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Chromium Species and 3D-Fluorescence Spectroscopy in a Soil Irrigated with Industrial Wastewater

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Abstract

Irrigation of agricultural land with wastewater is beneficial because it incorporates organic matter into the soil, as well as organic ions (such as nitrates, sulfates, and phosphates). However, long-term application causes negative effects such as the accumulation of heavy metals. The wastewater used in the agricultural soils, also incorporates organic refractory compounds, which affect the microbial population and fertility. This chapter aimed to identify the chromium species present in agricultural soil irrigated with wastewater (679.6 mg/L for total chromium and 559.5 mg/L for Cr VI), and characterize the dissolved organic matter in the saturated solution soil. In the soil-saturated solutions (pH 6), the most stable Cr (III) species was Cr_2O_3. These species precipitate and accumulate in the soil in combination with natural organic matter. The highest accumulation of chromium occurred in the first 10 cm of the soil column. The 3D fluorescence analysis exposes the presence of aromatic proteins, microbiological degradation products, and humic and fulvic acids in the soil profile. The excitation-emission matrix (EEM) showed that Cr (VI) species were complexed with humic acids. In the X-ray diffraction analysis, the species Cr_2O_5, Cr_5O_{12}, CrO_2, and Cr_7C_3 were found at depth with the greatest amount of organic matter.

Keywords: wastewater, chromium, agriculture, irrigation, environment, aromatic proteins, humic acid

1. Introduction

Wastewater reuse in farming Mexican represents a valuable resource in agricultural production due to the irrigation supply and considerable nutrients input to the soil. Negative environmental effects may result from long-term wastewater application due to heavy metal accumulation in soils, increasing amounts of highly mobile, and easily mobilizable metal fractions, as well as crops uptake [1, 2]. Among the solid reactive components present in the soil, organic matter (OM), which has a high sorption capacity for metal ions [2–5], plays a very important role in soil fertility. The positive effects of organic matter are due to the fact that it benefits the aggregation of soil particles, improving aeration, permeability, resistance to erosion, and water retention. Regarding the chemical function of organic matter, it is based on its high cation retention capacity, which contributes greatly to the control of soil acidity, nutrient recycling and the detoxification of dangerous compounds such as heavy metals that are incorporated into soils by industrial wastewater [6]. Chromium is among the metals that may be present in wastewater.

Chromium is a trace component in the Earth's crust (0.02%) that is essential for animal and human life, but not for plants. It is a natural element present in water, sediments, rocks, soils, plants, biota, animals, and volcanic emissions. The main oxidation forms of chromium are trivalent chromium and hexavalent chromium, each with opposite properties [7]. The total concentration of chromium in the lithosphere is between 69 and 100 mg/kg [7, 8]. The two forms of chromium have different effects on living organisms: Chromium (III) is apparently useful and harmless at reasonable concentrations, while Chromium (VI) is extremely toxic. Moreover, Chromium (III) is not mobile in soil; therefore, the risks of leaching are negligible.

In solution, Cr (VI) can exist in three different ionic forms: $HCrO_4^-$, CrO_4^{2-}, and $Cr_2O_7^{2-}$. It can also exist in the form of complex anions that are soluble in water and may persist in it. In surface water rich in organic content, Cr (VI) has a much shorter shelf life [9]. The presence of each ionic form of chromium in solution depends on the pH [10]. Chromium is present in soils as water-insoluble $Cr_2O_3.H_2O$ [11]; only a small part of it can be leached from soil. Chromium (VI), mainly present as chromate ions (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$), is generally mobile and is sometimes part of crystalline minerals [7, 12]. In soil, Cr (VI) tends to be reduced to Cr (III) by organic matter. The chromium present in the environment is mainly derived from human activities.

Chromium (III) converts to Chromium (VI) only in some soils, particularly those that are rich in manganese oxides, poor in organic matter and with high oxidation–reduction potential. In contrast, the conversion of Chromium (VI) to Chromium (III) is very common and easy, and is thus very difficult to find hexavalent chromium forms in the soil solution or in leaching waters [7, 13]. The mobility of chromium in the lithosphere can only be evaluated by considering the adsorption and reduction capacity of soils [4, 13].

Accordingly, the aim of this study was to identify the chromium species present in soil and the saturated solution during irrigation with wastewater and characterize the dissolved organic matter, through the 3D fluorescence spectroscopy analysis, and its evolution in the soil profile.

2. Materials and methods

2.1. Soil sampling and irrigation

Three soil samples were taken in an agricultural area, previously conditioned with the addition of organic matter in order to ensure a high content of organic matter in the soil. Sampling was performed vertically by inserting a PVC tube 10 cm in diameter at a depth of 50 cm at a random point in the area, so that three complete soil columns were obtained. The sampling and transfer was carried out hermetically to guarantee the inviolability of the sample until the arrival at the laboratory. The first profile was used to determine the physicochemical characteristics of the soil: pH, Ce, CEC, MOS, moisture, and texture.

The other two profiles were irrigated with wastewater from an electroplating industry (559.5 mg/L Cr VI and 20.1 mg/L de Cr III); the irrigation was carried out on a single occasion in order to saturate the soil with Cr. About 10-cm deep holes were successively drilled in the soil profiles until reaching a depth of 50 cm. A sample of the saturated solution was obtained from each of these holes to observe the decrease of the concentration of chromium in the saturated solution after crossing 10 cm of soil. The ORP, Cr VI concentration [14], and 3D fluorescence spectrum were determined in the collected solution samples.

