

Article

Influence of Physicochemical Properties and Parent Material on Chromium Fractionation in Soils

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Abstract: Chromium is an element that possess several oxidation states and can easily pass from one to another, so its behavior in soils is very complex. For this reason, determining its fate in the environment can be difficult. In this research work we tried to determine which factors affect the chromium fractionation in natural soils, conditioning chromium mobility. We paid special attention to the parent material. For this purpose, extraction experiments were carried out on spiked soils incubated for 50–60 days, using H₂O, CaCl₂ and diethylenetriaminepentaacetic acid (DTPA). The most efficient extraction rate in all soils was achieved using water, followed by CaCl₂ and DTPA. We obtained models with an adjusted R² of 0.8097, 0.8471 and 0.7509 for the H₂O Cr, CaCl₂ Cr and DTPA Cr respectively. All models were influenced by the amount of chromium added and the parent material: amphibolite and granite influenced the amount of H₂O Cr extracted, and schist affected the other two fractions (CaCl₂ and DTPA). Soil texture also played an important role in the chromium extraction, as well as the amounts of exchangeable aluminum and magnesium, and the bioavailable phosphorus. We concluded that it is possible to make relatively accurate predictions of the behavior of the different Cr fractions studied, so that optimized remediation strategies for chromium-contaminated soils can be designed on the basis of a physicochemical soil characterization.

Keywords: heavy metal; modeling; predict; spiking; extraction; H₂O; CaCl₂; DTPA



Citation: Campillo-Cora, C.; Rodríguez-González, L.; Arias-Estévez, M.; Fernández-Calviño, D.; Soto-Gómez, D. Influence of Physicochemical Properties and Parent Material on Chromium Fractionation in Soils. *Processes* **2021**, *9*, 1073. <https://doi.org/10.3390/pr9061073>

Academic Editor: Juan Francisco García Martín

Received: 18 May 2021
Accepted: 17 June 2021
Published: 20 June 2021

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1. Introduction

Chromium is one of the most common elements on earth: it occupies the seventh position in terms of abundance, but most of this element is found in the earth's core or in the mantle [1]. The average concentration in the earth's crust is around 185 mg Kg⁻¹, and it is usually associated with basic and ultrabasic rocks. Human activities (burning of fossil fuels and incineration of rubbish, production of parts for the aerospace industry, pulp and paper processing, production of metallic chrome, leather tanning, etc.), have also contributed to an increase in chromium levels in the air and in the water [2].

The behavior of ionic chromium is complex since it has several oxidation states (between -2 and +6) and easily switches from one state to another [3]. The most stable and common forms in nature are the trivalent, Cr(III) and the hexavalent chromium, Cr(VI) [4]. Both species of Cr present very different characteristics, and their movement and retention in the soil is conditioned by different factors: for example, the retention of Cr(III) is greatly affected by the texture, and it is more retained in silty soils that present high pH; while Cr(VI) is better retained when the soil pH drops, or when organic matter or iron oxides are added (materials positively charged) [5].

Cr(III) is an essential trace element for humans, involved in the metabolization of carbohydrates and lipids [6]. It is a metal that can remain trapped in soils, be assimilated by crops and bioaccumulate along the food chain, posing risks to human health [7]. In addition, it is an element that does not have any known role in the development of plants, but its presence in the environment is associated with certain problems: Cr(VI) can cause reductions in the growth, alterations in the chloroplasts and inhibition of the photosynthesis [8]. The remediation methods for soils contaminated by Cr are based on immobilizing it by reducing Cr(VI) to Cr(III), which is less toxic and less mobile. For this aim, materials such as biochar from chicken manure or black carbon have been successfully tested: materials that act as electron donors and provide energy to the soil organisms that take part in this reduction reaction [9]. In addition, these type of reactions are associated with an increase in pH [10] which as we mentioned previously, favors the retention of Cr(III).

It is important to know how soil properties (parent material, pH, organic matter content, texture, etc.) affect the movement and availability of Cr, especially for the remediation of contaminated soils. Therefore, the objectives of this research work are (i) to analyze the (natural) occurrence of this metal in forest soils developed over various parent materials, (ii) to determine how the characteristics of the soil affect chromium fractionation, and (iii) to develop models that allow us to predict the fractionation of this metal in soils.

