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Chelating compounds influence the chemical properties of post-harvest chromium contaminated soil after maize and mustard

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Abstract
Pot experiments were conducted in the net house of Department of Soil Science and Agricultural Chemistry, Institute of Agricultural Sciences, B.H.U., Varanasi in alluvial soil during 2015-16 using maize-mustard cropping sequence to study the effect of chelating compounds on chemical properties of post-harvest chromium contaminated soil after maize and mustard. Five levels of chromium viz. 0, 5, 10, 20, and 30 ppm with and without five types of chelating compounds viz. EDTA, DTPA, Oxalic Acid, Citric Acid, and Humic Acid were applied. All the treatments of chelating compounds were applied to maize in *kharif* season and mustard was taken in *rabi* season as residual crop after harvesting of maize crop. pH, EC (dSm^{-1}), organic carbon (%), N, P, K and Cr content in chromium contaminated post-harvest soil were determined after harvesting of maize and mustard crops. Results indicated that pH, EC, OC, N, P and K content decreased with increasing level of chromium. It was also found that pH, EC, OC, N, P and K content increased with application of chelating compounds, however; DTPA, humic acid and oxalic acid buildup the post-harvest N, P and K content but not significantly. Soil from maize and mustard harvested pot trending toward increasing DTPA extractable chromium with increasing rate of chromium. It was noticed that DTPA extractable chromium decreased in post-harvest soil after maize and mustard harvesting with application of chelating compounds.

Keywords: chelating compounds, chemical properties, chromium, maize, mustard

Introduction
The increasing concentration of heavy metals in agricultural soil is an important environmental issue which can limit future land-use options as the heavy metals are toxic and non-biodegradable (Sharma and Pandey, 2014; Habiba *et al*., 2015) [22]. Among various heavy metals, chromium (Cr) is the seventh most abundant element of the earth's crust (Afshan *et al*., 2015; Ertani *et al*., 2017) [2]. Chromium is one of the most toxic, non-essential carcinogenic heavy metals (Atta *et al*., 2013; Mantry and Patra, 2017) [35]. Chromium is a transition element and can be found in six different oxidation states (Ahemad, 2015; da Costa *et al*., 2016) [2]. Extensive use of Cr in industrial processes such as, metallurgy, refractory materials, tanning, mining, and electroplating are the main sources of soil Cr contamination where it can exert deleterious ecological effects (Tripathi *et al*., 2016; Farid *et al*., 2017) [50]. Cr is a nonessential element for plants and induces toxicity in many plant species (Zeng *et al*., 2011; Gill *et al*., 2015) [56]. Higher concentration of Cr in plants caused reduction in root growth and biomass, chlorosis, photosynthetic impairment, and finally plant death (Das *et al*., 2014) [11]. Many researchers extensively reviewed the Cr toxic effects in different plant species at morphological, physiological, biochemical, and molecular levels (Singh *et al*., 2013) [45]. Thus, remediation of Cr-contaminated soil has become an important environmental issue worldwide (Ali *et al*., 2012) [3]. Cr (III) occurring in a contaminated natural environment is insoluble, and characterized by a low level of mobility; however, in the presence of organic ligands, the complexation of Cr (III) takes place, which increases its solubility, thus influencing its higher mobility and availability to living organisms (Yilmaz and Soylak, 2016) [55]. Metal (loid) s can accumulate in humans through the food chain and can lead to ailments due to their carcinogenic, mutagenic, and toxicological effects (Shukla *et al*., 2018) [43]. The elevated concentration of these metal (loid) s can result in growth inhibition and toxicity symptoms, such as DNA damage, inhibition of cell division, protein denaturation, damage to membranous structure of the cell, and displacement of the essential micro- and macro-elements (Srivastava

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et al., 2011 and Awasthi et al., 2017) [6, 47]. Chromium is a heavy metal with risk to human health. Its presence in agricultural soils can be attributed to the use of industrial effluents for irrigation. Increase of world population has resulted in the pollution of the environment. Chromium is highly toxic non-essential element for microorganism and plants. The contamination of the soil environment with chromium compounds is more and more frequently occurring problem throughout the world (Radziemska and Wyszkowski, 2017) [41]. Chromium pollution of soil and water is a serious environmental concern due to potential carcinogenicity of hexavalent chromium [Cr (VI)] when ingested (Choudhary et al., 2017) [9]. Chromium, due to its structural similarity with some essential elements, can affect mineral nutrition of plants in a complex way. Interactions of Cr with uptake and accumulation of other inorganic nutrients have received maximum attention by researchers (Kumar et al., 2016) [31].

Organic and inorganic amendments are used for immobilization of metals in the soils with varying benefits but organic amendments could be better option due to improvement of physical, chemical, biological properties and fertility status of the soil. The mobility and toxicity of Cr6+ can be reduced by converting it to the reduced state of Cr3+ by means of organic matter and inorganic reducing agents in the soil (Kumar and Sharma, 2018) [30]. The Organic sources may be organic manures, green manure, rural wastes, crop residues, biofertilizers and vermicompost (Kumar et al., 2018) [30]. The capability of phytoextraction process can be optimized by the addition of some organic and inorganic chelators which enhance the mobility and availability of Cr by making chelator+Cr soluble complexes (Wiszniewska et al., 2016; Kumar et al., 2014) [28, 52].

