

Chromium behavior in aquatic environments: a review

Josselin Gorny, Gabriel Billon, Catherine Noiriél, David Dumoulin, Ludovic Lesven, and Benoît Madé

Abstract: The fate of chromium (Cr) – a redox sensitive metal – in surface sediments is closely linked to early diagenetic processes. This review summarizes the main redox pathways that have been clearly identified over recent decades concerning the behavior of Cr(III,VI) in aquatic environments, and applies them to surface sediments where data for redox speciation remain limited. Overall, abiotic redox reactions that govern the speciation of Cr involve manganese (Mn) (III,IV) (hydr)-oxydes for Cr(III) oxidation, Cr(VI)-reducing species (dissolved iron (Fe) (II) and hydrosulfide (HS⁻), and Cr(VI)-reducing phases (ferrous and sulfide minerals, as well as Fe(II)-bearing minerals). Bacterial activity is also responsible for the redox interconversion between Cr(III) and Cr(VI): biotic reduction of Cr(VI) to Cr(III) is observed through either detoxification or dissimilatory reduction. Whereas Mn(II)-oxidizing bacteria are known to promote indirect oxidation of Cr(III) to Cr(VI), the reaction mechanisms are unresolved. Conversely, oxygen (O₂), nitrate (NO₃⁻), and nitrite (NO₂⁻) do not appear to play any role in Cr(III) oxidation. Additionally, Mn(II) and ammonium (NH₄⁺) are not known to promote Cr(VI) reduction. Once reduced, the mobility of Cr(III) in sediments is significantly restricted and regulated by precipitation and sorption processes. Finally, even if the role of natural organic matter in sediment has been determined, further research is required to identify the complexation mechanisms.

Key words: chromium, redox gradient, aquatic system, sediment, speciation.

Résumé : Le devenir du chrome – un métal sensible à l'oxydo-réduction – dans les sédiments de surface est étroitement lié aux processus de la diagenèse précoce. Cette article résume les voies d'oxydo-réduction qui ont été clairement identifiées au cours des récentes décennies, et ce, concernant le comportement du chrome (III et VI) dans des milieux aquatiques, et les transpose à des sédiments de surface pour lesquels les données de spéciation demeurent limitées. En général, les réactions d'oxydo-réduction abiotiques régulant la spéciation du chrome impliquent les (hydr)-oxydes de manganèse (III,IV) pour l'oxydation du Cr(III), les espèces réductrices du Cr(VI) [Fe(II) et HS⁻ sous formes dissous] et les phases réductrices de Cr(VI) [minéraux ferreux et sulfurés, ainsi que des minéraux renfermant Fe(II)]. L'activité bactérienne est aussi responsable de l'interconversion redox entre Cr(III) et Cr(VI) : la réduction biotique de Cr(VI) en Cr(III) est observée soit par la détoxification ou la réduction dissimilatrice. Alors qu'il est précisé que les bactéries oxydatives du Mn(II) promeuvent l'oxydation indirecte du Cr(III) en Cr(VI), les mécanismes de réaction sont non résolus. Au contraire, O₂, NO₃⁻ et NO₂⁻ ne semblent jouer aucun rôle dans l'oxydation du Cr(III). De plus, Mn(II) et NH₄⁺ ne sont pas reconnus comme permettant la réduction du Cr(VI). Une fois le Cr(VI) réduit en Cr(III) dans les sédiments, la mobilité du chrome est énormément limitée et déterminée par des processus de précipitation et de sorption. Finalement, même si le rôle de la matière organique naturelle dans les sédiments a été démontré, peu d'études sont dédiées à la détermination des mécanismes de complexation et ceci requiert des recherches approfondies. [Traduit par la Rédaction]

Mots-clés : chrome, gradient d'oxydo-réduction, système aquatique, sédiment, spéciation.

1. Introduction

Chromium (Cr) is the tenth most abundant element in the earth's mantle (Fendorf 1995) and is considered to be a trace element in river sediments with a median total content of 64 mg·kg⁻¹ (De Caritat and Reimann, 2012). The accumulation of Cr in sediments is mainly linked to industrial and urban sources and is the primary cause of Cr pollution. The use of Cr in industrial processes mainly involves Cr(VI) compounds due to their toxic and (or) corrosion inhibitor properties (the reduction of Cr(VI) to Cr(III) produces Cr(III) precipitate layers, which are relatively more stable under various chemical conditions). For these reasons, Cr is widely used in wood preservation, leather treatment, cement and paint production, metal dipping, and electroplating (Reid 2011). Accidental leakage, improper disposal, or industrial effluents represent

the main sources of Cr(VI) in aquatic environments (Kotas and Stasicka 2000; Kumar and Riyazuddin, 2011).

Monitoring of Cr pollution is an important environmental issue due to its adverse impacts on aquatic organisms. Cr(VI) is considered toxic as it readily passes through the cell membrane via non-specific anion channels, whereas Cr(III) is absorbed through passive diffusion or phagocytosis. Intracellular damage by Cr(VI) is mostly caused by reactive oxygen species such as superoxide, hydroxyl radicals, and hydrogen peroxide (IPCS 2009). The final product of Cr(VI) metabolism, Cr(III), forms stable coordination complexes with nucleic acids and proteins. Therefore, inside the cell, Cr(VI) reduction is the activation event that causes genotoxic damage and other forms of toxicity (Salnikow and Zhitkovich 2008). In addition, Cr(VI) is highly mobile in aquatic systems,

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whereas Cr(III) tends to precipitate and (or) be adsorbed onto minerals, especially aluminosilicates, resulting in a gradual accumulation within sediments (Rai et al. 1989). Because of these differences between Cr(VI) and Cr(III), it is important to identify the redox reactions that may influence the oxidation state of Cr in aquatic environments.

