

## Retention and Transport of Hexavalent Chromium in Calcareous Karst Soils

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**Abstract:** Hexavalent chromium, which is a highly toxic and soluble form of the element chromium, is a common soil and groundwater contaminant found in many contaminated sites throughout the world and poses a serious risk to human health when released into environment. The objective of this study was to determine transport and retention behaviour of aqueous Cr(VI) species in a highly calcareous and alkaline top soil of a karst system that is vulnerable to contamination. Batch sorption studies and column experiments conducted at both saturated and unsaturated steady-state flow conditions were used to evaluate the sorption/desorption and the transport of Cr(VI) in the alkaline soil conditions. The results of batch experiments indicated that Cr(VI) sorption was linear up to 200 mg L<sup>-1</sup> of Cr(VI) initial concentration. K<sub>d</sub> values obtained from both batch and column studies showed that Cr(VI) sorption was relatively low. The average K<sub>d</sub> value obtained from batch studies (0.53 L Kg<sup>-1</sup>) was about six times higher than the average K<sub>d</sub> value (0.09 L Kg<sup>-1</sup>) obtained from column studies. The results of the column experiments showed that transport of Cr(VI) was slightly retarded compared to non-reactive tracer at both saturated and unsaturated flow conditions. Extraction studies conducted on the soil columns also revealed that Cr(VI) oxyanions (dominantly CrO<sub>4</sub><sup>-2</sup>, HCrO<sub>4</sub><sup>-</sup>) were only temporarily retained by adsorption to easily exchangeable sorption sites in the soil and the sorption was reversible. Low retardation factors and K<sub>d</sub> values obtained from column experiments suggest that Cr(VI) species are very mobile and bioavailable in highly calcareous soil conditions. This increases the spreading of contamination in such contaminated systems with Cr(VI) and contamination risk of groundwater resources. However, if the bioavailability is a key factor for remediating Cr(VI) contaminated soil, as in phytoremediation, increased availability of Cr(VI) for plant uptake in calcareous soil will enhance its removal.

**Key Words:** Hexavalent chromium, calcareous soil, sorption, desorption, solute transport, heavy metal, contamination, column experiment

### Karbonatlı Karst Topraklarda Hekzavalent Krom'un Taşınımı ve Tutunumu

**Özet:** Krom'un yüksek derecede zehirli (toksikiteli) ve çözünürlüklü bir türü olan krom(VI), dünyada birçok kirlenmiş sahada yaygın olarak bulunan toprak ve yeraltı suyu kirleticisidir; çevreye bırakıldığında insan sağlığı için ciddi bir risk teşkil etmektedir. Bu çalışmanın amacı, kirlenme riski yüksek bir karst akifer sistemi üzerindeki yüksek miktarda karbonat içeren alkali örtü toprağında Cr(VI) türlerinin taşınma ve tutunma davranışlarını belirlemektir. Statik tutunma (sorpsiyon) deneyleri ve ayrıca doygun ve doygun olmayan duraylı akım koşullarında gerçekleştirilmiş kolon deneyleri, alkali toprak koşullarında Cr(VI)'nin tutunma, geri bırakma (desorpsiyon) ve taşınımını değerlendirmede kullanılmışlardır. Statik tutunma deneylerinin sonuçları krom(VI)'nin sorpsiyonunun 200 mg L<sup>-1</sup> Cr(VI) başlangıç konsantrasyonuna kadar doğrusal olduğunu göstermiştir. Statik tutunma ve kolon deneylerinden elde edilen K<sub>d</sub> değerleri Cr(VI) sorpsiyonunun oldukça düşük olduğunu göstermiştir. Statik tutunma deneylerinden hesaplanan ortalama K<sub>d</sub> değeri (0.53 L Kg<sup>-1</sup>) kolon deneylerinden elde edilen ortalama K<sub>d</sub> değerinden (0.09 L Kg<sup>-1</sup>) altı kat daha büyüktür. Kolon deneylerinin sonuçları hem doygun hem de doygun olmayan akım koşullarında, krom(VI)'nin tepkili (reaktif) olmayan klora göre göreceli taşınımının çok az derece gecikmeye uğradığını göstermiştir. Kolon toprakları üzerinde gerçekleştirilen katı-sıvı ayırma (ekstraksiyon) çalışmaları, Cr(VI) anyonlarının (baskın olarak CrO<sub>4</sub><sup>-2</sup>, HCrO<sub>4</sub><sup>-</sup>) topraktaki kolayca değişebilen tutunma yüzeylerine geri bırakmayla geçici olarak tutunduklarını ve tutunmanın tersinir olduğunu ayrıca ortaya koymuştur. Kolon deneylerinden elde edilen düşük geçirme (reterdasyon) katsayıları ve K<sub>d</sub> değerleri, Cr(VI) türlerinin yüksek oranda karbonat içeren toprak koşullarında çok hareketli (mobil) ve biyolojik alım için oldukça elverişli olduklarını önermektedir. Bu durum krom(VI) ile kirlenmiş benzer topraklarda kirlenmenin yayılmasını ve yeraltı suyu kaynaklarını kirletme riskini artırmaktadır. Ancak, biyolojik alım için elverişli olmak, fitoyileştirmede (fitoremediyasyonda) olduğu gibi, krom (VI) ile kirlenmiş toprakların temizlenip eski haline dönüştürülmesi için önemli bir etken ise bitki alımı için Cr(VI) elverişliliğinin artması Cr(VI)'nin topraktan uzaklaştırılmasını hızlandıracaktır.

**Anahtar Sözcükler:** Hekzavalent krom, karbonatlı toprak, sorpsiyon, desorpsiyon, taşınım, ağır metal, kirlilik, kolon deneyi

## Introduction

Chromium is a ubiquitous contaminant of soils and groundwater and is derived from both natural and anthropogenic sources (Françoise & Alain 1991). Chromium is released into the environment primarily through its widespread use in industrial processes, including ore refining, production of steel and alloys, pigment manufacture, plating metal, corrosion inhibition, leather tanning, wood preservation, and combustion of coal and oil (Adriano 2001; Papp 2001).

In the environment, chromium is commonly found in two most stable oxidation states as Cr(III) and Cr(VI), each characterized by distinctly different chemical properties, bioavailability, and toxicity. Trivalent chromium is an essential element for living beings, relatively insoluble, and strongly partitioned into the solid phases, while hexavalent chromium is very toxic, carcinogenic, and mutagenic to both animals and humans and may cause liver and kidney damage and internal respiratory problems (Doisy *et al.* 1976; Yassi & Nieboer 1988; USDH 1991; Fendorf 1995). Due to its high solubility and adverse health effects, Cr(VI) poses a significant environmental hazard. Hence, Cr(VI) contamination of soil and groundwater is considered a major environmental concern.

The concentration, transport, and toxicity of Cr(VI) in the soils and groundwater are controlled by numerous mechanisms including transformation reactions (i.e., chemical or biological reduction), sorption, precipitation, or various combinations of these processes. These processes are governed by many factors including soil composition (electron donor availability, soil texture, soil mineralogy, competing ions, adsorption capabilities, etc.) and conditions in the soil (pH, Eh, moisture content, and the presence of vegetation) (Zachara *et al.* 1989; Hanson *et al.* 1993; James 1994; Milacic & Stupar 1995; Chen & Hao 1996; Banks *et al.* 2006).

Hexavalent chromium (i.e., chromate) sorption by soils is a multifaceted phenomenon due to the presence of many soil components (i.e., clays, Fe, Mn oxides and hydroxides, organic matter, carbonate, etc.), their unique surface configuration, the multicomponent nature of solute and soil interactions, and potential reduction of Cr(VI) to Cr(III), with subsequent precipitation or sorption of Cr(III) species (Eary & Rai 1991; Echeverria *et al.* 1999). Due to its anionic nature, Cr(VI) is strongly

adsorbed by clays and iron and manganese oxides and hydroxides, favourably in acidic media due to increase in positively charged sorption sites at mineral surfaces (Bartlett & Kimble 1976; Zachara *et al.* 1987, 1988, 1989; Aide & Cummings 1997). Retention of Cr(VI) species ( $\text{CrO}_4^{-2}$ ,  $\text{HCrO}_4^-$ ,  $\text{Cr}_2\text{O}_7^{-2}$ ) in these environments decreases with increasing pH, therefore these anionic species are weakly sorbed into soils under alkaline to neutral conditions (Wittbrodt & Palmer 1995), resulting in increased mobility in the subsurface, especially in the presence of other competing anions such as  $\text{SO}_4^{-2}$ ,  $\text{H}_4\text{SiO}_4$ ,  $\text{HCO}_3^-$ , and  $\text{PO}_4^{-2}$  (Bartlett & Kimble 1976; Zachara *et al.* 1987, 1989; Avundainayagam *et al.* 2001; Banks *et al.* 2006). On the other hand, the presence of competing cations in the soils may increase Cr(VI) sorption. In alkaline soil, the presence of  $\text{Ca}^{+2}$  in the system favours greater retention and lesser mobility of Cr(VI) compared to water (Avundainayagam *et al.* 2001). Cd, Ni, Zn, and especially Cu, also favour the sorption of Cr(VI) in calcareous soils (Echeverria *et al.* 1999). Cr(VI) sorption by manganese dioxide in aqueous solution is increased in the presence of cations such as Cd, Pb, and Ni by the accumulation of positive surface charges that attract anions more effectively (Bhutani *et al.* 1992).

