Control of Chromium Concentrations in Food Plants. 2. Chemistry of Chromium in Soils and Its Availability to Plants

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Soluble Cr is converted to insoluble forms when added to soil. Chromium(VI) is reduced to Cr(III). This reduction is more rapid in acid than in alkaline soils. Insoluble Cr in soils appears to be hydrated oxides of Cr(III) mixed with or occluded in iron oxides. The low concentration of Cr(VI) that must be in soil may be the Cr source available for plant uptake. Addition of Cr to soils in order to increase dietary Cr for people will be very inefficient in terms of recovery by food crops of the Cr added to soil.

In order to effectively increase the chromium (Cr) concentration in food crops a fairly high supply of available Cr must be provided the plants (Cary et al., 1977). Experiments reported here were directed toward evaluating techniques for maintaining plant available Cr in soil. Attention was also directed toward characterization of the residual Cr resulting from the addition of different soluble Cr sources to soils.

EXPERIMENTAL SECTION

General Methods. The soils used, their pH values, and native Cr concentrations are given in Table I. Radioactivity measurements were made using a well-type scintillation counter (Nuclear-Chicago automatic γ well counting system) equipped with a NaI crystal. Radioactively labeled Cr species were prepared using reagent grade chemicals and carrier-free ^{51}Cr by equilibrating them at 80 °C overnight and their charge was verified by electrophoresis. All plant samples were dried at 70 °C and ground through a 20-mesh Cr-plated screen in a Wiley mill. Seeds were air-dried and washed but not ground before analysis. Total Cr analysis was done using the method of Cary and Olson (1975). The National Bureau of Standards orchard leaf sample (NBS 1571) was found to contain 2.47 ± 0.14 ppm of Cr by this method compared to the certified value of 2.6 ± 0.1 ppm of Cr.

Movement of Cr in Soil Columns. In order to characterize the persistence of soluble forms of Cr(VI) in soils, a study of the downward movement of ^{51}CrO$_4{}^{2-}$ during percolation through soil columns was conducted. Four glass cylinders 26 mm in diameter were partially filled with the Mardin soil. In two of these the soil had been adjusted to pH 7.5 with CaCO$_3$ and the other two contained this soil at its original pH of 4.7. Prior to packing in the cylinders the soils were treated with 8 ppm of unlabeled Cr to saturate some Cr-binding sites. This was added to the soil as aqueous K$_2$CrO$_4$, and the moist soil was mixed and allowed to equilibrate with the Cr for 4 weeks before being air-dried and packed into the cylinders. Soil (310 g) was packed into a volume of 286 ml and distilled water was added to the saturation point and allowed to drain.

Radioactively tagged Cr was added to each soil pH treatment in a 0.001 M Ca(NO$_3$)$_2$ solution containing either 25 or 75 ng/ml of Cr. Chromium additions were made in 25-ml aliquots, added at 15 separate times spread out over a period of 22 days. After each 25-ml aliquot of the ^{51}CrO$_4{}^{2-}$ solution was added, the first 5 ml of leachate was

Table I. Soil Classification and Native pH

Classification		pH[a]	Total Cr, ppm
Mardin silt loam	Typic fragiochrept	4.7	44
Dalton silt loam	Typic fragiochrept	5.6	44
Lima silt loam	Glossoboric hapludalfs	7.4	33

[a] 1:1 soil:water ratio.

checked for ^{51}Cr activity. After 22 days the soil was frozen, extruded from the tubes by air pressure, and cut into 2-cm sections. The ^{51}Cr activity in each section was determined. These sections were then extracted with unlabeled 0.02 M K$_2$CrO$_4$.

^{51}Cr activity was not detected in leachate from any columns. In the acid soil ^{51}Cr was retained largely in the upper 6 cm of soil at both rates of ^{51}Cr addition (Figure 1). In the alkaline soil ^{51}Cr from the low rate of addition was retained in the top 10 cm of soil. On the high rate of ^{51}Cr addition to the alkaline soil, about 90% of the activity was retained in the upper 12 cm of soil, but there were detectable amounts below that level. Downward movement was more affected by soil pH than by rate of Cr addition.