Surface sediments are a highly heterogeneous and complex medium. First, the sediment matrix is a combination of pore waters, inorganic solid particles, organic matter, and living organisms (especially bacteria that form biofilms on solid surfaces), where numerous transfers between different phases can take place (Berner 1980). Since the sediment compartment can be spatially heterogeneous, it is often difficult to extrapolate its characteristics over an entire study area and (or) to monitor a specific location as a function of time. Second, strong redox gradients can occur in sediments, specifically in surface sediments where the mineralization of biodegradable organic matter by bacterial activity takes place, involving the consumption of dissolved oxygen and other oxidants (e.g., nitrates (NO_3^-), iron (Fe) hydroxides, sulfates (SO_4^{2-})) (Froelich et al. 1979). This process, also called early diagenesis, tends to disturb the balance between the different phases. However, an approximate local equilibrium is assumed. The features of local equilibrium are important when studying redox sensitive element speciation and parameters that modify their forms (global physical, chemical, and biological forcing) (Borch et al. 2010).

Assessing the speciation of Cr in surface sediments is therefore important, especially when present at trace levels. Many speciation methods concentrate on quantifying only the amount of either monomeric species of Cr(III) or Cr(VI), and then calculating the amount of other species present as the difference remaining from the total Cr measurement (Marqués et al. 2000; Michalski et al. 2011). This approach is not completely correct because it neglects polymeric Cr(III) species (intermediate step during the slow transition from free ions to $\text{Cr}^{\text{III}}(\text{OH})_3$ precipitates), and (or) complexes between Cr(III) and dissolved organic matter (DOM). It can therefore lead to bias in estimating the fate and toxicity of Cr (Walsh and O'Halloran 1996; Hu et al. 2016).

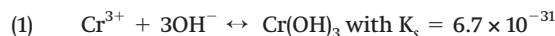
The quantification of both Cr species simultaneously remains a challenge because of the high reactivity of Cr species and the presence of interfering ions and substances, such as carbonate (CO_3^{2-}), chloride (Cl^-), and humic acid, which can dramatically interfere with the chromatographic separation of Cr(III) (Séby et al. 2003; King and Beauchemin 2010). Complementary methods have been tested to take into account the difficulties in directly attaining speciation of Cr in pore water samples contaminated by tannery effluent (Burbridge et al. 2012). As a consequence, the literature contains only a few references concerning the identification of reactions that influence the redox speciation of Cr in aquatic environments (Table 1). However, alternative sampling and in situ measurements should improve future environmental studies on Cr (Ernstberger et al. 2002; Pan et al. 2015; Devillers et al. 2016; Suárez et al. 2016). This review summarizes the main processes that have been clearly identified concerning the behavior of Cr in aquatic environments, including redox transformations, complexations, adsorptions, and precipitations. It also gives suggestions for future research to improve the understanding of the biogeochemical cycle of Cr in surface sediments.

2. Chromium speciation in aquatic systems

Chromium species exist under several oxidation states ranging from +II to +VI, with the predominance of trivalent (Cr(III)) and hexavalent (Cr(VI)) species in aquatic environments (Table 1).

In the environmental pH range (i.e., $5 < \text{pH} < 9$), $\text{Cr}^{\text{III}}(\text{OH})_3$, $\text{HCr}^{\text{VI}}\text{O}_4^-$, and $\text{Cr}^{\text{VI}}\text{O}_4^{2-}$ represent the main free aqueous Cr species (Rai et al. 1989; Kotas and Stasicka 2000). Contents of polynuclear complexes ($\text{Cr}^{\text{III}}_2(\text{OH})_2^{4+}$, $\text{Cr}^{\text{III}}_3(\text{OH})_4^{5+}$, $\text{Cr}^{\text{III}}_4(\text{OH})_6^{6+}$,

$[\text{Cr}^{\text{III}}(\text{OH})_4]_n^{n-}$, and $\text{Cr}^{\text{VI}}_2\text{O}_7^{2-}$) and mixed ligand complexes ($\text{Cr}^{\text{III}}(\text{OH})\text{Cl}^+$, $\text{Cr}^{\text{III}}(\text{SO}_4)^+$) are never significant in solution because their formation requires high Cr concentrations and (or) pH values out of the environmental range (Shen-Yang and Ke-An 1986; Rai et al. 1989; Torapava et al. 2009; Rakhunde et al. 2012). Cr(III) can be complexed by various natural organic ligands, which increases the low solubility of trivalent Cr (eq. 1).



Several complexation constants between Cr(III) and synthetic chelating agents are available in the literature (Selmer-Olsen 1962; Ogino et al. 1975; Martell et al. 2004; Carbonaro and Stone 2005; Carbonaro et al. 2008); however, interactions with natural organic matter are not well known (Gustafsson et al. 2014). This can present an obstacle for modelling Cr(III) behavior in the aquatic environment. Cr(VI) exists as oxyanions ($\text{HCr}^{\text{VI}}\text{O}_4^-$ and $\text{Cr}^{\text{VI}}\text{O}_4^{2-}$), but also as a relatively soluble neutral inorganic species that can be formed in the presence of the main cations present in pore waters of sediments (e.g., calcium (Ca^{2+}), potassium (K^+), sodium (Na^+), ammonium (NH_4^+)) (Kimbrough et al. 1999).

3. Redox reactions

The fate and mobility of Cr in surface sediments is controlled by redox reactions. The redox couples that are believed to change the redox speciation of Cr are: $\text{O}_2/\text{H}_2\text{O}$, Mn(IV)/Mn(II) (including the metastable Mn(III) species), NO_3^-/N_2 , $\text{NO}_3^-/\text{NO}_2^-$, Fe(III)/Fe(II), and $\text{SO}_4^{2-}/\text{HS}^-$. In Fig. 1, a simple redox potential diagram shows what are, from a thermodynamic point of view, the main theoretical oxidants of Cr(III) (dissolved oxygen, Mn(III,IV) (hydr)-oxides, nitrates, nitrites, and sulfates) and the main theoretical reducers of Cr(VI) (ferrous Fe and sulfides) at pH 7. In the following sections, characterizations of chemical oxidants and reducers that are able to change the redox speciation of Cr in surface sediments are described. Bacterial activity that is involved in these redox transformations will also be discussed.