Although retention and transport behaviour of Cr(VI) is well-characterized in the presence of Fe, Mn, and Al oxides and hydroxides as well as organic matter in the soils, the effect of the carbonate fraction on the sorption of Cr(VI) species in soil, with limited presence of aforementioned phases, has merited less attention. Liming the soil to pH 7 or higher is the common practice for remediation of heavy metals (i.e., Pb, Cu, Cd, etc.) in contaminated soils via stabilization method. However, there is also limited understanding of the effect of liming on the retention and transport behaviour of transition metals such as chromium whose toxicity and mobility depend on its speciation in the environment (Bolon & Thiagarajan 2001). In Turkey, approximately 80% of the soils have a pH greater than 7, and 11% of Turkish soils have lime contents greater than 25% (DPT 2001). Soils enriched with carbonates often exist as a cover soil layer over karst bedrock, which may have great potential for groundwater resources. Understanding of Cr(VI) retention and leaching characteristics in such soil conditions is critical for assessing the risk associated with groundwater contamination. The objective of this study is to determine the sorption and transport behaviours of

Cr(VI) species in a highly calcareous and alkaline soil under variably saturated flow conditions through a series of batch and column studies.

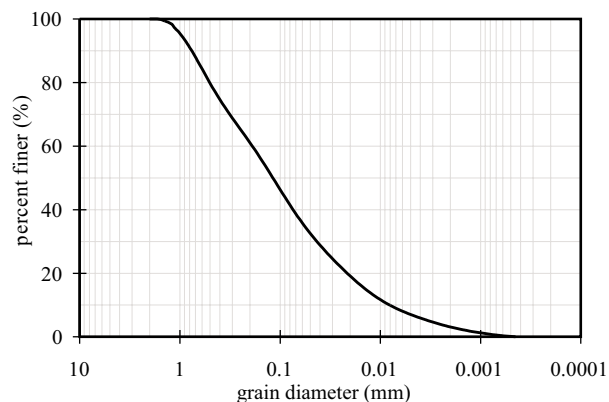
## Materials and Methods

### Soil

The porous medium used in all experiments was a calcareous soil collected from a karstic travertine plateau near Antalya located along the Turkish Mediterranean coast. Samples that are representative of the weathered form of limestone were taken at depths of 10–50 cm from the cover of travertine. Homogenized soil samples were dried at 105 °C for 48 hours and sieved before batch and column experiments. The soil fraction less than 2 mm grain diameter was used in all experiments. Relevant physical and chemical characteristics of the soil are summarized in Table 1. The soil was poorly-sorted sandy loam with a mean particle diameter of 118 µm (Figure 1). Chemical analysis of the soil indicates that it has an alkaline character (pH of 8.4) and contains relatively large amounts of calcium carbonate (73%), medium organic carbon content (0.94%) and very little chromium as Cr(III) (6.61 mg/kg).

**Table 1.** Physical and chemical properties of calcareous soil used in column and batch experiments.

particle-size distribution, % (w/w)	
sand	67.39
silt	29.5
clay	3.11
texture	Sandy loam
mean grain diameter, $d_{50}$ (µm)	118.21
coefficient of uniformity, $C_u$	23.64
bulk density $_{\text{disturbed}} \rho_b$ (g/cm <sup>3</sup> )	1.25
specific surface area, m <sup>2</sup> /g	0.383
soil chemical composition	
pH $_{\text{deionized}(1:1)}$	8.37
TOC (%)	0.97
TIC (as CaCO <sub>3</sub> ) (%)	73
Cr(III) (ppm)	6.61
Mn (ppm)	50
Fe (%)	0.24
Ca (%)	33.6
Mg (%)	0.32
Na (%)	0.01
K (%)	0.03
Al (%)	0.23
S (%)	0.24



**Figure 1.** Particle-size distribution of calcareous soil.

### Solutions

A 5 mM solution of CaCl<sub>2</sub>·2H<sub>2</sub>O (Mol Wt. 147.02, Riedel-Dehaën) was used as a background electrolyte solution in column experiments, so avoiding colloid mobilization in the eluted fractions. All solutions used in batch and column experiments were prepared in background electrolyte solution. Aqueous chromate [Cr(VI)] solutions were prepared from reagent-grade K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (Mol. Wt. 294.19; Sigma Chemical Co.) and used as reactive tracer in the experiments. A 100 mM solution of chloride as CaCl<sub>2</sub> was used as non-reactive tracer to assess the hydrodynamic characteristics of the packed columns. Chemical compositions of solutions used in the experiments are shown in Table 2. All system components (tubing, filters, column etc.) and glassware used in the experiments were acid-washed and then rinsed with deionized water prior to each experiment.

### Batch Sorption Experiments

Batch experiments were performed at 20 °C (±2) to determine the sorption capacity of the soil with respect to Cr(VI) contamination and also to quantify the sorption affinity of Cr(VI) to the calcareous soil under equilibrium conditions, in the absence of physical transport processes. Five grams of soil samples were weighed into 50 ml polyethylene centrifuge vials, to which were added 25 ml of aliquots of chromium solution containing 0.0, 0.1, 0.5, 1.0, 2.0, 5.0, 10, 50, 100 and 200 mg/L of Cr(VI). Similarly, a set of soil-free vials were also prepared as a control to account for Cr(VI) losses in the absence of porous media during experiment. The vials were

Table 2. Chemical composition of solutions used in the experiments.

solution	EC(dS/m) at 25 °C	pH	Ca <sup>+2</sup> (mmol L <sup>-1</sup> )	K <sup>+</sup> (mmol L <sup>-1</sup> )	Cl <sup>-</sup> (mmol L <sup>-1</sup> )	Cr(VI) mg L <sup>-1</sup>
background electrolyte	1.22	7	5	–	10	–
non-reactive tracer	8.91	7	50	–	100	–
chromate	1.22	7	5	0.019	10	1
			5	0.19	10	10
			5	1.92	10	100

prepared in triplicate at each concentration. Sample vials were shaken at reciprocal shaker (150 rpm) for 48 hours, which was a sufficient time to reach equilibrium based on previous batch studies. After achieving sorption equilibrium, vials were centrifuged at 6000 rpm for 30 minutes. The supernatants were then filtered through 0.45 µm pore size cellulose acetate membrane (Whatman) for the analysis of Cr(VI) described later. The adsorbed concentration of Cr(VI) was calculated by subtracting the equilibrium concentration from initial aqueous concentration taking into account a 1:5 soil-water ratio. Average concentration of Cr(VI) at both equilibrium and sorbed phases was then calculated within a 95% confidence interval.

**Miscible Displacement Experiments**

Miscible displacement experiments were both conducted with a non-reactive tracer (Cl) to characterize the hydrodynamic properties of the packed media and were performed with Cr(VI) to evaluate the degree of Cr(VI) retention and transport in the calcareous soil. Miscible displacement experiments were conducted at both saturated and unsaturated steady-state flow conditions under a range of flow rates and Cr(VI) initial concentrations. Pertinent characteristics of these experiments are provided in Table 3. The column was made of PVC, 3 cm in inner diameter and 13.5 cm long, and closed at both ends with threaded PVC caps. For unsaturated column experiments, membranes with pore

Table 3. Experimental conditions used in the column experiments and the results of temporal moment analysis.

Column Experiments	Q	θ <sub>v</sub>	n	ρ <sub>b</sub>	PV	t <sub>0</sub>	v	RT	R <sub>moment</sub>	K <sub>d</sub>	Input mass recovery
	cm <sup>3</sup> /min	cm <sup>3</sup> /cm <sup>3</sup>	cm <sup>3</sup> /cm <sup>3</sup>	g/cm <sup>3</sup>	cm <sup>3</sup>	hr	cm/hr	hr	[–]	L/Kg	%
<b>saturated</b>											
Cl tracer	0.8	0.58	0.58	1.28	55	24.03	11.78	1.04	1	0	98.46
1 mg/L Cr(VI)	0.8	0.58	0.58	1.28	55	24.03	11.78	1.39	1.34	0.15	97.10
10 mg/L Cr(VI)	0.8	0.58	0.58	1.28	55	24.86	11.78	1.30	1.25	0.11	97.56
Cl tracer (repeat)	0.8	0.59	0.59	1.26	56	23.76	11.57	1.22	1	0	100.6
100 mg/L Cr(VI)	0.8	0.59	0.59	1.26	56	23.76	11.57	1.27	1.04	0.02	97.88
<b>unsaturated</b>											
Cl tracer	0.8	0.52	0.60	1.25	50	6.13	12.96	1.12	1	0	99.5
1 mg/L Cr(VI)	0.8	0.53	0.60	1.25	51	17.87	12.71	1.45	1.29	0.12	97.95
1 mg/L Cr(VI)*	0.8	0.54	0.60	1.25	52	6.08	12.46	–	–	–	–
Cl tracer	0.08	0.53	0.59	1.26	51	47.92	1.24	9.29	0.85	0	98.7
1 mg/L Cr(VI)	0.08	0.53	0.59	1.26	51	47.92	1.24	12.43	1.34	0.14	94.9
1 mg/L Cr(VI)*	0.08	0.53	0.59	1.26	51	44.33	1.24	–	–	–	–
Cl tracer	0.08	0.51	0.59	1.26	49	47.58	1.32	7.88	0.77	0	99.93
100 mg/L Cr(VI)	0.08	0.51	0.59	1.26	49	47.58	1.32	8.41	1.07	0.03	101.39
100 mg/L Cr(VI)*	0.08	0.50	0.59	1.26	48	144.11	1.32	–	–	–	–

