chrome smelter waste to be particularly phytotoxic and resistant to revegetation. The waste was largely a mixture of Cr(VI) as calcium chromate and calcium hydroxide. Soil pH varied from 10 to 12. Gemmell (1973b) recommended chemical reduction of chromate with $FeSO_4$, addition of sewage sludge, and placement of a layer of subsoil over the waste. The subsoil layer was added to prevent movement of Cr(VI) vertically to growing roots.

The Cr content of sewage sludges varies widely, being dependent on the ratio of industrial to domestic influent and the types of industry served by the treatment plant in question. Blakeslee (1973) gives

the range in Cr content of 57 sewage sludges from Michigan treatment plants as 22 to 30,000 ppm. The mean and median values for this group of sludges were 2031 and 380 ppm Cr respectively.

The compounds of Cr in sewage sludge have not been well characterized though the Cr is thought to be present generally as Cr(III) in most sludges (Chaney, 1973). Though influent may contain appreciable quantities of Cr(VI), reduction due to the presence of large quantities of organic matter and subsequent precipitation of Cr as $Cr(OH)_3$ due to high pH accounts for the high Cr content of sludges and the low waste water effluent concentrations of Cr. Leeper (1972) concluded that Fe(III) and Cr(III) are precipitated so completely in sludges that binding to organic colloids was not important. He also stated that hydrolysis and precipitation are considerably more important in the soil reactions of Cr(III) and Fe(III) than Al(III) and could also account for the small relative importance of these cations in the exchange reactions of inorganic colloids.

Bloomfield and Pruden (1975) found that liming increased the solubility of Cr in sludge-soil mixtures as measured in water, HOAc, and EDTA extractions. Chromium extraction from sludge by water, HOAc, and EDTA increased with the length of anaerobic incubation time. Aerobic incubation increased the water and acetic acid extractability of sludge Cr.

Plant-Chromium Relationships

Considerably more work has been completed and published concerning plant responses to varying levels of naturally occurring and different forms of applied Cr. Reviews by the National Research Council

(1974), Lisk (1972), Mertz (1969), Allaway (1968), and Pratt (1966), provide a general insight into the earlier work on Cr uptake by plants.

Reports of increased yields due to Cr application to soils have been cited in the reviews listed above. Leep (1974) found that corn plants grown on a muck soil treated with Cr(III) had a higher yield than control plants. Cr(III) as a foliar spray has been found to increase the yields and sugar content, lower the acidity, and enhance the maturation of grapes (Shcheglov and Baev, 1973; Dobrolyubskii and Viktorova, 1974). Kusaka et al. (1971) found that turnips grown on soils treated with 400 ppm experienced no difference in yield from controls.

The essentiality of Cr to all plants is in doubt. Huffman and Allaway (1973a) found that Cr was not required for the normal growth of romaine lettuce, wheat, tomato, or bean. Due to Cr contamination of the atmosphere and the fact that the level of Cr in control solutions could not be lowered below 3.8×10^{-4} μM, the question of essentiality was not resolved. The required levels of Cr would be lower than those of any known essential element, however. Brown et al. (1972) notes that vegetational differences clearly mark serpentine soil areas. Some plants, termed "serpentinophytes", have adapted to these soils via the process of natural selection. Shewry and Peterson (1974) felt that Cr could well be essential for the growth of serpentine plants.

Reports of growth reduction due to Cr application or to high naturally occurring Cr were cited by Pratt (1966) and Mertz (1969) in their reviews. Turner and Rust (1971) found 0.5 ppm Cr(VI) in nutrient culture or 5 ppm Cr(VI) in soil culture induced toxicity symptoms in soybeans. Schueneman (1974) found that 50 ppm Cr(III) applications to

sandy soil retarded the growth of 70% of all treated crops. At 100

ppm Cr(III) treatment levels, 100% of the plants were adversely

affected. Ghini and Vercellino (1966) found that both trivalent and

hexavalent Cr had a strong adverse effect on the growth of wheat at

levels as low as 1 ppm solution Cr.

Mortvedt and Giordano (1975) reported that Cr(VI) as 20, 80, and

320 ppm soil Cr lowered the dry matter yield of corn. They also found

that 80 ppm Cr was more toxic as Cr(VI) than as Cr(III) and that Cr(VI)

toxicity was greater on a soil of pH 7.0 than on a soil of pH 5.5.

Toxicity symptoms of Cr vary among plant species. Some investi-

gators (Hewitt, 1953; Anderson et al., 1973) found Fe chlorosis to be

the predominate symptom which would imply a Cr-Fe interaction in the

soil during plant uptake or during translocation. Hewitt (1953) was

able to bring about plant recovery by foliar applications of ferrous

sulfate.

Other researchers found severe wilting of plants to be the

general symptom of toxicity (Turner and Rust, 1971; Schueneman, 1974).

Vercellino and Ghini (1966) found that treatments of 0.1 ppm Cr as

Cr(III) and Cr(VI) inhibited water absorption by wheat seeds after

planting.

Various information regarding the plant physiological aspects of

Cr addition to soils has been reported. Plant roots tend to accumulate

Cr and translocation in minimal (Lyon et al., 1969b; Turner and Rust,

1971; Tiffin, 1972; Huffman and Allaway, 1973b; Myttenaere and Mousny,

1974; Mortvedt and Giordano, 1975; Cary et al., 1977a). Chromium EDTA

behaves differently than other Cr compounds (Myttenaere and Mousny,

1974; Cary et al., 1977a); little Cr EDTA was taken up by plants,

but shoot ^{51}Cr/root^{51}Cr ratios were much larger.

Shewry and Peterson (1974) found that less than 1% of the ^{51}CrO$_4^{2-}$ absorbed was transported to the shoots of barley seedlings. Uptake of the Cr(VI) anion was linear over a twenty-four hour time period. The absorbed ^{51}Cr was found as a "soluble non-particulate" in root cell vocuoles. Sulfate was found to inhibit chromate uptake. Turner and Rust (1971) found that Cr(VI) inhibited the uptake of several plant nutrients and that a specific (Cr-P or Cr-Fe) interaction was not indicated by the data. Schueneman (1974) and Leep (1974) found that plant Mn was increased at low Cr(III) treatment levels.

Lyon et al. (1969a), using Na$_2$CrO$_4$ as a ^{51}Cr carrier, were able to isolate three anions of Cr in the leaf tissue of Leptospermun scoparium (Manuka tea plant). The dominant one of these was the tri-oxalatochromium(III) ion. They also found that ^{51}CrO$_4^{2-}$ was the only ^{51}Cr ion in xylem exudate. This would indicate that Cr(VI) is absorbed from soil solution, transported in the xylem fluid to the leaves, and is there metabolized (reduced) to the oxalate complex of Cr(III). They pointed out the analogy between Cr, S, and P; the latter nutrients also being transported in xylem sap primarily as anions. The Manuka tea plant is a known Cr accumulator found on New Zealand's serpentine soils (Lyon et al., 1968, 1970).

Huffman and Allaway (1973b) found that seeds of wheat and bean plants contained 0.02 to 0.1% of the total ^{51}Cr in the plant. Uptake and translocation of ^{51}Cr varied little between Cr(III) and Cr(VI) sources.

Concern over anthropogenically added Cr in the environment has led to a number of plant studies in this area. Purves (1972) has

written a general commentary on the trace-element contamination of soils. Desbaumes and Ramaciotti (1968) found that an acid Cr(VI) mist being vented from an electro-plating operation was causing damage to surrounding vegetables and fruit trees.

Chromium containing sludges have come under considerable scrutiny. The general consensus is that while sludge Cr incorporation increases plant uptake of Cr, there is no reduction in yield attributable to the Cr content of sludge (Alther, 1975; Bolton, 1975; Cunningham et al., 1975a, 1975b, 1975c; Dowdy and Larson, 1975; Mortvedt and Giordano, 1975). Dowdy and Larson (1975) found that total Cr uptake by barley seedlings was greater on an acid soil. Incubation of sludge amended acid and alkaline soils resulted in greater plant removal of Cr.

Cunningham et al. (1975b) found that the dry matter yields of several crops grown in succession on sludge amended soils actually increased as sludge Cr application rates increased. They felt that Cr might be inhibiting the uptake or translocation of other metals, and tissue analyses tended to substantiate this assertion.

Schroeder (1968) presented evidence on the essentiality of Cr to animals, and by logical extension, to humans. Consequently, researchers have tried to derive methods by which the Cr content of plants may be increased. Allaway (1968) noted the problems associated with increasing the Cr content of food and feed crops and presented several possible alternative solutions to the problem of increasing the Cr content of the human diet. Huffman and Allaway (1973b) reported that edible seed crops tended to "restrict the movement of nutritionally effective forms of Cr from the soil into human and animal diets." They called for a general

search to find plant species that would accumulate this nutritionally effective form of Cr in edible tissues. Cary et al. (1977a) found that leafy vegetables could have their Cr content enhanced, but that the Cr content of edible seeds could not be raised by similar methods. Research indicates that Cr compounds in leaf tissue are not nutritionally effective forms of Cr (Huffman and Allaway, 1973b).

Animal and Human-Chromium Relationships

Trivalent Cr is the only trace metal known to be essential to just the higher animals (Davies, 1972). Mertz (1969) has published a comprehensive review on the role of Cr in biological systems where he describes work conducted by his group and that of Schroeder which establishes Cr(III) as a cofactor with insulin in the necessary mechanisms of glucose utilization. Tipton (1960) found Cr to be the only element depleted in concentration in most tissues with advancing age. Canfield and Doisy (1976) reported that total Cr excretion in the urine of elderly people (median age, 68) was 25% that of younger individuals (median age, 31) under study. Diabetics also excreted much less (35-45% of normal) total Cr in the urine. Mertz (1974b) has discussed the correlations between Cr metabolism and diabetes. Other reviews on Cr nutrition and metabolism have appeared (Underwood, 1971; Davies, 1972; Scott, 1972; World Health Organization, 1973; Hambidge, 1974; National Research Council, 1974; Doisy et al., 1976).

Average daily urinary excretion of Cr ranges between 5 and 10 µg (World Health Organization, 1973). This must be replaced to prevent Cr depletion in tissues. The absorption of Cr(III) as the trichloride has been found to be only 0.5 to 0.7% of the orally given dose (Mertz,

1974b). The average individual's daily Cr intake in the United States is 60 µg (Mertz, 1974b; National Research Council, 1974). The Cr supply in the body would be rapidly repleted if the availability of food Cr was as low as that of inorganic salts. That is obviously not the case; the Cr depletion has been found to be occurring at a much slower rate. Mertz (1969) found that a Cr compound called glucose tolerance factor (GTF), isolated from brewer's yeast, was highly available when supplied as an oral dose. Fully twenty-five percent of the GTF-Cr was absorbed by the gastrointestinal tract.

Other foods supply appreciable quantities of GTF-Cr, especially spices such as black pepper (Doisy et al., 1976) and thyme (Davies, 1972). Meats, vegetables, and fruits provide lesser amounts of Cr (Doisy et al., 1976). The refining of sugar and the milling of wheat flour removes most of the Cr in these foodstuffs, concentrating it in the molasses and the bran and germ, respectively (Mertz, 1969; Underwood, 1971; Doisy et al., 1976).

One of the major problems in understanding the biochemistry of Cr is that the chemical structure of the GTF-Cr complex is not completely known. Mertz (1974b) reported that GTF contains two nicotinic acid residues per Cr atom, is of low molecular weight, and is heat stable and dialyzable.

As is the case with several other essential metals, dosages of Cr can be raised to toxic levels. Luckey et al. (1975) presented the following dose-response diagram of an essential element:
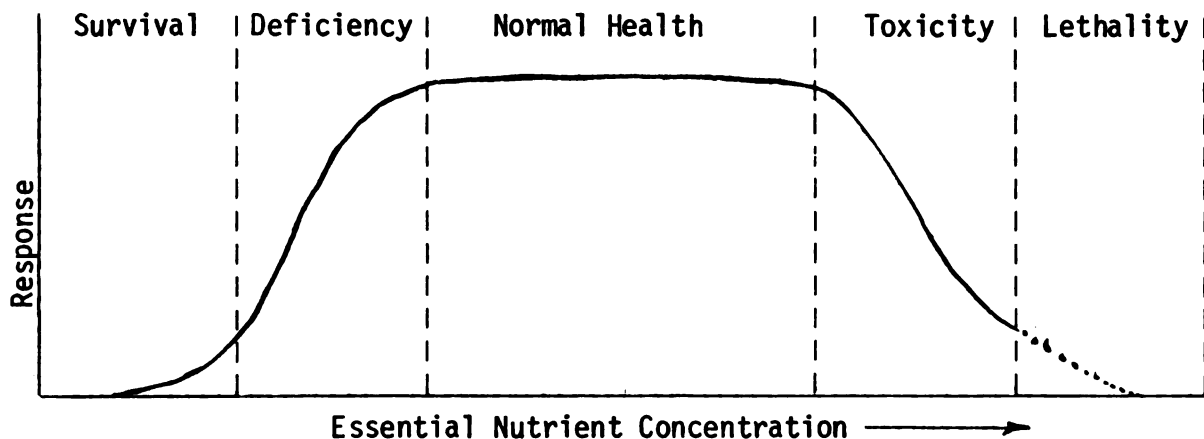
Smith (1972), Baetjer (1956), and the National Research Council (1974) have reviewed the toxicology of Cr in animals and humans. Early work was concerned with the effects of prolonged exposure to Cr, especially for workers in the chromate industry.

Baetjer (1956) presented some important findings in this regard. Hexavalent chromium remains soluble at body pH, while Cr(III) does not. Trivalent chromium compounds do not bring about serious damage to body tissues, while Cr(VI) compounds are corrosive, irritating, and sometimes toxicological. Industrial exposures affect the skin and respiratory tracts, causing skin ulcers and dermatitis, perforation of the nasal septum, and other respiratory ailments. Allergic reactions to Cr(VI) compounds have been found to occur in some individuals. Duration of exposure resulting in allergic symptoms was highly variable. Most important, deaths due to cancers of the respiratory regions are significantly correlated with work involving Cr(VI) compounds in industry.

