

## Original Research

### Effect of organic amendments on chromium speciation in chromium contaminated soils (Maize field)

by

Sunitha, R\*<sup>1</sup> and S. Mahimairaja<sup>1</sup>

<sup>1</sup>Department of Environmental Science, Tamil Nadu Agricultural University, Coimbatore – 641 003.

Author Address: Dr. Sunitha Rangasamy, Research Associate, Department of Nano Science and Technology, Tamil Nadu Agricultural University, Coimbatore – 641 003.

Office : +91 422 6611567, Fax : +91 422 6611567, Mail address: [drsunithaens@gmail.com](mailto:drsunithaens@gmail.com)

Co-author address: Professor, Department of Environmental Science, Tamil Nadu Agricultural University, Coimbatore – 641 003, Mail address: [rajasmahimai@yahoo.co.in](mailto:rajasmahimai@yahoo.co.in)

#### Abstract

The distribution and mobility of chromium in the soils surrounding a tannery waste dumping area was investigated to evaluate its vertical and lateral movement of operational speciation which was determined in five steps to fractionate the material in the soil and sludge into (i) water soluble, (ii) exchangeable, (iii) reducible, (iv) oxidizable, and (v) residual phases. In this study the speciation of Cr was determined in soil after the harvest of crops by a sequential fractionation procedure. The result showed that, initially, in maize field soils, about 41 per cent of Cr was found as exchangeable form (as extractable by  $\text{KNO}_3$ ) followed by 33.8 per cent in residual forms. A reduction of only 28 per cent from the initial concentration of Cr in the surface soils under maize was observed due to the addition of organic amendments. Such reduction is attributed to the formation of either organo-chromic complexes (Immobilization) or chelates. Significantly higher amounts Cr were found in the subsurface soils of maize field due to greater amount of Cr leaching. The predicted (cumulative) net drainage of 483 mm computed for maize and the sandy loam nature of the soil appeared to have facilitated greater leaching and transport of Cr to the subsurface soil. The results showed greater risk for groundwater contamination due to Cr in these contaminated soil.

*Key words: Cr speciation, organic amendments, Cr contaminated soil, immobilization*

#### Introduction

The average concentration of chromium in non-polluted soils is around 100 mg  $\text{kg}^{-1}$ . Much higher contents of

several thousand mg  $\text{kg}^{-1}$  can be found in soils of old sites of chrome plating plants and sewage farms of leather industry. In order to assess the potential hazards

emanating from such contaminations it is essential to determine the speciation of chromium. In the environment, this metal exists as Cr (III) and Cr (VI) with both forms being chemically completely different. Trivalent Cr forms hydrolysis products and co-precipitates with ferric iron (Schwertman *et al*, 1989). It also forms stable complexes with amino groups in organic material and is therefore used for leather tanning (Gauglhofer and Bianchi, 1991). In soils, Cr (III) is relatively immobile. Cr (VI) exists as the chromate anion which as a strong oxidizing agent is considered to be 100 to 1000 times more toxic than Cr (III) (Gauglhofer and Bianchi, 1991). Chromate is much more mobile in soils because it is only weakly bound by sorption reactions (Rai *et al*, 1989). Both forms, Cr (III) and Cr (VI), interact with soil constituents and can co-exist depending on the soil Eh-pH conditions. Chromate is reduced to Cr (III) by soil organic matter and ferrous iron. Cr (III) can be oxidized to Cr (VI) by Mn (IV) oxides (Manceau and Charlet, 1990) or even by oxygen at neutral to alkaline conditions (Gauglhofer and Bianchi, 1991). In the present study, we attempted to determine the speciation of chromium in a highly contaminated soil and

to devise procedures for removing and immobilizing the contamination.

Tanning is one of the oldest and fastest growing industries in India. There are about 2,000 tanneries located at different centers with a total processing capacity of 600,000 tons of hides and skins per year (Raju and Tandon, 1986). Two major sources of Cr contamination are sludge-treated/amended soil (Dreiss, 1986) and uncontrolled disposal of wastes (Makdisi, 1991). It is estimated that in India alone, about 2000–3000 tons of Cr escape into environment annually from the tanning industries, with Cr concentration ranging between 2000 and 5000mg/L in the aqueous effluent, compared to the recommended permissible limit of 2mg/L while 0.05mg/L in drinking water (Mohan, 2006).