Q— flow rate, θ<sub>v</sub>— average volumetric water content, n— porosity, ρ<sub>b</sub>— bulk density, PV— pore volume, t<sub>0</sub>— injection duration, v— average pore-water velocity, RT— solute residence time, R<sub>moment</sub>— retardation factor calculated from temporal moment analysis, K<sub>d</sub>— distribution coefficient. \* represents the column experiments that were terminated after breakthrough of Cr(VI) to determine the Cr(VI) distribution in soil fractions.

diameters of 38  $\mu\text{m}$  and 5  $\mu\text{m}$  were placed at the top and bottom ends of the column, respectively, to provide support for the packed media and to attain the boundary conditions imposed on the column. For saturated column experiments, both ends of the column contained 5  $\mu\text{m}$  pore size membrane filters. The column inlet was connected to a peristaltic pump (ATTO Corp., JA) using teflon tubing with a two-way valve to switch between background electrolyte and Cr(VI) solutions.

The columns were uniformly packed with soil in incremental steps to a dry bulk density of  $1.25 \text{ g cm}^{-3}$  and average porosity of  $0.6 \text{ cm}^3 \text{ cm}^{-3}$ . The columns were then saturated from the bottom with electrolyte solution at a flow rate of  $0.8 \text{ ml min}^{-1}$  to reduce the entrapped air in the column.

For saturated experiments, after achieving column saturation, a pulse of non-reactive tracer (Cl) or Cr(VI) solution was introduced into the system from the bottom until effluent (outlet) concentration of solute (C) reached the inlet concentration ( $C_0$ ). Following completion of the non-reactive tracer or Cr(VI) pulse, the column was flushed with background electrolyte to elute the tracer or Cr(VI) solution from the system. Effluent samples were collected periodically during each experiment and analyzed immediately after sampling for the solute of interest [Cl or Cr(VI)]. The experiments were terminated after effluent reached background concentrations. Saturated column experiments were conducted with initial Cr(VI) concentrations ( $C_0$ ) of 1, 10, and  $100 \text{ mg L}^{-1}$  at an average pore-water velocity of  $11.5 \text{ cm h}^{-1}$  (Table 3). Cr(VI) injection concentrations were selected from the range over which sorption was linear based on the results of batch studies.

The experimental setup for the unsaturated column experiments has some differences from the saturated experiments. Unsaturated displacement studies were conducted using a modified laboratory apparatus described by Rambow & Lennartz (1993). The design of the column setup was illustrated in Figure 2. Experimental setup consists of a packed column, peristaltic pump, vacuum chamber, separating funnel, manometer, vacuum pump and regulator. The top cap of the column had a small venting hole to keep the soil surface at atmospheric pressure. The outlet of the column was connected to the vacuum chamber and separating funnel, both of which were kept under suction sequentially during the experiment. The vacuum

chamber, which also serves as an outlet reservoir, was used to establish a constant head boundary for water flow at the bottom of the column and to achieve stable soil water contents for given flow rates. A separating funnel was used for sampling effluent. To maintain the boundary conditions at the column outlet during sampling, two segments of three-way valves were placed in lines between the column outlet and the vacuum pump. One of them was used to switch the flow direction of effluent between the separating funnel and vacuum chamber, while the other was used to divert the vacuum applied between the two simultaneously. During the sampling event, a vacuum was only applied to the separating funnel. For other times, a vacuum was applied to the column outlet through the vacuum chamber; this gave an opportunity to take the sample accumulated in the separating funnel and clean the reservoir prior to subsequent sampling.

For unsaturated experiments, once the column reached water saturation from bottom, the inlet solution line was switched to the top of the column and the column drained by applying suction at the lower end of the column through the vacuum chamber, while the soil surface was kept under atmospheric pressure. Steady-state unsaturated flow conditions were accomplished by adjusting flow rates and suction until the specified water content was reached in the column. The lowest water saturation that could be achieved in the sandy loam was about eighty percent for the given flow rates (i.e.,  $Q = 0.08$  and  $0.8 \text{ cm}^3 \text{ min}^{-1}$ ) under steady-state flow conditions. This ratio was kept similar in all unsaturated transport experiments. After steady-state flow and equilibrium water content were established in the system, a pulse of non-reactive tracer (Cl) or Cr(VI) solution was introduced into the system from an inlet until the effluent (outlet) concentration of solute (C) reached the inlet concentration ( $C_0$ ). Following the completion of non-reactive tracer or Cr(VI) pulse, the column was flushed with background electrolyte to elute the tracer or Cr(VI) solution from the system. Effluent samples were collected periodically during each experiment and analyzed immediately after sampling for the solute of interest [Cl or Cr(VI)]. The experiments were terminated after effluent reached background concentrations. Unsaturated Cr(VI) transport experiments were conducted at two different flow rates ( $0.8$  and  $0.08 \text{ cm}^3 \text{ min}^{-1}$ ) and initial concentrations ( $1$  and  $100 \text{ mg L}^{-1}$ ) (Table 3).

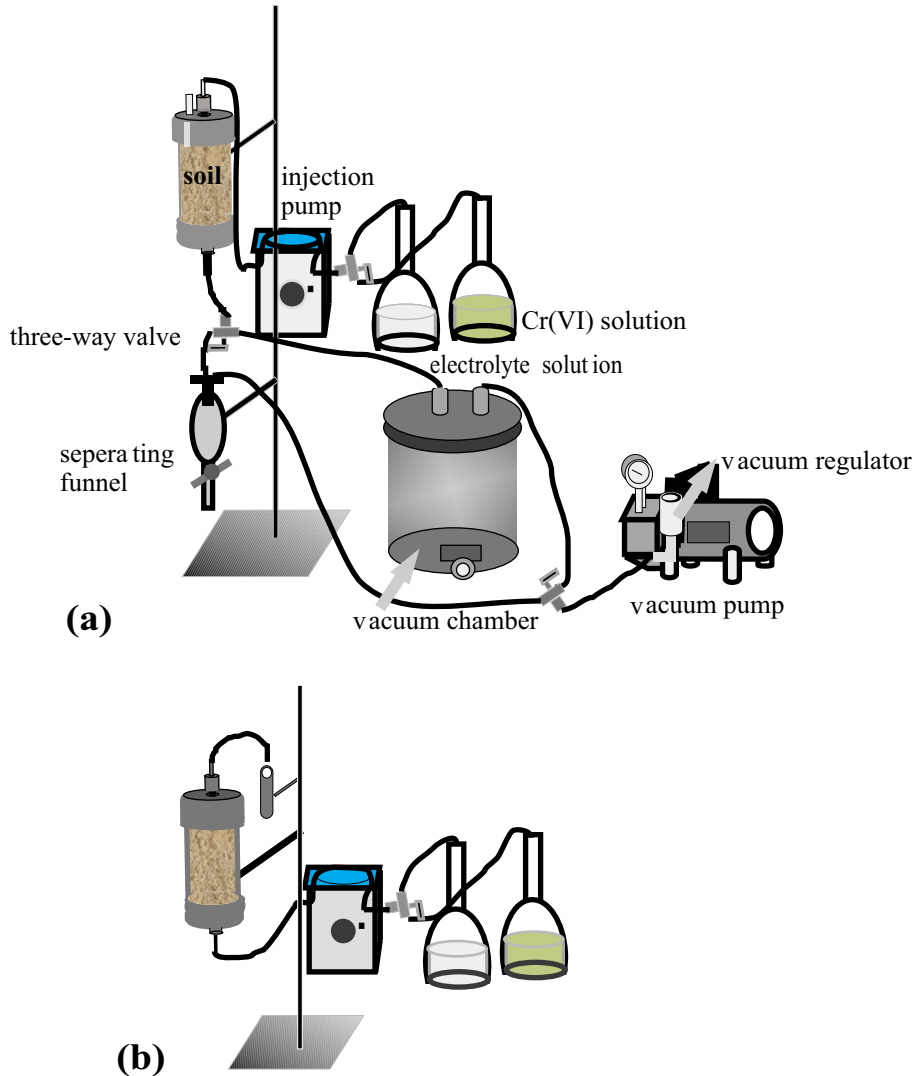


Figure 2. Experimental setup used in (a) unsaturated column and (b) saturated column experiments.

During each experiment, columns were weighed regularly to confirm the existence of stable water content in the system and flow rate measurements were taken occasionally to ensure the persistence of steady-state flow conditions. Effluent pH was also monitored. The column effluent during all experiments varied from pH 6.8 to 7.2.