Less than 8% of the ^{51}Cr retained in the top 2 cm of soil was removed by extraction with unlabeled K$_2$CrO$_4$ and no exchange was noted in sections below 6 cm.

Removal of Added Cr from Soil by Different Extractants. One part per million and 10 ppm of Cr as ^{51}CrCl$_3$ and 1 ppm and 10 ppm of Cr as K$_2{}^{51}$CrO$_4$ were added to a 100-g sample of Mardin soil with no treatment, with 2% ground alfalfa, with 2% CaCO$_3$, and with both CaCO$_3$ and alfalfa. The alfalfa and CaCO$_3$ treatments were permitted to equilibrate with the soil at 0.1-bar H$_2$O tension for 41 days prior to ^{51}Cr additions. The Cr treatments were then added in H$_2$O with thorough mixing. On the day Cr was added to the soil, five 1-g (dry weight) samples of each soil × Cr treatment were removed and these were extracted once with 9.0 ml of 0.1 N HCl, 0.1 N NH$_4$OH, 0.01 M Ca(NO$_3$)$_2$, 0.01 M CrCl$_3$, or 0.01 M K$_2$CrO$_4$. Each sample was weighed into a test tube and the ^{51}Cr activity in the tube was measured. Then 9 ml of extracting solution was added, the tube was shaken end-over-end for 15 h and centrifuged, and the clear supernatant was carefully decanted. The ^{51}Cr activity remaining in the tube was then measured, and the ^{51}Cr removed in each extracting solution was calculated from the difference in activity for individual tubes before and after extraction. The extraction procedures were repeated at 6, 19, 46, and 90 days after the Cr addition. The soil moisture was maintained at 0.1-bar H$_2$O tension during the experiment.

The percentages of ^{51}Cr removed by the various extractants from soils treated with 1 or 10 ppm of Cr were very similar in all cases so only the data for the 1-ppm

Table II. Removal by Different Reagents of Added ^{51}Cr as Affected by Soil Treatments, Time after ^{51}Cr Addition, and Form of Cr Added

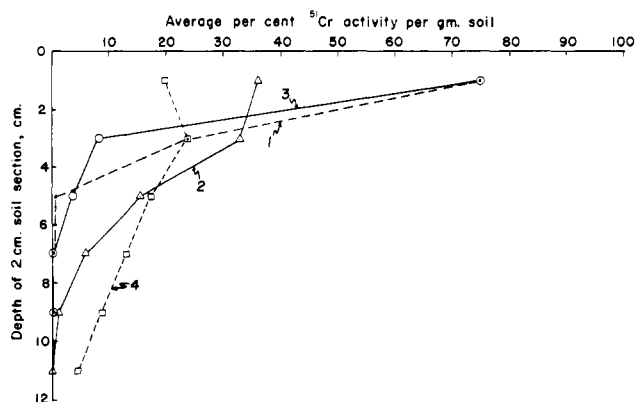|		Soil treatment, %							
		Control		2% alfalfa		2% CaCO$_3$		Alfalfa + CaCO$_3$	
	Days	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)
0.01 M CrCl$_3$	1	11	18	9	14	2	2	0	3
	7	4	10	4	9	0	3	1	2
	19	3	3	4	3	3	1	1	1
	46	4	2	6	4	2	1	2	0
	90	2	3	4	8	2	1	1	1
0.01 M K$_2$CrO$_4$	1	16	0	8	4	23	5	7	8
	7	3	2	4	4	2	4	2	5
	19	2	1	4	3	2	4	1	3
	46	3	3	4	4	4	0	3	2
	90	1	1	3	3	4	5	2	3
0.1 N HCl	1	40	40	37	38	40	56	40	57
	7	26	31	26	32	31	53	31	51
	19	22	20	26	21	30	38	31	38
	46	22	19	22	19	29	38	30	39
	90	18	22	21	22	26	40	29	39
0.1 N NH$_4$OH	1	32	22	27	23	26	11	15	14
	7	20	23	20	21	8	9	8	13
	19	17	19	18	17	6	8	8	10
	46	6	14	7	15	3	7	4	6
	90	23	3	20	4	6	3	7	3
0.01 M Ca(NO$_3$)$_2$	1	0	0	0	1	6	1	0	2
	7	0	0	2	0	0	1	1	2
	19	2	2	1	2	0	1	0	2
	46	1	0	4	0	2	2	3	1
	90	0	1	2	3	0	2	3	2