2. Materials and Methods

2.1. Soil: Sampling and Characterization

The soils used in this article were sampled in northern Spain. Samples were taken from ten forest soils developed over four different parent materials (amphibolite, schist, granite, and limestone), and found in areas not contaminated by metals. The soils were selected based on the parent material, in order to obtain samples with different physical and chemical characteristics. The sampling areas were chosen using geological maps [11]. The sampling was carried out in the surface layer of the soil, using an Edelman probe (between 0 and 20 cm). Each soil sample was subjected to a homogenization process before air drying and sieving: soil particles smaller than 2 mm were used to carry out the experiments.

Taking into account that the ultimate purpose of the article is to analyze the influence of soil properties on chromium fractionation, a characterization of each soil sample was carried out to determine the texture (relative amount of sand, silt and clay), pH (both in H₂O and KCl), the amount of organic matter (OM), dissolved organic carbon (DOC), exchangeable cations (Ca, Mg, K, Na and Al), phosphorus, and different forms of aluminum and iron (crystalline forms, non-crystalline form associated with oxyhydroxides, and forms associated with organic matter). The procedure by which the above parameters have been determined can be consulted in Campillo-Cora et al. [12].

The data obtained for each of these soils is summarized in Tables 1 and 2, adapted from Campillo-Cora et al. [12]. Furthermore, the characteristics of the different parent materials appear in Paz-González et al. [13].

Table 1. Summary of the soil properties used in this study.

	Sand (%)	Silt (%)	Clay (%)	pH	pHK	P (mg kg ⁻¹)	OM (%)	Ca (mg kg ⁻¹)	Mg (mg kg ⁻¹)	K (mg kg ⁻¹)	Na (mg kg ⁻¹)	Al (mg kg ⁻¹)
1	71.1	12.6	16.3	3.96	2.97	18.7	13.6	1.87	1.03	0.14	0.17	4.80
2	61.9	19.0	19.1	4.63	3.80	105.5	14.1	3.40	1.22	0.19	1.59	2.69
3	50.2	24.7	25.1	4.79	4.23	6.5	11.6	1.88	0.39	0.18	0.17	3.19
4	47.3	35.3	17.4	4.85	4.47	2.0	12.0	1.68	0.25	0.06	0.18	0.88
5	68.2	16.2	15.7	4.85	4.24	101.1	11.2	0.38	0.14	0.11	0.05	1.21
6	19.1	67.1	13.8	6.35	5.76	11.7	14.4	21.40	1.21	0.66	0.16	<d.l.
7	20.4	51.9	27.7	7.47	6.85	2.9	14.8	27.76	1.06	0.14	0.11	<d.l.
8	31.5	36.8	31.7	5.04	4.54	3.0	10.0	2.10	0.36	0.29	0.18	1.13
9	45.5	35.1	19.4	4.70	4.32	5.2	19.6	3.30	0.37	0.23	0.26	2.59
10	31.0	45.4	23.7	4.93	4.44	6.2	29.1	3.72	0.44	0.40	0.45	1.86

Adapted from Campillo-Cora et al. [12]. This table includes texture (as percentage of sand, silt and clay), determination of pH in water and KCl, amount of phosphorus, proportion of organic matter (OM), and amount of calcium, magnesium, potassium, sodium and aluminum (in mg kg⁻¹). On the left side are soil ID numbers assigned (randomly) to each soil sample. <d.l., below detection limit.

Table 2. Summary of other soil properties considered in this study.

	FeOM (mg kg ⁻¹)	FeIA (mg kg ⁻¹)	FeC (mg kg ⁻¹)	AlOM (mg kg ⁻¹)	AlIA (mg kg ⁻¹)	AlC (mg kg ⁻¹)
1	799	47	526	1186	225	391
2	2086	<d.l.	544	2937	<d.l.	396
3	4343	2123	17,592	11,440	<d.l.	5037
4	4631	2052	24,556	8993	1141	12,239
5	927	48	588	4239	<d.l.	936
6	907	2555	37,397	3323	5268	<d.l.
7	1531	3670	32,209	1530	2954	<d.l.
8	6567	2161	45,893	10,724	3506	6503
9	5559	2757	50,229	11,027	3787	<d.l.
10	4359	1367	47,501	16,966	7224	<d.l.

Adapted from Campillo-Cora et al. [12]. Table includes amount of iron and aluminum forms associated with organic matter (FeOM and AlOM, respectively), amount of amorphous inorganic iron and aluminum forms (FeIA and AlIA, respectively), and amount of crystalline iron and aluminum forms (FeC and AlC, respectively). On the left side are soil ID numbers assigned (randomly) to each soil sample. <d.l., below detection limit.