2.2. Sampling and characterization of wastewater

The water sampling was carried out in the discharge of wastewater from an electroplating industry, located in the City of Toluca, State of Mexico. A sample composed of 5 L of residual water was collected, which was integrated with five individual samples of 1 L each, taken from the wastewater discharge every 15 min. The parameters, determined according to standard methods [14], were pH, electrical conductivity (EC), nitrates (NO_3-), sulfates (SO_4^2), chlorides (C^{1-}), total chromium (by atomic absorption spectrometry) and chromium VI (by diphenylcarbazide spectrophotometry) [14].

2.3. Fluorescence spectroscopy and X-ray diffraction

The 3D fluorescence analysis was performed [15–17]. A Perkin Elmer fluorescence spectrophotometer LS55 was used, with 150 watts xenon lamp as excitation source. In the characterization of the samples, 45 individual emission spectra were obtained at emission wavelengths (λem) between 250 and 600 nm with intervals of 5 nm and, collected at excitation wavelengths (λexc) between 200 and 450 nm. The samples were analyzed at a concentration < 2 mg/L COD [15, 17]. A 290 nm filter was used in all analyses to eliminate Raleigh peak light interference. The excitation-emission matrix (EEM) of distilled water was subtracted from the EEM of the industrial wastewater samples to eliminate interference caused by Raman peaks. In order to verify the presence of chromium retained in the soil, the X-ray diffraction analysis was performed.

2.4. Chromium retention capacity of soil

Batch tests were carried out to determine the Cr accumulation capacity of soil; 1 g of dry soil, sieved to a particle size of 0.002 mm, was placed in a glass tube together with 10 ml of a chromium

(Cr VI) solution at standard concentrations of 5, 10, 15, 20, and 25 mg/L, in continuous stirring and constant temperature of 25°C. Five tests were performed for each depth of the soil column, with a contact time of half an hour. Subsequently, the tubes were centrifuged at 2500 rpm, and the supernatant was filtered, collected, and acidified for Uv–visible spectroscopy [14].

3. Results and discussion

3.1. Physicochemical characteristics of the soil

Figure 1 shows the physico-chemical characteristics of the soil profile. The data obtained show a slight increase of pH as depth increases, with a value of 7.3 in the most superficial area and 7.5 at a depth of 50 cm. These pH values show that the soil is moderately alkaline, suggesting a medium availability of nutrients. The results of the electrical conductivity tests show a remarkable decrease along the soil column; the surface area has a value of 255.09 µS/cm and the deepest layer of 112.95 µS/cm. The lowest conductivity value (105.13 µS/cm) was observed at a depth of 30–40 cm (**Figure 1**). The cation exchange capacity remained constant throughout the soil column, with values of 30.20 Cmol/kg at a soil depth of 40–50 cm, and up to 38.21 Cmol/kg at 10–20 cm depth.

The content of organic carbon (OC) gradually decreased as the depth of the soil column increased: from 9.96 g/kg in the surface layer to 2.29 g/kg a depth of 40–50 cm. The percentage of organic matter (OM) also decreased with increasing depth; the highest value (17.17%) was observed in the surface layer, and the lowest value (3.95%) in the deepest layer. The percentage of humidity, like the OC content, decreased along the soil column by up to 29%, from 22.83% in the surface layer to 16.27% at a depth of 30–40 cm.

Regarding the texture of the different layers of the soil column, we obtained the following results: the most superficial layer (0–10 cm) had sandy loam soil; at depths of 10–20 and 30–40 cm, the soil had a loamy texture, and in the intermediate layers of the column (20–30 cm) and in the lowest layer 40–50 cm, the soil had a loamy-clay texture (**Table 1**).

In general, all layers of the soil column had a loam texture. The literature on the subject states that a soil with medium alkaline pH is a sandy soil; this agrees with the texture data obtained in the present study, which showed a high sand content in all soil samples (**Table 2**). The results of this study also agree with the low amount of natural organic matter reported for these types of soils, as well as with deficiencies of B, Cu, Fe, Mn, Zn, and P [18].