Figure 1. Percent of total activity applied remaining in 2-cm soil sections. Chromium rate (parts per billion) and soil pH, respectively: curve 1 (•– –•), 75, 4.7; 2 (△—△), 25, 7.6; 3 (○—○), 25, 4.7; 4 (□---□), 75, 7.6.

treatments are shown in Table II. Extraction with 0.01 M Ca(NO$_3$)$_2$ was used to estimate water-soluble Cr. In no case did this solution remove more than 6% of the added Cr, and most values were 3% or less. Most of the added Cr was quickly converted to forms that are not water soluble.

Extractions with unlabeled CrCl$_3$ and K$_2$CrO$_4$ estimate isotopically exchangeable Cr that might be present. Apparently by the end of the first week there was very little labile Cr in any of the treatments and therefore the sorbed or precipitated Cr in soils is stable and tightly bound. The CrCl$_3$ solutions were not highly buffered. The pH values of the mixtures of CrCl$_3$ solution and CaCO$_3$ treated soil were slightly alkaline; thus, the solubility of Cr(III) would have been very low. Thus, measurements of labile or isotopically exchangeable Cr(III) may be limited to acid soils or to buffered acid Cr(III) solutions.

After day 1, the percent of the ^{51}Cr removed by K$_2$CrO$_4$ was quite similar regardless of whether or not Cr(VI) or Cr(III) had been added to the soil. This indicates that most of the Cr(VI) added to these soils may have been

converted to Cr(III) by day 7, and that less than 5% of added ^{51}Cr(III) was oxidized to Cr(VI) within 90 days. The amount of ^{51}Cr removed on day 1 by extraction with unlabeled K$_2$CrO$_4$ was lower on the soils treated with alfalfa, indicating an enhancement of Cr(VI) reduction by the extra organic matter present.

Extraction of the soils with 0.1 N HCl dissolved excess CaCO$_3$ and part of the Fe, Al, and Mn oxides. These percentages of the ^{51}Cr removed by 0.1 N HCl declined steadily as the experiment progressed but even on day 90 they exceeded extraction by any of the other reagents. More Cr was extracted from soils treated with CaCO$_3$ than from the acid soils. The amounts of ^{51}Cr extracted by HCl were similar for soils treated with ^{51}Cr(VI) and ^{51}Cr(III) indicating that the residual Cr in these soils was similar regardless of whether Cr(VI) or Cr(III) was initially added. Hydrous oxides of Cr(III) may constitute the majority of this residual Cr. In the acid soils these hydrous oxides of Cr(III) are more tightly bound, less olated, or perhaps occluded in sesquioxide particles, whereas in soils treated with CaCO$_3$ highly olated Cr tends to be present on the surface of CaCO$_3$ or sesquioxides, and is therefore more susceptible to dissolution by HCl.

Extraction of the soils with 0.1 N NH$_4$OH was intended to estimate soluble organic complexes of Cr(III). It would also solubilize Cr(OH)$_3$ (Novikov, 1962). Comparison of percentages of ^{51}Cr extracted by NH$_4$OH from acid vs. CaCO$_3$ treated soils is subject to a possible error because NH$_4$OH extracts of acid soils were brown and may have contained suspended colloidal material, while those from CaCO$_3$ treated soils were clear. The percentages of ^{51}Cr extracted by NH$_4$OH generally declined as the experiment progressed. This would not be expected from the known tendency of Cr(III) to slowly form complexes with organic ligands (Mertz, 1969). However, this could be a result of the aging of Cr(OH)$_3$ type compounds. Furthermore, the percentages of ^{51}Cr extracted by NH$_4$OH were less from soils treated with alfalfa than from soils without alfalfa additions. Therefore, if the ^{51}Cr extracted by NH$_4$OH was indeed organic complexes of Cr, the formation of these

complexes was not enhanced by alfalfa additions. In the two unlimed Cr(VI) soil treatments, the amount of ^{51}Cr extracted by NH_4OH increased from less than 10% to more than 20% of the total ^{51}Cr present during the 46–90-day period. This increase could have been due to formation of organic complexes of Cr late in the experiment, but if so, it is difficult to explain why this increase was not shown by the Cr(III) treatments on the unlimed soils nor by either Cr(VI) or Cr(III) treatments on the limed soils. In summary of the NH_4OH extractions, it appears that there is some evidence, but no definite proof, that organic Cr complexes may have been present in these soils. Definite proof of the presence of organic complexes in the supernatants might be obtained by chromatographic or electrophoretic studies of the supernatant solutions.