Low-molecular weight organic acids (LMWOAs) such as citric, malic, succinic, and fumaric acid participate as crucial components in several cellular biochemical pathways such as energy production and amino acid synthesis. At the whole plant level, they play a role in metal tolerance, cope with nutrient deficiencies, and regulate rhizospheric plant–microbe interactions (Kaur et al., 2017) [27]. Among LMWOAs, citric acid (CA), an important intermediate of the tricarboxylic cycle, plays a crucial role in respiratory and other biochemical pathways and its exogenous application reduces heavy metal toxicity and improves phytoextraction (Najeeb et al., 2011) [36]. Also CA-enhanced phyto xtraction of Cd is reported in B. juncea (Quartacci et al., 2005) [39], Solanum nigrum (Gao et al., 2010) [17], and Sedum alfredii (Lu et al., 2013) [34]. In addition to heavy metal tolerance, its role is also implicated in other abiotic stresses (Sun and Hong 2011; Hu et al., 2016). Although most of heavy metals have low bioavailability in soils, there is a need to meet stringent cleanup targets. To overcome the limitations of natural phytoextraction has led to several studies on different chelates that increase the bioavailability of heavy metals (Evangelou et al., 2007) [14]. For this purpose, different synthetic and natural chelators are used to enhance the bioavailability of metals in contaminated medium. Among synthetic chelating agents, ethylene diamine tetra acetic acid (EDTA) and diethylene triamine pentaacetic acid (DTPA) are commonly used as they are efficient in complexing metals and increasing their concentration in the upper plant parts (Kanwal et al., 2014) [26]. However, they are non-biodegradable and can cause ground water contamination due to uncontrolled leaching in the soil (Anwer et al., 2012;

Bareen, 2012) [4, 7]. Organic acids could be an interesting alternative to the persistent synthetic chelating agents described above. Organic chelating agents are low molecular-weight organic acids such as citric acid (CA) and can form complexes with heavy metals and have higher degree of biodegradability and less leaching hazard as compared to synthetic chelating agents (Bareen, 2012) [7]. Recently, it has been reported that citric acid (CA) significantly enhances metal solubility and uptake by plants (Yeh and Pan 2012; Freitas et al., 2013) [16, 54]. To date, many studies have reported the effects of organic chelating agents on the extraction of heavy metals from the solution cultures (Gunawardana et al., 2011; Das et al., 2014; Ehsan et al., 2014) [11, 21, 12]; there are few reports on the role of these chelating agents during phyto extraction of heavy metal from contaminated soils (Chigbo and Batty 2013) [8]. Thus, we need longer term (as compared to hydroponic cultures) and more realistic soil-based studies to better understand the practical implications of chelating agents mediated phyto extraction and tolerance of metals so that successful field experiments can be conducted (Afshan et al., 2015) [1].

Chelating agents such as EDTA, DTPA, citric acid, oxalic acid and humic acid are added to soil to increase the bioavailability of heavy metals in soil for uptake by plants (Lai and Chen, 2004; Kant et al., 2018) [32].

Material and Methods
To conduct the pot experiment, the bulk of soil was collected from the Agricultural Research Farm, Institute of Agricultural Sciences, Banaras Hindu University; Varanasi U.P. Soil was air dried gently, ground to pass through 2 mm sieve and homogenized. Chemical properties of soil are depicted in table 1.

Table 1: Chemical properties of the initial soil

Parameter	Values	Parameter	Values
pH_w(1:2.5)	7.94	N (mg kg^{-1})	72.00
EC_w (1:2.5) (dS/m)	0.11	P (mg kg^{-1})	12.00
Organic Carbon (%)	0.46	K (mg kg^{-1})	100.00
CEC (C mole (p^+) kg^{-1})	20.10	Cr (mg kg^{-1})	0.48

Treatment details
The pot experiments were conducted in FCRD with five levels of chromium and with and without five types chelating compounds –

A.	Chromium Levels (mg/kg soil)	Symbol
1)	Control	Cr_0
2)	5 ppm	Cr_1
3)	10 ppm	Cr_2
4)	20 ppm	Cr_3
5)	30 ppm	Cr_4
B.	Chelating compound	Symbol
1)	Control	C_0
2)	EDTA (10 m Mole kg^{-1})	C_1
3)	DTPA (10 m Mole kg^{-1})	C_2
4)	Citric Acid (20 m Mole kg^{-1})	C_3
5)	Oxalic Acid (20 m Mole kg^{-1})	C_4
6)	Humic acid (1g kg^{-1})	C_5

Treatment combinations for pot experiment

Treatments	Control C_0	EDTA (10 mMole kg^{-1})	DTPA (10 mMole kg^{-1})	Citric Acid (20 mMole kg^{-1})	Oxalic Acid (20 mMole kg^{-1})	Humic acid (1g kg^{-1})
Cr_0 0.0 ppm	$Cr_0 C_0$ 1	$Cr_0 C_1$ 2	$Cr_0 C_2$ 3	$Cr_0 C_3$ 4	$Cr_0 C_4$ 5	$Cr_0 C_5$ 6
Cr_1 5.0 ppm	$Cr_1 C_0$ 7	$Cr_1 C_1$ 8	$Cr_1 C_2$ 9	$Cr_1 C_3$ 10	$Cr_1 C_4$ 11	$Cr_1 C_5$ 12
Cr_2 10.0 ppm	$Cr_2 C_0$ 13	$Cr_2 C_1$ 14	$Cr_2 C_2$ 15	$Cr_2 C_3$ 16	$Cr_2 C_4$ 17	$Cr_2 C_5$ 18
Cr_3 20.0 ppm	$Cr_3 C_0$ 19	$Cr_3 C_1$ 20	$Cr_3 C_2$ 21	$Cr_3 C_3$ 22	$Cr_3 C_4$ 23	$Cr_3 C_5$ 24
Cr_4 30.0 ppm	$Cr_4 C_0$ 25	$Cr_4 C_1$ 26	$Cr_4 C_2$ 27	$Cr_4 C_3$ 28	$Cr_4 C_4$ 29	$Cr_4 C_5$ 30