**Chemical Analysis**

Non-reactive tracer (Cl) concentration in the elution was monitored using a conductivity meter. There is a linear

relationship between electrical conductivity (EC) of soil solution to tracer concentration within the range of tracer concentrations (0–50 mM CaCl<sub>2</sub>) used in this study [EC(dS/m)= 0.1778 \* C(mM), R<sup>2</sup>= 0.99, n= 10]. Therefore, relative EC can be used to obtain relative tracer concentration (C/Co). Relative concentration of tracer (C/Co) at a specific time was calculated by

$$\frac{C_t}{C_0} = \frac{EC}{EC_0} = \frac{[EC_t - EC_i]}{EC_0 - EC_i} \tag{1}$$

where  $EC_t$  is the EC measured at time 't' at the outlet of the column,  $EC_0$  is the EC of the initial concentration of the tracer pulse, and  $EC_i$  is the baseline EC before and after the tracer application (Kachanoski *et al.* 1992).

Cr(VI) concentration in aqueous samples and soil extracts was determined using the diphenylcarbazide colorimetric method (EPA 1992) with a UV-VIS spectrophotometer (Varian Cary 50) at wavelength 540 nm. Analysis of Cr(VI) was performed immediately after sampling to avoid possible reduction of Cr(VI) to Cr(III). The lower detection limit for Cr(VI) in this method is  $10 \mu\text{g L}^{-1}$ .

A polarographic method was also used to determine the chromium speciation [Cr(III) and Cr(VI)] in the effluent samples in a single analysis. The measurements were performed using TraceLab 50 polarographic system (Radiometer Anal., France), which consists of POL150 polarographic analyzer and MDE150 electrode stand, and controlled by a personal computer. A HMDE (Hanging Mercury Drop Electrode) working electrode, Pt auxiliary electrode, and Ag/AgCl/3M KCl reference electrode were used. Chromium was determined by Differential Pulse Polarography (DPP). An appropriate amount of standard or sample was added to the analysis vessel, making the total volume 5 ml, followed by addition of 0.8 ml of Ammonia buffer to provide a supporting electrolyte. While stirred, the sample was purged with  $\text{N}_2$  for 360s (seconds) to remove oxygen prior to sample analysis. After the stirring and purge were stopped, three drops of mercury were formed. Following a 15s equilibration time, chromium determination was performed by potential scanning in the cathodic direction from  $-0.5$  to  $-1.65$  V versus an Ag/AgCl reference electrode with a 5 mV step potential,  $-50$  mV modulation amplitude, 40 ms pulse width, and  $50 \text{ mV s}^{-1}$  scan rate. Cr(VI) ions are first reduced to Cr(III). Then, at a more negative potential, all the Cr(III) ions are reduced [Cr(tot) = Cr(III) free + Cr(III) coming from the Cr(VI) reduction]. The Cr(VI) peak appeared at  $-265$  mV while the Cr(tot) peak appeared at  $-1390$  mV. Cr(III) concentration is determined by the difference:  $\text{Cr(III)} = \text{Cr(tot)} - \text{Cr(VI)}$ . The optimum pH for analysis is pH 9–10. The lower detection limit of both Cr(VI) and Cr(tot) in the polarographic method is  $50 \mu\text{g L}^{-1}$ . Relative standard deviations of the measurements range from 0.07% to 3.11% with an average of 1.10%.

### Cr(VI) Extraction in Soil

Cr(VI) extraction was performed on the soils from column experiments wherein Cr(VI) loading was just carried out (experiments marked with \* in Table 3). Following the completion of Cr(VI) loading ( $C/C_0 = 1$ ), the soil removed from these column systems was thoroughly mixed and allowed to dry for 24 hr at  $105^\circ\text{C}$ . An alkaline digestion procedure (EPA 1996) was then performed on the triplicate sub-samples to determine the amount of Cr(VI) sorbed. In this method, 2.5 g of soil sample was added to a beaker containing 50 ml of 0.28 M  $\text{Na}_2\text{CO}_3$ /0.5 M NaOH extracting solution and heated at  $95^\circ\text{C}$  for 60 minutes with continuous stirring. Each sample was then gradually cooled with continued agitation and filtered through a  $0.45 \mu\text{m}$  cellulose acetate membrane filter. The supernatant was adjusted to pH of  $7.5 \pm 0.5$  with 5 M  $\text{HNO}_3$  and then analyzed for Cr(VI) using the diphenylcarbazide method.

To determine the amount of Cr(VI) in easily exchangeable sites, soil was also extracted with 8 ml of 1 M  $\text{MgCl}_2$  solution adjusted to a pH of 7 (Tessier *et al.* 1979). In this method, one gram of soil sample was added in triplicates to the polyethylene centrifuge tubes containing extraction solution. The tubes were shaken for 1 hr at  $25^\circ\text{C}$  on a reciprocating shaker and then centrifuged at 6000 rpm for 30 min. The supernatant was collected, filtered ( $0.45 \mu\text{m}$  membrane filter), and analyzed for Cr(VI) using the diphenylcarbazide method.

### Data Analysis

Non-reactive tracer (Cl) and Cr(VI) breakthrough curves (BTCs) obtained from all column experiments were analyzed using methods of moments to calculate the retardation factors and the input mass recovery in the system. The total mass of solute eluted from the column, which was determined by integrating under the solute breakthrough curve (zeroth temporal moment), was normalized to the injected known mass to obtain the mass recovery in the system. The mean travel time of solute in the system was determined by subtracting one-half of the injection pulse width from the ratio of first moment to zeroth moment. The ratio of Cr(VI) and non-reactive tracer travel times was used to obtain the retardation factor.

PHREEQC Version 2 geochemical model, developed by United States Geological Survey (Parkhurst & Appelo 1999), was also used to examine aqueous speciation of chromium and mineral saturation-indices in our system. The Minteq v.4 thermodynamic database was used in equilibrium speciation calculations. Aqueous speciation of 100 mg L<sup>-1</sup> Cr(VI) in 5 mM CaCl<sub>2</sub> background electrolyte solution was carried out in pH 6.8 to 7.2.

### Mathematical Modelling

Both deterministic equilibrium and physical nonequilibrium (two region) solute transport models were used to simulate the breakthrough curves of conservative (non-reactive) and Cr(VI) tracers. The governing equation for a one-dimensional, steady-state flow, equilibrium model with linear sorption can be expressed in non-dimensional form as

$$R \frac{\partial C^*}{\partial T} = \frac{1}{P} \frac{\partial^2 C^*}{\partial X^2} - \frac{\partial C^*}{\partial X} \quad (2)$$

where non-dimensional parameters are defined as

$$C^* = \frac{C}{C_0}, \quad X = \frac{x}{L}, \quad T = \frac{vt}{L}, \quad P = \frac{vL}{D} \quad (3)$$

$$R = 1 + \frac{\rho_b K_d}{\theta}, \quad D = \alpha v + D^*$$

where  $C$  and  $C_0$  are the effluent concentration and input solute concentration [M L<sup>-3</sup>], respectively,  $C^*$  is the relative solute concentration [-],  $X$  is the dimensionless distance [-],  $x$  and  $L$  are the distance and the column length [L],  $T$  is the pore volume [-],  $P$  is the pecelet number [-],  $v$  is the mean pore-water velocity [L T<sup>-1</sup>],  $t$  is the time [T],  $D$  is the hydrodynamic dispersion coefficient [L<sup>2</sup> T<sup>-1</sup>],  $D^*$  is the molecular diffusion coefficient [L<sup>2</sup> T<sup>-1</sup>],  $\alpha$  is the dispersivity [L],  $R$  is the retardation factor [-],  $\rho_b$  is the soil bulk density [M L<sup>-3</sup>],  $K_d$  is the distribution coefficient [L<sup>3</sup> M<sup>-1</sup>],  $\theta$  is the volumetric water content [L<sup>3</sup> L<sup>-3</sup>].

A two-region transport model including a first order solute exchange (i.e., diffusion) process between mobile and immobile regions and linear sorption (Wierenga & Van Genuchten 1989) can be written in dimensionless form as

$$\beta R \frac{\partial C_m}{\partial T} = \frac{1}{P_m} \frac{\partial^2 C_m}{\partial X^2} - \frac{\partial C_m}{\partial X} - \omega (C_m - C_{im}) \quad (4)$$

$$(1 - \beta)R \frac{\partial C_{im}}{\partial T} = \omega (C_m - C_{im}) \quad (5)$$

where

$$P_m = \frac{v_m L}{D_m}, \quad \beta = \frac{\theta_m + f \rho_b K_d}{\theta + \rho_b K_d}, \quad \omega = \frac{\alpha L}{\theta v} \quad (6)$$

The subscripts  $m$  and  $im$  refer to the mobile and immobile liquid phases, respectively,  $D_m$  is the dispersion coefficient of the mobile liquid phase,  $v_m$  is the mean pore-water velocity of the mobile region,  $\theta_m$  and  $\theta_{im}$  are the volumetric water content of mobile and immobile liquid phases, respectively ( $\theta = \theta_m + \theta_{im}$ ),  $\alpha$  is the first-order mass transfer coefficient between mobile and immobile regions,  $f$  is the fraction of adsorption sites in mobile region,  $\omega$  is the dimensionless mass transfer coefficient,  $\beta$  is the mobile water fraction,  $C_m$  and  $C_{im}$  are the solute concentration in the mobile and immobile phases, normalized to input solute concentration.