CHAPTER II

EXTRACTABLE CHROMIUM AS RELATED TO
SOIL pH AND APPLIED CHROMIUM

Abstract

The chromium (Cr) nutrition of men and animals has come under increasing scrutiny. Cr has been implicated in the infertility of some serpentine soils. High Cr-containing sewage sludges are being incorporated or considered for incorporation into agricultural soils.

The objective of this study was to evaluate the soil chemistry of added Cr(III), Cr(VI), and sludge Cr as affected by initial soil pH. Treatments of 0, 50, 100, and 500 ppm Cr as $CrCl_3$ and CrO_3, and sludge Cr at rates of 700 and 1400 ppm Cr were applied to Rubicon sand (pH 4.7), Morley clay loam (pH 6.0) and limed Morley clay loam (pH 7.5). Pots were sampled at 24 hours, 1, 2, 4, 8, and 16 weeks of incubation. Soil samples were extracted in succession with distilled water, 1 M NH_4Cl, 0.1 $\underline{M}$ $CuSO_4$, 0.3 $\underline{M}$ $(NH_4)_2C_2O_4$, and citrate-dithionite-bicarbonate.

Chromium (III) addition reduced soil pH while sludge Cr raised soil pH. Chromium (VI) treatment initially lowered soil pH, but then raised it above the pH of control soils after a short time period. Water soluble Cr(III) decreased with time, though more rapidly as soil pH increased. Water soluble Cr(VI) also decreased with time, but less rapidly as soil pH increased. Exchangeable and organic bound

Cr were negligible. Oxalate and dithionite extractions removed large quantities of Cr from all treatments. Water soluble Cr compounds are converted to insoluble compounds of Cr(III) in soils. Sludge Cr is probably a colloidal precipitate prior to incorporation.

Introduction

The chromium (Cr) concentration of most tissues in the human body decreases with advancing age. Chromium is the only known element to exhibit this behavior (Tipton, 1960). Mertz (1969), Hambidge (1974), and Doisy et al. (1976) have published reviews on the role of Cr in biological systems and the Cr nutritional requirements of mankind. Toxicological reviews (Baetjer, 1956; National Research Council, 1974) are also available.

Much work has been done in the determination of plant response to varying levels of naturally occurring and applied Cr. Pratt (1966) has reviewed earlier work on Cr uptake. Turner and Rust (1971) found that 5 ppm Cr(VI) in soil culture brought about toxicity symptoms in soybeans. Mortvedt and Giordano (1975) reported that 20 ppm Cr(VI) applied to soils reduced the dry matter yield of corn.

The essentiality of Cr for plant growth is in doubt. Huffman and Allaway (1973) found that Cr was not required for the normal growth of romaine lettuce, wheat, tomato, or bean. Due to Cr contamination of the atmosphere, and the fact that the level of Cr in control solutions could not be lowered below 3.8×10^{-4} $\mu\underline{M}$, the question of essentiality was not resolved. At this level in solution, the plant nutritional requirement for Cr would be lower than that known for any other essential element. Soils derived from ultra-basic (serpentine) rocks may contain several percent total Cr. Brown et al. (1972) notes that vegetational differences clearly mark serpentine soil areas. Some plants, termed "serpentinophytes", have adapted to these soils. Shewry and Peterson (1974) feel Cr could be essential to the growth of serpentine species.

Chrome is an important component of sludges emanating from sewage treatment plants with tanneries and/or plating plants as major contributors of influent load. Large amounts of sludge are being incorporated into agricultural soils. Until recently little research had been published involving the soil chemistry of Cr. Bartlett and Kimble (1976a, 1976b) reported that organo-Cr(III) complexes were appreciable in quantity, stable, and soluble as the soil pH was raised to levels where Cr(III) normally precipitates. They found analogous behavior between Cr(III) and Al(III), and also between CrO_4^{2-} and orthophosphate.

Cary et al. (1977) reported that soluble Cr is rapidly converted to insoluble forms of Cr in soils of widely varying pH. These insoluble forms had properties of mixed hydrous oxides of Cr(III) and Fe. Further similarities between Cr(III) and Fe(III) chemistry in soils were noted in this work.

The chemistry of naturally occurring and added Cr compounds in soils is important as this influences plant uptake and subsequently, animal and human nutrition. The objective of this study was to arrive at some general conclusions regarding the soil chemistry of added Cr(VI), Cr(III), and sludge Cr via extraction partitioning methods.

Materials and Methods

Rubicon sand from Muskegon County, Michigan and Morley clay loam from Ionia County, Michigan were obtained from the top 2 and 4 inches, respectively. The soils were passed through a 2 mm plastic sieve, air-dried, and divided into 1 kg portions. Rubicon sand is a sandy, mixed, frigid Entic Haplorthod, while Morley clay loam is a fine,

illitic, mesic Typic Hapludalf. Important chemical parameters are

given in Table 1. Determinations of pH were made in solutions of

10 g soil/10 ml deionized, distilled H_2O. Organic matter contents were

determined by a Leco Carbon Analyzer (Allison et al., 1965). Total

Cr was determined on nitric-hydrofluoric-perchloric acid digests of

soils and sludge (Pratt, 1965).

TABLE 1-Characteristic chemical properties of Rubicon sand, A Horizon and Morley clay loam, Ap horizon.

Soil	pH	Organic Matter	Total Cr[‡]
		%	ppm
Rubicon sand	4.7	2.2	N.D.[*]
Morley clay loam	5.4	4.2	16.0

[‡] Average of 12 replications.
[*] Non-detectable.

A third "soil" was created by liming the Morley soil to a pH of

7.5 with calcium hydroxide.

Chromium sources were as follows: Cr(III) as the trichloride, (

Cr(VI) as the oxide, and sludge Cr. The sludge came from the Grand

Haven, Michigan municipal treatment facility and contained 12,500 ppm Cr.

Three replications of 0, 50, 100, and 500 ppm Cr as Cr(III) and

Cr(VI) were applied to all three soils in the initial wetting water.

Wet sludge was added at rates of 57 and 113 g air-dry sludge per

kilogram of soil; equivalent to 700 and 1400 ppm Cr on a dry weight

basis. Sludge amended soils were then air-dried and deionized, dis-

tilled water was added to bring them to the constant moisture tension of

all the pots, +100 cm water. This moisture tension corresponds to mois-

ture contents of 14 and 29% for the Rubicon and Morley soils, respective-

ly. All pots were thoroughly mixed, covered with polyethylene to mini-

mize water vapor loss, and placed in a constant temperature (25° C)

chamber.

Pots were sampled at 24 hours, 1, 2, 4, 8, and 16 weeks. All samples (5 g) were extracted on an end-over-end shaker in succession with the regime detailed in Table 2. The citrate-dithionite-bicarbonate extraction is that of Mehra and Jackson (1960). The extractants listed in Table 2 were selected to remove water soluble, exchangeable, organic bound, amorphous precipitated, and more crystalline precipitated Cr. After each extraction the samples were centrifuged at 27,000 g for 15 minutes and decanted. Corrections for extracted Cr present in subsequent extractions were made.

TABLE 2-Regime of extractants used in the successive extraction of Rubicon sand, A horizon and Morley clay loam, Ap Horizon.

Extractant	Solution/Soil	Shaking Time
	ml/gm	min.
Deionized, distilled water	5	30
1 M NH_4Cl	5	60
0.1 M $CuSO_4$	5	60
0.3 $\bar{M}$ $(NH_4)_2C_2O_4$	7.5	120
Na_3 citrate/Na_2 dithionite/ Na bicarbonate	62.5*	15‡

* Final ratio after complete reaction.
‡ Duration of reaction time.

All Cr determinations were conducted on a model 303 Perkin Elmer Atomic Absorption Spectrophotometer. Aliquots of extracts were brought to volume in 0.1 $\underline{M}$ K_2SO_4 to minimize ionic strength effects and to "swamp" possible interferences. The detection limit of this method was 0.1 ppm solution Cr.

The results of the Cr(III) and Cr(VI) treatments were analyzed by standard analysis of variance procedures carried in the statistical programs of the Michigan State University Computer Laboratory.

Results

Tables 3 and 4 demonstrate the existence of significant differences in the pH and extractable Cr data.

TABLE 3-Analysis of variance for extractable chromium.

Source of Variance	Approx. Significance Probability of F Statistic
Soil (S)	<0.029
Cr Source (Cr)	<0.0005
S x Cr	<0.0005
Time (T)	<0.0005
S x T	<0.0005
Cr x T	<0.0005
S x Cr x T	<0.0005
Extractant (E)	<0.0005
S x E	<0.0005
Cr x E	<0.0005
T x E	<0.0005
S x Cr x E	<0.0005
S x T x E	<0.0005
Cr x T x E	<0.0005
S x Cr x T x E	<0.0005

TABLE 4-Analysis of variance for soil pH.

Source of Variance	Approx. Significance Probability of F Statistic
Soil (S)	<0.0005
Cr Source (cr)	<0.0005
S x Cr	<0.0005
Time (T)	<0.0005
S x T	<0.0005
Cr x T	<0.0005 .
S x Cr x T	<0.0005

Fig. 1 to 6 show the amount of Cr extracted from 500 ppm Cr(III) and 500 ppm Cr(VI) applications. Treatments of 50 and 100 ppm trivalent and hexavalent Cr gave results similar to the 500 ppm applications, though at lower absolute levels of extractable Cr, and are not included here. Eighty-five to one hundred-ten percent of the applied Cr was extracted from all treatments on all soils.

Ammonium chloride and $CuSO_4$ extractable fractions were generally negligible, eighty to ninety-nine percent of all extractable Cr being present in the water, oxalate, and the dithionite extractions. Although early extractions of the acid Rubicon soil yielded appreciable quantities of NH_4Cl and $CuSO_4$ soluble Cr, these fractions declined to near zero levels on all soil-Cr source treatment combinations with time.

Fig. 1--Extractable Cr vs. time for 500 ppm Cr(III) treated Rubicon sand.
+ Average of three replications.
‡ Corrected for Cr content of controls.

Fig. 2--Extractable Cr vs. time for 500 ppm Cr(III) treated Morley clay loam.
+ Average of three replications.
‡ Corrected for Cr content of control.

Fig. 3--Extractable Cr vs. time for 500 ppm Cr (III) treated Morley clay loam (limed).
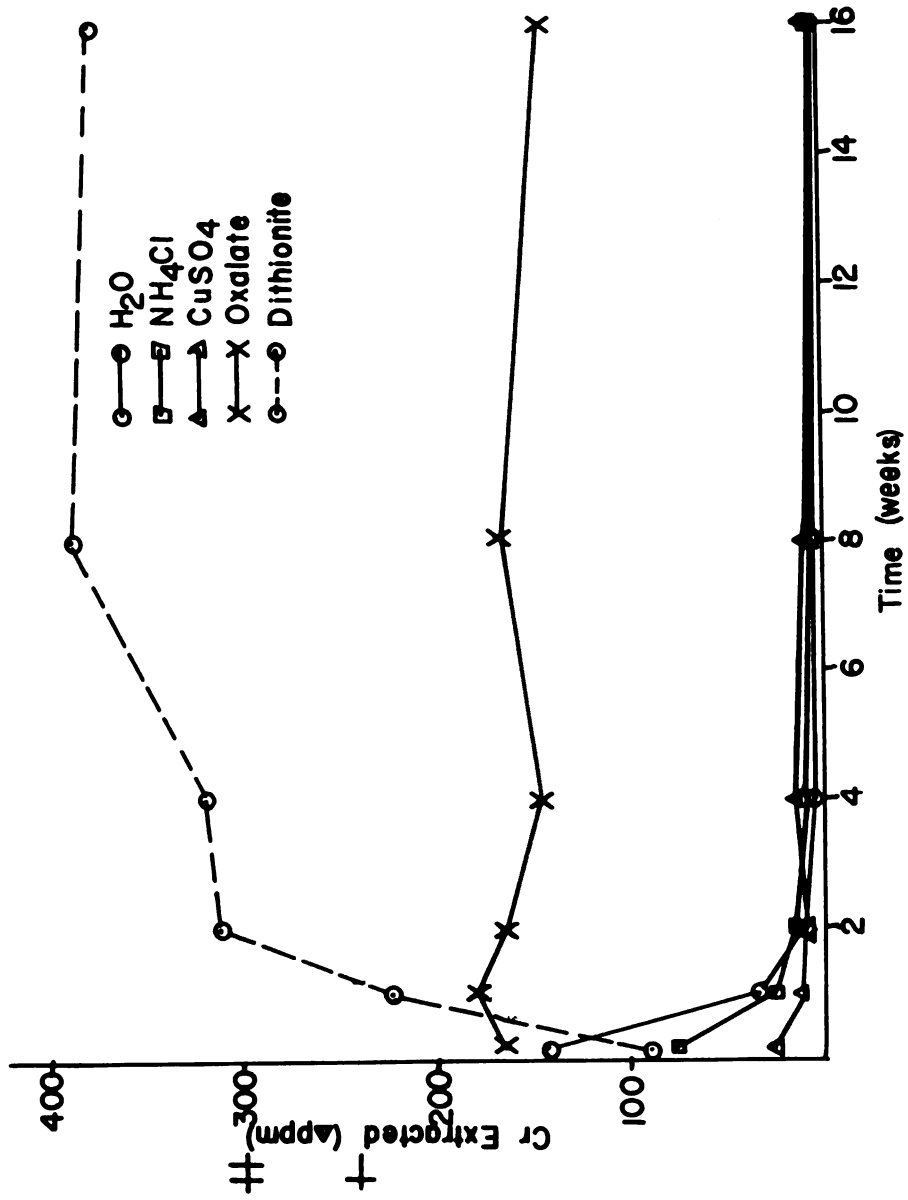† Average of three replications.
‡ Corrected for Cr content of controls.