After 90 days, the treatments receiving 10 ppm of Cr were sampled and exhaustively extracted with 0.03 N NH_4F in 0.025 N HCl, 0.5 N neutral NH_4F, 0.1 M $(NH_4)_3C_6H_5O_7$ (pH 4.8), or 0.1 M $(NH_4)_2C_2O_4$ (pH 4.8). The decrease in ^{51}Cr activity of the soil was determined after each successive extraction.

Exhaustive extraction of soil after 91 days of reaction time with dilute acid–fluoride indicated that less than 10% of the ^{51}Cr added as Cr(III) was bound with surface layers of iron or aluminum. Neutral 0.5 N NH_4F, which would remove more of the Al component without extracting Fe, removed less than 15% of the Cr. Only slightly more ^{51}Cr was removed by these treatments when soils treated with Cr(VI) were extracted. Citric acid and oxalic acid removed 85 to 90% and 75 to 80% of the ^{51}Cr, respectively, from the Cr(III) and Cr(VI) treated soils. This suggests that the Cr was largely associated with hydrous oxides of Fe or possibly of Mn.

Addition of High Rates of Cr(III) to Dalton Soil. In order to determine whether or not residual Cr(III) can build up to the point of increasing the Cr concentration in plants for extended periods of time, heavy applications of freshly precipitated $Cr(OH)_3$ were made to Dalton soil. The Cr(III) was added as a solid in order to maximize coating of the soil particles with Cr and minimize occlusion of the Cr by sesquioxides.

Chromium hydroxide was prepared from Cr_2K_2-$(SO_4)_4 \cdot 2H_2O$ by precipitation with NaOH. The precipitate was washed free of sulfate and mixed (wet) with 3 kg (dry wt) of soil. Rates of $Cr(OH)_3$ additions were 0.03, 0.08, 0.1, 0.3, 0.6, and 1.0% Cr on a dry soil basis. After initial mixing, the soil was passed through a 1-mm screen and mixed for 20 min in a twin-shell blender. After addition of 3 g of NH_4NO_3 and 2.9 g of KH_2PO_4, the soil was again blended for 20 min. Three replications of the soil were potted in plastic nondraining pots and seeded to Chris wheat. After germination, the plants were thinned to five plants per pot. One month after germination, 0.07 g of $MgSO_4$ was added. Wheat was harvested at maturity by taking the entire aerial portion of the plant cut 2 cm above the soil. The soil was allowed to dry and the crowns of the wheat plants were removed before inoculated Saranac alfalfa was seeded. After germination, plants were thinned to five per pot. One week later 1.5 g of KH_2PO_4 and 0.18 g of $MgSO_4$ were added. Three successive cuttings of alfalfa were taken at one-tenth bloom. The soil was then frozen for 1 month and repotted after removing the alfalfa crowns. NH_4NO_3 (3.7 g) and KH_2PO_4 (1.3 g) were added in 700 ml of water. Buckwheat (New York Common) was seeded, germinated, and then thinned to three plants per pot. These were harvested 12 weeks after germination.