2.2. Spiking and Extraction

Each of the 10 soils was contaminated with seven different concentrations of Cr: 2000, 1000, 500, 250, 125, 62.5, 31.25 mg of Cr Kg⁻¹ of soil, plus a control with no Cr added. The concentrations used range from natural values to high concentrations that can occur in soils developed over ultramafic rocks [14]. For this purpose, K₂Cr₂O₇ solutions with different concentrations were added to the air-dried soil samples, until a moisture content between 50–70 % of its field capacity was obtained. A spatula was used to distribute the solution in the soil, mixing manually until a homogeneous paste was obtained. Once the samples were contaminated with chromium, they were incubated for 50–60 days in the dark, at 22 °C.

After incubation, the extraction was not carried out sequentially: one-gram aliquots were taken from each contaminated soil, and a different extractant was used with each aliquot. In other words, a one-step single extraction was performed using three extractants: H₂O, CaCl₂ and DTPA. The composition of each of the extractants, as well as their properties or the changes they induce in the soil, will condition the retention/release of chromium ions.

Water extraction was performed by adding 10 mL of distilled water to 1 g of soil. The resulting mixture was shaken for 2 h on a mechanical shaker at 0.73 g and centrifuged for 15 min (2000 g). The supernatant was filtered through acid-washed paper, and the chromium concentration (H₂O Cr) was determined by atomic absorption spectrophotometry (AAAnalyst 200, PerkinElmer, Boston, MA, USA). The same procedure was repeated with the other two extractants: 10 mL of a 0.01 M CaCl₂ solution (to obtain CaCl₂ Cr) [15], and with a solution composed of DTPA 0.005 M, triethanolamine 0.1 M and CaCl₂ 0.01 M, whose pH was adjusted to 7.3 with HCl 6 M (to obtain DTPA Cr) [16].

2.3. Statistical Analysis

Data obtained from the controls (samples with no amount of Cr added) were used to discuss the natural chromium levels in the soil as a function of the parent material and physicochemical characteristics.

The data obtained from the soil characterization were compared with the results of the extractions, and correlations were sought using Pearson's method. For this purpose, we decided to use the extracted concentrations on a logarithmic scale and to discard those samples where the chromium levels were below the detection limit.

Finally, SPSS software was used to develop multiple regression models to determine the concentration of the different Cr fractions using soil characteristics (parent material, pH, OM content, etc.), as well as the total amount of Cr added (Cr_T). For this purpose, we used the variables that offered the better correlations with each Cr fraction. The backward stepwise regression was employed.

The models created have a predictive purpose but were also made to analyze the effect and weight of the different soil properties. If the models obtained are to be applied for remediation work, it is important to consider that the Cr concentrations are in logarithmic values.

3. Results

3.1. Extraction Results

Table 3 summarizes the results of the Cr fractions extracted from the different soils as a function of the concentrations added. As can be seen, in the case of the controls (0 mg Kg⁻¹ of Cr added), we were able to extract small amounts of this metal only in soils developed from amphibolite and in some of the granitic soils. In amphibolite soils, the presence of this metal in relatively high quantities is frequent [17], while in granitic rocks the quantities that usually appear are lower (between 3 and 22 mg Kg⁻¹) [18], but there is a possibility that the Cr obtained in the extraction has reached the soil by alteration of the rocks and not by contamination. In some works [13] it has been seen that soils developed on amphibolite have a greater amount of iron and manganese oxides, which facilitates the retention of this metal [19]. When analyzing the data of the contaminated soils according to the parent material, we observed that in the soil developed from schist the mobility of Cr (both H₂O, CaCl₂ and DTPA) is higher than in other soils. The behavior of chromium in this soil may be due to the low concentration of phosphorus, an element that causes chromium to precipitate [20]. The type of organic matter present in this soil can also be the cause of the greater mobility of this metal. As happened in the same soil for Zn and Cu [12], there is a large amount of aluminum and iron associated with organic matter, forming soluble organometallic complexes.

Table 3. Results of Cr extraction using H₂O, CaCl₂ and DTPA, as a function of the added concentration, for the ten soils used. The parent material of each soil as also been included in the bottom.