Fig. 4--Extractable Cr vs. time for 500 ppm Cr(VI) treated Rubicon sand.
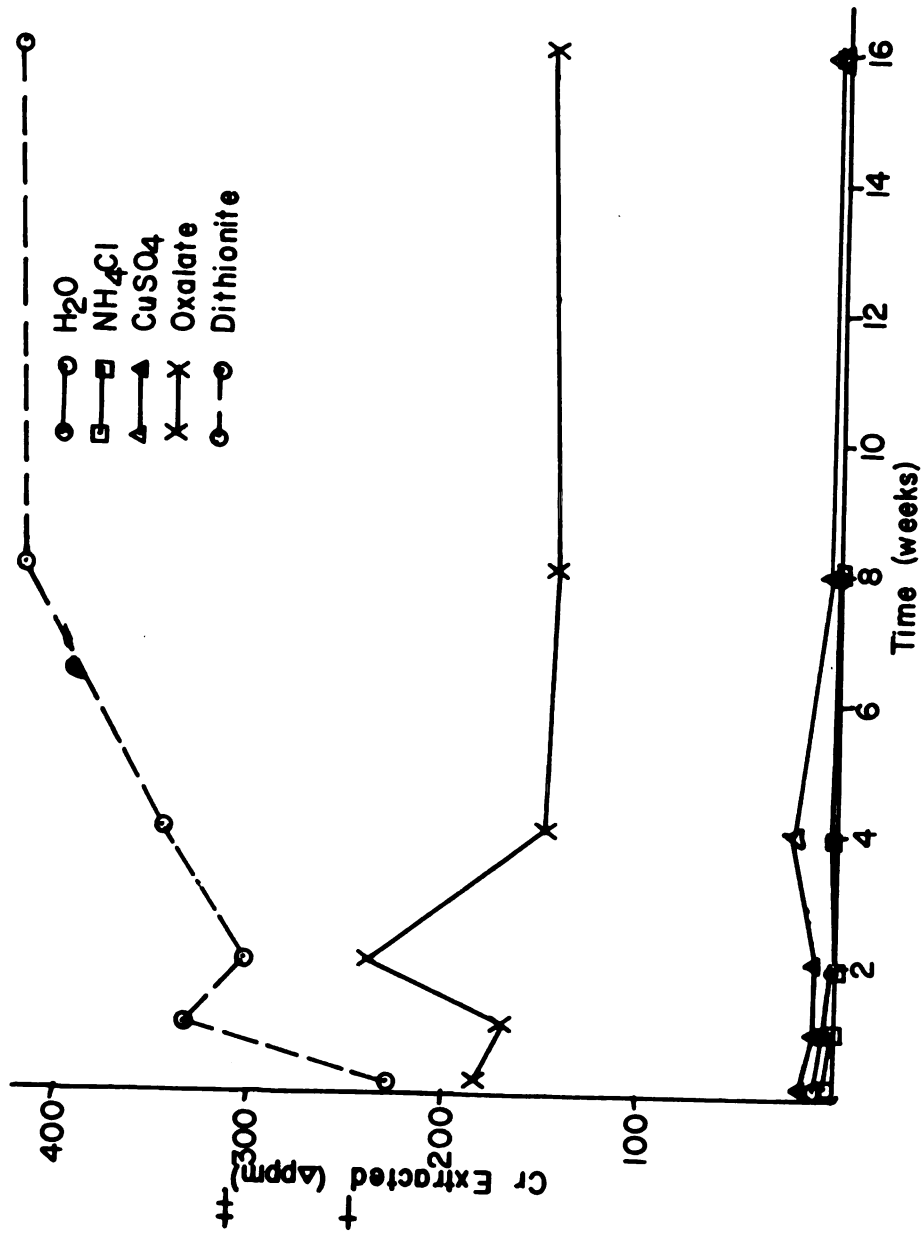+ Average of three replications.
‡ Corrected for Cr content of controls.

Fig. 5--Extractable Cr vs. time for 500 Cr (VI) treated Morley clay loam.
+ Average of three replications.
‡ Corrected for Cr content of controls.

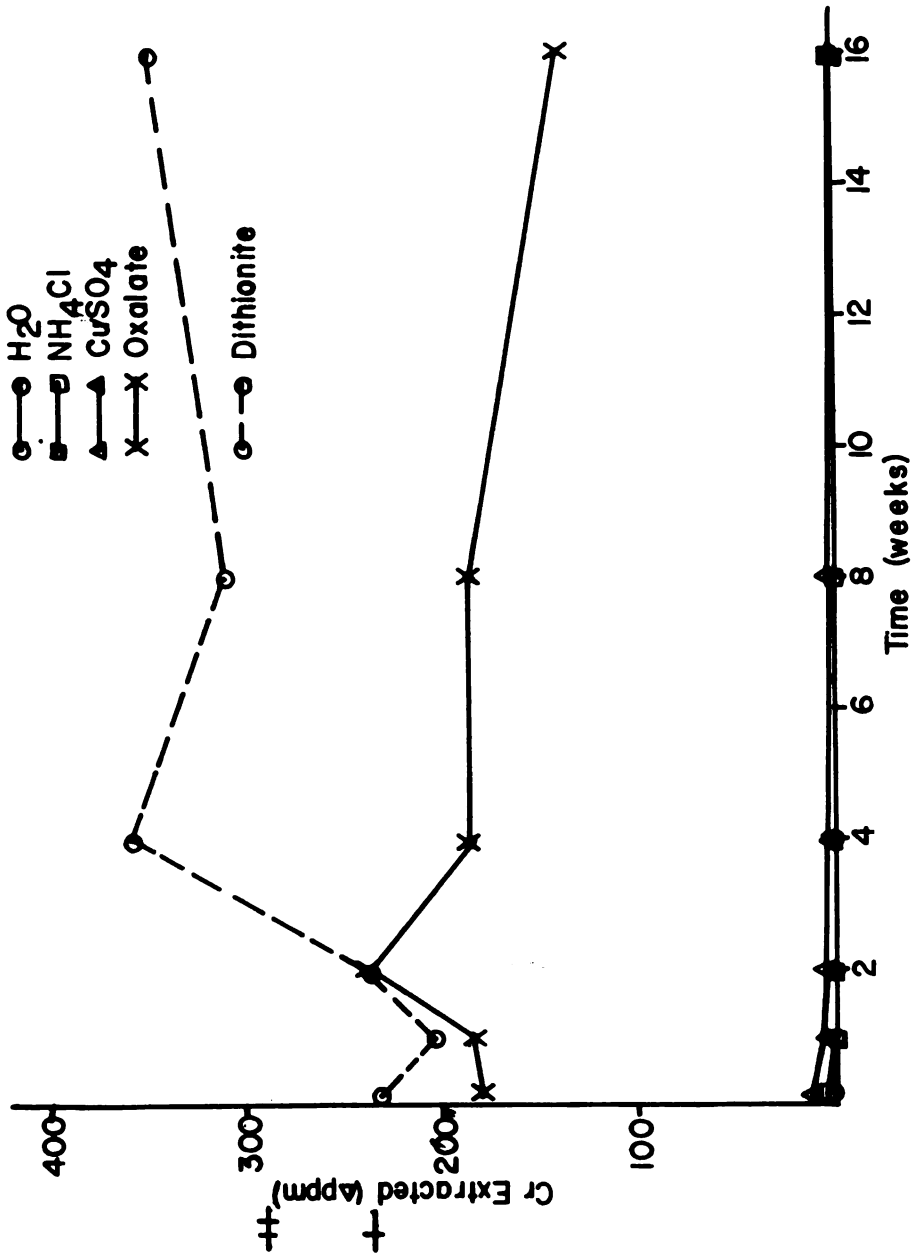Fig. 6--Extractable Cr vs. time for 500 ppm Cr (VI) treated Morley clay
loam (limed).
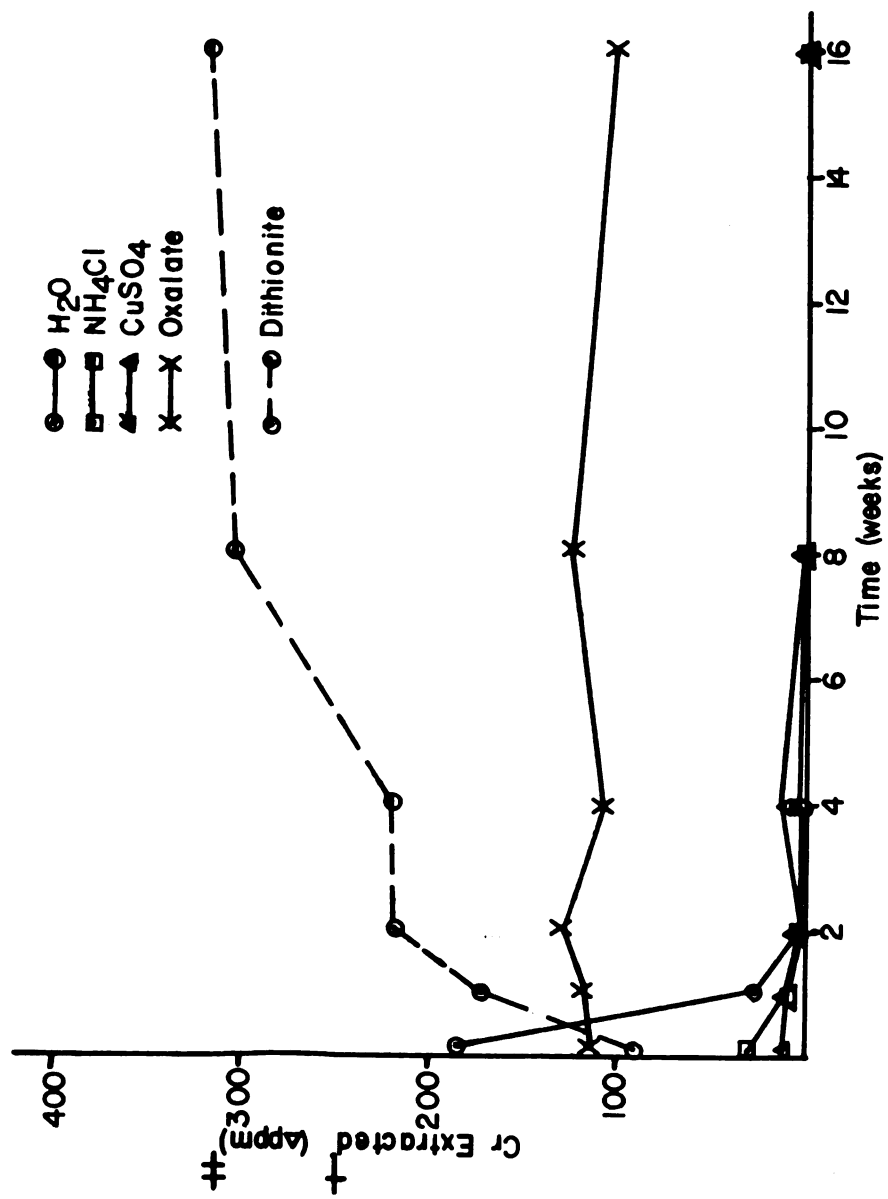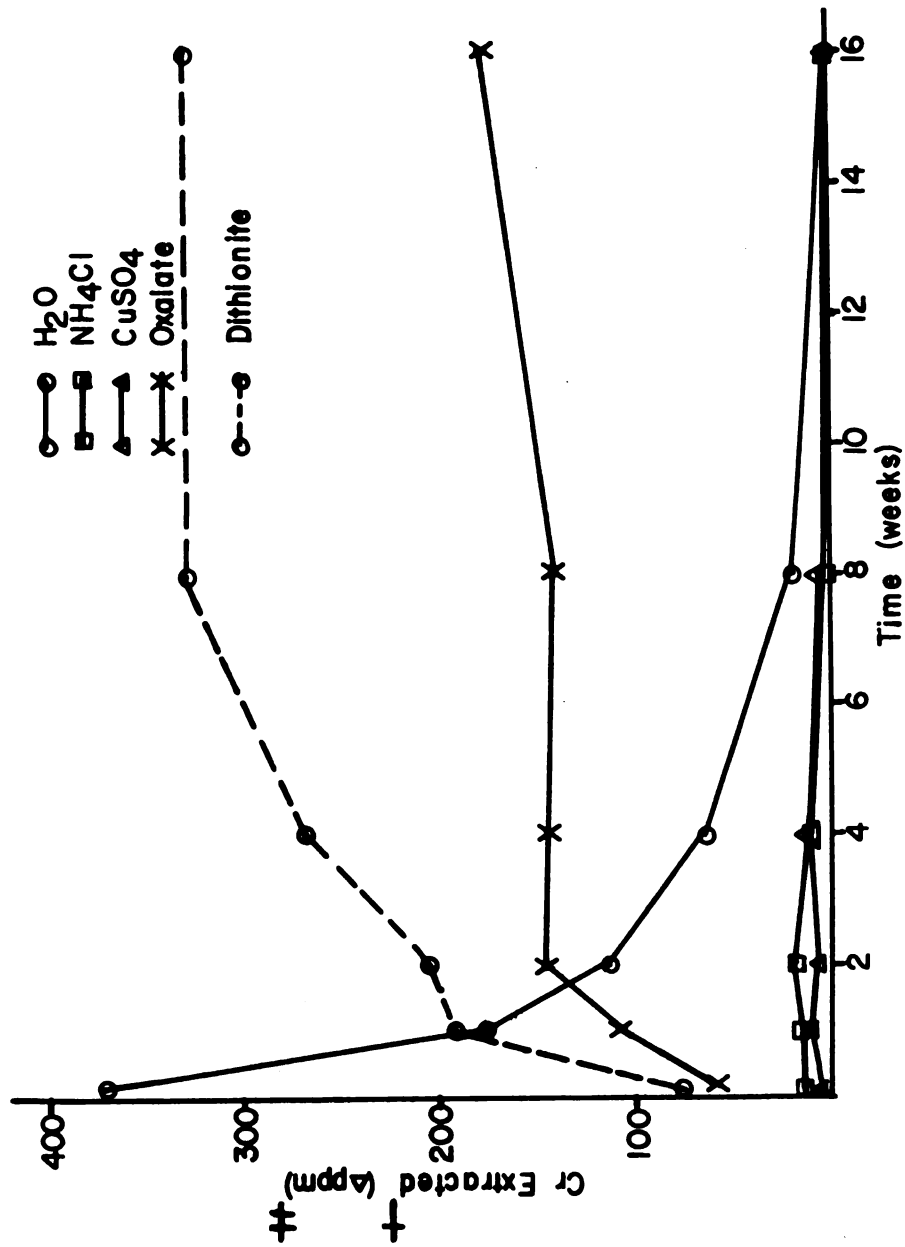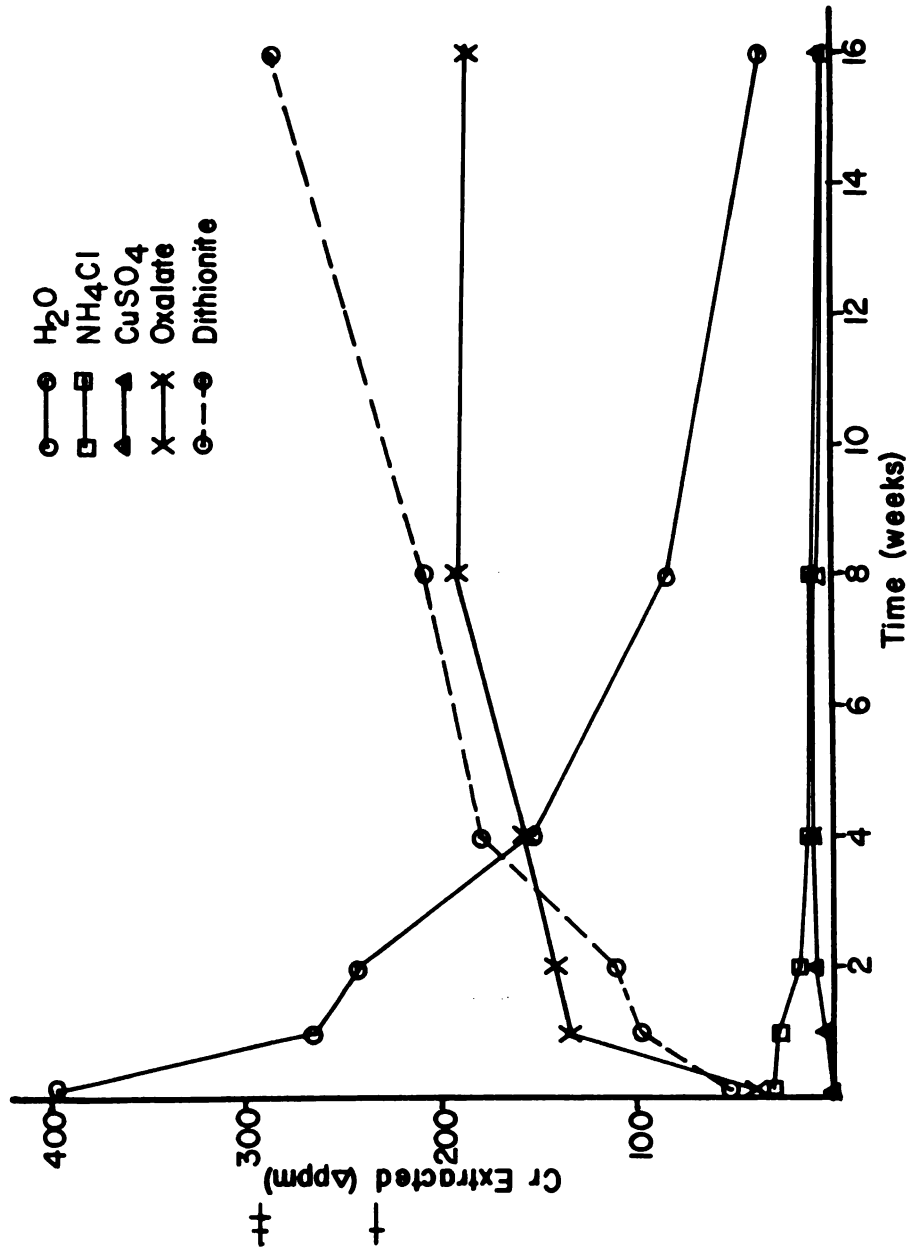+ Average of three replications.
‡ Corrected for Cr content of controls.