3.1. Oxidation of Cr(III) species

In sediments, particularly close to the water-sediment interface, numerous oxidants are able to oxidize Cr(III) into Cr(VI) (Fig. 1). However, dissolved oxygen has been proved to be an inactive (indirect) oxidant due to slow oxidative kinetics (Schroeder and Lee 1975). Nitrates and nitrites are never cited as potential oxidants, although redox reactions appear to be thermodynamically possible for these two species. Concerning sulfates, their reduction by Cr(III) is not thermodynamically conceivable (Fig. 1). Finally, only Mn(III,IV) (hydr)-oxides (Fendorf 1995) are able to significantly oxidize the Cr(III) species present in both liquid and solid phases.

3.1.1. Oxidation by dissolved oxygen

Although aerobic oxidation of Cr(III) to Cr(VI) is thermodynamically possible (Apte et al. 2005), this reaction (eq. 2) occurs very slowly in aquatic environments.



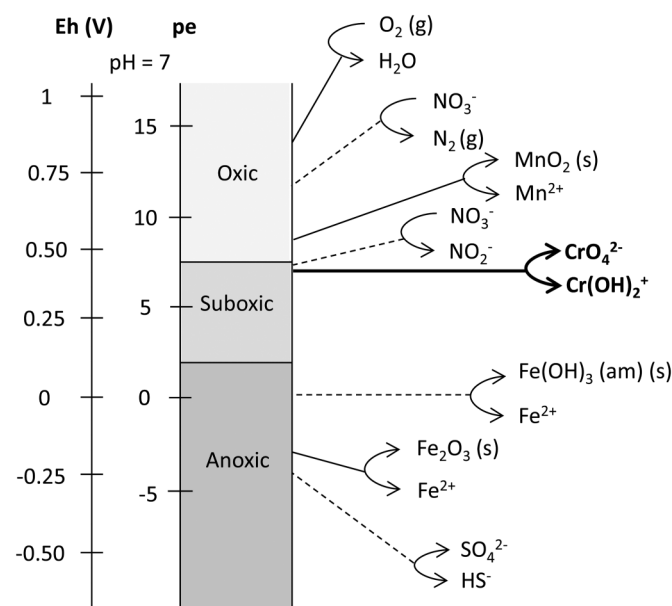
Schroeder and Lee (1975) observed that, where the concentration range was $1.9\text{--}2.4 \mu\text{mol}\cdot\text{L}^{-1}$, only 2%–3% of Cr(III) was oxidized over a 2 week period. This not only occurred in buffered solutions with a pH ranging from 5.5 to 9.9, but also in natural lake waters at pH 8.3–8.7. Eary and Rai (1987) reported no redox reaction in $\sim 2 \mu\text{g}\cdot\text{L}^{-1}$ Cr(III) solutions saturated with dissolved oxygen at pH 4, 12, and 12.5 after a period of 24 days. The production of dissolved Cr(VI) is never significant in buffer solutions containing amorphous Cr(III) hydroxides at $1 \text{g}\cdot\text{L}^{-1}$ (Namgung et al. 2014); while not

Table 1. Summary of relevant studies dedicated to Cr behavior in surface sediments.

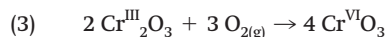
Environmental compartment	pH range	Particulate phase					Surface waters/ Groundwaters ([Cr] range $\mu\text{g}\cdot\text{L}^{-1}$)	Cr speciation		
		Total Cr (mg kg^{-1})	Exch (%)	Red (%)	Oxi (%)	Res (%)		Species detected	Where and why	References
Lake	8.1–9.6	<85 10^3	—	—	—	—	—	Only Cr(III)	Conditions at the study site favor the reduction of Cr(VI) to Cr(III)	Burbridge et al. 2012
Aquifer	7–9	<15 10^3	—	—	—	—	35–91	Cr(III and VI)	[Cr(VI)] > [Cr(III)]	Dermatas et al. 2015
River	—	30–720	—	—	—	—	<50	Cr(III and VI)	Mn(III,IV) (hydr)-oxide in SPM modify Cr speciation. [Cr(III)] \geq [Cr(VI)]	Szalinska et al. 2010
Esutary	7.6–8.1	—	—	—	—	—	3.6	Cr(III), DOM-Cr(III)	DOM-Cr(III) is the main species	Walsh and O'Halloran 1996
River	7.9–8.5	—	—	—	—	—	<90	Cr(III and VI)	[Cr(III)] \geq [Cr(VI)]	Bobrowski et al. 2004
River	—	—	—	—	—	—	<2	Cr(III and VI)	[Cr(III)] \geq [Cr(VI)]	Sumida et al. 2005
Sea	—	—	—	—	—	—	<1	Cr(III and VI)	Cr(III)/Cr(VI) ratios vary according to the origin of seawater samples	Abu-Saba and Flegal 1995
River	—	—	—	—	—	—	<10	Cr(III and VI)	[Cr(III)] \geq [Cr(VI)]	Wen et al. 2002
Sea	—	—	—	—	—	—	<1	Cr(III and VI)	[Cr(VI)] > [Cr(III)]; Cr(III) production through photoreduction?	Van Den Berg et al. 1994
Sea	—	—	—	—	—	—	<1	Cr(III and VI)	[Cr(VI)] > [Cr(III)]	Connelly et al. 2006
River	—	18	1	2	42	55	—	—	—	Davidson et al. 1994
Lake	—	18	0	0	43	57	—	—	—	Davidson et al. 1998
River	—	2.5–25	0	~5	~30	~65	—	—	—	Nemati et al. 2011
Sea	6–7	20–90	0	0	0	~100	—	—	—	Yuan et al. 2004
Sea	7–8	35–110	0	~20	~80	~80	—	—	—	Guevara-Riba et al. 2004
River	—	75–130	0	0	~10	~90	—	—	—	Filgueiras et al. 2004
Sea	—	74–124	0	~15	~15	~70	—	—	—	Yu et al. 2010
River	7.5–8	30–110	0	~5	~15	~80	—	—	—	Davutluoglu et al. 2011
River	7.5–8	—	~5	~15	~40	~40	—	—	—	Lesven et al. 2010