Cr _T mg Kg ⁻¹		H ₂ O Cr (mg Kg ⁻¹)								
2000	<d.l.	<d.l.	1312.33	40.19	517.93	32.15	179.20	147.92	124.39	31.46
1000	<d.l.	<d.l.	407.19	10.74	171.74	<d.l.	32.28	21.49	19.03	11.90
500	<d.l.	<d.l.	135.52	3.17	21.09	<d.l.	14.99	8.51	6.15	7.26
250	<d.l.	<d.l.	33.22	3.40	<d.l.	<d.l.	11.38	3.05	10.16	4.65
125	<d.l.	<d.l.	8.85	6.26	<d.l.	<d.l.	6.31	3.09	11.85	6.56
62.5	<d.l.	<d.l.	1.61	3.47	<d.l.	<d.l.	6.16	6.90	13.74	5.43
31.25	<d.l.	<d.l.	<d.l.	1.47	<d.l.	<d.l.	7.08	10.25	10.43	2.72
0	<d.l.	<d.l.	<d.l.	1.16	6.64	<d.l.	<d.l.	7.58	12.08	4.25
		CaCl ₂ Cr (mg Kg ⁻¹)								
2000	<d.l.	<d.l.	881.21	14.07	195.33	7.12	88.10	39.77	29.94	5.26
1000	<d.l.	<d.l.	210.19	3.07	30.47	<d.l.	4.22	3.63	3.33	1.81
500	<d.l.	<d.l.	66.61	<d.l.	2.00	<d.l.	1.52	0.24	0.33	0.64
250	<d.l.	<d.l.	15.86	<d.l.	<d.l.	<d.l.	0.85	0.35	<d.l.	<d.l.
125	<d.l.	<d.l.	1.45	<d.l.	<d.l.	<d.l.	0.46	<d.l.	<d.l.	<d.l.
62.5	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	0.41	0.66	<d.l.	<d.l.
31.25	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	0.46	0.37	<d.l.	<d.l.
0	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	0.30	<d.l.	<d.l.
		DTPA Cr (mg Kg ⁻¹)								
2000	5.65	5.34	419.98	10.36	170.91	4.35	30.94	22.79	26.26	6.98
1000	4.14	3.10	154.53	4.20	51.18	0.53	1.69	4.99	4.91	2.89
500	2.83	2.90	51.85	2.40	11.30	<d.l.	0.07	1.31	1.42	1.52
250	1.07	1.63	18.07	1.10	2.34	<d.l.	<d.l.	0.61	0.19	0.53
125	0.37	0.34	4.83	<d.l.	0.20	<d.l.	<d.l.	<d.l.	<d.l.	0.10
62.5	<d.l.	<d.l.	0.53	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	0.95
31.25	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	0.75
0	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	0.56
Parent material	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10
	Gra.	Gra.	Sch.	Amp.	Gra.	Lim.	Lim.	Amp.	Amp.	Amp.

Cr_T is the total amount of Cr added to the soil, Gra. granite, Sch. schist, Amp. amphibolite, and Lim. limestone. # indicates the number of the soil (randomly assigned and used for easy identification). <d.l., below detection limit.

On the contrary, in two of the granite soils studied (#1 and #2) no Cr concentration was extracted with water or with CaCl_2 , and extraction with DTPA was minimal. If we exclude the schist soil, the rest of the soils showed quite a lot of variability independently of the parent material, so it seems that this factor does not condition the retention too much (or that there are other factors that have more weight).

If we compare the results obtained with the different extractants, the amounts of Cr extracted with water are much higher than those obtained with CaCl_2 or DTPA. For example, in soil #8 we obtained 7.58 mg Kg^{-1} of $\text{H}_2\text{O Cr}$, whereas we are only able to extract 0.3 mg Kg^{-1} of $\text{CaCl}_2 \text{ Cr}$ (about 25 times less). This trend is maintained if we compare the data of the samples that have been subjected to a spiking process: the extraction of $\text{H}_2\text{O Cr}$ is between 1.5 and 35.5 times higher than the extraction of $\text{CaCl}_2 \text{ Cr}$; and it is between 1.3 and 227.7 times higher than the extraction of DTPA Cr (if soils #1 and #2 are not considered). These results differ from those obtained for other metals (Ni, Zn, Cu and Pb), using the same soils and the same procedure [12]. However, these metals are in solution in cationic form, whereas chromium use to remain as chromate and dichromate anions. These ions precipitate easily in the presence of metal cations [21], which could explain the difference between H_2O and CaCl_2 extraction. As for DTPA, its low efficiency as an extractant (compared to CaCl_2 and EDTA) has already been observed in previous works [22,23], and can be explained by the difference in pH between the extractants: DTPA has a pH adjusted to 7.2, slightly higher than the other two extractants, which causes $\text{Cr}_2\text{O}_7^{2-}$ ions to precipitate [24].