The governing equations for equilibrium and nonequilibrium models were solved using a third-type inlet boundary condition involving flux-averaged concentrations (Van Genuchten & Parker 1984), a zero concentration gradient at infinity and an initially solute-free soil profile:

$$C^*(X, 0) = 0 \quad (7)$$

$$C^*(0, T) - \frac{1}{P} \frac{\partial C^*(0, T)}{\partial X} = C_0^*(T), \quad \frac{\partial C^*}{\partial X}(\infty, T) = 0 \quad (8)$$

A nonlinear least-squares optimization program, CXTFIT (Toride *et al.* 1995) implemented in software STANMOD v.2.2 (Simunek *et al.* 1999) was employed to fit the measured column data to the analytical solutions of the advective-dispersive equation for estimating transport parameters. For the equilibrium model (MODE= 1), the value of the hydrodynamic dispersion coefficient ( $D$ ) calibrated from non-reactive tracer data was used to simulate Cr(VI) BTCs. For a two-region model (MODE= 2),  $D$ ,  $\beta$ , and  $\omega$  parameter values optimized from calibration of the model to non-reactive tracer data were

employed to simulate Cr(VI) data. Retardation factor values estimated independently from the moment analysis were also used in both models as an input parameter to simulate Cr(VI) BTCs.

## Results

### Batch Experiments

Sorption capacity of calcareous soil for Cr(VI) was determined with a series of batch experiments. The results of batch experiments are illustrated in Figure 3. Linearity of Cr(VI) sorption isotherm was evaluated at different ranges of Cr(VI) concentration (0–10 mg L<sup>-1</sup>, 0–100 mg L<sup>-1</sup>, and 0–200 mg L<sup>-1</sup>). The results showed that Cr(VI) sorption isotherm was linear in the all ranges of Cr(VI) concentration examined with the correlation coefficient values ranging between 0.97 and 0.99. Therefore, Cr(VI) influent concentrations (1, 10, 100 mg L<sup>-1</sup>) used in the column experiments were selected within this linear range. The average distribution coefficient ( $K_d$ ) obtained from linear sorption isotherms within the three different Cr(VI) concentration ranges was  $0.53 \text{ L Kg}^{-1} \pm 0.18$ , which corresponds to an average Cr(VI) retardation factor of  $2.11 \pm 0.37$  with 95% confidence interval.

### Miscible Displacement Experiments

Miscible displacement experiments were conducted under both saturated and unsaturated flow conditions. The experimental conditions are summarized in Table 3. Soil-water saturation in the column experiments ranged from 85% to 100%. For the flow rates used in the unsaturated column experiments, the lowest soil-water

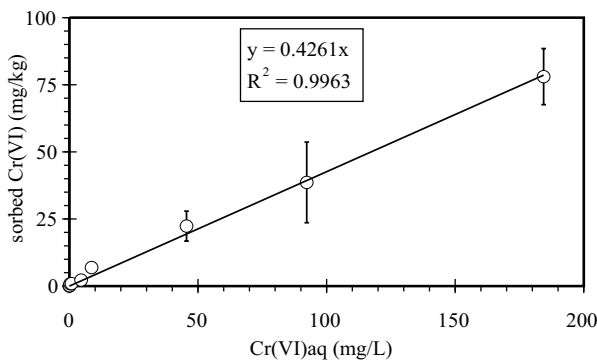


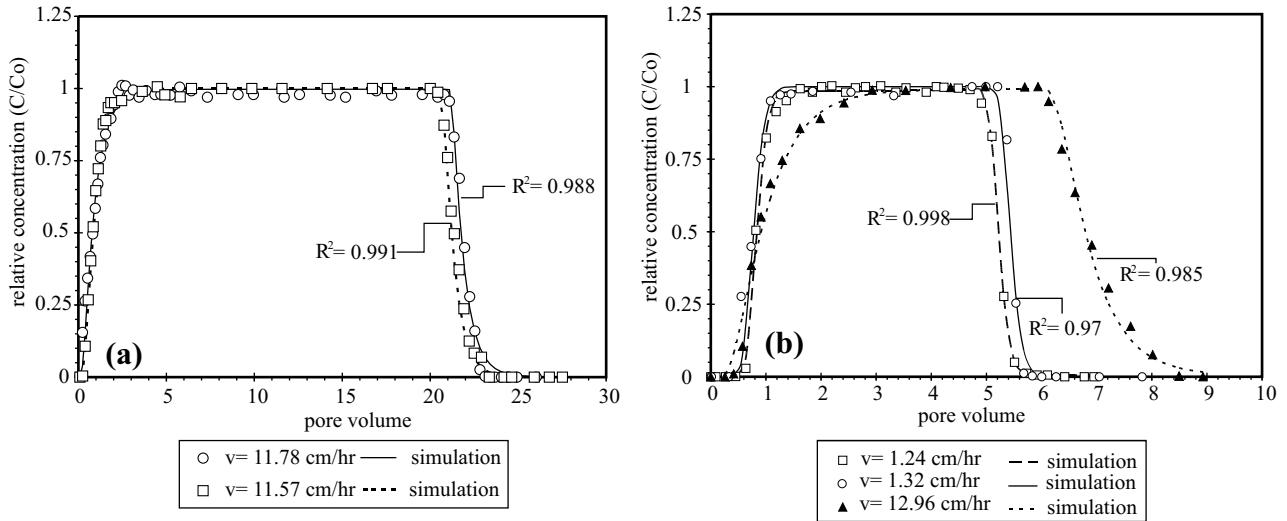
Figure 3. Equilibrium sorption isotherm of Cr(VI) obtained from batch experiments. Errors bars indicate the 95% confidence intervals.

saturation that could be achieved under steady-state flow conditions was limited by the greater fraction of finer-size soil particles in the calcareous soil. Solute residence times in the column system ranged from 1.04 hr to 12.43 hr depending on the flow rates. Steady-state flow conditions and stable water content in the system were accomplished throughout all displacement experiments. The distribution of soil water content along the column for unsaturated displacement experiments was checked by taking soil samples for gravimetric water content determination at different locations in the system after the termination of the experiment. Although slightly non-uniform soil-water content distributions were determined along the column (Table 4), the average soil-water content in the system was stable during the experiment. Previous studies showed that solute breakthrough curves were simulated accurately using average water content measurements under the prevailing conditions (De Smedt & Wierenga 1978; De Smedt *et al.* 1986; Hutchison *et al.* 2003).

*Non-reactive Tracer Transport.* Prior to each Cr(VI) transport experiment, non-reactive tracer tests were conducted to characterize the hydrodynamic properties of the column. The results of these experiments are shown in Tables 3 & 5. Under saturated steady-flow conditions ( $v = 11.78$  &  $11.57 \text{ cm hr}^{-1}$ ), the breakthrough curves (BTCs) of the non-reactive tracer (chloride) were symmetrical, indicating ideal transport behaviour in the column (Figure 4a). As expected, the retardation factor of the chloride tracer obtained from moment analysis of BTCs was equal to one, suggesting the absence of preferential flow and anion exclusion mechanisms in the system. Moment analysis of tracer BTCs also show that

Table 4. An example to distribution of soil water content along the column length under unsaturated steady-state flow conditions.

distance from the column inlet (cm)	gravimetric water content ( $\theta_g$ )
0 – 1	19.2 %
3.5 – 5	21.5 %
7 – 8.5	22.2 %
11.5 – 13.5	24.2 %
average	22.5 %



**Figure 4.** Measured and simulated breakthrough curves for non-reactive tracer transport in the (a) saturated column experiments (1 PV~ 1.16 hr) and (b) unsaturated column experiments (1 PV equals to 10.90 hr, 10.21 hr and 1.06 hr for 1.24 cm/hr, 1.32 cm/hr and 12.96 cm/hr experiments, respectively).

**Table 5.** Experimental conditions obtained from the simulation of non-reactive tracer (Cl) and Cr(VI) data. Numbers in parentheses represent 95% confidence interval ( $2\sigma$ ). Parameter values italicized represent the physical non-equilibrium in the system like the conditions at the relevant Cl tracer experiments.

experiments	modelling parameters						
	v	D	$\alpha$	$\beta$	$\omega$	P	CXTFIT
<b>saturated</b>	cm/hr	cm <sup>2</sup> /hr	cm	[ ]	[ ]	[ ]	r-squared
Cl tracer	11.78	44.7	3.77	–	–	3.58	0.988
1 mg/L Cr(VI)	11.78	44.7	3.77	–	–	3.58	0.987
10 mg/L Cr(VI)	11.78	44.7	3.77	–	–	3.58	0.991
Cl tracer	11.57	29.7	2.57	–	–	5.26	0.991
100 mg/L Cr(VI)	11.57	29.7	2.57	–	–	5.26	0.994
<b>unsaturated</b>							
Cl tracer	12.96	27.3	2.11	–	–	6.41	0.985
1 mg/L Cr(VI)	12.71	27.3	2.15	–	–	6.28	0.912
Cl tracer	1.24	0.30	0.24	0.85 (0.84–0.86)	0.015 (2.5E–3–0.028)	56.36	0.998
1 mg/L Cr(VI)	1.24	0.30	0.24	0.85 (0.84–0.86)	1E–7 (0–0.048)	56.36	0.974
Cl tracer	1.32	0.38	0.29	0.79 (0.76–0.82)	1E–7 (0–0.048)	46.53	0.979
100 mg/L Cr(VI)	1.32	0.38	0.29	0.79 (0.76–0.82)	1E–7 (0–0.048)	46.53	0.969

v– mean pore-water velocity, D– hydrodynamic dispersion coefficient,  $\alpha$ – dispersivity,  $\beta$ – mobile water fraction,  $\omega$ – dimensionless mass transfer rate coefficient P– pecelet number.

mass recovery in the system was greater than 98%. As shown in Figure 4a, the results of tracer experiments were fairly consistent with each other and reproducible.