3.2. Physicochemical characterization of industrial wastewater

Table 3 shows the physicochemical characteristics of the wastewater used for irrigation of the soil columns. The concentration of total Chromium and Cr VI in the wastewater was high: 679.6 mg/L for total chromium and 559.5 mg/L for Cr VI. The concentration of copper was 18.5 mg/L; 0.64 mg/L for nitrates; 360.3 mg/L for sulfates; and 272.3 mg/L for chlorides. Electrical conductivity was 1576 µS/cm due to the presence of metals such as chromium, copper, chlorides, and sulfates. The pH of the water (3.4) is congruent with the presence of
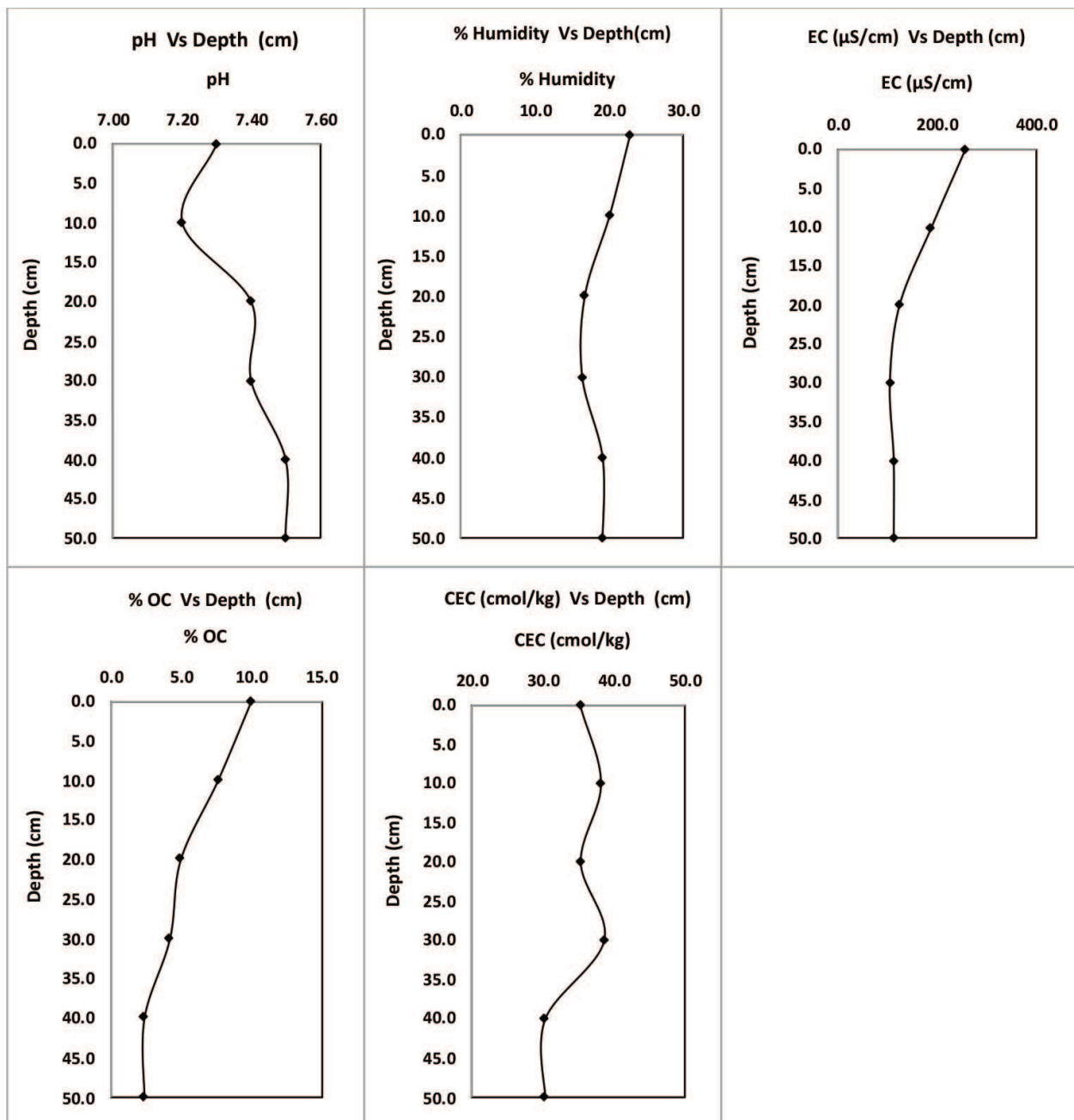
Figure 1. Physical and chemical characteristics of the soil sample as a function of depth. EC = electric conductivity, OC = organic carbon, CEC = cation exchange capacity.

chromium VI, since the species distribution diagram for chromium indicates that the chromium species present in waters with pH values ranging from 1 to 5 is chromium VI. The wastewater studied here came from an electroplating plant in the city of Toluca.

3.3. Concentration of chromium VI in the soil solution throughout the soil column

The concentration of chromium in samples of the soil-saturated solution collected from the soil profile at depth intervals of 10 cm (**Table 4**); it also shows the amount of chromium accumulated in each section of the soil column. The initial concentration of Cr VI in the water used

Soil	Depth (cm)	pH	EC (μS/cm)	CEC (Cmol/Kg)	OC (g/Kg)	OM %	Humidity %
M1	0–10	7.30	255.09	35.22	9.96	17.17	22.83
M2	10–20	7.20	187.93	38.21	7.57	13.05	20.02
M3	20–30	7.40	124.74	35.29	4.90	8.45	16.63
M4	30–40	7.40	105.13	38.66	4.13	7.12	16.27
M5	40–50	7.50	112.91	30.20	2.29	3.95	19.08

M sample.

Table 1. Physicochemical characteristics of the soil column under study.

Sample	Depth (cm)	Clay (%)	Loam (%)	Sand (%)
M1	0–10	10.0	30.0	60.0
M2	10–20	18.0	42.0	40.0
M3	20–30	41.0	46.0	13.0
M4	30–40	11.0	45.0	44.0
M5	40–50	34.0	54.0	12.0

M sample.

Table 2. Textural characteristics of the soil column under study.

Characteristic	Value
pH	3.4
Electrical conductivity (μS/cm)	1576
Cr VI (mg/L)	559.5
Cu (mg/L)	18.5
Nitrates (mg/L)	0.64
Sulfates (mg/L)	360.3
Chlorides (mg/L)	272.3
Total Chromium (mg/L)	*679.6*

Table 3. Physicochemical characteristics of the wastewater used for irrigation.

for irrigation was 559.5 mg/L. The results show that the greatest accumulation of Cr occurred between 0 and 10 cm depth (299 mg/L), followed by the layer at 30–40 cm, with 160 mg/L Cr, a 50% decrease in the concentration of chromium VI present in soil solution.

The data on soil texture showed that the percentage of clay is low at 10–20 cm depths (10%), while at 20–30 cm is four times greater (41%). The percentage of organic matter is 17.17 and 8.45%. The CEC, however, is 35.22 and 35.29%, similar to the rest of the soil column. The highest

amount of accumulated chromium was found in the surface layer, which had the lowest percentage of clay. This demonstrates the participation of organic matter in the accumulation of chromium (**Table 4**).