Chromium converted rapidly to the oxalate and dithionite
extractable fractions, although less rapidly to the dithionite fraction.
The oxalate fraction appeared to level off as the incubation period
was extended. The dithionite fraction rose to dominate all other frac-
tions on all soil-Cr source treatment combinations.

Water soluble Cr declined in importance on all soils with time,
but showed several interesting relationships. The water solubility
of Cr(III) declined more rapidly than that for Cr(VI) on all soils.
The amount of water soluble Cr(VI) decreased more rapidly on acid than
alkaline soils, but just the opposite phenomena was observed for the
water soluble Cr(III) fraction.

Sludge amended soils contained very little water soluble, NH_4Cl,
or $CuSO_4$ extractable (Table 5). The oxalate and dithionite fractions
predominated, together accounting for about 99% or more of the total Cr
extracted. No ratio of constancy between these two fractions could be
established for any or all soils. The dithionite fraction predominated
with time, similar to inorganic Cr treatments.

TABLE 5-Average[+] extractable Cr: 1400 ppm sludge Cr.

Soil	H_2O-Cr	NH_4Cl-Cr	$CuSO_4$-Cr	Oxalate-Cr	Dithionite-Cr
			----ppm----		
Rubicon	2.73	2.09	0.12	568.	666.
Morley	0.93	0.51	0.20	635.	814.
Morley-limed	0.82	0.28	0.23	569.	705.

[+] Average over incubation period-6 extraction times x 3 replications.

Data for soil pH's is presented in Fig. 7 to 9. Data for 50 and
100 ppm Cr additions is not presented due to similarities with 500 ppm
treatment levels. The 1400 ppm sludge Cr treatment is not included for
similar reasons.

Chromium (III) addition reduced soil pH on all soils with the
greatest decrease observed on the Rubicon soil. Chromium (VI)

Fig. 7--Soil pH vs. time for selected treatments on Rubicon sand.
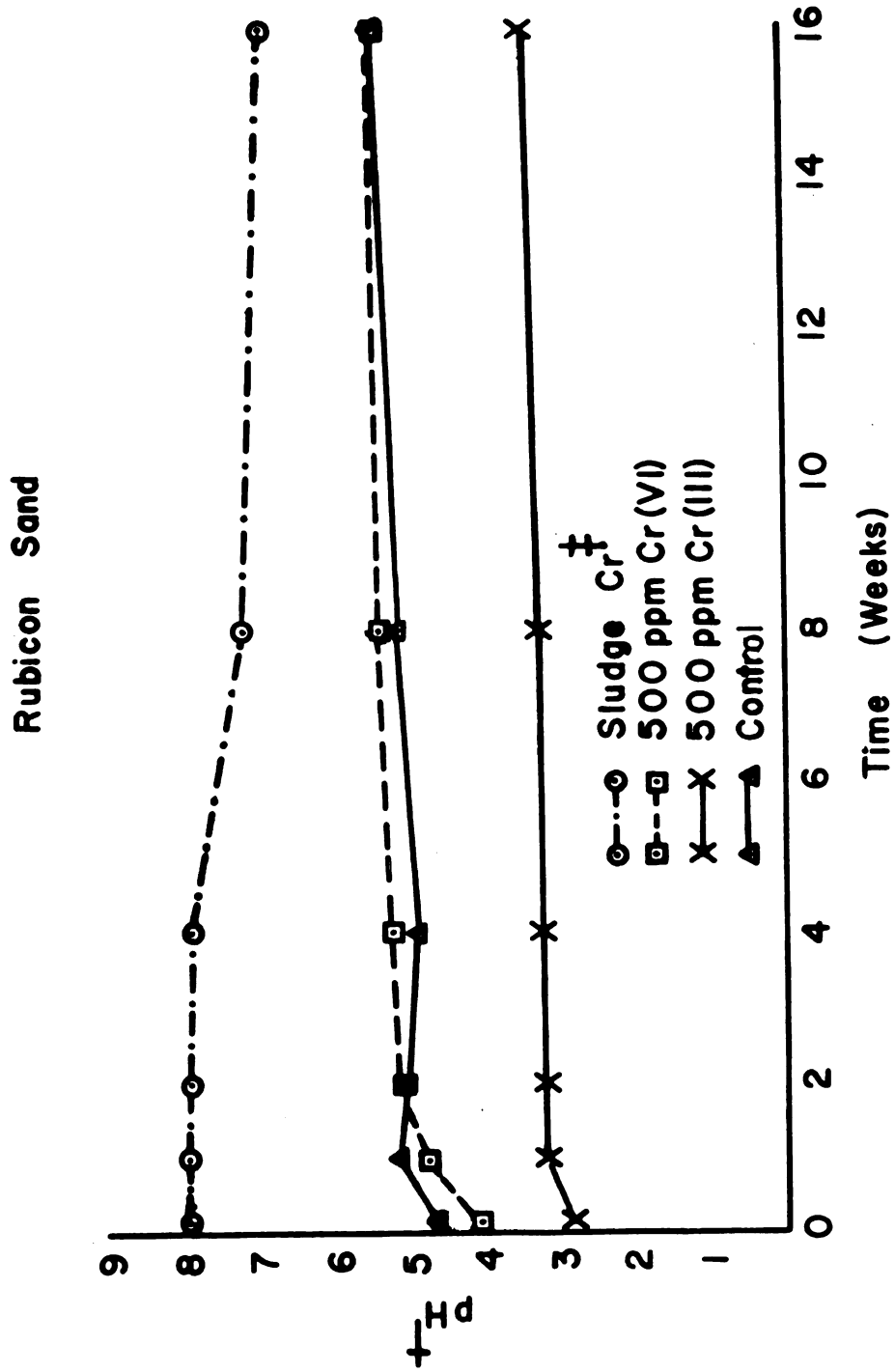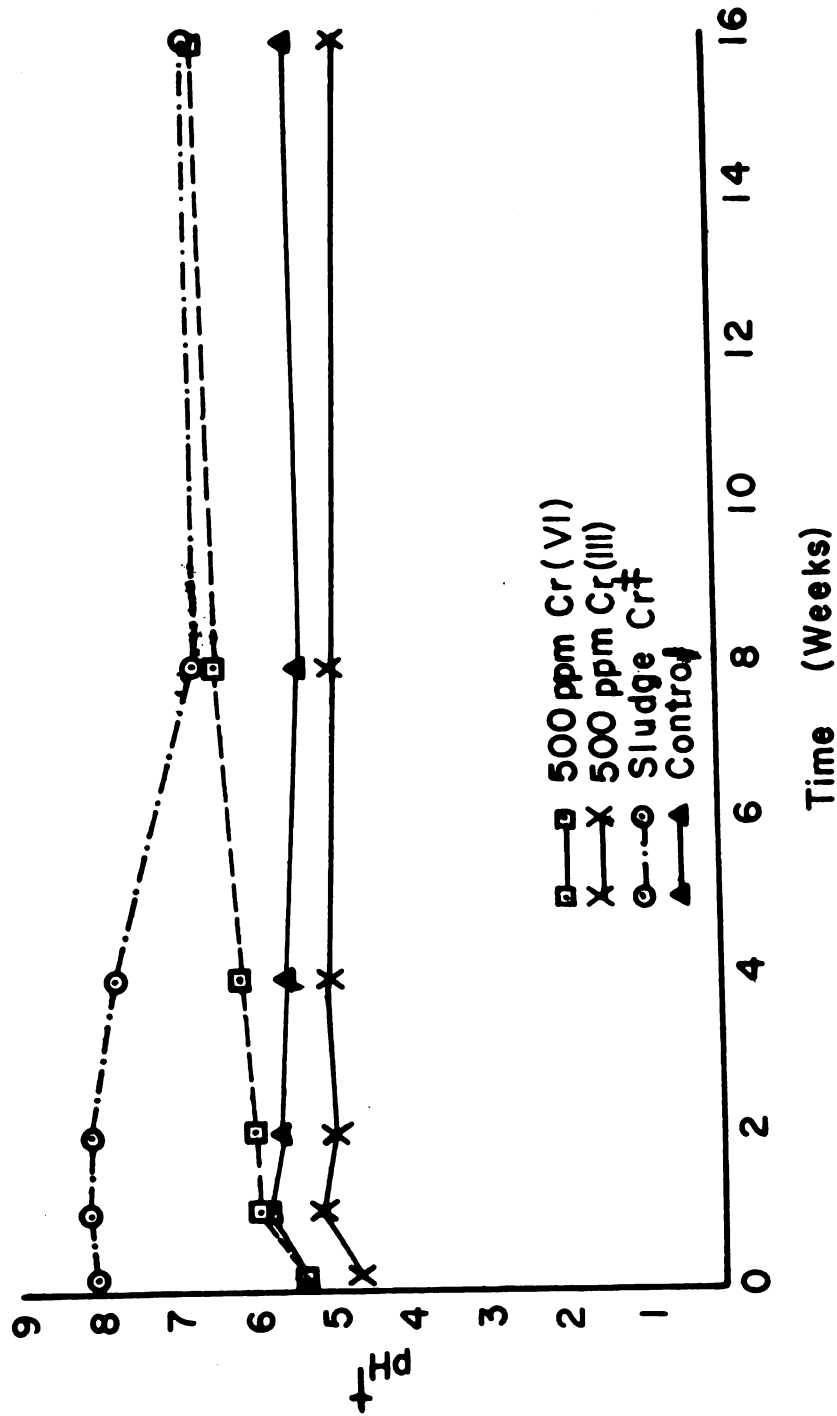+ Average of three replications.
‡ 57 gm dry sludge/kg amended soil.