Under unsaturated flow conditions, BTCs of the non-reactive tracer vary depending on the pore-water velocity (Figure 4b). At high pore-water velocities ( $v= 12.96 \text{ cm hr}^{-1}$ ), BTCs of the tracer exhibit relatively more spreading compared to those at slower pore-water velocities ( $v= 1.24 \text{ \& } 1.32 \text{ cm hr}^{-1}$ ) (Figure 4b). A similar degree of spreading was also observed in the tracer BTCs of high pore-water velocity experiments at saturated flow conditions (Figure 5). As mentioned previously, the porous media used in the experiments is poorly sorted soil (Figure 1) which has a relatively high value of uniformity coefficient ( $C_u= 23.64$ , Table 1). In such soils, the degree of velocity variation in the pore scale is much larger at the high pore-water velocities than those at the slow-pore-water velocities. Mechanical dispersion that contributes to solute spreading in porous media increases with an increase in velocity variation. Therefore, spreading observed in tracer BTCs at high-pore water velocities becomes more pronounced than those at slow-pore water velocities (Figures 4b & 5). The degree of spreading observed in these experiments was also estimated using a curve fitting program, CXTFIT. Modelling results show that hydrodynamic dispersion coefficients obtained for the high pore-water velocity tracer experiments ( $D= 27.3 \text{ cm}^2 \text{ hr}^{-1}$ ) are approximately 70 to 90 times larger than those for the slow pore-water

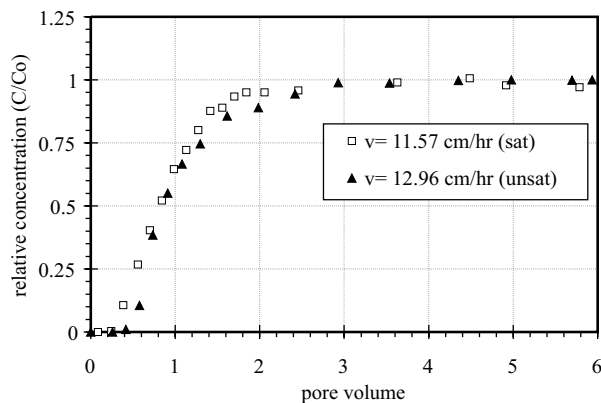


Figure 5. Arrival part of the non-reactive tracer breakthrough curves at the high pore-water velocities under saturated and unsaturated flow conditions. See Table 3 for the details of experimental conditions used in these column experiments (1 PV  $\sim$  1.06 hr).

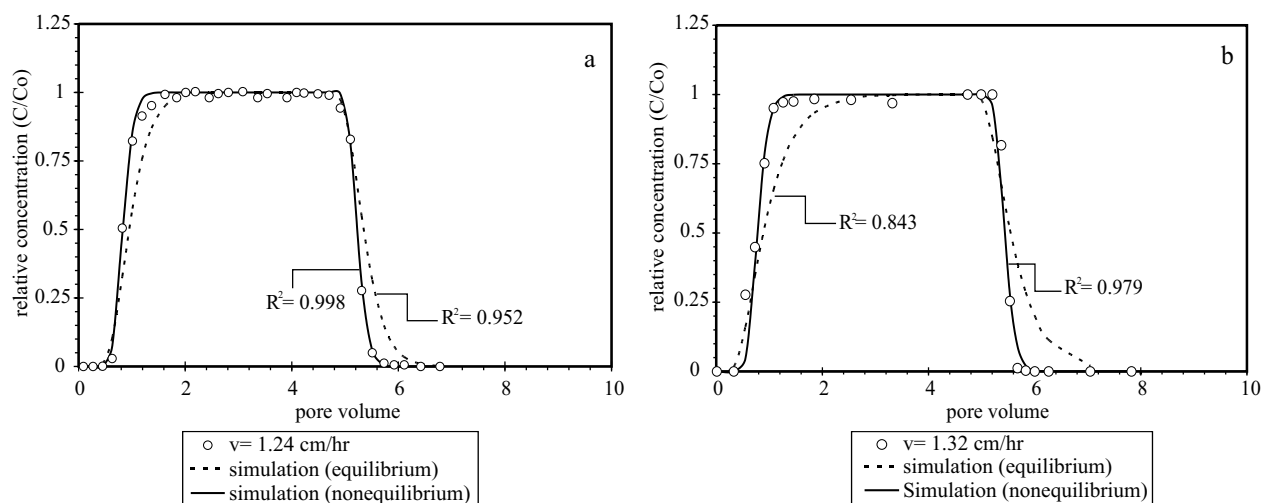
velocity tracer experiments ( $D= 0.30, 0.38 \text{ cm}^2 \text{ hr}^{-1}$ ) (Table 5). The contribution of mechanical dispersion to hydrodynamic dispersion was also calculated using the molecular diffusion coefficient of the non-reactive tracer chloride ( $D^*= 0.054 \text{ cm}^2 \text{ hr}^{-1}$ , Griffioen *et al.* 1998). The degree of contribution was about 84% on average at the slow-pore water tracer experiments while it was about 99.8% at the high-pore water tracer experiments.

At slow pore water velocities ( $v= 1.24 \text{ \& } 1.32 \text{ cm hr}^{-1}$ ), BTCs of non-reactive tracer show early breakthrough, suggesting preferential flow characteristics in the column, though one would expect that at relatively higher pore-water velocities (i.e.,  $v= 12.96 \text{ cm hr}^{-1}$ ).

Under unsaturated flow conditions, retardation factors obtained from temporal moment analyses of tracer data for  $0.08 \text{ cm}^3 \text{ min}^{-1}$  were 0.77 and 0.85. R values smaller than unity for non-reactive tracer are attributed to the existence of immobile water regions that are not participating in solute transport in the column (Gaudet *et al.* 1977; Seyfried & Rao 1987; Kamra *et al.* 2001). Despite the physical nonequilibrium conditions in the column, BTCs of non-reactive tracer at slow pore-water velocities show no sign of tailing but display ideal transport behaviour. This is due to the fact that diffusive mass transport between mobile and immobile water regions is much slower than advective transport, hence not allowing sufficient time for mass transfer to occur. Therefore, BTCs of the tracer display resemblance to those at equilibrium conditions in spite of physical nonequilibrium conditions in the column. These results were also verified by the outcomes of both the equilibrium and the physical nonequilibrium modelling of tracer data. As shown in Figure 6, tracer BTCs were well characterized by the deterministic two-region model ( $R^2= 0.979, 0.998$ ) as compared with the equilibrium model ( $R^2= 0.843, 0.952$ ). Calibration of the two-region model to the tracer data indicated that mobile water fraction ( $\beta$ ) in the column was 0.79–0.85, while mass transfer coefficient was relatively low ( $\omega= 1.5 \times 10^{-2}, 1 \times 10^{-7}$ ) (Table 5).

### Speciation of Cr(VI) in the Initial Solutions

Aqueous speciation of  $100 \text{ mg L}^{-1}$  (1.92 mM) Cr(VI) in 5 mM  $\text{CaCl}_2$  background electrolyte solution was evaluated using PHREEQC geochemical modelling in the pH of 6.8



**Figure 6.** Comparison of two region model simulation with deterministic equilibrium model simulation for non-reactive tracer data obtained from low pore-water velocity experiments conducted at unsaturated flow conditions. 1 PV equals to 10.90 hr and 10.21 hr for 1.24 cm/hr and 1.32 cm/hr experiments, respectively.

to 7.2, which corresponds to a typical pH range measured in the column effluent during the experiments. Speciation and mineral saturation calculations were carried out using the chemical composition of the solution used in the experiments. The calcareous soil used in the experiments has a pH of 8.37, which decreased to 6.8–7.2 after conditioning the soil columns with background electrolyte and saturating with Cr(VI) solution. In this pH range, the predominant aqueous chromium species were predicted to be  $\text{CrO}_4^{2-}$  (73 to 87.3%) and  $\text{HCrO}_4^-$  (25.4 to 12.1%). During the Cr(VI) transport experiments, Cr(III) species were not detected in the column effluent, indicating lack of Cr(VI) reduction in the system. Mineral saturation indices calculated from geochemical modelling also showed that water was undersaturated with respect to  $\text{CaCrO}_4$  (Chromatite), which was expected due to its relatively high solubility value ( $163 \text{ g L}^{-1}$  at  $20 \text{ }^\circ\text{C}$ ). All these results suggest that fate and transport of Cr(VI) were not influenced by the mineral precipitation and the redox (i.e., reduction/oxidation) reactions in the alkaline calcareous soil used herein.