3.2. Relationships between Chromium Fractionation and Soil Properties

When analyzing the correlations obtained between chromium fractions and soil properties, it is important to bear in mind that the extraction values are on a logarithmic scale and that the degrees of freedom depend on the fraction considered (since we have discarded the data where the amount of chromium extracted was below the detection limit).

$\text{CaCl}_2 \text{ Cr}$ fraction is the one that offers the higher correlation values with soil properties. This fraction seems to be strongly conditioned by the soil texture, as it shows significant correlations with the percentage of sand ($R = 0.48$), silt ($R = -0.415$), and clay ($R = -0.362$). Sand has a low specific surface area, so its retention capacity will be lower (compared to materials of smaller diameter such as silts or clays). However, it also tends to have a higher isoelectric point than silts and clays (slightly less acidic), so at the pH at which the soil is found (between 4.5 and 7.5), it will have a higher proportion of positive charges, which will reduce electrostatic repulsion and favor the retention of anions such as dichromate [25]. Good correlations have also been found between this Cr fraction (CaCl_2) and the crystalline forms of iron ($R = -0.509$), and the non-crystalline forms of aluminum ($R = -0.470$). Cr(VI) is usually adsorbed to crystalline forms of Fe [26,27], and its desorption can rapidly occur (in both acid and basic soils). Amorphous forms of aluminum are also important chromium sorbents [28], and nanocomposites of this material have been developed to treat waters contaminated with hexavalent chromium [29]. Finally, $\text{CaCl}_2 \text{ Cr}$ is also related to the amount of exchangeable aluminum ($R = 0.388$). This may be indirectly caused by pH: both Cr(VI) and Al are more soluble as pH increases [30], so it is common for certain crops to show simultaneous stress to both metals.

Some (non-significant) trends were observed between DTPA Cr and texture parameters (amount of sand and silt) and basic cations (Ca, Na, K and Mg). However, there is only a really significant relationship with the amount of amorphous aluminum ($R = -0.348$), which as mentioned in the previous paragraph, is able to adsorb Cr(VI). On the other hand, $\text{H}_2\text{O Cr}$ offers a significant correlation with the amount of crystalline forms of Fe ($R = -0.291$). This shows the same sign as in the case of $\text{CaCl}_2 \text{ Cr}$ and can be explained by the same reason. In addition, the amount of $\text{H}_2\text{O Cr}$ also correlates significantly with the amount of phosphorus ($R = -0.298$). Ding et al. [20] pointed out that phosphorus can form stable precipitates with Cr, which would cause a decrease of its concentration in suspension.

3.3. Model Development

For the model development we tried to use all the data (considering all metal concentrations and all soils), but for H₂O Cr we had to reduce it to 50 values, those in which the extracted chromium was above the detection limits and, therefore, could present toxicity problems associated. We obtained a model (Equation (1)) with an adjusted R² of 0.8097 (*F*-value = 25.597, sig. = 0.000) (Figure 1).

$$\begin{aligned} \text{Ln H}_2\text{O Cr} = & (3.235 \pm 0.659) & + (0.002 \pm 0.000) & + (25.462 \pm 8.621) & + (1.017 \pm 0.231) \\ & (p < 0.010) & (p < 0.010) & (p < 0.010) & (p < 0.010) \\ & - (1.114 \pm 0.247) & - (0.244 \pm 0.085) & - (0.038 \pm 0.018) & \\ & \text{Amphibolite} & \text{P} & \text{Sand} & \\ & (p < 0.010) & (p < 0.010) & (p = 0.039) & \end{aligned} \quad (1)$$

where Ln H₂O Cr is the natural logarithm of the water extracted chromium concentration, Cr_T is the Cr concentration added to the soil (in mg Kg⁻¹), Amphibolite and Granite are dummy variables for the parent materials, Al is the amount of exchangeable aluminum (in mg Kg⁻¹), P is the amount of available phosphorus (in mg Kg⁻¹), and Sand is the amount of sand (in percentage).