Additional to the irrigation with wastewater, one irrigation was done with a compost solution (100 g of compost/1 L water) in order to observe the effect of dissolved organic matter on the accumulation of chromium in the soil column. The results showed that chromium was absent from the soil-saturated solution at any depth of the soil profile, indicating that the chromium was being immobilized or retained. After this irrigation, one more irrigation was carried out, maintaining the concentration of chromium in the water entering the soil profile at 559.5 mg/L (**Table 5**). In these irrigations, the concentration of Cr VI in the saturated water collected at the outlet of the soil column was lower than in the first irrigation, suggesting a higher accumulation of chromium.

The theoretical amount of chromium that precipitated and accumulated in the soil during the first irrigation was 299 mg; when dissolved organic matter was added to the irrigation water, that amount increased to 326 mg. Using the solution containing dissolved organic matter improved the soil reduction conditions, causing the reduction of Cr (VI) to Cr (III), which produced a precipitate of chromium, either an oxide or hydroxide, that accumulated in the

Depth (cm)	Irrigation		Kd	T (°C)	pH	ORP (mV)
	Ce_s	A				
0–10	260.0	299.0	11.5	23.0	5.7	102.1
10–20	240.0	20.0	0.8	22.0	5.7	103.3
20–30	80.0	160.0	2.0	22.0	5.8	96.5
30–40	40.0	40.0	40.0	22.0	5.9	92.4
40–50	40.0	0.0	0.0	21.0	5.9	91.2

Ce: concentration of Cr in the saturated solution at every 10 cm of depth (mg/L) A: amount of chromium retained (mg).

Table 4. Concentration of Cr VI in the soil-saturated solution (Ce). Retention capacity of Cr. Distribution coefficient of Kd, pH, and ORP along the soil column (q).

Samples	Intensity of fluorescence (Excitation/Emission (nm))			
	Peak A	Peak B	Peaks C and D	Peak F
0–10	158 (340/412)	313 (210/407)	ND	121 (280/414)
10–20	255 (340/412)	540 (210/409)	ND	177 (280/412)
20–30	33 (320/438)	ND	ND	
30–40	67 (335/442)	200 (210/420)	ND	
40–50	93 (330/440)	206 (225/435)	ND	

ND Undefined.

Table 5. 3D-fluorescence characterization of the soil solution.

soil matrix [18, 19]. Of the 559.5 mg/L of chromium that were added to the soil column with the first irrigation, 53% was retained; after adding dissolved organic matter to the irrigation water, the retention percentage reached 58%.

3.4. Irrigation with wastewater

It was observed that the concentration of chromium (VI) in the wastewater decreased along the soil column. **Table 4** shows the concentration of chromium (VI), the oxidation–reduction potential and pH along the soil column. The samples show a direct effect of dissolved organic matter on the soil conditions that facilitate the accumulation of chromium. The irrigation results show that dissolved organic matter improved the soil reduction conditions, which promoted the accumulation by precipitation of chromium species. The soil reduction conditions are represented by the ORP values in the soil-saturated solution at the outlet of the soil column during direct irrigation.

The initial ORP value of the irrigation water was 274.9 mV; it decreased by up to 66% with each additional 10 cm of depth. The pH of the irrigation water changed from 3.4 to 5.6. It should be mentioned that the wastewater used for irrigation stayed in the soil column for 15 min, which shows that the soil had good drainage.

3.5. Chromium species in wastewater and soil solution along the soil profile

The species distribution diagram of Cr VI and Cr III were built based on the ORP and pH data, using the Hydra and Medusa programs [19]. **Figure 2** shows the Eh-pH diagram of chromium in the wastewater; it shows that the $HCrO_4^-$ ion is the Cr VI species that predominated in both oxidized and reduced environments at pH values of 0–6.6. The CrO_4^{2-} ion predominated at values of pH > 6.0. According to the diagram, the Cr III species that predominated in the solution, depending on the pH of the water, was Cr^{3+}. Thus, Cr VI species such as $HCrO_4^-$, and Cr III species such as Cr^{3+}, entered the soil with the irrigation water, the latter in smaller quantities.
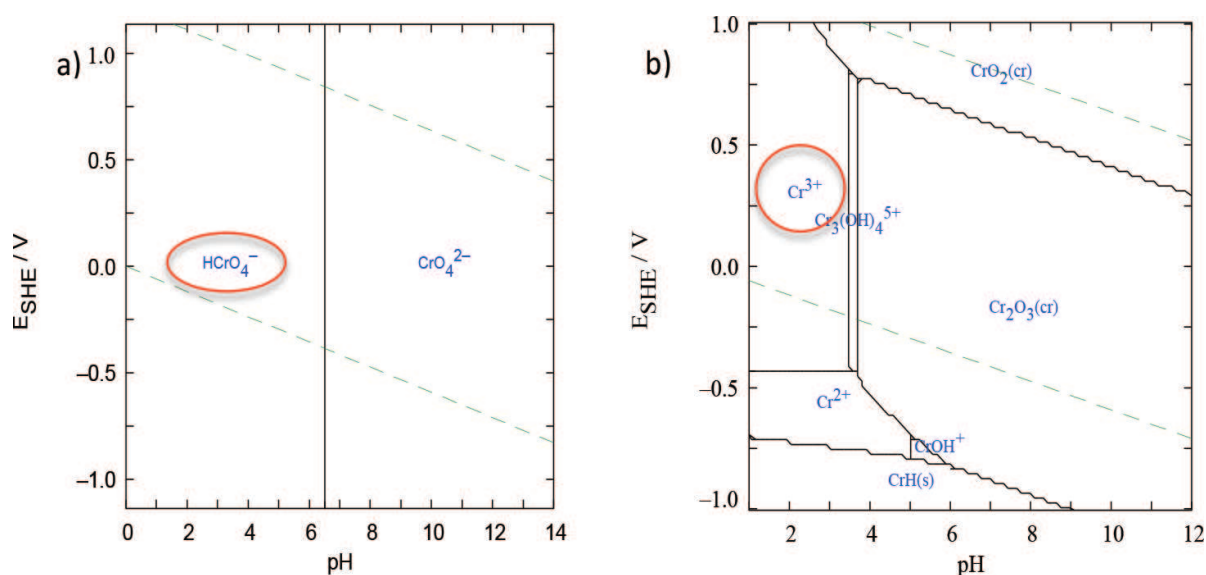

Figure 2. Stability diagram of chromium species (Eh-pH) in wastewater with high chromium content. Cr VI concentration: 10.78 mM; Cr III concentration: 2.31 mM; pH 3.4. (a) Cr VI species and (b) Cr III species.