Collection of soil sample
After harvesting of maize and mustard crop, represented soil sample from each pot was collected with spud by cutting one cm slice from bulk of pot soil.

Processing of soil sample
Collected soil samples of the pot experiment were brought into laboratory in a separate one kg polythene bag and dried at room temperature. After drying, broken clods were ground on wooden plank with wooden roller and passed through a 2 mm sieve. The soil samples were then stored in polythene bags. The homogenized soil samples were analyzed for selected chemical properties.

Soil chemical analysis
Soil pH
A soil-water suspension was prepared in the ratio of 1:2.5 (10 g soil with 25 mL of distilled water) and pH was measured with the help of pH meter (Sparks, 1996) [46].

Electrical conductivity
The soil water suspension prepared for determination of pH was used to estimate the electrical conductivity of the soil. Soil suspension was allowed to settle till supernatant become clear. Electrical conductivity was measured with the help of EC meter and expressed as dSm^{-1} (Sparks, 1996) [46].

Organic carbon
Organic Carbon was determined by the method given by Walkley and Black (1934) [51]. One gram of soil was taken in a 500 ml of conical flask; ten mL of 1 N $K_2Cr_2O_7$ solution was added and mixed. Then 20 mL of Conc. H_2SO_4 was added, the flask was swirled 2-3 times and allowed to stand for 30 minutes on an asbestos sheet for the reaction. The suspension was diluted with 200 mL with distilled water. Ten mL of 85% H_3PO_4 and 1 mL of diphenyl amine indicator were added and titrated against 0.5 N Ferrous Ammonium Sulphate solution till colour changed from violet to bright green. A blank titration was also carried out.

Calculation

$$\% \text{ Organic Carbon in soil} = \frac{(B-T) \times 0.003 \times 100 \times 1.3}{\text{wt. of soil}} \times \frac{10}{B}$$

Where, B = Volume of 0.5 N FAS solution used for blank titration
T = Volume of 0.5 N FAS solution used for sample titration

Available Nitrogen
Available nitrogen was determined by the method given by Subbiah and Asija (1956) [48], where 5 gram air dried soil was taken into a Kjeldahl tube; 25 ml 0.32 % $KMnO_4$ and 2.5% NaOH each were added. This was connected to automated KEL PLUS distillation unit and liberated ammonia was swiped and collected into 20 ml of 2% Boric acid. The blue colour of boric acid was titrated with 0.02N H_2SO_4 to its original brick red colour. A blank titration was also carried out.

Calculation

$$\text{Mineralizable N (kg/ha)} = \frac{(S-V) \times 0.02 \times 14 \times 1000 \times 2.24}{5}$$

Where, S = Sample titration reading   V = Blank titration reading

Available phosphorous
Available phosphorous was determined by the method given by Olsen et al. (1954) [38], in this method phosphorous was extracted with 0.5N $NaHCO_3$ (pH 8.5). Initially reagent A was prepared by ammonium moly date, antimony potassium tartarate and H_2SO_4. Then reagent B was prepared by using reagent A and ascorbic acid. 2.5 gram soil was taken into a 150 ml conical flask, a pinch of Draco G-60(Activated Charcoal) and 50 ml of Olsen's reagent (0.5N $NaHCO_3$) were added and contents of flask was shaken for 30 minute on a mechanical shaker. It was filtered through what a man No. 1 filter paper. 5 ml of aliquot was transferred into a 25 ml volumetric flask and acidified by 5 N H_2SO_4 to pH 5.0. Than 10 ml distilled water and 4 ml of reagent B were added and volume was made up to 25 ml with distilled water. The intensity of blue colour was measured spectrophotometrically at 660 nm.
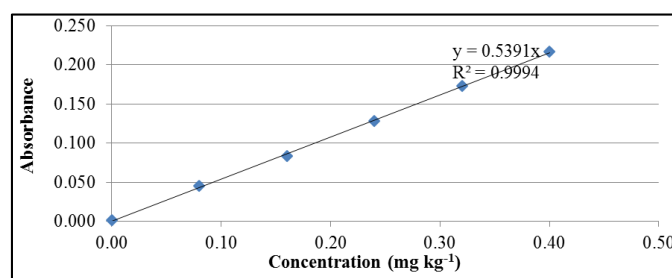
Calculation
2.5 g soil was extracted with 50 mL of 0.5 N $NaHCO_3$ solution Hence,
First dilution = (50/2.5) =20 times
5 mL of aliquot was taken and final volume was made up to 25 mL
Hence, Second dilution = (25/5) = 5 times
Therefore, total dilution factor (DF) = 20 x 5 = 100 times

From the graph,

y = 0.5391 x

Where, x = concentration

y = absorbance

m = 0.5391 (slope)

Available Phosphorous (kg/ha) = R x Dilution Factor x 2.24

Where, R = µg P in the aliquot (obtained from standard curve) = $\frac{y(\text{absorbance})}{m(\text{slope})}$

Available potassium
Available potassium content of soil was determined by Flame

Photometer (1 N ammonium acetate extract) method given by Hanway and Heidal (1952) [23]. Five gram of soil was taken in a 100 ml conical flask and 25 ml of 1 N ammonium acetate solution was added and shaken for 5 minutes. The suspension was then filtered through Whatman No. 1 filter paper and potassium concentration in the filtrate was measured using flame photometer. First standard reading was taken followed by sample reading.