Note: Solid speciation of Cr is determined by the Bureau Community of Reference sequential extraction (Rauret et al. 1999). Exch, exchangeable fraction/bound to carbonates; Red, reducible fraction bound to Fe(III) and Mn(III,IV) (hydr)-oxides; Oxi, oxidizable fraction bound to organic matter; Res, residual fraction; SPM, suspended particulate matter; DOM, dissolved organic matter.

Fig. 1. Redox scale of environmentally relevant redox couples. The Eh and pe values (with Eh = 0.059 pe) are calculated at pH 7 with a total concentration of dissolved species equal to 10^{-5} M except for Cr (15×10^{-6} M).

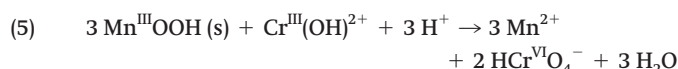


detected at pH 7, Cr(VI) was measured after 20 days at a concentration of 0.9 and 1.9 μM at pH 8 and 9, respectively. Apte et al. (2006) observed that the aerobic oxidation of $\text{Cr}^{\text{III}}_2\text{O}_3$ to $\text{Cr}^{\text{VI}}\text{O}_3$ (eq. 3) occurs only in harsh conditions (at high temperatures ranging from 200 to 300 $^\circ\text{C}$). Temperature is therefore one of the limiting parameters for generating aerobic oxidation of Cr(III) in aquatic environments.



3.1.2. Oxidation by Mn(III,IV) (hydr)-oxides

As presented in eqs. 4 and 5, Manceau and Charlet (1992) reported the oxidation of Cr(III) to Cr(VI) by various natural or synthetic Mn(III,IV) (hydr)-oxides. The latter can be birnessite $[(\text{Na}, \text{K}, \text{Mg}, \text{Ca})\text{Mn}^{\text{III,IV}}_2\text{O}_4 \cdot n\text{H}_2\text{O}]$, busenite $[\text{Na}_4\text{Mn}_{14}\text{O}_{27} \cdot 9\text{H}_2\text{O}]$, cryptomelane $[(\text{K})\text{Mn}^{\text{II,IV}}_8\text{O}_{16}]$, hausmanite $[\text{Mn}^{\text{II,III}}_3\text{O}_4]$, manganite $[\gamma\text{-Mn}^{\text{III}}\text{OOH}]$, lithiophorite $[(\text{Al}, \text{Li})\text{Mn}^{\text{III,IV}}\text{O}(\text{OH})_2]$, pyrolusite $[\beta\text{-Mn}^{\text{IV}}\text{O}_2]$, romanechite $[\text{Ba}_2\text{H}_2\text{O}_2\text{Mn}^{\text{III,IV}}_5\text{O}_{10}]$, and todorokite $[(\text{Na})\text{Mn}^{\text{III,IV}}_4\text{O}_{12} \cdot 3 \text{H}_2\text{O}]$ (Eary and Rai 1987; Johnson and Xyla 1991; Silvester et al. 1995; Kim et al. 2002; Weaver et al. 2002; Feng et al. 2006).



The oxidizing capacities of Mn(III,IV) (hydr)-oxide species differ according to their physico-chemical and surface properties, including pH_{PZC} , Mn valence, and the degree of crystallinity. Kim et al. (2002) performed several batch experiments over a 12 h period, in pH 4 and 7 solutions containing different Mn(III,IV) (hydr)-oxides and dissolved Cr(III) species at initial concentrations of 0.4–0.8 $\text{g}\cdot\text{L}^{-1}$ and 200 $\mu\text{mol}\cdot\text{L}^{-1}$, respectively. The decrease of the Cr(III)-oxidizing capacity of Mn(III,IV) (hydr)-oxides can be classified as follows: birnessite > todorokite > lithiophorite > pyrolusite. Weaver and Hochella (2003) have also shown that birnessite is a stronger oxidant than lithiophorite and pyrolusite under quite similar experimental conditions: birnessite > hausmanite >>

romanechite > cryptomelane >> manganite ~ pyrolusite >> lithiophorite. At higher concentrations of Cr(III) (4 $\text{mmol}\cdot\text{L}^{-1}$) and Mn(III,IV) (hydr)-oxides (20 $\text{g}\cdot\text{L}^{-1}$), and with a lower pH (pH = 4.5), the Cr(III)-oxidizing capacities of Mn(III,IV) (hydr)-oxides are found to change as follows: birnessite > cryptomelane > todorokite > hausmanite (Feng et al. 2007). Overall, the most reactive Mn precipitate towards Cr(III) remains birnessite.