Figure 3 shows the stability diagrams of chromium (Eh-pH) along the soil column during irrigation with wastewater with high chromium content. As observed in **Figure 4**, and based on the pH values of each soil solution, the predominant Cr III species was Cr_2O_3, and there was no presence of Cr VI species, confirming that chromium III species precipitate and accumulate in soil as chromium oxide combined with natural organic matter [18, 19]. The redox potential measured in the soil solution during the irrigation was between 91.2 and 103.3 mV, with pH values between 5.67 and 5.90. In the species distribution diagram of chromium, these intervals correspond to the area of predominance of Cr_2O_3. The amount of chromium in the solution decreased along the soil profile.

3.6. 3D-fluorescence of dissolved organic matter in the soil solution

The 3D fluorescence spectra of the soil-saturated solution, based on the fluorescence data obtained (**Table 5**), show two peaks: A and B (**Figure 4**). These peaks are located within a
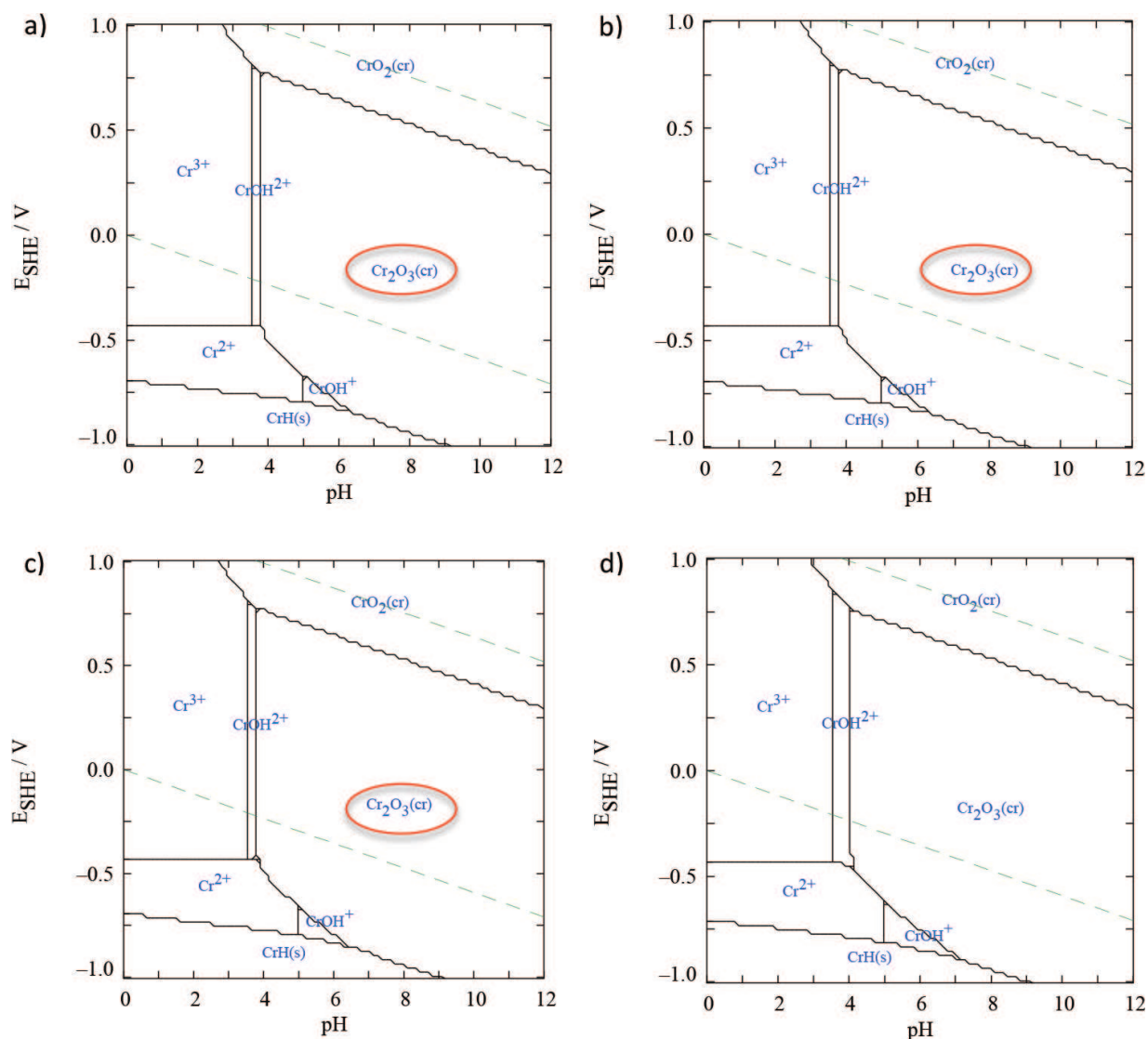