#### *Transport of Cr(VI) at Saturated Flow Conditions*

Cr(VI) transport experiments under saturated flow conditions were conducted at a high pore water velocity (i.e.  $v = 11.78, 11.57 \text{ cm hr}^{-1}$ ) for three different Cr(VI)

concentrations (1, 10,  $100 \text{ mg L}^{-1}$ ). Measured breakthrough curves of Cr(VI) are shown in Figure 7. The Cr(VI) breakthrough curves were quite symmetrical and exhibited ideal transport behaviour. The transport of Cr(VI) was slightly retarded compared to that of the non-reactive tracers (Table 3). Retardation factors of Cr(VI) for 1, 10, and  $100 \text{ mg L}^{-1}$  were 1.34, 1.25, and 1.04, respectively. The observed decrease in the retardation as the influent concentration of Cr(VI) increased suggests nonlinear sorption, however, sorption isotherm obtained from batch studies indicated linear behaviour for the concentration range used in the column experiments. Sorption linearity was further evaluated by comparing the shapes of the arrival and elution parts of Cr(VI) breakthrough curves for each influent concentration. A characteristic aspect of nonlinear sorption is that the breakthrough curves are asymmetrical with a sharply rising front and a relatively more dispersed elution part. Therefore, the arrival and inverted elution parts of the breakthrough curves do not coincide. Comparison of elution and arrival parts of the breakthrough curves for different Cr(VI) influent concentrations are presented in Figure 8. Arrival and elution curves for each Cr(VI) concentration were fairly coincident. This shows that sorption nonlinearity had no significant influence on the transport of Cr(VI) in the calcareous soil in the concentration range examined.

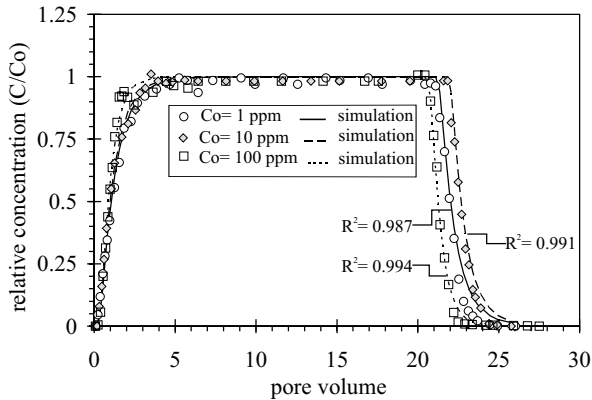


Figure 7. Measured and simulated breakthrough curves for Cr(VI) transport at different influent concentrations at saturated column experiments (1 PV ~ 1.16 hr).

The average value of  $K_d$  obtained from the saturated column experiments equals  $0.097 \text{ L Kg}^{-1}$ , which indicates that sorption affinity of aqueous Cr(VI) species to the calcareous soil is relatively low (Table 3). Mass recovery of Cr(VI) in the column experiments was around 98%, which shows that sorption was also reversible (Table 3). The average value of  $K_d$  calculated from the column experiments was approximately six times lower than the average  $K_d$  value obtained from batch studies ( $K_d = 0.53 \text{ L Kg}^{-1}$ ). Such differences in the parameter values estimated from batch vs. column experiments were often noted in the literature (Maraqa *et al.* 1999; Porro *et al.* 2000; Gamedinger *et al.* 2001; Hutchison *et al.* 2003). This observed difference could be attributed to the differences in soil/water ratio and limitations in availability of sorption sites in dynamic (column) vs static (batch) experiments (Maraqa *et al.* 1999; Gamedinger & Kaplan 2001).

#### Transport of Cr(VI) at Unsaturated Flow Conditions

Cr(VI) transport experiments under unsaturated flow conditions were performed at two different influent concentrations ( $1, 100 \text{ mg L}^{-1}$ ) for a range of pore-water velocities given in Table 3. As in the saturated column experiments, transport of Cr(VI) under unsaturated flow conditions was slightly retarded compared to that of the non-reactive tracers (Table 3). The 1 ppm Cr(VI) experiments were conducted at two different pore-water velocities, although a nearly nine-fold increase was observed in solute residence time (*i.e.*, 1.45 to 12.43 hr),

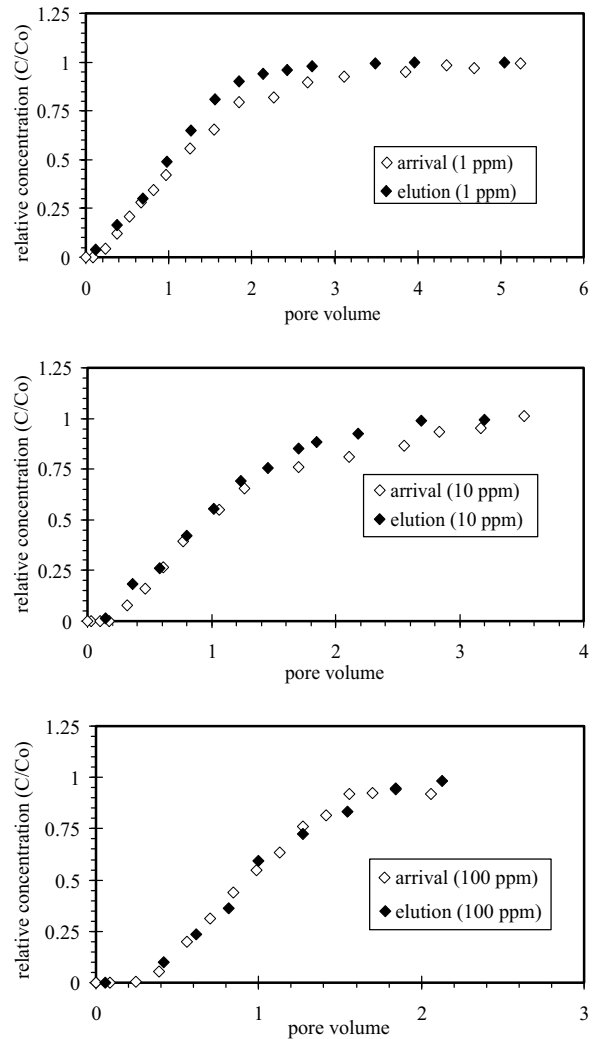


Figure 8. Comparison of arrival and inverted elution parts for measured Cr(VI) breakthrough curves at different influent concentrations in the saturated column experiments (1 PV ~ 1.16 hr).

retardation factor of Cr(VI) increased slightly from 1.29 to 1.34, which is the highest retardation observed in the unsaturated column experiments (Table 3). These results indicate that the magnitude of solute residence time or pore-water velocity had only a minimal impact on the sorption of Cr(VI) in the calcareous soil under alkaline conditions.

At the slow pore-water velocity experiments, retardation factors of Cr(VI) calculated for 1 and  $100 \text{ mg L}^{-1}$  influent concentrations were 1.34 and 1.07, respectively. These were quite similar to the R values obtained from 1 and 100 ppm Cr(VI) experiments

conducted at the high pore-water velocities under saturated flow conditions (Table 3). Measured breakthrough curves of Cr(VI) at the slow pore-water velocity experiments are shown in Figure 9. They were relatively sharp and symmetrical and exhibit no tailing, indicating the presence of chemical equilibrium in the system. The existence of physical nonequilibrium conditions in these experiments, which was discussed in a previous section, had no significant impact on the retention of Cr(VI) in the system because advective mass transport of Cr(VI) was faster than the diffusive mass transfer between mobile and immobile phases in the system; However, the existing nonequilibrium condition decreased the travel time of Cr(VI) in the system to some degree (Table 3).

Sorption affinity of Cr(VI) to the calcareous soil at the unsaturated flow conditions was determined to be quite low (average  $K_d = 0.093 \text{ L Kg}^{-1}$ ), as at the saturated flow conditions (Table 3). Mass balance calculation showed that Cr(VI) recovery in the unsaturated column experiments was almost complete (i.e., 98% or greater), suggesting that Cr(VI) sorption was reversible.

Low  $K_d$  and  $R$  values of Cr(VI) suggest that easily exchangeable sites present in the calcareous soil are probably responsible for the observed weak sorption behaviour of Cr(VI) in the examined concentration range. This was confirmed by performing several extraction

procedures on the soils from column experiments wherein Cr(VI) loading was just carried out (experiments marked with \* in Table 3). For instance, after Cr(VI) loading was completed at the 100 ppm Cr(VI) experiment, conducted at a slow pore-water velocity ( $v = 1.32 \text{ cm hr}^{-1}$ ) under unsaturated flow conditions, the amount of Cr(VI) mass retained in the soil was estimated to be  $39.38 \pm 1.75 \text{ mg/kg}$  from alkaline digestion procedure. To determine the amount of Cr(VI) in easily exchangeable sites, soil was also extracted with 8 ml of 1 M  $\text{MgCl}_2$  solution adjusted to pH of 7. Almost the entire mass of Cr(VI) was recovered from the soil in the later extraction procedure ( $39.81 \pm 3.60 \text{ mg/kg}$ ). All these results indicate that Cr(VI) is highly mobile and available to biological systems in the calcareous soil at alkaline soil pH values. The presence of a high amount of carbonate fraction or moderate organic matter content in the soil (Table 1) did not have any significant effect on Cr(VI) retention in the alkaline soil conditions.