This difference in Cr(III)-oxidizing capacities is related to the structure of the Mn(III,IV) (hydr)-oxides, especially their degree of crystallinity (Kim and Moon 1998) and, to a lesser extent, the valence of Mn and the surface charge of Mn(III,IV) (hydr)-oxides. While oxidation of Cr(III) by manganite, lithiophorite, and pyrolusite is observed, the surface sites of these Mn(III,IV) (hydr)-oxides are positive (i.e., $\text{pH}_{\text{PZC}} > \text{pH}$; see Section 6). From an electrostatic point of view, the complexation between the cationic Cr(III) species (existing for pH < 5) and the positive surface sites of Mn(III,IV) (hydr)-oxides species is theoretically not favorable due to the charge repulsion. This suggests that the chemical potential outweighs the electrical potential in sorption processes (Sparks 1998), though the sorption mechanism onto Mn(III,IV) (hydr)-oxides remains unclear (Feng et al. 2006). In addition to the valence of Mn, Nico and Zasoski (2000) have established the importance of Mn(III) availability in birnessite on the oxidation rate of Cr(III), while performing experiments in N_2 -sparged solutions (pH 3–6) with birnessite and dissolved Cr(III) at initial concentrations of 0.1 $\text{g}\cdot\text{L}^{-1}$ and 50 $\mu\text{mol}\cdot\text{L}^{-1}$, respectively. They have also shown that, at a concentration of 1 $\text{mmol}\cdot\text{L}^{-1}$, pyrophosphate ($\text{P}_2\text{O}_7^{4-}$), a powerful complexing agent of Mn(III) ($\log K = -20$, (Klewicki and Morgan 1998)), inhibits the oxidation of Cr(III) by Mn(III) present on birnessite. The inhibition rate of Cr(III) oxidation due to the formation of $\text{Mn}^{\text{III}}\text{HP}_2\text{O}_7$ increases as a function of pH, and is equal to 35%, 75%, 80%, and 90% at pH 3, 4, 5, and 6, respectively.

The oxidation of Cr(III) by (hydr)-oxides occurs following three main steps: (i) sorption of aqueous Cr(III) species onto a surface site of Mn(III,IV) (hydr)-oxides; (ii) electron transfer leading to the generation of Cr(VI) and Mn(II); and (iii) desorption of the reaction products (i.e., dissolved Cr(VI) and Mn(II)) (Richard and Bourg 1991). However, there is still a lack of information on the reaction mechanisms, particularly concerning Cr(III) sorption (see Fendorf et al. (1992), Manceau and Charlet (1992), Silvester et al. (1995) and Banerjee and Nesbitt (1999)). Generally, the reaction kinetics are initially fast regardless of the Mn(III,IV) (hydr)-oxide, then slow down significantly due to the passivation of the (hydr)-oxide surface at pH > 4.5 (see next paragraph). For instance, at pH 4, with initial concentrations of manganite $[\gamma\text{-Mn}^{\text{III}}\text{OOH}]$ and Cr(III) fixed at 0.03 $\text{g}\cdot\text{L}^{-1}$ and 0.5 $\mu\text{mol}\cdot\text{L}^{-1}$, respectively, half of the Cr(III) is oxidized within the first 50 s of the reaction, whereas oxidation is approximately 80% complete after 180 s (Johnson and Xyla 1991).

Passivation of the Mn(III,IV) (hydr)-oxide surface stems from various factors. At pH > 5, the formation of $\text{Cr}^{\text{III}}(\text{OH})_3$ precipitate on the oxide surface inhibits further redox reactions. The precipitate coating also acts as an efficient sink for soluble Cr(III) species (see Section 3.1.4) and forms a physical barrier between dissolved Cr(III) and the reactive Mn(III,IV) (hydr)-oxide surface (Fendorf 1995). The chemical reactivity of Mn(III,IV) (hydr)-oxides can be affected by the presence of Mn^{2+} in dissolved phase, and (or) generated during an oxidation reaction with Cr(III). Several assumptions have been proposed to explain this process: (i) Mn^{2+} could occupy a surface site on Mn(III,IV) (hydr)-oxides, thereby limiting Cr(III) sorption; (ii) Mn^{2+} could reduce Cr(IV) and Cr(V) (intermediate products of the oxidation reaction between Cr(III) and Mn(III,IV) (hydr)-oxides); or, (iii) incorporation of Mn^{2+} into the structure of Mn (hydr)-oxides could prevent access to oxidant surface sites (Carbonaro and Stone 2014).

In aquatic environments, other abiotic processes can also limit the oxidation of Cr(III) to Cr(VI): (i) competition between trace

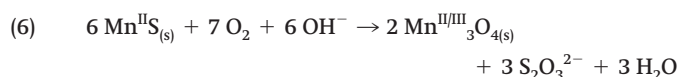
metals (cadmium (Cd), cobalt (Co), lead (Pb), zinc (Zn)) for sorption onto Mn(III,IV) (hydr)-oxides; (ii) formation of surface precipitates onto Mn(III,IV) (hydr)-oxides (e.g., aluminum (Al) and Fe(hydr)-oxides at pH \geq 4, calcite (CaCO₃), and (or) organic matter coating) (Sass and Rai 1987; Fendorf et al. 1993; Gorny et al. 2015); (iii) specific dissolution of Mn(III) mineral phase and (or) surface complexation of surface Mn(III) sites by various ligands (e.g., citrate, EDTA, pyrophosphate, and siderophore) (Kostka et al. 1995; Klewicki and Morgan 1998; Klewicki and Morgan 1999; Trouwborst et al. 2006); and (iv) reductive dissolution of Mn(III,IV) precipitates under anoxic conditions by Fe(II) (Burdige et al. 1992) and HS⁻ (Burdige and Nealson 1986).

The oxidation rate of Cr by Mn(III,IV) (hydr)-oxides in aquatic environments also depends on the initial speciation of Cr(III). Results from batch experiments with the soil fraction containing Mn(III,IV) (hydr)-oxides indicate that Cr(VI) production decreases according to the following initial form of Cr(III): freshly precipitated Cr(OH)₃ > Cr-citrate complex > aged-precipitated Cr(OH)₃ in citrate > aged-precipitated Cr(OH)₃ (James and Bartlett 1983). Dai et al. (2009) supplemented these results by adding other Cr(III) precipitates; their stability during oxidation by Mn(III,IV) (hydr)-oxides was found to decrease as follows: Cr(OH)₃ > CrFe(OH)₆ > CrPO₄.