Figure 3. Stability diagram of chromium (Eh-pH) in the soil solution: (a) depth (0–10 cm), ionic strength 0.005 M, [Cr VI] 5.01 mM, [Cr III] 1.07 mM; (b) (10–20 cm), ionic strength 0.004 M [Cr VI] 4.62 mM and [Cr III] 0.99 mM; (c) (20–30 cm), ionic strength 0.001 M [Cr VI] 0.77 mM and [Cr III] 0.17 MM; (d) (30–50 cm), ionic strength 0.001 M [Cr VI] 0.77 mM and [Cr III] 0.17 mM for the entire pH range and for the range of pH measurements and redox potential of the samples.
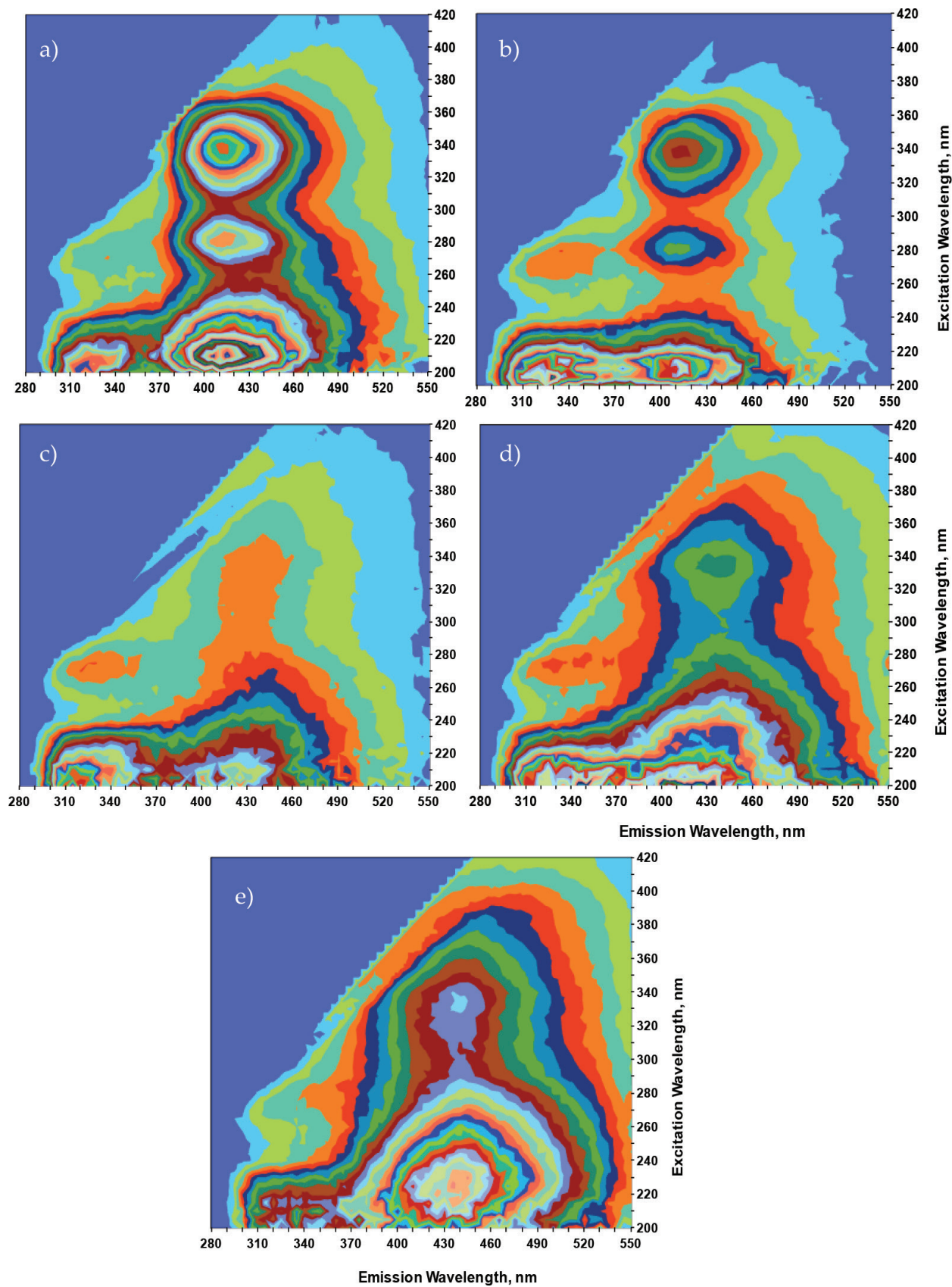
Figure 4. 3D fluorescence spectra of the soil-saturated solution along the soil profile.

range of excitation/emission wavelengths of 320–340 ex/412–440em and 210–225ex/407–435em, with intensities of 33–255 and 200–540, respectively. The A and B peaks are within the regions corresponding to humic and fulvic acids [16]. The spectra did not show peaks of type C and D, which are associated with the presence of organic material of anthropogenic origin. However, a peak (F) between the peaks A and B could be considered a humic acid, given the region in which it is located, although it could also be associated with some organic synthetic material or a complex of Cr and humic acids.

The highest fluorescence intensity was recorded at a depth of 0–20 cm, in agreement with the fact that the surface layer had the greater presence of natural organic matter (**Figure 4**). As mentioned before, the chromium accumulated in the soil profile may combine with two types of natural organic matter, humic and fulvic acids. The fluorescence spectra showed the evolution of humic substances [15, 17]. In the first 20 cm of the soil profile, the fluorescence intensity of humic acids is high (158 at 10 cm and 255 at 20 cm), but decreases with increasing depth by up to 87%. The fluorescence intensity of fulvic acids is higher than that of humic acids (313 and 540) and decreases less with depth (62%).