Hence, in 1995, the Supreme Court of India ordered the closure of hundreds of tanneries in Tamil Nadu for failing to treat their effluents (Kennedy, 1999). The Tamil Nadu Pollution Control Board (TNPCB) estimates that about 150,000 tons of solid wastes accumulated over two decades of plant operation were stacked in an open yard (three to five meters high and on 2 hectares of land) on the facility premises. It is common conception nowadays that the total concentrations of metals in soils are not a

good indicator of phytoavailability (Tessier, 1979), or a good tool for potential risk assessment, due to the different and complex distribution patterns of metals among various chemical species or solid phases (Elzinga and Cirimo, 2010). Wang *et al.* (2004) reported that correlation was better between plant growth and available Cr than between plant growth and total Cr. It has long been recognized that the soluble, exchangeable, and loosely adsorbed metals are quite labile and hence more bioavailable for plants (Lasat, 2002). Also, clayey soil might have high sorption capacity for Cr than other types of soils (Adriano, 1986).

Total metal content of soils is useful for many geochemical applications but the speciation (bioavailability) of these metals is more valuable agriculturally because this form of metal will be bioavailable for plant uptake or extractable to groundwater or animal/human consumption (Ratuzny *et al.*, 2009). Since mineralogy and chemistry of the soil sample determine the phases or forms of metal salts present, the solubility of these metal salts mostly depends on ionic strength or chemical composition of the extractants. Metal can exist in water soluble, carbonate and sulfide bound, reducible (Fe and Mn oxide bound), oxidisable (organic matter bound), and residual (lattice bound)

forms in soils and sludge. Data on metal concentration in each phase are urgently important to access its bioavailability and mobility in underground soil strata under different geochemical environments. No single extractant can leach all forms of metal phases in soil, and hence other chemical speciation techniques (Sarkar and Datta, 2004) are not suitable except Sequential Extraction Procedures (SEP).

There are several SEP available in the literature (Zimmerman and Weindorf, 2010). Despite the nonselectivity of the reagents used, handling of sediment prior to extraction, sediment-reagent ratio, and length of extraction lead to dubious data collected from SEP and even ends up with inconsistent results using repeatedly the same SEP, these techniques are unanimously accepted and adopted for speciation of metal bound to different salts in soils.

## **Materials and methods**

### **Sample collection**

The experimental soil was a sandy loam and belongs to *Fluventic Haplustepts* in USDA classification. The experimental field was ploughed well, leveled and divided into 21 plots of 20 m<sup>2</sup> of area. The bioremediation technology was introduced in this chromium contaminated soils. After the crop harvest period the soil samples

were collected from the maize experimental field and analyzed the different chromium species presented in soil.

### **Speciation of Heavy metals**

A sequential extraction procedure was followed to quantify the relative proportion of different species of Cr. It is helpful in determining the biotoxicity of Cr as species determine the toxicity of heavy metals. Sequential extraction is a series of chemical extractions performed on same sample. The extractants used in the first few steps of a sequential extraction tend to selectively target specific components of adsorbent structure whereas extractants used in the last step are less specific and more vigorous and destructive (Beckett, 1989).

A method described by Noble and Hughes (1991) was employed to determine the species of retained Cr in the soil as outlined below.

**Step 1 (Water soluble fraction):** One gram of air-dried soil sample was weighed in a 50 ml polypropylene centrifuge tube and added 25 ml of double distilled water. It was shaken in an end-over-end shaker for 2 hrs at  $25\pm 2^{\circ}\text{C}$ . Then centrifuged the tubes at 8000 rpm for 10 mint and filtered through Whatman No.40 filter paper. The soluble Cr in the water extract was determined using an Atomic Absorption Spectrophotometer with

air- acetylene flame of new VARIAN, AA240 (USEPA, 1979a).

**Step 2 (Exchangeable fraction):** To the residue from step 1, 25 ml of 0.5 M  $\text{KNO}_3$  was added and shaken it for 16 hrs. The centrifugation, filtration and measurement were followed as in step 1.

**Step 3 (Organic fraction):** Added 25 ml of 0.5 M NaOH to the soil remaining after the exchangeable fractions (step 2) and shaken it for 16 hrs. The centrifugation, filtration and measurement were followed as in step 1.

**Step 4 (Organic plus iron-oxide bound fraction):** The residue from step 3 was shaken with 0.05 M  $\text{Na}_2\text{EDTA}$  for 6 hrs and followed centrifugation, filtration and measurement as in step 1.