Even at the highest rates of $Cr(OH)_3$ the Cr concentration in the grain of wheat planted immediately after Cr

Table III. Effects of $Cr(OH)_3$ Addition to Dalton Soil on the Cr Concentration in Successive Crops

Rate of Cr addition, % Cr	Cr concn in plants, ppb of Cr				
	Wheat			Alfalfa (av of 3 harvests)	Buckwheat entire plant
	Grain	Stem	Leaf		
0	11	29	258	101	211
0.03	13	107	263	103	167
0.08	15	64	303	102	170
0.10	15	64	315	101	351*
0.3	11	118	615	147*[a]	247
0.6	16	198	678	220*	526*
1.0	13	105	535	209*	486*

[a] The asterisk means significantly (5%) different from means in same columns with no asterisk by Duncan's multiple range test.

addition was not increased (Table III). The Cr concentration in the stems and leaves was increased on some of the $Cr(OH)_3$ treatments but these increases were variable and not consistent with the rates of Cr applied. In the alfalfa and buckwheat crops, only those receiving higher rates of Cr addition showed significantly increased Cr concentrations.

These Cr concentrations are similar to those found in plants growing on high Cr serpentine soils. Wheat and oats collected from soils formed in alluvium from serpentine in California contained 0.4 to 1.8 ppm of Cr in vegetative tissue, but Cr concentrations in the grain were similar to those found in low Cr areas (Welch and Cary, 1975). It is apparent from these results that very high applications of Cr(III) compounds would be required to provide a lasting increase in the Cr concentration in crops, and the increases obtained would not occur in cereal grains.

The yields of wheat grain grown immediately after Cr additions were significantly higher than the controls at all levels of Cr addition except the 1.0% level. The yield increases on Cr-treated pots were not correlated with Cr concentrations in the plant tissue. It seems possible that these increases are an indirect effect of Cr additions on the availability to the wheat of some other element, or perhaps due to effects of the Cr additions upon some soil-borne pathogen, rather than to effects of Cr as a plant nutrient (Turner and Rust, 1971). Pratt (1966) reported that crop yield increases previously reported for plants grown on Cr-treated soils may be due to indirect effects.

Influence of Time of Application of Cr to Soil on Cr Uptake by Plants. A greenhouse pot experiment was conducted to determine the rate at which Cr added to soil would revert to forms that are not available to plants. Mardin soil (3500 g (dry weight) per pot) was mixed with 11 g of $CaCO_3$, 0.08 g of $CaSO_4$, 3.7 g of NH_4NO_3, and 1.3 g of KH_2PO_4 in a twin-shell blender for 20 min. The treatments applied in triplicate were: aqueous $CrCl_3$ and aqueous K_2CrO_4 applied 5 days before seeding and at boot stage at rates of 0.5 and 2.0 ppm of Cr (soil dry weight basis). Chris wheat was planted, germinated, and thinned to four plants per pot. The plants were harvested 99 days after planting.

Preplant soil treatment of Cr to the Mardin soil as $CrCl_3$ or as K_2CrO_4 had no measurable effect on yield or Cr concentration in wheat (Table IV). An aqueous addition to the soil of 2.0 ppm (soil dry weight) of Cr(VI) at boot stage increased the concentration of Cr in stems and leaves. Other Cr additions at the boot stage had no significant effect on the Cr concentration found in wheat.

Effect of pH on the Availability of Cr(III) and Cr(VI) to Wheat and Buckwheat. Mardin soil at pH

Table IV. Yield and Concentration of Cr in Wheat Grain and Straw as Affected by Cr Addition to the Mardin Soil Limed to pH 6.3

Treatment, ppm			Wt, g		Cr concn, ppb	
Source	Level	Time	Grain	Straw	Grain	Straw
Control			13.5	13.5	17	183
Cr(III)	0.5	Boot	11.5	13.8	26	328
	0.5	Preplant	13.3	13.9	16	208
	2.0	Boot	12.8	13.5	24	180
	2.0	Preplant	11.2	11.4	27	196
Cr(VI)	0.5	Boot	12.4	11.6	27	542
	0.5	Preplant	12.5	13.3	18	287
	2.0	Boot	13.4	15.6	43	1353*[a]
	2.0	Preplant	12.6	12.8	19	199

[a] The asterisk indicates significantly (5%) different from means in the same column with no asterisk by Duncan's multiple range test.