Fig. 8--Soil pH vs. time for selected treatments on Morley clay loam.
+ Average of three replications.
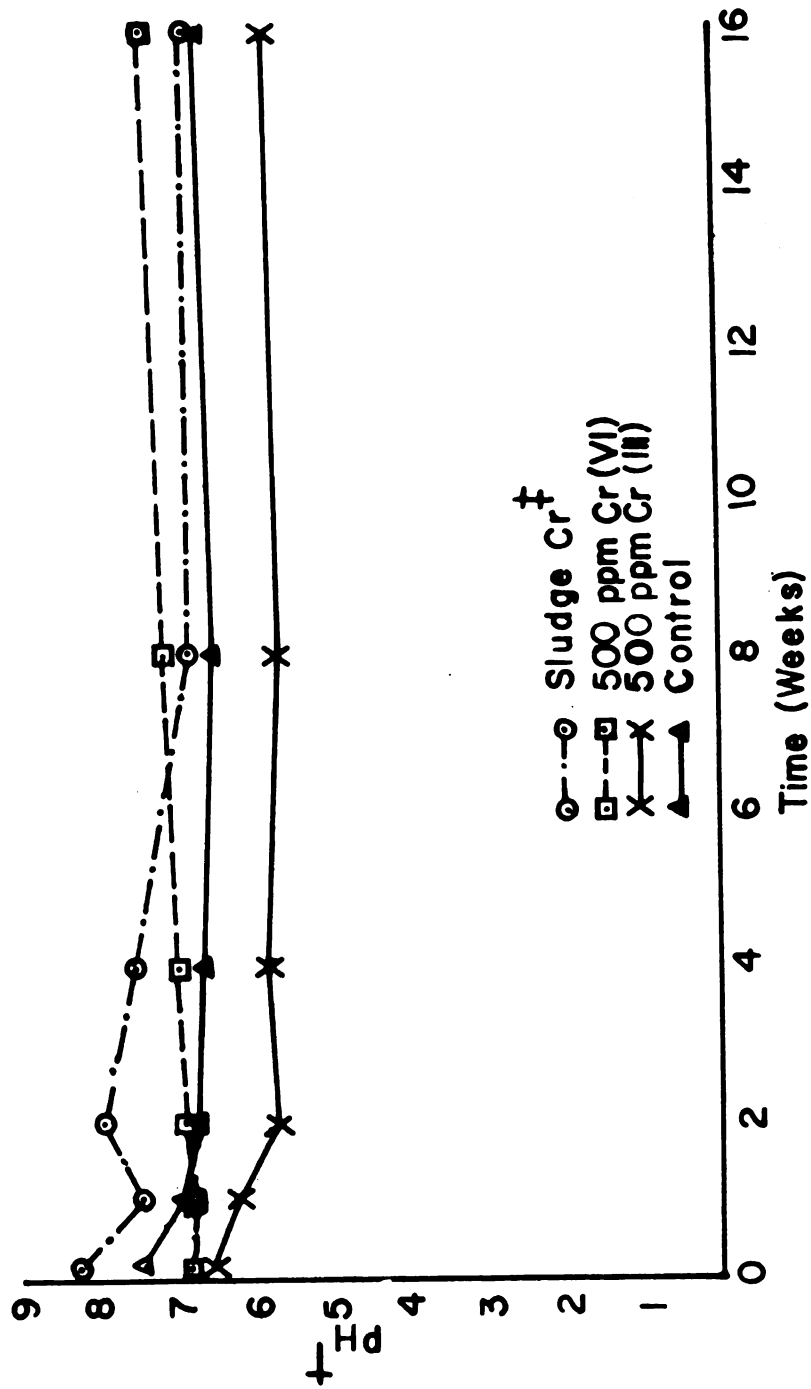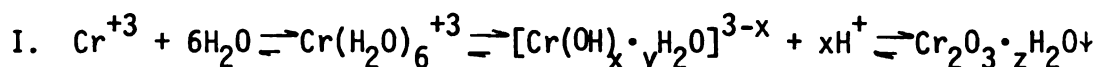‡ 57 gm dry sludge/kg amended soil.

Fig. 9--Soil pH vs. time for selected treatments on Morley clay loam (limed).
+ Average of three replications.
‡ 57 gm dry sludge/kg amended soil.

initially lowered soil pH but then raised it relative to control on all soils. Sludge amended soils had very high pH's initially which then declined with time.

Discussion

Trivalent Chromium

The following reaction path for water soluble Cr(III) compounds added to soils is proposed:

I. $Cr^{+3} + 6H_2O \rightleftharpoons Cr(H_2O)_6^{+3} \rightleftharpoons [Cr(OH)_x \cdot yH_2O]^{3-x} + xH^+ \rightleftharpoons Cr_2O_3 \cdot zH_2O\downarrow$

This mechanism accounts for the pH decrease found on Cr(III) treated soils and the subsequent insolubility of the resulting soil Cr compounds with the first three extractants used. While the compound $Cr(OH)_3$ is a stoichiometric possibility, Udy (1956) points out that the indeterminate hydrous oxide is produced upon precipitation of Cr(III) solutions. The acid Rubicon soil slows movement of Cr(III) through this pathway by providing protons that compete with those dissociated from the aquo complex. The solubility product of $Cr(OH)_3$ is 7×10^{-31} in neutral solution (Murrman and Koutz, 1972), indicative of the driving force towards precipitation experienced by the Cr(III)-Rubicon system. The water solubility of Cr(III) compounds will be reduced even more severely in the more alkaline Morley soils, which is in agreement with the findings of Cary et al. (1977).
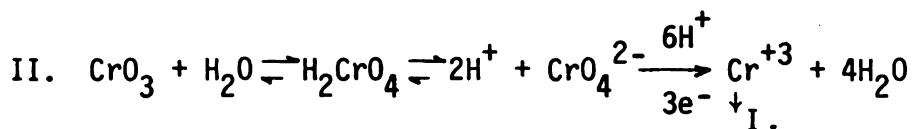
Organic bound Cr appears to be negligible. While hexacoordinate complexes of Cr(III) are very stable, it is this stability that mitigates against entrance of organic ligands into the coordination sphere of the aquo complex. The effectiveness of $CuSO_4$ as an extractant for

organic bound Cr may be questionable. Divalent ions are not noted for their ability to displace trivalent ions from the organic complex. Copper(II) organic complexes do possess a high stability constant (Stevenson and Ardakani, 1972), and the high concentration of this ion and the lengthy extraction time used in this study were chosen to maximize the exchange reaction of Cu(II) for Cr(III) in organic complexes. The data gives strong evidence to the contrary, but is not conclusive as regards the existence of organo-Cr(III) complexes.

Water soluble Fe data indicating that a Fe-Cr coprecipitation compound is formed when Cr(III) compounds are added to soils can be found in Chapter III. Other similarities between Cr(III) and Fe(III) chemistry led these investigators to use the oxalate and dithionite extractions for precipitated Cr compounds. The oxalate acts to reduce Fe(III), breaking up the amorphous matrix that may contain or hold Cr(III), and to chelate and stabilize metal ions released during the extraction. Cr (III) is not reduced by either oxalate or dithionite. These agents act on different portions of the solid matrix, the more crystalline compounds being attacked by the dithionite.

Hexavalent Chromium

The proposed mechanism of Cr(VI) reaction in soils is given below:

$$\text{II.} \quad CrO_3 + H_2O \rightleftharpoons H_2CrO_4 \rightleftharpoons 2H^+ + CrO_4^{2-} \xrightarrow[3e^-]{6H^+} Cr^{+3} + 4H_2O$$

$$\downarrow I.$$

The acid anhydride hydrolyzes quickly and then dissociates. This initial acid character explains the observed lowering of pH relative to controls. The critical step is the reduction step since both protons

and electrons must be present for this to occur. In these soils the electron donors, probably organic compounds, do not appear to be limiting. Bartlett and Kimble (1976b) found that a lack of soil organic matter could inhibit Cr(VI) reduction in soils.

Hydrogen ion activity is the determining factor in the reduction of Cr(VI) added to the three soils in this study. After Cr(VI) is reduced to Cr(III), the most stable oxidation state of Cr, the reduced Cr then enters reaction path I. Subsequent Cr(III) precipitation generates protons, but does not meet the requirements for hydrogen ions in the Cr(VI) reduction reaction, causing the soil pH to rise above control.

Sludge Chromium

Sludge Cr exhibits the chemistry of trivalent chromium, suggesting that the Cr in the sludge was a precipitated Cr(III) compound(s). Upon addition to soils, the sludge Cr changed little in its chemical character, remaining largely in insoluble forms.

The results suggest a management strategy by which Cr(VI) chemical spills on soils may be contained. If such contamination occurred, acidification agents such as sulfur and reducing agents such as leaf litter or acid compost could be incorporated to speed Cr(VI) reduction. After reduction is complete, liming to further precipitate and crystallize Cr(III) compounds might be necessary. Gemmell (1973) has suggested a similar scheme for the revegetation of chrome smelter waste piles.

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CHAPTER III

EXTRACTABLE IRON AND MANGANESE AS RELATED
TO SOIL pH AND APPLIED CHROMIUM

Abstract

Metal-metal interactions in soils can be very important in determining the composition and yield of plants. Chromium application has been shown to effect plant Mn concentrations and uptake, and Fe deficiency symptoms have been associated with Cr toxicity by some workers.

The objectives of this study were to evaluate the changes in soil Mn and Fe resulting from added Cr(III), Cr(VI), and a high Cr content sludge. Treatments of 0, 50, 100, and 500 ppm Cr as $CrCl_3$ and CrO_3, and sludge Cr at rates of 700 and 1400 ppm Cr were applied to Rubicon sand, a sandy, mixed, frigid Entic Haplorthod (pH 4.7), Morley clay loam, a fine, illitic, mesic Typic Hapludalf (pH 6.0), and limed Morley clay loam (pH 7.5). Pots were sampled after 24 hours, 1, 2, 4, 8, and 16 weeks of incubation. Soil samples were extracted in succession with deionized, distilled water, 1 $\underline{M}$ NH_4Cl, 0.1 $\underline{M}$ $CuSO_4$, 0.3 $\underline{M}$ $(NH_4)_2C_2O_4$, and citrate-dithionite-bicarbonate.

Water soluble Fe was reduced on all soils by Cr(III) and sludge amendment. Sludge amendment increased oxalate soluble Fe. Chromium (VI) initially lowered water soluble Fe, later raising this fraction above control soil levels.

41

Water soluble Mn increased on all soils as the quantities of added Cr(III) increased. Chromium (VI) initially raised water-soluble Mn; later lowering this fraction to levels not significantly different from control pots. Sludge amended soils produced more water soluble Mn as the incubation study progressed in time.

Addition of inorganic Cr compounds to soils induced changes in soil pH, subsequently effecting the soil chemistry of Mn. A Cr-Fe coprecipitation reaction was indicated by the data.

Introduction

Soil chemical interactions of trace elements can be important in determining resultant plant composition and yield (Knezek and Greinert, 1971; Olsen, 1972). Also, work of this nature can lend support to predicting, by analogy, the effects and fate of other substances applied to various soils (Lisk, 1972). Effects may be indirect, e.g., added chemicals bringing about changes in Eh or pH which can then induce a chemical redistribution of trace elements (Hodgson, 1963). These indirect effects can be important when considering fertilization methodologies to alleviate micronutrient deficiencies (Allaway, 1968; Giordano and Mortvedt, 1972).

The effect of applied Cr compounds on other soil constituents has not been extensively studied. Leep (1974) reported that soil Cr(III) additions significantly reduced 0.1 N HCl and 0.005 M DTPA extractable Fe below control treatments. Schueneman (1974) found that increasing Cr(III) application raised the Mn and lowered the Fe extracted by H_2O, NH_4OAc, and DTPA.

Changes in plant composition due to the presence of Cr have been reported. Turner and Rust (1971) found Cr(VI) to interfere with Ca, K, P, Fe, Mg, and Mn uptake and tissue concentrations in nutrient culture and plant Ca, K, Mg, P, B, and Cu in soil culture. Cary et al. (1977a) describe a Cr-Fe interaction in plants and postulate a similar or related process of translocation for the two elements. Cropper (1967) found decreased Fe, P, and Zn uptake by corn on a soil amended with a sludge containing large amounts of Cr. Manganese content was twice that of control. Schueneman (1974) and Leep (1974) reported higher Mn contents of plants and greater yields where low levels of

$CrCl_3$ were applied to soils.

Deficiency symptoms can be indicative of nutritional inter-
actions occurring either within the plant or in the surrounding soil.
Soane and Saunder (1959) felt that Cr(III) and Fe(III) acted analogously
in causing the acute P deficiency symptoms they observed in sand
culture experiments with oats. Hewitt (1953) and Anderson et al. (1973)
found Fe chlorosis to be the primary symptom of high Cr presence.
Cunningham et al. (1975) found that increasing sludge Cr content
correlated with decreasing plant tissue concentrations of Cu, Zn, Ni,
Cd, and Mn. They attribute this phenomena to a possible blockage of
plant absorption sites or interference in the translocation processes
of the plant.

The objective of this research was to ascertain the changing
soil chemistry of Fe and Mn resulting from additions of Cr compounds to
soils. Extraction methods were used to follow the changes in Fe and
Mn chemistry of incubating soils.

Materials and Methods

Soil treatments, extractants, extraction and sampling methods,
and incubation procedures are described in a preceding paper (see Chap.
II). Table 1 gives the total Fe and Mn in the soils and sludge used in
the incubation study. Fe and Mn were determined directly on all extracts
using a model 303 Perkin Elmer Atomic Absorption Spectrophotometer.
Detection limits were 0.5 and 0.1 ppm in solution for Fe and Mn, res-
pectively. Due to missing data problems only the 24 hour, 1 week, 8
week, and 16 week data were included in the analysis of variance of
Cr(III) and Cr(VI) soil treatments.

TABLE 1-Total Fe and Mn‡ of Rubicon sand and Morley clay loam.

Soil/Sludge	Total Fe	Total Mn
	----------ppm------------	
Rubicon sand	5600	323
Morley clay loam	7640	1450
Sludge	27000	528

‡ Average of six determinations.

Results

Tables 2 and 3 demonstrate the existence of significant differences in the extractable Fe and Mn data.

TABLE 2-Analysis of variance for extractable Fe.

Source of Variance	Approx. Significance Probability of F Statistic
Soil (S)	<0.0005
Cr Source (Cr)	<0.0005
S x Cr	<0.0005
Time (T)	<0.0005
S x T	<0.0005
Cr x T	<0.0005
S x Cr x T	<0.0005
Extractable Fe (Fe)	<0.0005
S x Fe	<0.0005
Cr x Fe	<0.0005
T x Fe	<0.0005
S x Cr x Fe	<0.0005
S x T x Fe	<0.0005
Cr x T x Fe	<0.0005
S x Cr x T x Fe	<0.0005

TABLE 3-Analysis of variance for extractable Mn.