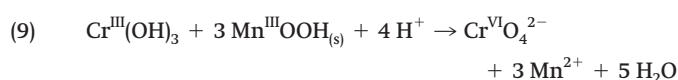
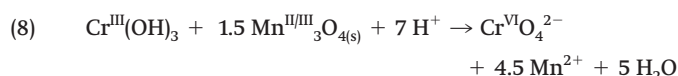
The complexation of Cr(III) by organic matter is kinetically slow and pH dependent (Dai et al. 2009; Gustafsson et al. 2014). However, organic Cr(III) complexes are generally more stable and resistant to oxidation than the hydrolysed forms of dissolved Cr(III) (Johnson and Xyla 1991). Using voltammetric measurements with diethylenetriamine pentaacetic acid (DTPA) as a Cr(III) complexing agent, Li and Xue (2001) observed that the organic complex of Cr(III) was slowest to oxidize. Carbonaro and Stone (2014) have pointed out that the oxidation rate of Cr(III) by Mn (hydr)-oxides tends to decrease in the presence of synthetic chelating agents in the following order: inorganic Cr(III) species > complex with nitrilotriacetic acid > complex with iminodiacetic acid.

3.1.3. The role of Mn cycling in surface sediments

Under anoxic conditions, the reduction of Mn(III,IV) (hydr)-oxides results in the formation of dissolved Mn²⁺ and Mn(II) precipitates, such as rhodocrosite (Mn^{II}CO₃; pKs = 9.3), Mn phosphate (Mn₃(PO₄)₂; pKs = 22) and to a lesser extent in sulfidic sediments, Mn sulfides (Mn^{II}S; pKs = 11.6 for pink Mn^{II}S and pKs = 12.6 for green Mn^{II}S) (Charlot 1983). Mn(II) can also be included in other minerals, such as calcite solid-solution Ca_{1-x}Mn_xCO₃ (with 0 < x < 1) (Billon et al. 2002). During resuspension of anoxic sediments in anoxic water column due to boat traffic, dredging, bioturbation, or flood events, oxygenation promotes changes in Mn speciation. For instance, the oxidation of Mn^{II}S by dissolved oxygen results in the formation of hausmanite (Mn₃^{IV}O₄) and manganite (Mn^{III}OOH) as illustrated in eqs. 6 and 7.



The redox transformations of Mn^{II}S to mixed valence Mn(II/III) (hydr)-oxides at pH > 7 cause the oxidation of Cr(III) (eqs. 8 and 9).



Wadhawan et al. (2015) highlighted the existence of such phenomena by carrying out batch experiments in N₂-sparged buffer solutions (pH 5–8) in the presence of Mn^{II}S suspension and Cr(VI) at initial concentrations of 1 g·L⁻¹ and 50 μmol·L⁻¹, respectively. After complete reduction of Cr(VI) to Cr(III) by sulfides (t = 50 h), the mixture was exposed to oxygen for 150 h. The production of Cr(VI) was shown to be highly pH dependent. The extent of Cr(VI) production was 8.5 μmol·L⁻¹ at pH 5.2, 2 μmol·L⁻¹ at pH 6.2, not detected at pH 7.1, and 0.5 μmol·L⁻¹ at pH 8. For pH < 7, the oxidation of Mn(II) by dissolved oxygen is strongly limited. In the absence of Mn(III,IV) (hydr)-oxides or dissolved Mn(III), it is unlikely that Cr(III) can be oxidized. One explanation might be that the Cr(III) oxidation by sulfur species was not clearly identified. Future research should be dedicated to their characterization. The recurrence of Cr(VI) production at pH > 7 was, in the present case, attributed to the oxidation of Cr(III) by mixed valence Mn(II/III) (hydr)-oxides, as no dissolved Mn(II) was detected in the solution.

In addition, Namgung et al. (2014) performed several batch experiments at pH 7–9 over a period of 21 days under oxic conditions in the presence of amorphous Cr(OH)_{3(s)} and dissolved Mn(II) at initial concentrations of 1 g·L⁻¹ and 50 μmol·L⁻¹, respectively. The concentration of Cr(VI) increased with increasing pH: below the limit of detection, 1.9–2.3, 4.3, and 7.2–8.2 μmol·L⁻¹ at pH 7, 8, 8.5, and 9, respectively. The expected oxidative process involving dissolved Mn²⁺ is divided into five steps: (i) sorption of dissolved Mn(II) onto the surface sites of Cr(III) hydroxides; (ii) surface oxidative precipitation of sorbed Mn(II) by the dissolved oxygen, thus leading to a mixed valence Mn(III/IV)-solid phase; (iii) sorption of dissolved Cr(III) at trace levels on surface sites of the Mn(III/IV)-solid phase; (iv) oxidation of Cr(III) to Cr(VI) and generation of Mn²⁺; and (v) desorption of Cr(VI) and Mn(II) from the surface. The oxidative process is certainly limited by the redox stability of Mn(II) at pH < 8 in the absence of Mn(II)-oxidizing bacteria or catalysts such as iron hydroxides (Diem and Stumm 1984; Davies and Morgan 1989; Morgan 2005). Moreover, the limited number of anionic surface sites on Cr(III) hydroxides (pH_{PZC} ~ 8) (Kosmulski 2011); see Section 6) are not favorable for the sorption of cationic Mn(II) species.