**Step 5 (Residual fraction):** The soil residue from step 4 was transferred to a 150 ml conical flask using a jet of water and dried in an oven. Then added 10 ml concentrated  $\text{HNO}_3$  and digested the contents at  $110^{\circ}\text{C}$ . After digestion, the contents were diluted and filtered before taking measurements.

The tube plus contents were weighed before and after extraction to calculate the volume of entrapped solution and transfer of heavy metal between extractants. The amounts of Cr extracted by each extractant were computed by using the following equation.

**Cr extracted ( $\mu\text{g g}^{-1}$ ) = C x (E+M) - (C' x M) / weight of soil**

Where,

C - Concentration of heavy metal in the extraction solution

M - Mass (g) of the entrained solution carried over from previous extraction

C' - Concentration of the heavy metal in the extraction solution of proceeding step of the sequence

E - Mass (g) of the extractant

## Results and discussion

Water soluble Cr was found in soil at harvesting stage and data presented in Table 1. The initial soil had  $0.1 \text{ mg kg}^{-1}$  of water soluble Cr,  $319.6 \text{ mg kg}^{-1}$  exchangeable form of Cr,  $115.4 \text{ mg kg}^{-1}$  of organic bound,  $12.1 \text{ mg kg}^{-1}$  of organic plus iron oxide bound and  $248.4 \text{ mg kg}^{-1}$  of residual Cr. The highest water soluble of Cr was observed in control ( $3.2 \text{ mg kg}^{-1}$ ) and the other treatment soils were recorded below detectable limit at harvesting stage. The exchangeable form of Cr was ranged from  $27.6$  to  $42.6 \text{ mg kg}^{-1}$ . The organically bound Cr, Organic plus oxide bound Cr and residual forms of Cr were ranged from  $34.5$  to  $109.9$ ,  $47.8$  to  $230.9$  and  $17.4$  to  $72.0 \text{ mg kg}^{-1}$  in the  $T_1$  to  $T_7$  respectively. Among the five steps the highest Cr was found in organic plus iron

oxide bound Cr step with organic manure amended soil treatments. The highest organically bound and iron bound Cr was recorded in poultry manure amended soil ( $T_2$ ) and the lowest was found in control.

Water soluble Cr was found in soil at harvesting stage and data presented in Table 2. The initial soil had  $0.03 \text{ mg kg}^{-1}$  of water soluble Cr,  $285.3 \text{ mg kg}^{-1}$  exchangeable form of Cr,  $102.9 \text{ mg kg}^{-1}$  of organically bound,  $17.9 \text{ mg kg}^{-1}$  of organic plus iron oxide bound and  $232.4 \text{ mg kg}^{-1}$  of residual Cr. The highest water soluble of Cr was observed in control ( $6.2 \text{ mg kg}^{-1}$ ) and the other treatment soils were recorded below detectable limit at harvesting stage. The exchangeable form of Cr was ranged from  $11.1$  to  $43.2 \text{ mg kg}^{-1}$ . The organically bound Cr, Organic plus oxide bound Cr and residual forms of Cr were ranged from  $14.8$  to  $104.4$ ,  $18.7$  to  $295.2$  and  $6.1$  to  $46.6 \text{ mg kg}^{-1}$  in the  $T_1$  to  $T_7$  respectively. Among the five steps the highest Cr was found in organic plus iron oxide bound Cr step with organic manure amended soil treatments. The highest organically bound and iron bound Cr was recorded in poultry manure amended with *Trichoderma viride* ( $T_3$ ) and the lowest was found in control.

### ***Effect of manures on speciation of chromium in maize experimental field soil (30cm)***

The Cr speciation was analysed at 30 cm depth of maize field experimental soil and data presented in Table 3. The water soluble Cr was observed and ranged from 5.1 to 8.2 mg kg<sup>-1</sup>. The exchangeable form, organically bound, organic plus iron bound Cr and residual Cr were ranged from 614.5 to 666.6, 74.5 to 144.4, 84.0 to 126.5 and 93.3 to 163.2 mg kg<sup>-1</sup> respectively. The highest Cr was found in vermicompost amended with *Pseudomonas fluorescens* which was in exchangeable form of Cr (666.6 mg kg<sup>-1</sup>). Among the five steps the exchangeable form of Cr was recorded the highest concentration followed by residual form, organically bound, organic bound plus iron oxide bound and water soluble form of Cr.