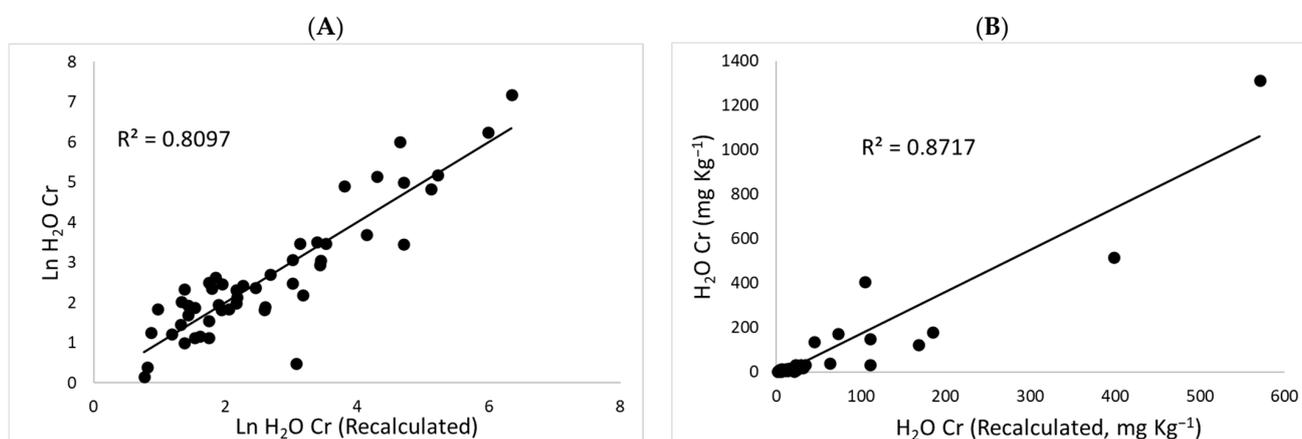


Figure 1. Goodness of fit for measured and recalculated fractions of H₂O Cr in (A) logarithmic scale and in (B) mg of Cr Kg⁻¹ of soil.

When modeling any chromium fraction (H₂O, CaCl₂ or DTPA) it is essential to include in the models the amount of chromium added (Cr_T). This is because the same amount of soil (1 g) is always used, and the soil has a limited capacity to store chromium, so the higher the amount of chromium added, the more chromium will be obtained with the different extractants. Exchangeable aluminum is not significantly related to H₂O Cr, but as mentioned above it has a similar behavior to Cr(VI), so both metals will react in a similar way to the soil properties. As for phosphorus, this negative relationship is observed with the amount of H₂O Cr since it is an element with which it can precipitate. Regarding the parent material, in all amphibolite soils we were able to extract a small amount of H₂O Cr, which indicates that this soil can retain quite a lot, but always leaving a small soluble part. According to a previous work [13], the amphibolite soils of the area have a lot of manganese and iron oxides, which may favor this retention [19]. Whereas, in the case of granite, this parent material seems to easily store Cr, except when the concentrations are high. In addition, this is what we see in Equation 1 (it should be remembered that samples with Cr below the detection limit have not been considered for the model development). Finally, sand seems to present a contradictory behavior, since, in theory, it is clays and silts that favor the immobilization of Cr, so we think that this is an effect caused by the relationship between sand and pH. There is a correlation between both variables (*R* = −0.781), which indicates that soils with low amount of sand have basic pHs, so that the solubility of Cr(VI) would increase. The pH was not introduced in the model development to avoid

collinearity. Moreover, it may also be a question of charge: in the previous section it was mentioned that at the pHs of the soils considered, sand has a higher isoelectric point and a higher proportion of positive charges that will favor the retention of anionic forms of chromium [25].

For the development of the CaCl_2 Cr model we used 31 sample values, and obtained a model (Equation (2)) with an adjusted R^2 of 0.8471 (F -value = 49.871, sig. = 0.000) (Figure 2).

$$\begin{aligned} \text{Ln CaCl}_2 \text{ Cr} = & -(1.923 \pm 0.479) & +(0.002 \pm 0.000) & +(2.858 \pm 0.498) \\ & (p < 0.010) & \text{Cr}_T & \text{Schist} \\ & +(0.025 \pm 0.013) & (p < 0.010) & (p < 0.010) \\ & \text{Sand} & & \\ & (p = 0.059) & & \end{aligned} \quad (2)$$

where Ln CaCl_2 Cr is the natural logarithm of the CaCl_2 extracted chromium concentration, Cr_T is the Cr concentration added to the soil (in mg Kg^{-1}), Schist is a dummy variable for the parent material, and Sand is the amount of sand (in percentage).