#### Modelling of Cr(VI) Transport

Cr(VI) transport under variably saturated conditions was modelled using both deterministic equilibrium and two-region physical nonequilibrium transport models coupling linear sorption. Physical transport parameters ( $D$ ,  $\beta$ ,  $\omega$ ) obtained from the calibration of non-reactive tracer data using CXTFIT program and  $R$  values calculated from

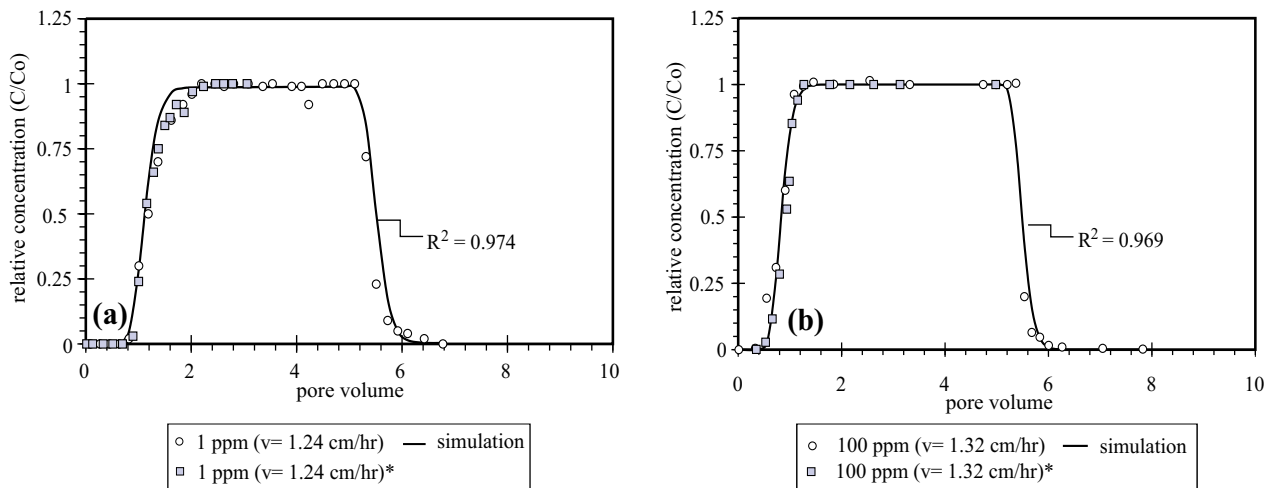
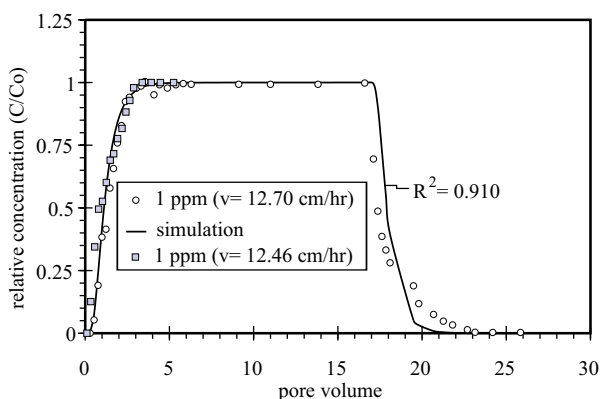


Figure 9. Measured and simulated breakthrough curves of Cr(VI) for a) 1 ppm Cr(VI) influent concentration (1 PV = 10.90 hr) b) 100 ppm Cr(VI) influent concentration (1 PV = 10.21 hr), at slow pore-water velocity experiments under unsaturated flow conditions. Two-region physical nonequilibrium model including linear sorption was used for the simulation of Cr(VI) data.

moment analysis of Cr(VI) data were used as input parameters in the transport models to simulate the Cr(VI) breakthrough curves and determine the correlation coefficient of the estimation. These parameters are tabulated in Table 5. Except for the slow velocity experiments conducted at unsaturated flow conditions, which exhibit the presence of physical nonequilibrium in the system (Figure 6), all other experiments were simulated with the deterministic equilibrium model (Figures 4, 7, 9 & 10). For the high pore-water velocity tracer experiment at the unsaturated flow conditions, physical nonequilibrium parameters ( $\beta$  and/or  $\omega$ ) optimized from the two-region model characterized the equilibrium conditions; therefore, the deterministic equilibrium model was preferred instead to simulate the tracer data (Figure 4b).

The models used in simulating Cr(VI) breakthrough curves generally provide a good match to measured data (Figures 7 & 9) in the majority of experiments. The correlation coefficients (*r*-squared) calculated for the simulations ranged from 0.97 to 0.99 (Table 5), suggesting that the processes included in the models represented the transport of Cr(VI) in the calcareous soil reasonably well. Only in one experiment, which was conducted at a high pore-water velocity under unsaturated flow conditions (Table 3), did the simulated breakthrough curve provide a poor match to the measured data with a *r*-squared value of 0.91 (Figure



**Figure 10.** Measured and simulated breakthrough curves of Cr(VI) for 1 ppm Cr(VI) influent concentration, at a high pore-water velocity experiment under unsaturated flow conditions. Deterministic equilibrium model including linear sorption was used for the simulation of Cr(VI) data (1 PV~ 1.06 hr).

10). In particular, the equilibrium model used was not able to provide a good fit to the elution part of the breakthrough curve. During the simulation, when the hydrodynamic dispersion coefficient (*D*) was not fixed to the value ( $D= 27.3 \text{ cm}^2 \text{ h}^{-1}$ ) obtained from the curve fitting of non-reactive tracer data, the correlation coefficient of the simulation was slightly improved ( $R^2= 0.938$ ,  $D= 72.7 \text{ cm}^2 \text{ h}^{-1}$ ). The BTC of Cr(VI) was also simulated with two-region model and one-site chemical nonequilibrium model separately to elucidate the processes causing observed elution behaviour; however, no further improvement was attained at the simulations and calculated nonequilibrium parameters showed a high degree of uncertainty (data not shown). Van Genuchten & Parker (1984) noted that BTCs obtained from nonequilibrium models diverge, especially when the Peclet number is less than 5. The *P* value used in the nonequilibrium modelling ( $P= 2.36$ ) was smaller than five, indicating the failure of models to incorporate the influence of any types of nonequilibrium in the system.

## Conclusion

The objective of this study was to evaluate transport and retention behaviours of aqueous Cr(VI) species in a highly calcareous and alkaline soil of a karst terrain. Batch sorption experiments and column experiments conducted at both saturated and unsaturated steady-state flow conditions were used to determine the Cr(VI) sorption and transport in the alkaline soil conditions. The results of batch experiments showed that sorption was linear up to  $200 \text{ mg L}^{-1}$  Cr(VI) initial concentration.  $K_d$  value obtained from both batch and column studies showed that sorption was relatively low. Average  $K_d$  value obtained from batch studies ( $0.53 \text{ L Kg}^{-1}$ ) was about six times higher than the average  $K_d$  value ( $0.09 \text{ L Kg}^{-1}$ ) obtained from column studies, which remained same at the saturated and the unsaturated flow conditions.

The results of the column experiments showed that transport of Cr(VI) was slightly retarded relative to non-reactive tracer at both saturated and unsaturated flow conditions. Low retardation factors and  $K_d$  values obtained from column experiments indicated that Cr(VI) species are very mobile and available to biological systems in highly calcareous and alkaline soil conditions. Extraction studies conducted on the soil columns also showed that Cr(VI) oxyanions (dominantly  $\text{CrO}_4^{-2}$ ,

$\text{HCrO}_4^-$ ) were only temporarily retained by adsorption to easily exchangeable sorption sites in the soil and that the sorption was reversible. In addition, both geochemical modelling and extraction studies indicated that mineral precipitation and redox processes (i.e. reduction) did not have any effect on the fate of Cr(VI) in the highly calcareous and alkaline soil used here. In Turkey, approximately 80% of soils have a pH greater than 7, and 11% of Turkish soils have lime contents greater than 25%. The soil used here was a cover soil sampled over karst bedrock and contained moderate amounts of organic carbon and low iron oxide contents. The results obtained from this study suggest that high mobility of Cr(VI) under such soils increases the rate of contaminant spreading and the potential risk of groundwater contamination. In soils contaminated with heavy metals such as divalent metals (i.e., Pb, Cu, Cd, Zn, etc.) lime

( $\text{CaCO}_3$ ) was generally added to the soil to stabilize the heavy metals. The results of this study showed that in such sites, Cr(VI) mobility will increase significantly by the addition of lime compared to the divalent metals. Increased bioavailability of Cr(VI) in calcareous soil is a key factor for remediation of Cr(VI) in such contaminated sites via phytoremediation, due to enhancement in Cr(VI) availability for plant uptake.

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