3.1.4. Bacterial activity

Few studies have been undertaken on the biological oxidation of Cr(III). For instance, in aerobic to partially anaerobic conditions, Mn(II)-oxidizing bacteria (e.g., *Bacillus* sp. Strain SG-1 (Murray and Tebo 2007) and *Pseudomonas putida* (Murray et al. 2005)) were shown to indirectly promote the oxidation of Cr(III) to Cr(VI), although the reaction mechanisms are unresolved. Bacterial oxidation of Mn(II) to Mn(IV) (hydr)-oxides occurs as a sequence of two enzymatically mediated one-electron transfer reactions (Webb et al. 2005), the enzyme Mn(III) intermediate being the potential Cr(III) oxidant (Murray and Tebo 2007).

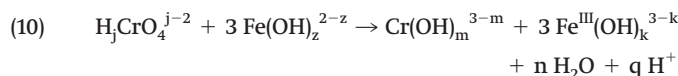
3.2. Reduction of Cr(VI)

The reduction process of Cr(VI) to Cr(III) is mainly effective in the presence of Fe(II), HS⁻, natural organic matter, and bacteria (Wittbrodt and Palmer 1996; Kim et al. 2001; Schlautman and Han 2001; Cheung and Gu 2007). The reduction of Cr(VI) is more effective in its soluble forms, thus the solubility of Cr(VI) can be a limiting factor in redox reactions in sediments since its dissolved concentrations depend on various elements in pore waters, especially barium (Ba(II)), Ca(II), Fe(III), K(I), and strontium (Sr(II)) (Baron et al. 1996; Olazabal et al. 1997; Buerge and Hug 1999; Kimbrough et al. 1999).

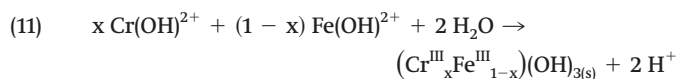
3.2.1. Fe(II)

As presented in eq. 10, the reduction of Cr(VI) to Cr(III) by dissolved Fe(II) under anoxic conditions occurs in two main steps: (i) three successive electron transfers progressively change the oxidation state of Cr from +VI to +III; and (ii) production of Cr(III)

and Fe(III). For pH values ranging from 5 to 9, Cr(III) production increases because the kinetics of Cr(VI) reduction increase with pH (Buerge and Hug 1997; Sedlak and Chan 1997; Pettine et al. 1998b; Schlautman and Han 2001). In anoxic solutions containing Cr(VI) and Fe(II) at initial concentrations of 20 and 50 $\mu\text{mol}\cdot\text{L}^{-1}$, respectively, the consumption of Cr(VI) was completed within about 6 days at pH 4, and within 1 day at pH 7.2 (Schlautman and Han 2001).



where the j , z , m , k , n , and q indexes denote the speciation of the possible hydrolyzed species, with $j = 0$ to 2, $z = 0$ to 3, $m = 0$ to 4, $k = 0$ to 4, $n = 4 + 3z - (3k + m)$, and $q = j + 3(2 - z) - (3k + m + 2n)$. The production of Cr(III) and Fe(III) species results in the precipitation of both separate hydroxide precipitates and solid solution chromic–ferric hydroxides (eq. 11), depending on the pH values as well as Cr(III) and Fe(III) speciation.



with $0 < x < 1$.

The marked pH dependence of Cr(VI) reduction by Fe(II) has been theoretically explained using the linear free energy relationship (LFER), by the high reactivity of Fe(II)-hydroxo complexes. Briefly, a LFER is usually assumed to reflect the sensitivity of a series of reactions occurring via the same mechanism to the composition of the reaction medium or to structural changes in the reagents and (or) products (Bonneville et al. 2009). Hydroxo ligands may stabilize Fe(III) and may donate electron density to Fe(II) through σ - and p - systems, resulting in a decrease of Fe(III)/Fe(II) redox potential values. Thus, the species $\text{Fe}^{\text{II}}(\text{OH})_x^{2-x}$ (with $x = 1$ or 2) appears to be a better reductant than hexaquo Fe^{2+} (Buerge and Hug 1997). The presence of DOM can also accelerate the rate of Cr(VI) reduction by stabilizing Fe(III) by complexation (Buerge and Hug 1998).

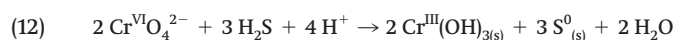
Numerous recognized Cr(VI)-reducing mineral phases containing Fe(II) are present in sediments, such as biotite (Chon et al. 2006), green rust (Loyaux-Lawniczak et al. 2000; Legrand et al. 2004; Skovbjerg et al. 2006), magnetite ($\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}_2\text{O}_4$) (Peterson et al. 1997b), ilmenite ($\text{Fe}^{\text{II}}\text{Ti}^{\text{IV}}\text{O}_3$) (White and Peterson 1996), and siderite ($\text{Fe}^{\text{II}}\text{CO}_3$) (Erdem et al. 2004). In addition, surface reactions of Fe(II)-bearing minerals such as CaCO_3 (Chakraborty et al. 2010), hematite ($\text{Fe}^{\text{III}}_2\text{O}_3$) (Buerge et al. 1999), goethite ($\text{Fe}^{\text{III}}\text{OOH}$) (Eary and Rai 1989), and phyllosilicates (chlorite, corrensite, montmorillonite) (Brigatti et al. 2000; Scheinost et al. 2008) can also contribute to the reduction of other redox sensitive trace elements (arsenic (As(V)), Cr(VI), antimony (Sb(V)), selenium (Se(IV)), uranium (U(VI))). Buerge and Hug (1999) showed that the reduction kinetics of Cr(VI) by Fe(II)-containing minerals decreases as follows: goethite \sim ferrihydrite \gg montmorillonite $>$ kaolinite \sim quartz \gg alumina. The enhanced reactivity of the adsorbed Fe(II) is commonly attributed to surface complexation of Fe(II) by hydroxo ligands on the mineral surface, which stabilize the Fe(III) oxidation state and lower the Fe(III)–Fe(II) redox potential values (Stumm et al. 1990; Williams and Scherer 2004). In addition, Deng and Stone (1996) have shown that aluminum oxides, goethite, and particularly titanium oxides present catalytic activities for Cr(VI) surface reduction in the presence of low molecular weight organic compounds.