Calculation

$$\% \text{ Organic Carbon in soil} = \frac{R \times \text{Volume of extract} \times 2.24}{\text{wt. of soil (g)}}$$

Where,   R = μg K in the aliquot (obtained from standard curve)

DTPA extractable chromium

Available chromium in soil samples were determined by the method of Lindsay and Norvell (1978). In this method, 10 g of soil was extracted with 20 mL DTPA (0.005M DTPA+0.01M+$CaCl_2.2H_2O$+0.1M TEA) extracting solution by shaking for 2 hrs. On a mechanical shaker. The suspension

was filtered and chromium was determined by atomic absorption spectrophotometer (Agilent Technologies 200 Series AA) using respective cathode lamps.

Statistical analysis and interpretation of data

For determining the significance between the treatment means and to draw valid conclusion, statistical analysis was made.The raw data observed during the whole experiment, were subjected to statistical analysis by adopting appropriate method of "Analysis of Variance". The significance of the treatment effect was judged with the help of 'F' test (Variance ratio). The difference of the treatments mean was tested using critical difference (CD) at 1% level of probability (Gomez and Gomez, 1984) [20] by following the Complete Randomized Design (CRD) to draw the valid differences among the treatments using SPSS software.

Results and Discussion

Effect on PH, EC and organic carbon

The data obtained in relation to pH, EC and organic carbon of post-harvest soil from both plant species influenced by different levels of chromium with organic and synthetic chelates presented in the Table 2.

Table 2: Effect of chelating compounds on pH, EC (dSm^{-1}) and organic carbon (%) content in chromium contaminated post-harvest soil

Treatment		After Maize Harvesting			After Mustard Harvesting		
		pH	EC	OC	pH	EC	OC
Control		7.53	0.195	0.431	7.61	0.190	0.445
Cr_0 + EDTA 10 mmol kg^{-1}		7.37	0.238	0.501	7.44	0.231	0.516
Cr_0 + DTPA 10 mmol kg^{-1}		7.47	0.245	0.525	7.52	0.238	0.541
Cr_0 + CA 20 mmol kg^{-1}		7.00	0.232	0.473	7.10	0.227	0.488
Cr_0 + OA 20 mmol kg^{-1}		7.16	0.228	0.450	7.21	0.226	0.465
Cr_0 + HA 1g kg^{-1}		6.90	0.253	0.557	6.99	0.256	0.574
5ppm Cr		7.40	0.190	0.415	7.46	0.185	0.428
5ppmCr + EDTA 10 mmol kg^{-1}		7.28	0.232	0.482	7.35	0.225	0.497
5ppmCr + DTPA 10 mmol kg^{-1}		7.37	0.239	0.505	7.39	0.232	0.521
5ppmCr + CA 20 mmol kg^{-1}		6.87	0.227	0.455	6.98	0.220	0.469
5ppmCr + OA 20 mmol kg^{-1}		7.07	0.222	0.433	7.15	0.220	0.447
5ppmCr + HA 1g kg^{-1}		6.84	0.246	0.535	6.97	0.250	0.552
10ppmCr		7.31	0.186	0.399	7.34	0.180	0.411
10ppmCr + EDTA 10 mmol kg^{-1}		7.00	0.226	0.463	7.05	0.220	0.477
10ppmCr + DTPA 10 mmol kg^{-1}		7.15	0.233	0.486	7.17	0.226	0.501
10ppmCr + CA 20 mmol kg^{-1}		6.85	0.221	0.437	6.96	0.215	0.451
10ppmCr + OA 20 mmol kg^{-1}		6.91	0.217	0.416	7.01	0.215	0.430
10ppmCr + HA 1g kg^{-1}		6.82	0.240	0.515	6.92	0.243	0.531
20ppmCr		7.20	0.182	0.384	7.24	0.177	0.396
20ppmCr + EDTA 10 mmol kg^{-1}		6.92	0.222	0.446	6.98	0.216	0.460
20ppmCr + DTPA 10 mmol kg^{-1}		7.06	0.229	0.468	7.11	0.222	0.482
20ppmCr + CA 20 mmol kg^{-1}		6.73	0.217	0.421	6.82	0.210	0.434
20ppmCr + OA 20 mmol kg^{-1}		6.77	0.213	0.401	6.84	0.210	0.414
20ppmCr + HA 1g kg^{-1}		6.64	0.236	0.496	6.72	0.239	0.511
30ppmCr		7.16	0.177	0.367	7.19	0.172	0.378
30ppmCr + EDTA 10 mmol kg^{-1}		6.75	0.216	0.426	6.85	0.210	0.439
30ppmCr + DTPA 10 mmol kg^{-1}		6.89	0.222	0.447	6.99	0.216	0.461
30ppmCr + CA 20 mmol kg^{-1}		6.60	0.211	0.403	6.71	0.205	0.415
30ppmCr + OA 20 mmol kg^{-1}		6.69	0.207	0.383	6.77	0.205	0.395
30ppmCr + HA 1g kg^{-1}		6.49	0.229	0.474	6.60	0.232	0.488
SEm±	Chromium	0.042	NS	0.004	0.040	NS	0.004
	Amendments	0.046	NS	0.004	0.043	NS	0.005
	Interaction	NS	NS	NS	NS	NS	NS
CD (P=0.01)	Chromium	0.12	NS	0.012	0.11	NS	0.012
	Amendments	0.13	NS	0.013	0.12	NS	0.013
	Interaction	NS	NS	NS	NS	NS	NS