5.2 and this same soil with 4% added $CaCO_3$ (pH 7.5) and Lima soil (native pH 7.2) were used in this experiment. All soils were treated uniformly with major and micronutrients to eliminate any deficiencies, and half the pots were planted to wheat (Sheridan variety hard red spring) and the other half to buckwheat (New York Common variety). Triplicate pots of each crop were treated as follows: no added Cr, Cr(III) added as $CrCl_3$, and Cr(VI) added as K_2CrO_4. The Cr additions consisted of 2.33 mg of Cr(III) or Cr(VI) in 300 ml of H_2O, added 30 days after seeding and each 4 or 5 days thereafter for a total of eight applications. There were 3500 g of dry soil in each pot so the total addition was 5.3 ppm of Cr on a dry soil weight basis. The moisture level in the pots was adjusted to 25% for the Lima soil and 30% for the Mardin soil. These moisture percentages approximated 0.05 bar tension, so well aerated conditions should have been maintained during plant growth periods. The Cr treatments, soil pH values, and soil aeration regimens were thus designed to promote maximum Cr uptake.

Buckwheat was harvested 101 days postseeding and wheat 110 days postseeding. There were no significant differences in yield due to Cr treatments. All pots were then left in the greenhouse for 90 days without watering. Then the stumps of the plants were removed. The surface of each pot was stirred to a depth of about 5 cm with a spatula, and buckwheat was planted in all pots with no additional Cr treatment. This buckwheat was harvested for Cr analysis 60 days after planting.

Higher Cr concentrations were in the tops of the plants grown with Cr(VI) treatments than with Cr(III) treatments (Table V), and Cr from both sources was taken up more from the two alkaline soils than from the acid soil. These results are consistent with those of the experiments on solubility of Cr in different extractants. The pH of the soil was not the only factor affecting Cr availability, however, since the Cr levels in plants grown on the Lima

soil at pH 7.2 were slightly higher than those on Mardin soil limed to pH 7.5.

Even though the Cr treatments were designed to maximize Cr concentrations in the plants, the seed of wheat contained only slightly more Cr than found in a survey of Cr in wheat from major wheat-producing areas (Welch and Cary, 1975). The seed of buckwheat contained higher concentrations of Cr than any other seed or fruit encountered so far in any of our studies of Cr in plants. Even so the concentration of Cr in the leaves of buckwheat was about one order of magnitude higher than in the seeds, indicating a substantial barrier to translocation of Cr from vegetative tissues to seeds even in plants that are relatively good Cr accumulators.

Plant available Cr in the soil decreased very sharply during the period prior to the planting of the second buckwheat crop even though the soil was dry and well aerated so as to minimize reduction of Cr(VI) to Cr(III). The low uptake of Cr by the second planting of buckwheat indicates that applications of Cr to these soils will have very little residual effects on Cr concentrations in plants.

DISCUSSION

The most consistent feature in all of the experiments reported here is the pronounced tendency of soluble Cr added to soils to revert to forms that are insoluble and unavailable for plant uptake. When considered with information on the chemistry of Cr, the results of these experiments offer some qualitative insights to the mechanisms involved in this reversion.

The equilibrium distribution of different forms of Cr in aqueous solution has been calculated as a function of pH and redox potential by Huffman (1973). His diagrams indicate that at pH values ranging from about 5 to 8 the E_h values at which Cr(VI) will convert to Cr(III) are close to the E_h values of aqueous environments in equilibrium with air. At pH 7 in a well-aerated soil the concentration of CrO_4^{2-} could be equal to the concentration of $Cr(OH)_2^+$. Data given by Frissel et al. (1975) indicate that E_h-pH relationships in most arable soils will favor the formation of Cr(III) over that of Cr(VI). Naturally occurring minerals of Cr(VI) are very rare and found only in highly oxidizing environments. Most of the occurrences of Cr are as Cr(III) in the mineral chromite, a mixed oxide of Cr(III) and Fe(II) (Goldschmidt, 1954). Thus, mixed oxides of Cr and Fe are more stable than Cr oxides, although we have not found reports of quantitative measurements. The oxides and hydroxides of Cr(III) are quite stable and insoluble. Mesmer and Baes (1975) indicate log K_S = -30 for the reaction $Cr(OH)_3 \leftrightarrows Cr^{3+} + 3(OH^-)$. The calculation of forms of Cr and concentrations of different forms in solution is complicated by very slow exchange rates of ligands coordinated with Cr(III) (Mertz, 1969).