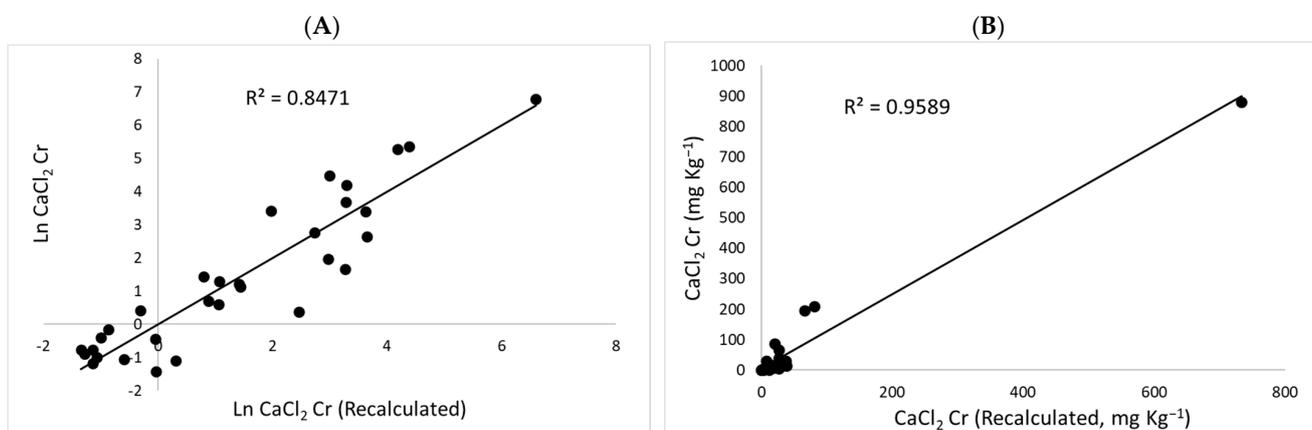


Figure 2. Goodness of fit for measured and recalculated fractions of CaCl_2 Cr in (A) logarithmic scale and in (B) mg Cr Kg^{-1} of soil.

In the CaCl_2 Cr model, the Cr_T is once again included, and the explanation is the same as that considered for the H_2O Cr. However, in this case a different parent material is introduced, schist, and the sand appears again but with another sign. Soil developed on schist seems to have difficulties in retaining chromium, and this may be the reason we could not find chromium in natural samples (Table 3). This can be caused by the low concentration of phosphorus in this soil (four times less than the average in other soils), an element that can cause chromium to precipitate, or it may also be due to the type of organic matter present: in this soil there are large amounts of iron and aluminum associated with organic matter. It can be concluded that the organic matter of this soil can easily form organometallic complexes that favor the solubility of the chromium, as observed in a previous article for Zn or Cu [12]. Finally, sand, as mentioned above, with its low specific surface area will difficult the retention and favor the passage of chromium to the soil solution [28].

The number of data used for the DTPA Cr model (Equation (3)) was 46, and we obtained an R^2 of 0.7509 (F -value = 11.739, sig. = 0.000) (Figure 3).

$$\begin{aligned} \text{Ln DTPA Cr} = & +(0.892 \pm 0.465) & +(0.002 \pm 0.000) & +(2.19 \pm 0.460) \\ & (p = 0.06) & \text{Cr}_T & \text{Schist} \\ & -(0.034 \pm 0.011) & (p < 0.010) & (p < 0.010) \\ & \text{Silt} & -(1.089 \pm 0.402) & \\ & (p < 0.010) & \text{Mg} & \\ & & (p < 0.010) & \end{aligned} \quad (3)$$

where \ln DTPA Cr is the natural logarithm of the DTPA extracted chromium concentration, Cr_T is the Cr concentration added to the soil (in $mg\ Kg^{-1}$), Schist is a dummy variable for the parent material, Silt is the amount of silt (in percentage), and Mg is the amount of exchangeable magnesium (in $mg\ Kg^{-1}$).