Source of Variance	Approx. Significance Probability of F Statistic
Soil (S)	<0.0005
Cr Source (Cr)	<0.0005
S x Cr	<0.0005
Time (T)	<0.0005
S x T	<0.0005
Cr x T	<0.0005
S x Cr x T	<0.0005
Extractable Mn (Mn)	<0.0005
S x Mn	<0.0005
Cr x Mn	<0.0005
T x Mn	<0.0005
S x Cr x Mn	<0.0005
S x T x Mn	<0.0005
Cr x T x Mn	<0.0005
S x Cr x T x Mn	<0.0005

Fig. 1 to 6 show the amount of extractable Fe from selected soils, Cr treatments, and extractants. The limed Morley soil generally exhibited the same behavior as the unlimed Morley though at lower absolute levels of extractable Fe. Lesser Cr(III) and Cr(VI) treatments were similar to the 500 ppm treatments. NH_4Cl and $CuSO_4$ extractable Fe accounted for less than 2% of the total Fe extracted and varied little from controls throughout the incubation.

Water soluble Fe (Fig. 1 and 2) was lowered below that of the controls by both Cr(III) and sludge addition. The Cr(VI) treatment initially lowered water soluble Fe, but later raised this fraction above control values.

Oxalate soluble Fe (Fig. 3 and 4) increased when sludge was added to these soils. Little difference between other treatments and the control could be found, and a general decline in this extractable Fe fraction occurred with time for all treatments and the control.

In contrast, dithionite extractable Fe (Fig. 5 and 6) increased with time for all treatments and the control. Behavior of this fraction on the Rubicon soil was erratic when Cr treatments and time factors are considered. The Morley soil, when treated with Cr(III), gave larger amounts of dithionite extractable Fe. Sludge addition resulted in significantly lower levels of dithionite-Fe.

Fig. 7-10 detail the changes in extractable Mn observed during the soil incubation. Selected soil-treatment combinations are not resented here as they contributed nothing to the elucidation of extractable Mn behavior as a function of added Cr.

The behavior of extractable Mn was very complex. Water soluble Mn increased as the quantity of added Cr(III) increased. The Rubicon
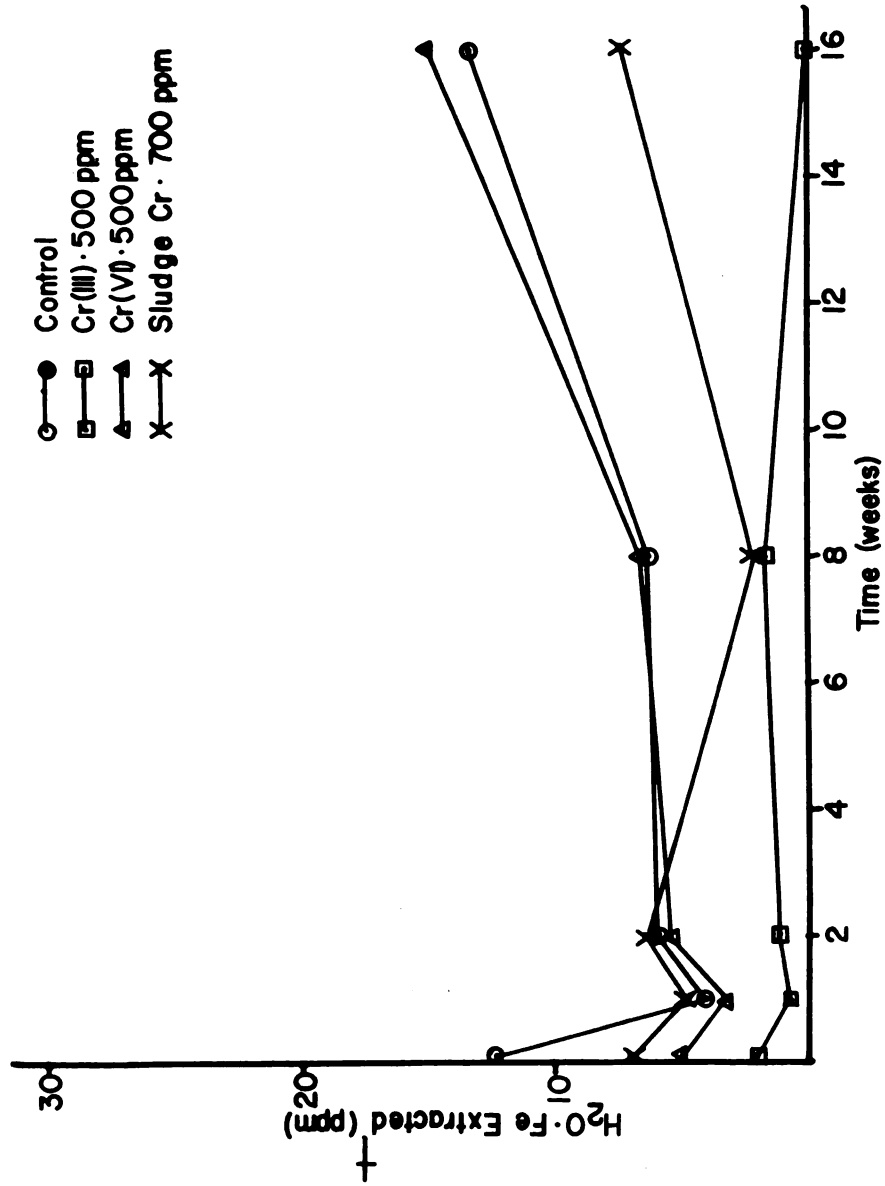
Fig. 1--Water soluble Fe vs. time for selected treatments on Rubicon sand.
+ Average of three replications.
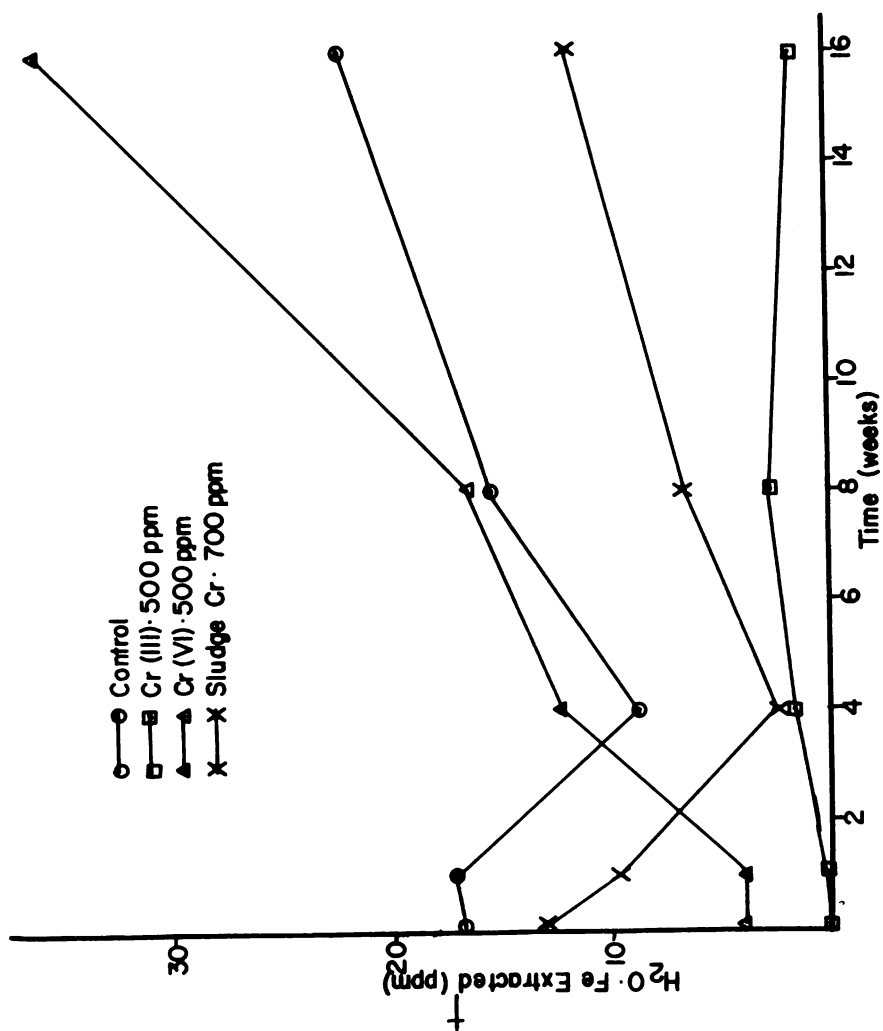
Fig. 2--Water soluble Fe vs. time for selected treatments on Morley clay loam.
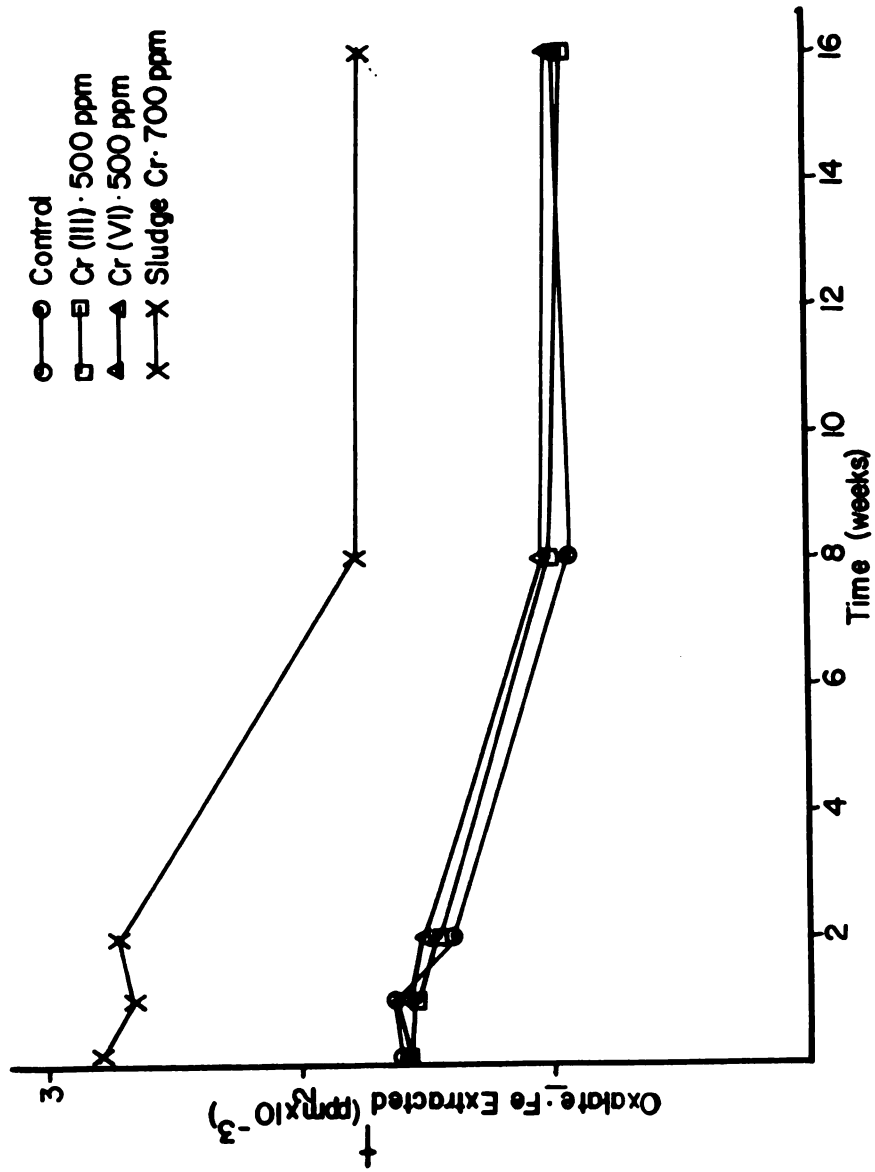+ Average of three replications.

49

Fig. 3--Oxalate extractable Fe vs. time for selected treatmens on Rubicon sand.
+ Average of three replications.

Fig. 4--Oxalate extractable Fe vs. time for selected treatments on Morley clay loam.
+ Average of three replications.

Fig. 5--Dithionite extractable Fe vs. time for selected treatments on Rubicon sand.
+ Average of three replications.
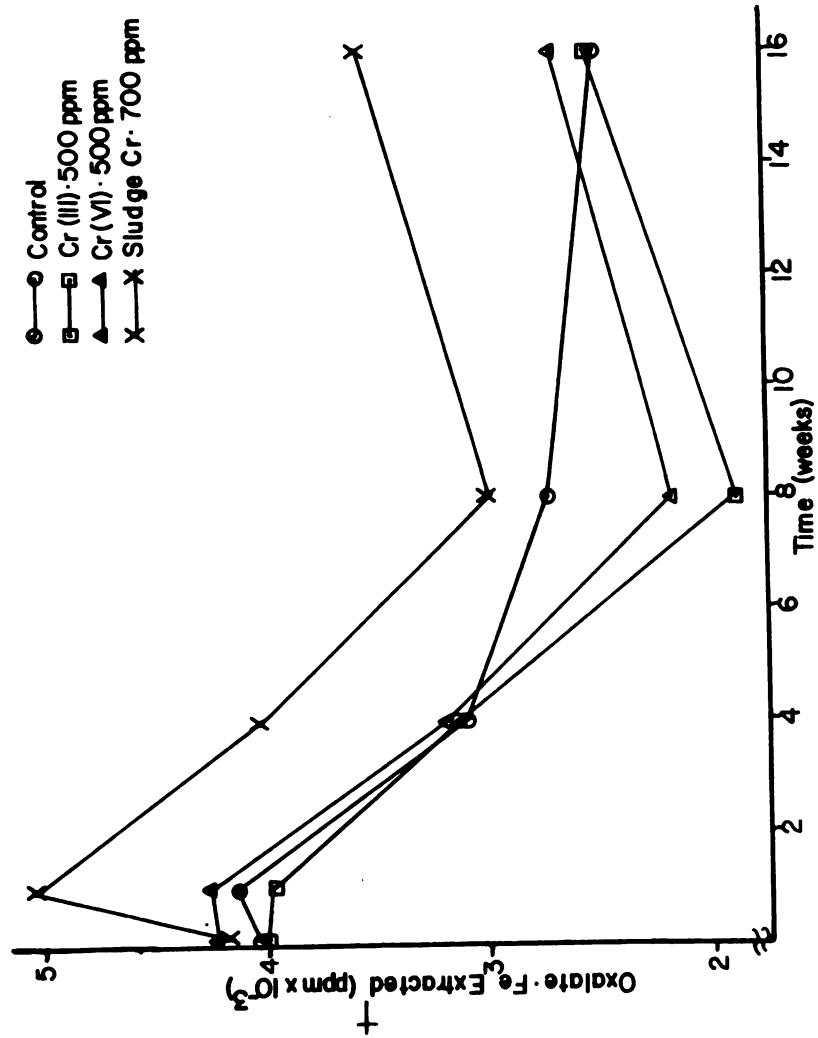
Fig. 6--Dithionite extractable Fe vs. time for selected treatments on Morley clay loam.
+ Average of three replications.