### ***Effect of manures on speciation of chromium in maize experimental field soil (60cm)***

The Cr speciation was analysed at 60 cm depth of maize field experimental soil and data presented in Table 4. The water soluble Cr was observed and ranged from 3.3 to 7.5 mg kg<sup>-1</sup>. The exchangeable form, organically bound, organic plus iron bound Cr and residual Cr were ranged from 559.4

to 626.0, 60.7 to 134.7, 84.1 to 126.8 and 168.6 to 193.8 mg kg<sup>-1</sup> respectively. The highest Cr was found in control which was in exchangeable form of Cr (626.0 mg kg<sup>-1</sup>). Among the five steps the exchangeable form of Cr was recorded the highest concentration followed by residual form, organically bound, organic bound plus iron oxide bound and water soluble form of Cr.

### ***Distribution of chromium species in soil***

In soil Cr exists in different species depending upon soil characteristics (SOC, redox potential, pH, CEC etc.). In this study the speciation of Cr was determined in soil after the harvest of crops by a sequential fractionation procedure. The result showed that, initially, in maize field soils, about 41 per cent of Cr was found as exchangeable form (as extractable by KNO<sub>3</sub>) followed by 33.8 per cent in residual forms. The organically bound Cr and organic plus Fe/Al oxide bound Cr constituted about 15 per cent and only a small concentration (<0.5%) was detected as soluble Cr (Figure 1 and 2). The total Cr as determined by the summation of Cr species ( $\sum Cr_{sp.}$ ) closely agreed with the value obtained by the single acid digestion ( $R^2 = 0.96$ , Figure 3) method, indicating a high recovery (> 95%) of Cr. Due to biotransformation, notable changes in the concentration of different depth

species were observed. In the control soil at 0-15 cm depth the concentrations were found reduced several folds in all the species which followed:

Maize soil = Na<sub>2</sub>EDTA-Cr > NaOH-Cr > KNO<sub>3</sub>-Cr > HNO<sub>3</sub>-Cr >>>>H<sub>2</sub>O-Cr

About 92 percent reductions in exchangeable Cr (KNO<sub>3</sub>-Cr) were observed in soils under maize crop. Similarly, a drastic reduction in organically bound Cr (NaOH-Cr) and residual Cr (HNO<sub>3</sub>) was also observed. The reduction in exchangeable Cr could be attributed to the crop removal and leaching in the soil profile. Whereas, due to the addition of poultry manure and vermicompost with or without microbial strains, the concentration of different species changed markedly. There was a significant reduction in KNO<sub>3</sub>-Cr and the concentration of H<sub>2</sub>O-Cr was below the detectable limit.

The concentration of organically bound-Cr (NaOH-Cr) and organic plus Fe/Al oxide bound Cr (Na<sub>2</sub>EDTA-Cr) was found significantly increased, indicating large amount of Cr could have adsorbed and also converted into organic form. The greater concentration of NaOH-Cr and Na<sub>2</sub>EDTA-Cr provide evidence for the occurrence of complexation reaction

resulting in the formation of large amount of organo-chromic complexes and chelates in the soil due to poultry manure and vermicompost. At subsurface soils (15-30 cm and 30-60 cm depth) the concentration followed:

KNO<sub>3</sub>-Cr > > HNO<sub>3</sub>-Cr > Na<sub>2</sub>EDTA-Cr > NaOH-Cr >>H<sub>2</sub>O-Cr

A concentration up to 6.8 mg kg<sup>-1</sup> was observed in relation to H<sub>2</sub>O-Cr (soluble Cr) in all the treatments, which indicates greater amount of soluble Cr (Cr VI) might have leached down in the soil profile and accumulated in the deeper layers. A high concentration in the H<sub>2</sub>O-Cr and KNO<sub>3</sub>-Cr at subsurface soils are of concern since these fractions represent the soluble and exchangeable and sorbed fraction that has the potential to leach down in the soil profile and contaminate the groundwater (Mahimairaja *et al.*, 2000).