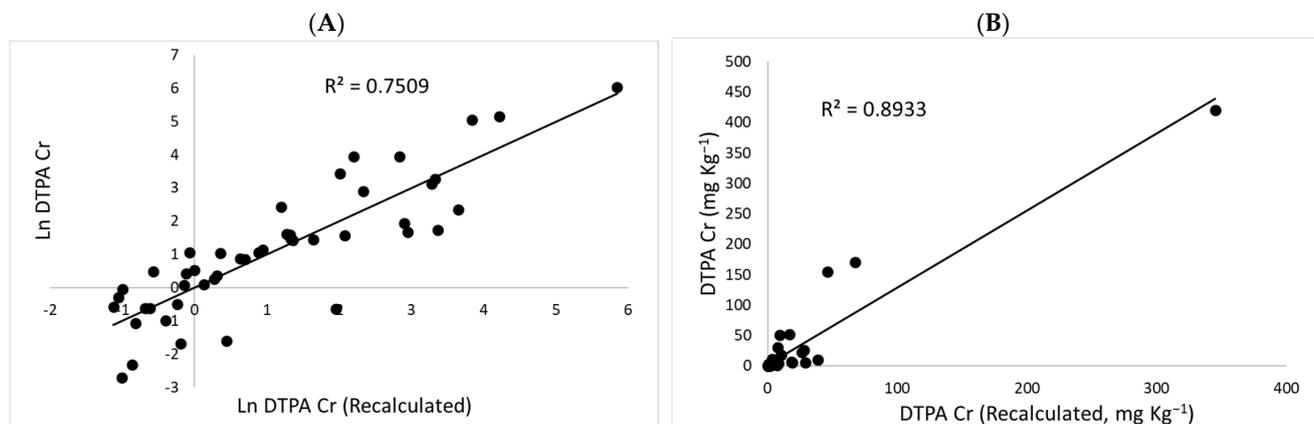


Figure 3. Goodness of fit for measured and recalculated fractions of DTPA Cr in (A) logarithmic scale and in (B) $mg\ Cr\ Kg^{-1}$ of soil.

In addition to the amount of Cr_T and schist as parent material (as in the case of $CaCl_2\ Cr$), the DTPA Cr model is influenced by the amount of silt and by the amount of exchangeable magnesium. Silt particles seem to be able to retain chromium even when an extractant such as DTPA is used. The three fractions show the same trends (or correlations) with the particles that determine soil texture: positive for the amount of sand, and negative for the amounts of silt and clays. This is related both to the specific surface area, and to the lower presence of positive charges that clays and silts have at the pHs of these soils. Finally, regarding the magnesium, the concentration of the four exchange bases (Ca, Mg, Na and K), as well as the cation exchange capacity, show a negative trend when compared to the amount of $CaCl_2$ or DPTA Cr extracted. This indicates that soils with a higher cation exchange capacity are more efficient when adsorbing Cr(III), a form of chromium reduced by the presence of organic matter [31].

4. Conclusions

The behavior of chromium in soils is very complex, since this element presents various oxidation states and has the capacity to easily pass from one to another. Throughout this article, we tried to determine how soil properties and parent material affect the fractionation of Cr, using samples of forest soils and three extractants: H_2O , $CaCl_2$ and DTPA. Water was the most efficient Cr extractant, followed by $CaCl_2$ and DTPA.

The three models developed (one for each Cr fraction) included the amount of total chromium added to the soil as a predictor variable. This variable presented a similar weight in all models. In the case of $H_2O\ Cr$, an adjusted R^2 of 0.8097 was obtained using, as predictive variables, the amount of total chromium added to the soil, two parent materials (granite and amphibolite), the percentage of sand and the amount of exchangeable aluminum and bioavailable phosphorus. The model obtained for $CaCl_2\ Cr$ presented an adjusted R^2 of 0.8471, and it was only necessary to include, in addition to the total amount of Cr added, the schist and the percentage of sand. The model obtained for DTPA Cr (adjusted R^2 of 0.7509) is very similar to the one obtained for $CaCl_2\ Cr$, but instead of sand percentage, the amount of magnesium and silt influenced the retention of this fraction.

Author Contributions: Conceptualization, M.A.-E.; methodology, D.F.-C.; formal analysis, C.C.-C., D.S.-G. and D.F.-C.; investigation, D.S.-G. and D.F.-C.; writing—original draft preparation, C.C.-C. and D.S.-G.; writing—review and editing, D.S.-G., D.F.-C. and L.R.-G.; funding acquisition, M.A.-E.,

and D.F.-C.; data curation: D.S.-G., C.C.-C. and L.R.-G.; supervision: M.A.-E. and D.F.-C.; project administration: D.F.-C. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Spanish Ministry of Economy and Competitiveness through the project CTM2015-73422-JIN. It was also supported by Xunta de Galicia via funding for research groups (ED431C 2017/62-GRC). D. Fernández-Calviño holds a Ramón y Cajal contract (Ministry of Economy, Industry and Competitiveness). Claudia Campillo-Cora holds a Predoctoral fellowship financed by Xunta de Galicia (ED481A-2020/084). Diego Soto Gómez was supported by a Postdoctoral fellowship from the Spanish Ministry of Education “Juan de la Cierva Formación: FJC2019-039176-I”.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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