Cr= Chromium, EDTA= ethylene diamine tetra acetic acid, DTPA= diethylene triamine penta acetic acid, OA= Oxalic Acid, CA= Citric Acid, HA= Humic Acid, CD = Critical Difference, SEm± = Standard error of mean

pH of soil showing a decreasing trend with increasing concentration of chromium in soil from 0 ppm to 30 ppm ranging from slightly alkaline than neutral to slightly acidic. Generally pH of soil from control pot (no chelating agent) was highest (7.53 and 7.61) followed by DTPA (7.47 and 7.52), EDTA (7.37 and 7.44) and humic acid with lower pH (6.90 and 6.99) at 0 ppm Cr in maize and mustard respectively. Furthermore, a high pH (7.40 and 7.46) was obtained with Cr_1C_0 followed by Cr_1C_3 (7.37 and 7.39), Cr_1C_2 (7.28 and 7.35) and decreasing up to Cr_1C_5 (6.84 and 6.97) at 5 ppm Cr in maize and mustard respectively. However, Cr_4C_5 (30 ppm Cr+ HA @ 1 g kg^{-1}) gives lower pH (6.49 and 6.60) in maize and mustard respectively. Moreover, the similar decreasing trend obtained with increasing level of contamination from 10 ppm, 20 ppm and 30 ppm with all chelating agent. Comparison between all treatment combinations post-harvest soil from mustard shows high pH than maize.

EC of soil showing a decreasing trend with increasing concentration of chromium in soil from 0 ppm to 30 ppm but at particular level of contamination it increases with organic chelates. Generally EC of soil from Cr_0C_5 (0 ppm Cr+ HA @ 1 g kg^{-1}) was highest (0.253 dSm^{-1} and 0.256 dSm^{-1}) followed by DTPA (0.245 dSm^{-1} and 0.0.238 dSm^{-1}), EDTA (0.238 dSm^{-1} and 0.231 dSm^{-1}) and control (Cr_0C_0) with lower EC (0.195 dSm^{-1} and 0.190 dSm^{-1}) at 0 ppm Cr for maize and mustard respectively. Furthermore, a high EC (0.246 dSm^{-1} and 0.250 dSm^{-1}) was obtained with Cr_1C_5 followed by Cr_1C_3 (0.239 dSm^{-1} and 0.232 dSm^{-1}), Cr_1C_2 (0.232 dSm^{-1} and 0.225 dSm^{-1}) and decreasing up to Cr_1C_0 (0.190 dSm^{-1} and 0.185 dSm^{-1}) at 5 ppm Cr for maize and mustard respectively. Moreover, the similar decreasing trend obtained with increasing level of contamination from 10 ppm, 20 ppm and 30 ppm with all chelating agent. When compare in all treatment combinations it was found that post-harvest soil from maize having higher electrical conductivity than mustard. OC (%) of soil showing a similar decreasing trend like pH with increasing concentration of chromium in soil from 0 ppm to 30 ppm but at particular level of contamination it increases with organic chelating agent. Generally OC of soil from Cr_0C_5 (0 ppm Cr+ HA @ 1 g kg^{-1}) was highest (0.557 % and 0.574 %) followed by DTPA (0.525 % and 0.541 %), EDTA (0.501 % and 0.516 %) and control (Cr_0C_0) with lower OC (0.431 % and 0.445 %) at 0 ppm Cr for maize and mustard respectively. Furthermore, a high percentage OC (0.535 % and 0.552 %) was obtained with Cr_1C_5 followed by Cr_1C_3 (0.505 % and 0.521 %), Cr_1C_2 (0.482 % and 0.497 %) and decreasing up to Cr_1C_0 (0.415 % and 0.428 %) at 5 ppm Cr for maize and mustard respectively. Moreover, the similar decreasing trend obtained with increasing level of contamination from 10 ppm, 20 ppm and 30 ppm with all chelating agent. When compare in all treatment combinations it was found that post-harvest soil from mustard having higher organic carbon percentage than maize.

Radziemska et al. (2018) [40] showed that the pH of soil solutions (contaminated with Cr) increased following the addition of amendment. However, with the addition of organic matter reduction in soil pH and degradation organic matter tends to increase organic carbon content thus the EC of soil (Wyszkowska, 2002) [53].

Effect on nitrogen, phosphorus and potassium content of post-harvest soil
Data pertaining to the effect of chelating agent on N, P and K content (mg/kg) in chromium contaminated post-harvest soil is presented in table 3.