The experiment on movement of ^{51}Cr in soil columns shows that Cr(VI) is converted to fixed forms within a

Table V. Concentration of Cr in Various Plant Tissues as Affected by Cr Additions to Soil

	ppb								
	Mardin soil (pH 5.2)			Mardin soil (pH 7.5)			Lima soil (pH 7.2)		
	None	Cr(III)	Cr(VI)	None	Cr(III)	Cr(VI)	None	Cr(III)	Cr(VI)
Wheat									
Leaf and stem	90	280	280	70	150	690	70	340	2 500
Seed	12	12	10	8	10	29	5	14	63
Buckwheat									
Leaf	150	330	1900	194	590	2490	234	2740	10 530
Stem	330	150	340	28	140	620	50	340	1 850
Seed	23	43	194	21	100	780	50	260	1 070
Buckwheat (2nd seeding)									
Whole plant	107	124	158	138	157	146	97	343	405

fairly short distance of penetration into the soil. This agrees with observations made by Frissel et al. (1975). The observation that very little of the added Cr was subject to isotopic exchange with Cr(VI) is evidence that reduction to Cr(III) was involved even if the initial immobilization of the added Cr(VI) had been due to coprecipitation of chromate ions on metal hydroxides (Plotnikov et al., 1967). Also, the slightly deeper penetration of Cr(VI) into the alkaline soil than into the acid soil is consistent with the E_h–pH diagrams of stability of different oxidation states of Cr. The experiments on extraction of Cr-treated soils with different solutions also provide evidence of conversion of Cr(VI) to Cr(III), followed by formation of mixtures of hydrated oxides of Cr and Fe.

The experiments involving Cr uptake by plants growing on Cr-treated soils indicate that the reversion of soluble Cr to forms that are generally unavailable to plants is essentially complete within one growing season after soluble Cr(VI) is applied to the soil. $Cr(OH)_3$ or other hydrated oxides of Cr(III) are so inert that they do not consititute an effective source of Cr for plants unless these hydrated oxides are present in the soil in very large amounts.

In summary, the chemistry of Cr in soils with reference to Cr uptake by plants appears to be dominated by a trend to form inert mixed oxides of Cr(III) and Fe. These mixed oxides have some of the characteristics of the mineral chromite. The rate at which soluble Cr(VI) will revert to inert forms of Cr(III) is slower in alkaline soils than in acid soils, as would be predicted from thermodynamic studies. Even though the concentration of Cr(VI) in soil solution may be extremely low it may be this anion that is taken up by the plant. There is some evidence for this given by Shewry and Peterson (1974).

We conclude from these experiments that the addition of Cr to soils as Cr(III) is not a promising method of enhancing human dietary intake of Cr, and will be inefficient even when used on soils for production of food crop species that are efficient Cr accumulators. The Cr concentration of plants growing in some soils could be increased by addition of Cr(VI) (Cary et al., 1977) to irrigation waters as Cr(VI) is fairly stable to reduction in water (Perkins et al., 1960). These experiments also indicate that the hazard of permanent damage to soils from inadvertent pollution with Cr in industrial or municipal wastes is very low.

In view of the similarity of the chemical properties of Cr(III) and Fe(III) the observation that plants may contain several hundred times as much Fe as Cr is striking. The reason for this difference may be the difference in the reduction potential of Fe(III) to Fe(II) as contrasted to the Cr(III)–Cr(II) couple if Cr enters the plant as a cation. According to Chaney et al. (1972), reduction of Fe(III) to Fe(II) followed by uptake of Fe(II) by the roots is a key process in Fe accumulation by plants. After passing root cell membranes Fe(II) may be oxidized to Fe(III) and be translocated to the top of the plant as ferric citrate (Tiffin, 1972). According to Huffman (1973) the E_h value for reduction of Cr(III) to Cr(II) is lower than the H_2O–H_2 couple and so this reduction is unlikely to take place in soils or plants. The relative ease of reduction of Fe(III) to mobile Fe(II) and the great difficulty of reducing Cr(III) to Cr(II) may be responsible for the mobility of Fe in soil–plant systems, and for the immobility of Cr in these systems.

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