### Conclusion

In the control soil, with the application only recommended NPK fertilizers, a reduction of about 76 per cent in Cr content of maize field was recorded. This explains why the Cr content and uptake by maize were greater when they were grown on the control soil. There observed a positive correlation between Cr

concentration in plants and Cr concentration in soil ( $R^2 = 0.837$ ). A reduction of only 28 per cent from the initial concentration of Cr in the surface soils under maize was observed due to the addition of organic amendments. Such reduction is attributed to the formation of either organo-chromic complexes (Immobilization) or chelates. Significantly higher amounts Cr were found in the subsurface soils (15-30 cm and 30-60 cm depth) of maize field due to greater amount of Cr leaching. The predicted (cumulative) net drainage of 483 mm computed for maize and the sandy loam nature of the soil appeared to have facilitated greater leaching and transport of Cr to the subsurface (15 to 30 and 30 to 60

cm) soil. The results showed greater risk for groundwater contamination due to Cr in these contaminated soil.

The total Cr as determined by the summation of Cr species ( $\sum Cr_{sp.}$ ) closely agreed with the value obtained by the single acid digestion ( $R^2 = 0.96$ ) method, indicating a high recovery ( $> 95\%$ ) of Cr. Due to biotransformation, notable changes in the concentration of different depth species were observed. A high concentration in the  $H_2O$ -Cr and  $KNO_3$ -Cr at subsurface soils is of concern since these fractions represent the soluble and exchangeable and sorbed fraction that has the potential to leach down in the soil profile and contaminate the groundwater.

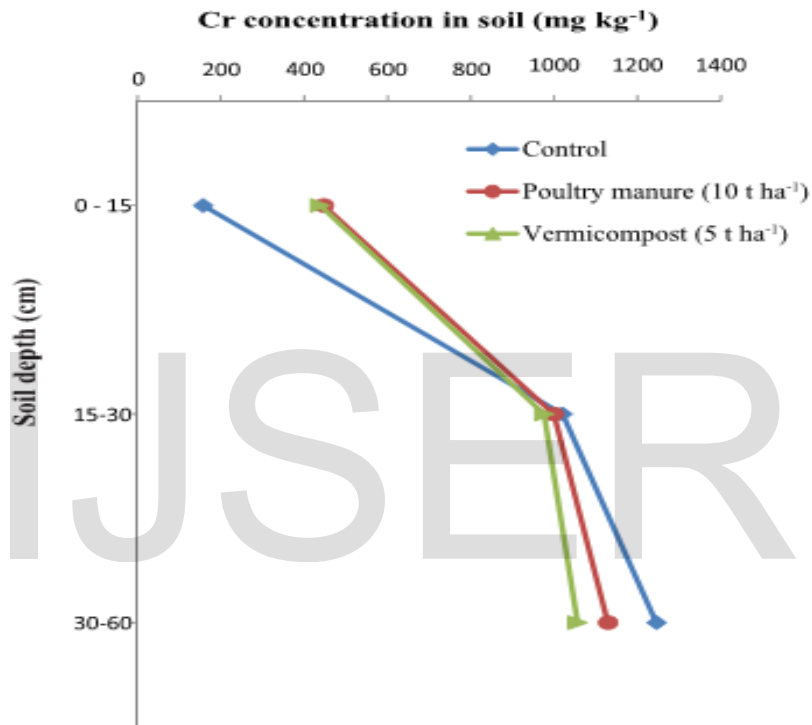
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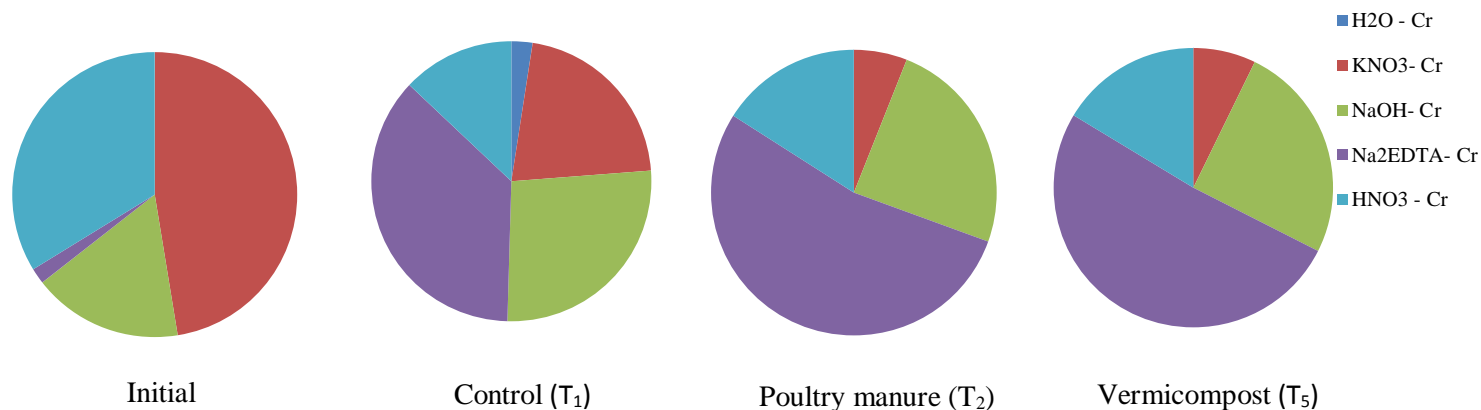