Table 3: Effect of chelating compounds on N, P and K content (mg kg^{-1}) in chromium contaminated post-harvest soil

Treatment	After Maize Harvesting			After Mustard Harvesting		
	N(mg kg^{-1})	P(mg kg^{-1})	P(mg kg^{-1})	N(mg kg^{-1})	P(mg kg^{-1})	P(mg kg^{-1})
Control	101.14	12.61	104.43	103.67	13.11	110.57
Cr_0 + EDTA 10 mmol kg^{-1}	91.30	9.63	97.82	93.58	10.02	103.57
Cr_0 + DTPA 10 mmol kg^{-1}	89.04	9.31	95.48	91.26	9.68	101.09
Cr_0 + CA 20 mmol kg^{-1}	95.08	10.70	100.23	97.46	11.14	106.12
Cr_0 + OA 20 mmol kg^{-1}	98.64	11.37	102.02	101.11	11.83	108.02
Cr_0 + HA 1g kg^{-1}	85.83	8.50	92.90	87.98	8.84	98.36
5ppm Cr	94.08	11.84	98.05	96.43	12.31	103.82
5ppmCr + EDTA 10 mmol kg^{-1}	84.93	9.04	91.85	87.05	9.41	97.25
5ppmCr + DTPA 10 mmol kg^{-1}	82.83	8.74	89.65	84.90	9.09	94.92
5ppmCr + CA 20 mmol kg^{-1}	88.45	10.05	94.11	90.66	10.46	99.65
5ppmCr + OA 20 mmol kg^{-1}	91.76	10.68	95.79	94.05	11.11	101.43
5ppmCr + HA 1g kg^{-1}	79.84	7.98	87.23	81.84	8.30	92.36
10ppmCr	87.52	11.11	90.79	89.70	11.56	96.13
10ppmCr + EDTA 10 mmol kg^{-1}	79.00	8.49	85.05	80.98	8.84	90.05
10ppmCr + DTPA 10 mmol kg^{-1}	77.05	8.21	83.01	78.97	8.54	87.89
10ppmCr + CA 20 mmol kg^{-1}	82.28	9.44	87.14	84.33	9.82	92.27
10ppmCr + OA 20 mmol kg^{-1}	85.36	10.02	88.70	87.49	10.43	93.91
10ppmCr + HA 1g kg^{-1}	74.27	7.49	80.77	76.13	7.79	85.52
20ppmCr	80.07	10.16	83.10	82.07	10.57	87.98
20ppmCr + EDTA 10 mmol kg^{-1}	72.28	7.76	77.84	74.09	8.08	82.42
20ppmCr + DTPA 10 mmol kg^{-1}	70.49	7.50	75.98	72.25	7.80	80.44
20ppmCr + CA 20 mmol kg^{-1}	75.27	8.63	79.76	77.16	8.98	84.45
20ppmCr + OA 20 mmol kg^{-1}	78.09	9.16	81.18	80.05	9.53	85.95
20ppmCr + HA 1g kg^{-1}	67.95	6.85	73.92	69.65	7.13	78.27
30ppmCr	73.79	9.36	76.60	82.07	9.73	81.11
30ppmCr + EDTA 10 mmol kg^{-1}	66.61	7.15	71.76	74.09	7.44	75.98
30ppmCr + DTPA 10 mmol kg^{-1}	64.96	6.91	70.04	72.25	7.19	74.16
30ppmCr + CA 20 mmol kg^{-1}	69.37	7.95	73.52	77.16	8.27	77.85
30ppmCr + OA 20 mmol kg^{-1}	71.97	8.44	74.84	80.05	8.78	79.24
30ppmCr + HA 1g kg^{-1}	62.62	6.31	68.15	69.65	6.56	72.15

SEm±	Chromium	0.58	0.12	0.27	0.49	0.11	0.28
	Amendments	0.63	0.13	0.29	0.54	0.12	0.31
	Interaction	NS	NS	NS	NS	NS	NS
CD (P=0.01)	Chromium	1.63	0.34	0.75	1.39	0.30	0.79
	Amendments	1.78	0.37	0.82	1.52	0.33	0.87
	Interaction	NS	NS	NS	NS	NS	NS

Cr= Chromium, EDTA= ethylene diamine tetra acetic acid, DTPA= diethylene triamine penta acetic acid, OA= Oxalic Acid, CA= Citric Acid, HA= Humic Acid, CD = Critical Difference, SEm± = Standard error of mean

Table 4: Effect of chelating compounds on DTPA Extractable Chromium (mg kg^{-1}) (AAS) in chromium contaminated post-harvest soil