53

Fig. 7--Extractable Mn vs. time for Cr(III) treatments on Rubicon sand.
+ Average of three replications.

Fig. 8--Extractable Mn vs. time for selected Cr(VI) and sludge Cr treatments on Rubicon sand.
+ Average of three replications.

Fig. 9--Extractable Mn vs. time for Cr(III) treatments on Morley clay loam.
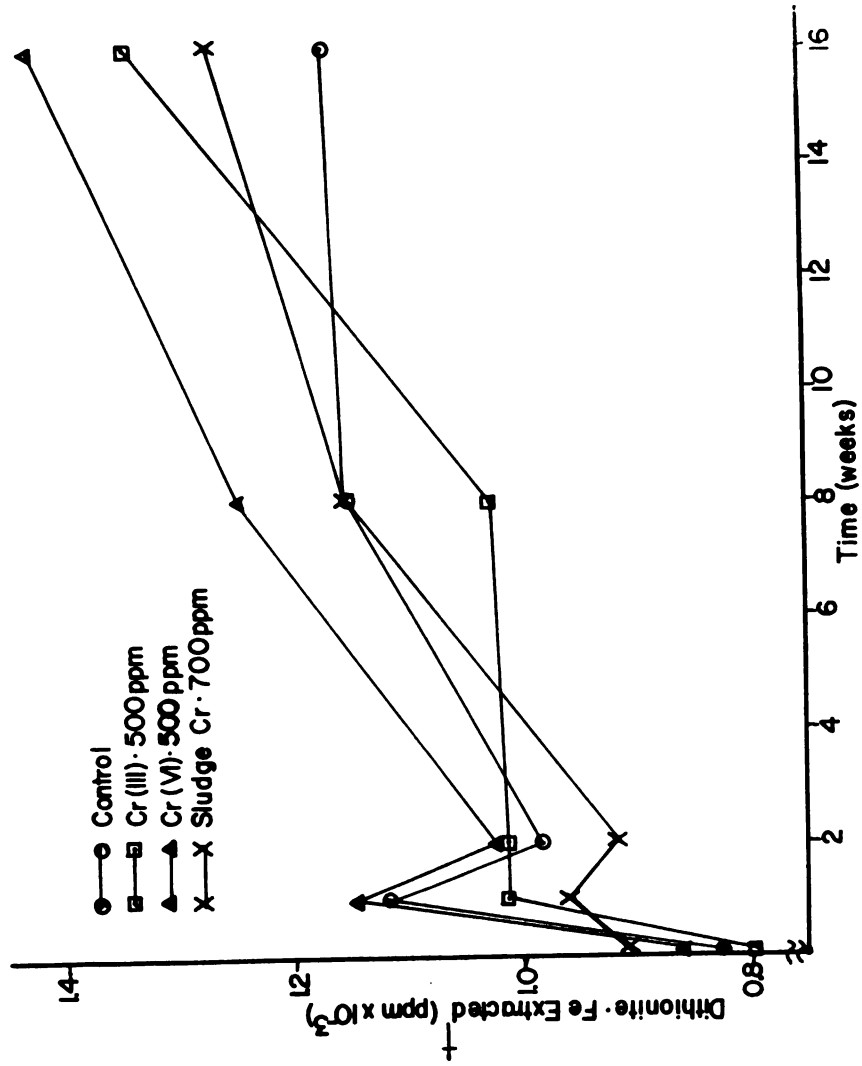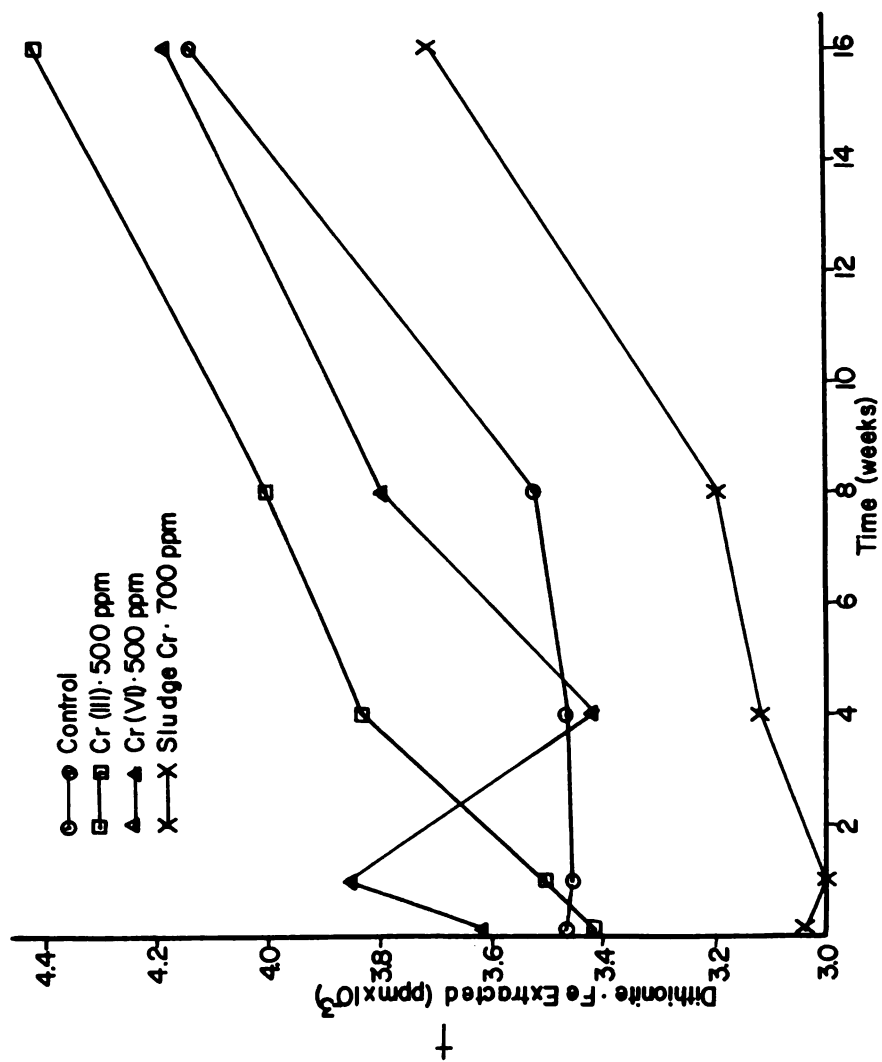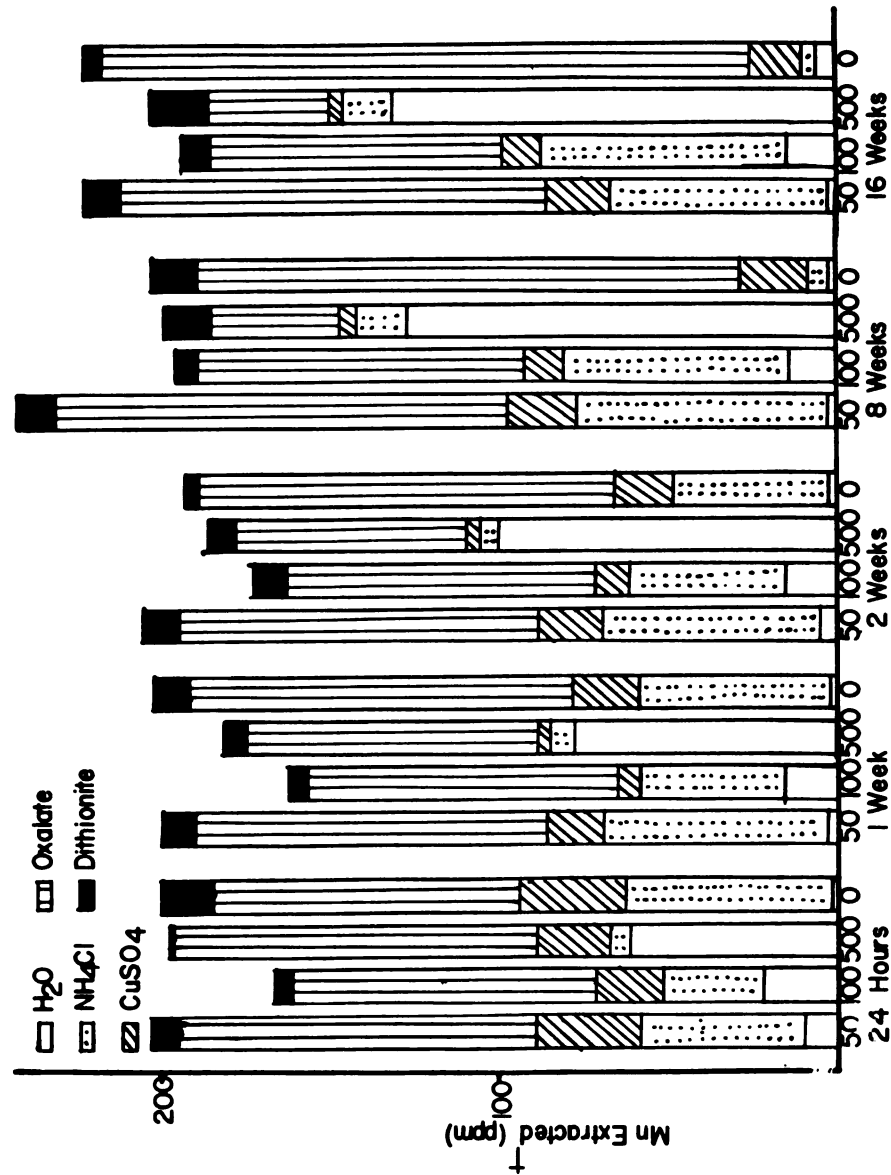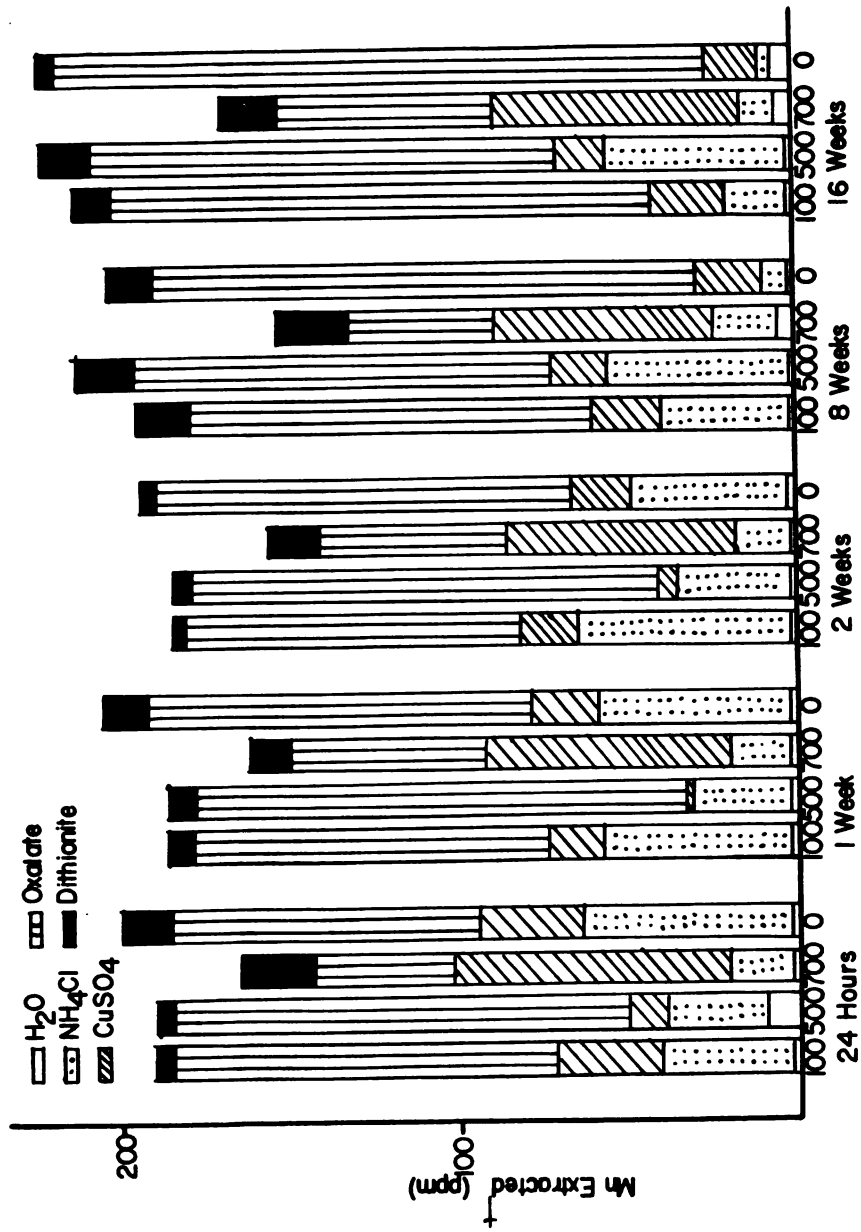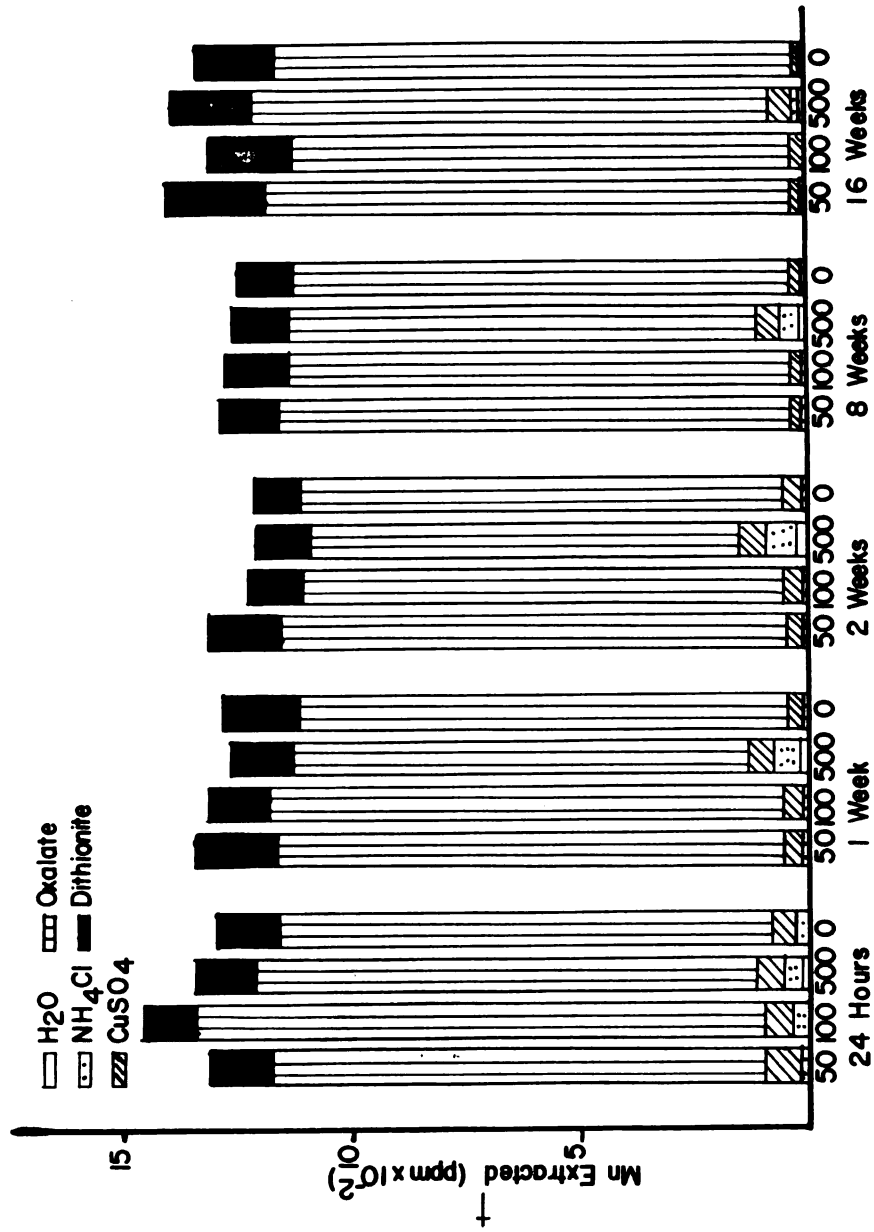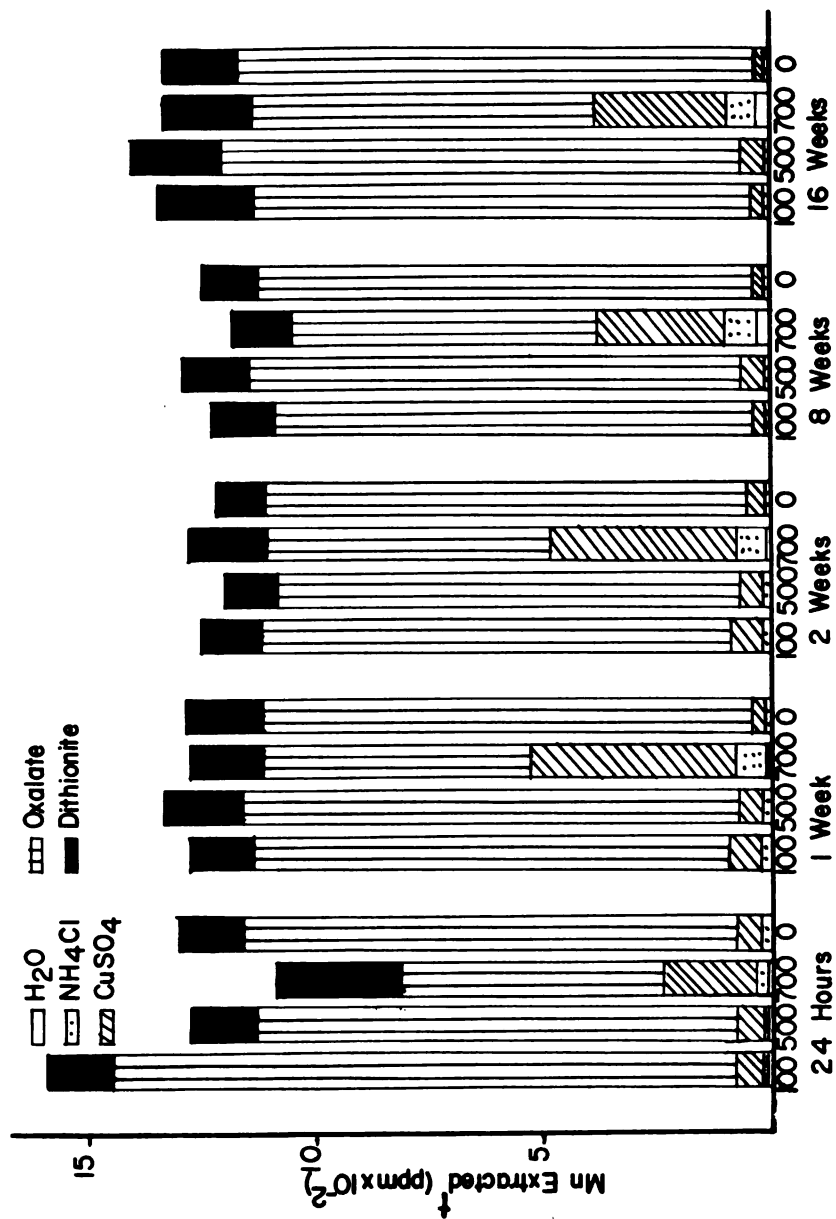+ Average of three replications.