Because fulvic acids are more mobile than humic acids, it is logical to find them throughout the soil profile (**Figure 4**). These acids can predominate in natural waters and have a high degree of anionic charge, which favors the formation of stable complexes with cations such as chromium [15, 20, 21]. It is worth noting the amount of chromium accumulated in the soil profile (**Table 6**); the greatest accumulation of chromium was observed in the first 10 cm of the column, where there was a greater presence of organic matter and where peak F was observed. At a depth 30–40 cm, the accumulated chromium was only 63% of the level found in the surface layer; however, at this depth, the organic matter content was 60% lower than on the surface layer, while the percentage of clay was the same in both layers.

The fluorescence spectra indicated that most of the dissolved organic matter present in the surface layer and at a depth of 30–40 cm were fulvic acids. As mentioned earlier, fulvic acids are more mobile and tend to form complexes with Cr (III) cations, which suggests that, given the low amount of Cr (III) present in the wastewater used for irrigation, it precipitated mostly in the first 20 cm of the soil profile, which explains its absence from the soil-saturated solution. The Cr (VI) species present in the solution collected at the outlet of the soil column may not have passed enough time in the soil column to convert to Cr (III).

3.7. Chromium retention capacity of the soil

Table 6 shows the chromium retention results of the soil, based on the retention capacity (q) and equilibrium concentrations (Ce) determined by Bach tests at different concentrations of chromium. The table shows that the retention capacity of the soil increased as the equilibrium concentration of chromium increased. However, a constant value was not reached, which is usually observed when the soil reaches a saturation point; this can be explained by the low concentration of chromium in the standard solutions. The results of the Bach tests showed that the dispersion coefficient of chromium in the soil was higher (Kd 8.36) in the surface layer

	0-10 cm			10-20 cm			20-30 cm			30-40 cm			40-50 cm		
Co	Ce	q	Kd	Ce	q	Kd	Ce	q	Kd	Ce	Q	Kd	Ce	q	Kd
(mg/L)	(mg/L)	(mg/Kg)		(mg/L)	(mg/Kg)		(mg/L)	(mg/Kg)		(mg/L)	(mg/Kg)		(mg/L)	(mg/Kg)	
5.00	2.72	22.79	8.38	4.00	9.99	2.50	4.61	3.90	0.85	4.35	6.49	1.49	4.12	8.79	2.13
10.00	7.26	27.41	3.78	8.64	13.65	1.58	8.09	19.09	2.36	7.33	26.68	3.64	7.78	22.24	2.86
15.00	11.18	38.19	3.42	12.74	22.57	1.77	12.03	29.72	2.47	11.28	37.18	3.30	11.26	37.41	3.32
20.00	15.90	41.04	2.58	17.12	28.76	1.68	15.21	47.90	3.15	14.14	58.60	4.14	13.09	69.14	5.28
25.00	18.92	60.82	3.21	21.80	32.00	1.47	19.44	55.60	2.86	17.12	78.80	4.60	16.88	81.20	4.81

Table 6. Results of Ce, q and Kd along the soil column.

of the soil column (0–10 cm depth), which had the largest concentration of organic matter and the lowest concentration of chromium (5 mg/L). This behavior shows the affinity of chromium for organic matter. At a depth of 20–30 cm, where the percentage of clay was the largest (41%) and the dispersion coefficient of chromium was Kd 0.85.

Starting at a depth of 20 cm, the dispersion coefficient increased while the concentration of chromium in the solution increased, except for interval of 20–30 cm depth, which showed an opposite behavior. Bach tests have been designed to study adsorption equilibria in a continuously stirred soil suspension. These tests are based on a physical model of a completely dispersed soil particle system where the entire surface of the soil is exposed and available to interact with chromium. These tests do not represent real natural conditions, since they assume a closed system in which soil particles have the highest adsorption capacity, and a practically null flow rate [21–23]. However, they are a good tool to try to represent and understand the behavior of contaminants. The Bach tests performed in this study were carried out with a contact time of 30 min, twice the residence time of the water in the soil column, in order to represent real conditions.

A linear isotherm was used to describe the adsorption processes that took place in the soil; this allowed us to describe the distribution of chromium between the soil and the solution [22, 23]. The isotherms generated by the Bach tests (**Figure 5**) show the retention capacity of chromium in the soil (q) versus the equilibrium concentration of chromium (Ce).

At low concentrations of chromium, the adsorption isotherm for the soil is linear. **Figure 5** shows that with a low concentration of chromium and a contact time range of 0–25 min, 45% of chromium is removed from the solution in the first 10 cm of the soil column, 20% at 10–20 cm, 7.8% at 20–30 cm, 13% at 30–40 cm, and 17% at 40–50 cm.