Treatment		After Maize	After Mustard
Control		**0.24**	**ND**
Cr_0 + EDTA 10 mmol kg^{-1}		0.21	ND
Cr_0 + DTPA 10 mmol kg^{-1}		0.21	ND
Cr_0 + CA 20 mmol kg^{-1}		0.22	ND
Cr_0 + OA 20 mmol kg^{-1}		0.23	ND
Cr_0 + HA 1g kg^{-1}		0.20	ND
5ppm Cr		0.49	0.130
5ppmCr + EDTA 10 mmol kg^{-1}		0.39	0.105
5ppmCr + DTPA 10 mmol kg^{-1}		0.36	0.097
5ppmCr + CA 20 mmol kg^{-1}		0.42	0.114
5ppmCr + OA 20 mmol kg^{-1}		0.45	0.122
5ppmCr + HA 1g kg^{-1}		0.31	0.084
10ppmCr		0.82	0.219
10ppmCr + EDTA 10 mmol kg^{-1}		0.66	0.177
10ppmCr + DTPA 10 mmol kg^{-1}		0.61	0.163
10ppmCr + CA 20 mmol kg^{-1}		0.71	0.191
10ppmCr + OA 20 mmol kg^{-1}		0.76	0.205
10ppmCr + HA 1g kg^{-1}		0.53	0.141
20ppmCr		1.79	0.480
20ppmCr + EDTA 10 mmol kg^{-1}		1.44	0.387
20ppmCr + DTPA 10 mmol kg^{-1}		1.33	0.356
20ppmCr + CA 20 mmol kg^{-1}		1.56	0.418
20ppmCr + OA 20 mmol kg^{-1}		1.67	0.449
20ppmCr + HA 1g kg^{-1}		1.15	0.310
30ppmCr		2.76	0.741
30ppmCr + EDTA 10 mmol kg^{-1}		2.23	0.597
30ppmCr + DTPA 10 mmol kg^{-1}		2.05	0.549
30ppmCr + CA 20 mmol kg^{-1}		2.40	0.645
30ppmCr + OA 20 mmol kg^{-1}		2.58	0.693
30ppmCr + HA 1g kg^{-1}		1.78	0.478
SEm±	Chromium	0.01	0.002
	Amendments	0.01	0.002
	Interaction	0.02	0.005
CD (P=0.01)	Chromium	0.03	0.006
	Amendments	0.03	0.007
	Interaction	0.07	0.015

Cr= Chromium, EDTA= ethylene diamine tetra acetic acid, DTPA= diethylene triamine penta acetic acid, OA= Oxalic Acid, CA= Citric Acid, HA= Humic Acid, CD = Critical Difference, SEm± = Standard error of mean

Nitrogen content of post-harvest soil
The data on nitrogen content of post-harvest soil showed that highest nitrogen (101.14 mg kg^{-1}and 103.67 mg kg^{-1}) was recorded with $Cr_0 C_0$ (control: no chelating agent) in both maize and mustard respectively was significantly higher over all the treatment combination, followed by treatment with oxalic acid @ 20 mMole kg^{-1} (98.64 and 101.11 mg kg^{-1}) and citric acid @20 mMole kg^{-1}(95.08 and 97.46 mg kg^{-1}). However, it was found significantly at par in treatment with EDTA (10 mMole kg^{-1}) and DTPA (10 mMole kg^{-1}) at all doses of chromium from 0 ppm to 30 ppm. Also, it was found lowest under $Cr_4 C_5$ with humic acid (62.62 and 69.65 mg kg^{-1}) in both maize and mustard harvested soil respectively. Thereby, decrease with increasing level of chromium in soil from 0 to 30 ppm in other treatment combinations with chelating agent.

Phosphorus content of post-harvest soil
The data on phosphorus content of post-harvest soil showed that highest phosphorus (12.61mg kg^{-1}and 13.11 mg kg^{-1}) was recorded with $Cr_0 C_0$ (control: no chelating agent) in both maize and mustard respectively was significantly higher over all the treatment combination. It was followed by treatment with oxalic acid @ 20 m Mole kg^{-1} (11.37 and 11.83 mg kg^{-1}) and citric acid @20 m Mole kg^{-1} (10.70 and 11.14 mg kg^{-1}). However, it was found significantly at par in treatment with EDTA (10 mMole kg^{-1}) and DTPA (10 mMole kg^{-1}) at all doses of chromium from 0 ppm to 30 ppm. Moreover, it found minimum and significantly lower under $Cr_4 C_5$ with humic acid (6.31 and 6.56 mg kg^{-1}) in both maize and mustard harvested soil respectively. Thereby, decrease with increasing level of chromium in soil from 0 to 30 ppm in other treatment combinations with chelating agent.

Potassium content of post-harvest soil

The data on potassium content of post-harvest soil showed that highest potassium (104.43mg kg^{-1} and 110.57 mg kg^{-1}) was recorded with $Cr_0 C_0$ (control: no chelating agent) in both maize and mustard respectively was significantly higher over all the treatment combination. It was followed by treatment with oxalic acid @ 20 m Mole kg^{-1} (102.02 and 108.02 mg kg^{-1}) and citric acid @ 20 m Mole kg^{-1}(100.23 and 106.12 mg kg^{-1}). However, it was found significantly at par in treatments with EDTA (10 m Mole kg^{-1}) and DTPA (10 mMole kg^{-1}) at all doses of chromium from 0 ppm to 30 ppm. Thereby, decrease with increasing level of chromium in soil from 0 to 30 ppm in other treatment combinations with chelating agent. Furthermore, it was found minimum under $Cr_4 C_5$ with humic acid (68.15 and 72.15 mg kg^{-1}) in both maize and mustard harvested soil respectively.

Comparison among maize and mustard post-harvest Nitrogen, Phosphorus and Potassium content soil

Comparison among post-harvest N, P, and K content of soil at all level of treatment combination. It can be inferred from table () that N, P and K content was found highest with Cr_0C_0 (no chelating agent and no chromium) (101.14, 12.61 and 104.43 mg kg^{-1}) and (103.67, 13.11 and 110.57 mg kg^{-1}) in maize and mustard respectively after harvesting. However, lowest (62.62, 6.31 and 68.15 mg kg^{-1}) and (69.65, 6.56 and 72.15 mg kg^{-1}) N, P and K was observed with Cr_4C_5 in mustard and maize respectively. However, DTPA and humic acid not significantly increase the post-harvest N, P, and K content of soil while control and oxalic acid buildup the post-harvest N, P, and K content but not significantly.