Fig. 10--Extractable Mn vs. time for selected Cr(VI) and sludge Cr treatments on Morley clay loam.
+ Average of three replications.

soil gave consistently larger amounts of water soluble Mn than the Morley soil when treated with Cr(III). At 500 ppm Cr(III) applied, the water soluble Mn fraction increased from 61.5 to 131 ppm and dominated the total extractable Mn of the Rubicon soil. This phenomena was not observed on the Morley soil or on the lower Cr(III) treatments of the Rubicon sand.

The Cr(VI) additions initially raised the level of water soluble Mn, which declined to control levels after one week of incubation for all soils. Sludge amendment resulted in larger amounts of water soluble Mn late in the incubation study on all soils, with the greatest occurring in the Morley clay loam soil. Control pots yielded little water soluble Mn for the duration of the incubation study.

Ammonium chloride extracted much less Mn as Cr(III) concentrations increased in the Rubicon soil, while the reverse effect was noted on the Morley clay loam. But the NH_4Cl fraction increased in importance on Cr(III) treated Rubicon sand, while it decreased on Cr(III) treated Morley soils. When Cr(VI) was applied to these soils, NH_4Cl-Mn behavior varied considerably as Cr(VI) treatment levels increased, but a general decline in this fraction was noted as the incubation of Cr(VI) treated soils proceeded. On sludge amended Rubicon, the NH_4Cl-Mn fraction decreased with time. Opposite results were found on the sludge amended Morley. Control pots also changed with time; the NH_4Cl-Mn declining on both soils with the drop being most rapid on the Rubicon. The NH_4Cl-Mn of control soils declined more rapidly with time than the same fraction on Cr(VI) or sludge amended soils.

The $CuSO_4$ extraction removed large quantities of Mn on sludge amended soils. The greater removal of Mn by $CuSO_4$ appeared to be at

the expense of the oxalate extraction which followed. $CuSO_4$ extractable Mn decreased as applied Cr(III) increased on Rubicon sand, but $CuSO_4$-Mn increased as applied Cr(III) increased on Morley clay loam. The $CuSO_4$-Mn behavior on Cr(VI) treated pots was erratic relative to control and unpredictable as a function of the amount of Cr(VI) applied.

Oxalate soluble Mn, as a fraction of total Mn extracted, was generally less on the Rubicon soil, though Rubicon control pots tend to refute this assertion as the incubation progressed in time. The oxalate-Mn fraction dominated in both soils. Oxalate-Mn decreased with time on 500 ppm Cr(III) Rubicon treatments but generally increased with time on all other soil-Cr treatment combinations.

Much less Mn was extracted by dithionite on the Rubicon soil than the Morley soil. This fraction of extractable Mn remained fairly constant with time, though sludge amended Rubicon soils generally gave larger amounts of dithionite-Mn than other Rubicon treatments. Overall, the total Mn extracted by the extracting regime was less on sludge amended soil.

Discussion

Extractable Iron

The decline in water soluble Fe due to added Cr(III) was similar to that reported by Schueneman (1974). A mixed hydrous oxide of Fe(III) and Cr(III) was probably formed. The precipitated compound was apparently quite stable at low pH for the duration of the incubation period (see Chap. II). Cary et al. (1977b) came to similar conclusions. The maintenance of the low water soluble Fe condition on the acid Rubicon soil was striking. The mixed oxide may be more stable at low pH than analogous pure Cr and Fe hydrous oxides.

The effect of added Cr(VI) on water soluble Fe is complex. The initial decline in the Fe fraction may be due to coprecipitation. The final increase above control values is challenging to explain, but could be due to the activity of soluble, low molecular weight organic compounds created by the oxidizing activity of Cr(VI). These compounds could act as chelating agents; solubilizing amorphous Fe precipitates to some small extent.

Sludge addition raised the soil pH to quite high levels on all soils (see Chap. II) and decreased the solubility of Fe in this manner. Much of the Fe in the sludge was precipitated, non-crystalline material which accounts for the large increase in oxalate soluble Fe observed on all soils.

As the precipitated Fe compounds in the Cr(III) and Cr(VI) treated soils aged, their crystalline order improved and the oxalate fraction declined as the dithionite fraction increased. The lower level of Fe extracted by dithionite on the sludge-amended soils is difficult to explain, though it may be due to a breakdown in buffering during extraction.

Extractable Manganese

The soil effect of applied water soluble Cr(III) on Mn was clearly demonstrated, and is consistent with Leep (1974) and Schueneman (1974). The mechanism by which Mn solubility was increased was most likely due to the lowered soil pH resulting from Cr(III) precipitation. Soluble organic chelates loosed from the coordination sphere of precipitating Fe may be a contributory factor in the increased Mn solubility, but not to any large extent. The extremely low pH of the

500 ppm Cr(III) treated Rubicon sand can account for the continuing solubilization of Mn and the decline of the oxalate-Mn and the $CuSO_4$-Mn pools observed. The initial acidity of added Cr(VI) (see Chap. II) causes the initial increase in water soluble Mn. Sludge amended soils dropped in pH as incubation time progressed; mineralization released Mn and/or caused it to be solubilized via the indirect pH effect, accounting for the small increase in water soluble Mn observed with time.

The first three extractants (water, NH_4Cl, and $CuSO_4$) should have extracted the more readily "available" Mn while oxalate and dithionite removed less available and precipitated Mn compounds. Addition of low levels of Cr(III) to the Rubicon soil caused shifts to more soluble Mn in the "available" pool. Only when enough Cr(III) had been added to increase hydrogen ion activity beyond a certain level were more of the precipitated Mn compounds attacked to a significant degree. The shifts within the more readily available pool are observed when comparing the NH_4Cl-Mn fractions of 50 and 100 ppm Cr(III). Declines in NH_4Cl-Mn fractions on Cr(VI) treatments were probably due to the heightened soil pH caused by Cr(VI) reduction. The soil pH effect accounts for the lower fraction of oxalate soluble Mn in the total extractable Mn on the acid Rubicon sand as compared to the less acid Morley clay loam.

The $CuSO_4$ apparently removed Mn bound in insoluble organic matter in these soils. The greater removal of Mn by $CuSO_4$ on sludge amended soils and the observation that extremely low pH brought about a reduction in this Mn fraction are consistent with this view. A more subtle lowering of pH on the Morley soil brought about an increase in

the $CuSO_4$-Mn fraction as precipitated Mn compounds are slowly solubilized.

The greater quantities of available Mn and the lesser amounts of water soluble Fe point to a Cr(III) induced Fe-Mn interaction in plants. This phenomena can account for the severe iron chlorosis associated with Cr(III) toxicity observed by several workers. At lower levels of application Cr(III) could stimulate growth and yield of plants where Mn was a limiting factor in the plant's mineral nutrition.

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CHAPTER IV

SUMMARY AND CONCLUSIONS

In a broad overview of the results of this study the following general conclusions concerning the soil chemistry of Cr and the effects of added Cr(III), Cr(VI), and sludge Cr on soil pH, Cr, Fe and Mn were drawn:

1. Water soluble Cr, when added to soils, is converted to much less soluble compounds. The rate of this precipitation is dependent on soil pH, the oxidation state of the added Cr, and the quantity of organic matter present (if Cr(VI) is added).

2. The soil pH is affected by water soluble Cr addition; being lowered by Cr(III) treatment and eventually raised by Cr(VI) incorporation.

3. Water soluble Fe is coprecipitated when Cr(III) is added to soils. The effectiveness of the oxalate extraction for Cr points to Cr adsorption into amorphous, hydrous oxides of Fe. Aging results in more intimate incorporation of adsorbed Cr into the precipitated Fe fraction, possibly as a bound layer about the Fe compound.

4. Sludge Cr exists largely as precipitated Cr(III) compounds of low solubility prior to soil incorporation.

5. Water soluble-organic-Cr(III) compounds are probably of little importance in soils. The stability of the aquo complex, the slow rate of ligand exchange, and a tendency to olate and precipitate, are

all chemical factors mitigating against significant quantities of these complexes being found in soil solution.

6. Changes in water soluble Mn are generally the result of pH changes in the soil induced by the addition of the water soluble Cr compounds. A slight lowering of pH results in mere shifts to greater solubility among the "available" Mn pools. A more drastic soil pH decline brings about solubilization of more precipitated soil Mn compounds.

7. Sludge either contains more "available" Mn or induces shifts in soil Mn to more readily soluble pools. The mineralization of the sludge lowers soil pH and releases low molecular weight organic anions. Either or both of these factors can contribute to the shifts in Mn solubility observed.

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