The removal percentage of chromium from the solution decreased as the concentration of chromium in the solution increased. The removal percentage of chromium also decreased throughout the soil column, with the highest percentage at 20–30 cm depth. Under nonequilibrium
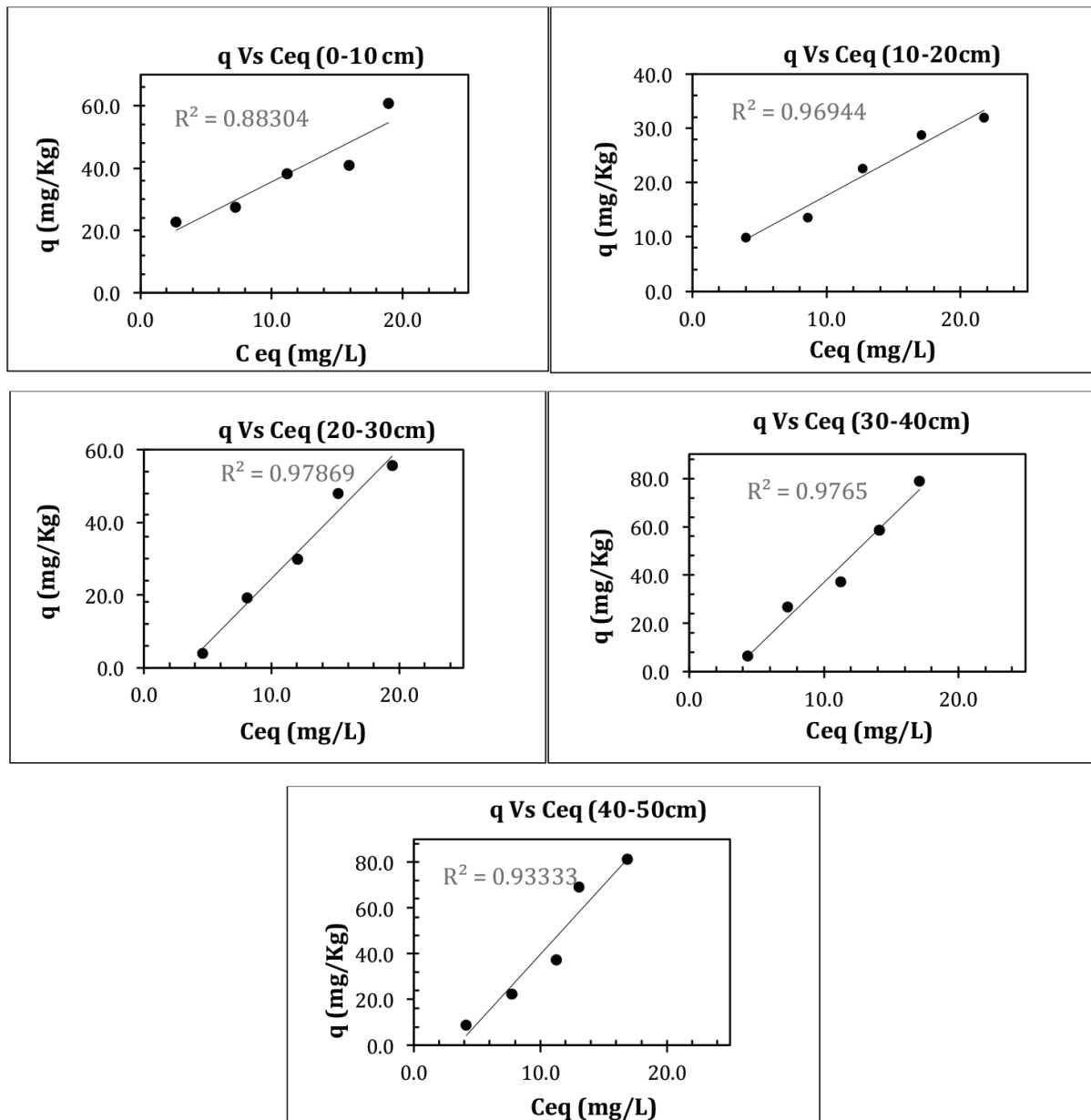
Figure 5. Chromium adsorption isotherms along the soil column. Contact time: 30 min. Temperature: 25°C.

conditions, the highest accumulation of chromium occurred in the first 10 cm of the soil column, in agreement with the results of the Bach tests, which showed that chromium has a high affinity for organic matter, as evidenced by the Kd value (**Table 6**). As mentioned before, the dispersion coefficients determined by the Bach tests decreases with depth in the soil column from 8.38 to 2.13. The fluorescence intensity of humic acids also decreased with depth; the highest fluorescence intensity of these humic substances was recorded in the first 10 cm of the soil column, where the dispersion coefficient was higher.

The dispersion coefficient of humic acids was similar to that of chromium, so it is possible to assume that Cr (VI) species complexed with humic acids or were reduced to Cr (III) in the

presence of these humic substances. Moreover, the R^2 values found along the soil column showed that the isotherm can describe the sorption or complexation behavior of chromium with humic acids.

An X-ray diffraction analysis was performed to verify the precipitation of chromium in the soil. The results showed the presence of the species Cr_2O_5, Cr_5O_{12}, CrO_2, and Cr_7C_3 in the soil layer with the greatest amount of organic matter, confirming the removal of chromium by precipitation. Considering that most of the reducers used here and reported in the literature are less effective at alkaline pH values [5], natural organic matter (humic acid) could be used for the remediation of soils and waters contaminated with Cr (VI).

4. Conclusions

The use of a dissolved organic matter solution had a direct effect on the soil reduction conditions, improving the reduction of Cr (VI) to Cr (III) and producing a precipitate of chromium that accumulated in the soil matrix.

In the species distribution diagram of chromium, the oxidation–reduction potential and pH values found in the soil-saturated solutions correspond to the area of predominance of Cr_2O_3, which is not water soluble and is thus difficult to leach.

The chromium accumulated in the soil profile may have combined with natural organic matter such as humic and fulvic acids.

The 3D fluorescence analysis of the soil-saturated solutions showed the presence of natural organic matter (humic and fulvic acids) throughout the soil profile.

The highest accumulation of chromium occurred in the first 10 cm of the soil column, suggesting, like the Bach tests, that chromium has a high affinity for organic matter, as evidenced by the Kd values.

The dispersion coefficient of humic acids was similarly to that of chromium, so it is possible to assume that Cr (VI) species may have complexed with humic acids.

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Conflict of interest

The authors declare is no conflict of interest regarding the publication of this paper.

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