This might be due to the fact of high degradability of chelating agent and high organic matter which insures the availability of N, P and K to plant thereby increasing growth, biomass and nutrient buildup to plant thus reduced soil nutrient content. Moreover, high affinity of chelating agent (HA> DTPA> EDTA) to metal reduce toxicity of metal even at higher concentration (Ghani et al., 2017) [18].

Effect on DTPA extractable chromium in chromium contaminated soil

Data pertaining to the effect on DTPA extractable chromium in chromium in chromium contaminated soil is presented in table 4. Soil from maize harvested pot trending toward increasing DTPA extractable chromium with increasing rate of chromium. Highest DTPA extractable chromium (2.76 mg kg^{-1}) was recorded with Cr_4C_0 followed by Cr_4C_0 (2.58 mg kg^{-1}), Cr_4C_0 (2.40 mg kg^{-1}) and Cr_4C_0 (2.23 mg kg^{-1}) at 30 ppm level of chromium contamination. DTPA extractable chromium followed a similar trend at 20 ppm, 10 ppm, and 5 ppm also. Moreover, a high amount DTPA extractable chromium (0.24 mg kg^{-1}) was observed with Cr_0C_0 and then decreasing in order Cr_0C_4 (0.23 mg kg^{-1}) >Cr_0C_3 (0.22 mg kg^{-1}) > Cr_0C_2 (0.21 mg kg^{-1}) > Cr_0C_1 (0.21 mg kg^{-1}) followed by lowest DTPA extractable chromium (0.20 mg kg^{-1}) at 0 ppm level of chromium contamination.

Soil from mustard harvested pot trending toward increasing DTPA extractable chromium with highest DTPA extractable chromium (0.741mg kg^{-1}) was recorded with Cr_4C_0 followed by Cr_4C_4 (0.693 mg kg^{-1}), Cr_4C_3 (0.645 mg kg^{-1}) and Cr_4C_1 (0.597 mg kg^{-1}) at 30 ppm level of chromium contamination. DTPA extractable chromium followed a similar trend at 20 ppm, 10 ppm, and 5 ppm also. Moreover, a high amount DTPA extractable chromium (0.130 mg kg^{-1}) was observed with Cr_1C_0 and then decreasing in order Cr_1C_4 (0.122 mg kg^{-1}) >Cr_1C_3 (0.114 mg kg^{-1}) > Cr_1C_1 (0.105 mg kg^{-1}) > Cr_1C_2 (0.97 mg kg^{-1}) followed by lowest DTPA extractable chromium (0.0.084 mg kg^{-1}) at 5 ppm level of chromium contamination. While at 0 ppm Cr DTPA extractable chromium was not detected.

Organic chelating agent cause a more increase in labile chromium in soil hence available for plant uptake as compare to synthetic chelating agent with high molecular weight in case of both maize and mustard (Nawab et al., 2016) [37]. High DTPA extractable chromium (2.76 mg kg^{-1}) with Cr_4C_0 was observed from maize harvested soil and mustard showed lowest DTPA extractable chromium (0.084 mg kg^{-1}) with Cr_1C_5. Thereby, maize showing a higher amount of DTPA extractable chromium when compare between all treatment combinations at particular level of chromium contamination in soil. Singh et al., (2007) [44] reported an increase in heavy metal concentration in soil with high Cr application and higher with organic chelates.

Conclusion

By comparing both maize and mustard it was found that pH, EC and organic carbon differ non-significantly. pH, EC and organic carbon decreased significantly with the increasing level of chromium. By comparing different rate of chromium contamination with different chelating compounds, significantly highest pH was recorded with control Cr_0C_0 (0 ppm Cr with no chelating agent) while, lowest by application of humic acid at 30 ppm level of chromium contamination. However, EC and organic carbon showed just opposite trend to that of pH and found significantly highest value by application of humic acid Cr_0C_5 (30 ppm Cr + 1 g kg^{-1}HA) and lowest with Cr_4C_0 (30 ppm Cr with no chelating agent). The NPK content from post-harvest soil decreased significantly with the increasing level of chromium. By comparing different rate of chromium contamination with different chelating compounds, significantly highest NPK content of soil were recorded with control Cr_0C_0 (0 ppm Cr with no chelating agent) while, lowest with Cr_4C_5 (30 ppm Cr + 1 g kg^{-1} HA). By comparing both maize and mustard NPK content was significantly higher in soil from mustard harvested pot. DTPA extractable chromium increased significantly with the increasing level of chromium contamination. By comparing different rate of chromium contamination with different chelating compounds, significantly highest DTPA extractable chromium was recorded with application of oxalic acid Cr_4C_4 (30 ppm Cr + 20 mMole kg^{-1}) while, lowest with Cr_0C_5 (0 ppm Cr + 1 g kg^{-1} HA). This might be due low affinity of low molecular weight toward metal to bind with and render to make available to plants. By comparing both maize and mustard DTPA extractable chromium was found significantly much higher in maize than mustard plants.

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