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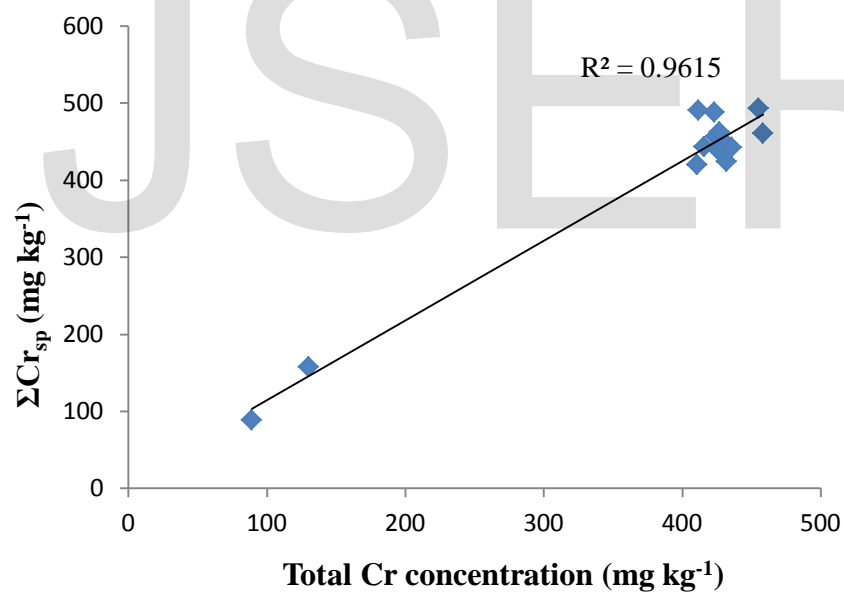
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**Fig. 1 Distribution of chromium in soil profile (Maize experimental field)**



**Fig. 2 Relative distribution of different species of chromium in soil under maize**



**Fig. 3 Relationship between total Cr as determined by summation of Cr species and total Cr determined by single acid digestion**

**Table. 1 Effect of organic manures on speciation of chromium in experimental field soil (15cm) of maize (mg kg<sup>-1</sup>)**

Treatments	Water Soluble – Cr (H <sub>2</sub> O - Cr)	Exchangeable - Cr (KNO <sub>3</sub> - Cr)	Organically bound - Cr (NaOH- Cr)	Organic + iron oxide bound – Cr (Na <sub>2</sub> EDTA- Cr)	Residual Cr (HNO <sub>3</sub> - Cr)
Initial (Before treatment implementation)	0.1	319.6	115.4	12.1	248.4
T <sub>1</sub> - Control	3.2	27.6	34.5	47.8	17.4
T <sub>2</sub> - Poultry manure (10 t ha <sup>-1</sup> )	0	30.2	105.7	230.9	68.8
T <sub>3</sub> - Poultry manure (10 t ha <sup>-1</sup> ) and <i>Pseudomonas fluorescens</i> (2.5 kg ha <sup>-1</sup> )	0	29.3	100.1	228.1	66.6
T <sub>4</sub> - Poultry manure (10 t ha <sup>-1</sup> ) and <i>Trichoderma viride</i> (2.5 kg ha <sup>-1</sup> )	0	30.1	104.8	212.5	68.4
T <sub>5</sub> - Vermicompost (5 t ha <sup>-1</sup> ) alone	0	30.6	107.8	218.5	69.5
T <sub>6</sub> - Vermicompost (5 t ha <sup>-1</sup> ) and <i>Pseudomonas fluorescens</i> (2.5 kg ha <sup>-1</sup> )	0	31.0	109.9	199.4	70.4
T <sub>7</sub> - Vermicompost (5 t ha <sup>-1</sup> ) and <i>Trichoderma viride</i> (2.5 kg ha <sup>-1</sup> )	0.9	42.6	104.2	213.2	72.0
<b>Mean</b>	0.5	67.6	97.8	170.3	85.2

**Table. 2 Effect of organic manures on speciation of chromium in experimental field soil (30 cm) of Maize (mg kg<sup>-1</sup>)**

Treatments	Water Soluble - Cr (H <sub>2</sub> O - Cr)	Exchangeable - Cr (KNO <sub>3</sub> - Cr)	Organically bound - Cr (NaOH- Cr)	Organic + iron oxide bound – Cr (Na <sub>2</sub> EDTA- Cr)	Residual Cr (HNO <sub>3</sub> - Cr)
T <sub>1</sub> - Control	5.5	617.4	136.1	121.9	163.2
T <sub>2</sub> - Poultry manure (10 t ha <sup>-1</sup> )	4.5	635.4	117.1	84.0	114.9
T <sub>3</sub> - Poultry manure (10 t ha <sup>-1</sup> ) and <i>Pseudomonas fluorescens</i> (2.5 kg ha <sup>-1</sup> )	6.5	614.5	144.4	119.7	156.1
T <sub>4</sub> - Poultry manure (10 t ha <sup>-1</sup> ) and <i>Trichoderma viride</i> (2.5 kg ha <sup>-1</sup> )	8.2	625.2	79.6	116.0	144.7
T <sub>5</sub> - Vermicompost (5 t ha <sup>-1</sup> ) alone	7.7	656.4	74.5	126.5	93.3
T <sub>6</sub> - Vermicompost (5 t ha <sup>-1</sup> ) and <i>Pseudomonas fluorescens</i> (2.5 kg ha <sup>-1</sup> )	7.4	666.6	79.7	116.3	143.1
T <sub>7</sub> - Vermicompost (5 t ha <sup>-1</sup> ) and <i>Trichoderma viride</i> (2.5 kg ha <sup>-1</sup> )	5.1	644.3	82.1	93.8	134.7
<b>Mean</b>	6.4	637.1	101.9	111.2	135.7

**Table. 3 Effect of organic manures on speciation of chromium in experimental field soil (60 cm) of Maize ( $\text{mg kg}^{-1}$ )**

Treatments	Water Soluble – Cr ( $\text{H}_2\text{O} - \text{Cr}$ )	Exchangeable - Cr ( $\text{KNO}_3 - \text{Cr}$ )	Organically bound - Cr ( $\text{NaOH} - \text{Cr}$ )	Organic + iron oxide bound – Cr ( $\text{Na}_2\text{EDTA} - \text{Cr}$ )	Residual Cr ( $\text{HNO}_3 - \text{Cr}$ )
T <sub>1</sub> - Control	3.3	626.0	130.7	111.9	192.6
T <sub>2</sub> - Poultry manure ( $10 \text{ t ha}^{-1}$ )	3.3	559.4	119.5	100.2	168.6
T <sub>3</sub> - Poultry manure ( $10 \text{ t ha}^{-1}$ ) and <i>Pseudomonas fluorescens</i> ( $2.5 \text{ kg ha}^{-1}$ )	4.6	615.1	134.7	94.5	175.7
T <sub>4</sub> - Poultry manure ( $10 \text{ t ha}^{-1}$ ) and <i>Trichoderma viride</i> ( $2.5 \text{ kg ha}^{-1}$ )	7.5	568.8	96.3	110.5	144.7
T <sub>5</sub> - Vermicompost ( $5 \text{ t ha}^{-1}$ ) alone	4.1	579.8	60.7	126.8	193.8
T <sub>6</sub> - Vermicompost ( $5 \text{ t ha}^{-1}$ ) and <i>Pseudomonas fluorescens</i> ( $2.5 \text{ kg ha}^{-1}$ )	7.2	577.5	67.3	116.6	183.0
T <sub>7</sub> - Vermicompost ( $5 \text{ t ha}^{-1}$ ) and <i>Trichoderma viride</i> ( $2.5 \text{ kg ha}^{-1}$ )	6.3	567.0	73.4	84.1	174.4
<b>Mean</b>	5.2	584.8	97.5	106.4	176.1