Under oxic conditions (cases encountered particularly at the water–sediment interface through bioturbation and resuspension events), dissolved oxygen is able to actively oxidize Fe(II) to Fe(III)

(Appelo and Postma 2005) resulting in the production of Cr(III), albeit it to a lesser extent (Morgan and Lahav 2007). The reaction kinetics decrease with increasing pH: for instance, the conversion of Fe(II) into Fe(III) takes several days at pH < 5 , whereas it takes less than 1 min at pH 7 (Appelo and Postma 2005).

3.2.2. Sulfides

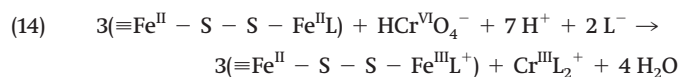
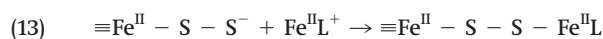
Dissolved sulfides reduce Cr(VI) to Cr(III) in three successive electron transfer steps. In the absence of dissolved oxygen, elemental sulfur is considered to be the main reaction product, as shown in eq. 12. To evaluate the pH dependence of this reaction, Kim et al. (2001) performed several experiments in N_2 -sparged phosphate buffer solutions (pH 6.6–7.3) containing Cr(VI) and S(-II) with initial concentrations of 20 $\mu\text{mol}\cdot\text{L}^{-1}$ and 200–800 $\mu\text{mol}\cdot\text{L}^{-1}$, respectively. The half-concentration was reached in less than 5, 10, and 30 min at pH 6.6, 7, and 7.3, respectively. The difference in kinetic rates is explained by the higher reactivity of H_2S compared to HS^- ($pK_a = 7$).



Lan et al. (2005) observed that, under anaerobic conditions, the production of elemental sulfur during Cr(VI) reduction subsequently improved the rate of Cr(III) production. The extent of Cr(VI) reduction was 69% in a 21 minute period ($[\text{Cr}(\text{VI})]_0 = 40 \mu\text{mol}\cdot\text{L}^{-1}$, $[\text{S}(-\text{II})]_0 = 800 \mu\text{mol}\cdot\text{L}^{-1}$, pH 7.6), whereas reduction was complete in 11 minutes once elemental sulfur was generated. The external addition of elemental sulfur provided similar results: the time for a complete Cr(VI) reduction ($[\text{Cr}(\text{VI})]_0 = 40 \mu\text{mol}\cdot\text{L}^{-1}$) at pH 7.6 decreased from more than 32 min to 12 min when 80 $\mu\text{mol}\cdot\text{L}^{-1}$ of elemental sulfur was initially added into the system.

Cr(VI) complexation by divalent cations ($\text{Me}^{\text{II}}\text{Cr}^{\text{VI}}\text{O}_4$) can change its own redox reactivity towards sulfides. Pettine et al. (1998a) observed an increase in Cr(III) production in the presence of the following divalent metals at μM levels: Ni $>$ Pb $>$ Cu $>$ Cd. To a lesser extent, Mn(II) and Mg (at $\text{mmol}\cdot\text{L}^{-1}$) also have significant effects on the reduction of Cr(VI) by sulfides. Oxygen affects the reaction by mainly oxidizing S^0 and to a lesser extent S(-II): the half-time of Cr(VI) reduction is 25 min in anaerobic conditions ($[\text{Cr}(\text{VI})]_0 = 40 \mu\text{mol}\cdot\text{L}^{-1}$, $[\text{S}(-\text{II})]_0 = 800 \mu\text{mol}\cdot\text{L}^{-1}$, pH = 7.6), whereas reduction is attained in 35 min in oxic conditions with $[\text{O}_2]_0 = 63 \mu\text{mol}\cdot\text{L}^{-1}$ (Pettine et al. 1998a). These results show that the reduction of Cr(VI) still occurs in oxic conditions, even if it is slightly limited.

Various sulfide minerals naturally present in sediments are reported to be reductant agents for Cr(VI), for example, amorphous Fe and Mn sulfides (Patterson et al. 1997; Wadhawan et al. 2015), mackinawite (FeS) (Mullet et al. 2004), and pyrite ($\text{Fe}^{\text{II}}\text{S}_2$) (Doyle et al. 2004). At pH > 5 , Fe sulfides are, in effect, reservoirs of Fe(II) and S(-II) due to their low dissolution. Their remobilization can, however, be limited due to surface passivation by Fe(III) and Cr(III) reaction products (Mullet et al. 2004; Rickard 2006; Lin and Huang 2008). Organic ligands can improve the reduction of Cr(VI) by: (i) removing surface oxides via the formation of soluble organometallic complexes; and (ii) eventually enhancing the reductive capacity of sulfide minerals by forming new surface sites, depending on the nature of the $\text{Fe}^{\text{II}}\text{L}^+$ complexes (eqs. 13 and 14). For example, Kantar et al. (2015) observed that the efficiency of organic ligands (L $^-$) on Cr(VI) consumption in the presence of pyrite decreases as follows: citrate \geq oxalate \sim tartrate $>$ EDTA $>$ salicylate \sim no organic ligands.



3.2.3. Particulate organic matter

Particulate organic matter (POM) is a significant reservoir of electron donors, which are able to reduce Cr(VI) to Cr(III) (Wittbrodt and Palmer 1995; Wittbrodt and Palmer 1997). However, the kinetics are much lower for these than they are for reduction reactions where Fe(II) or S(-II) are involved. The half-life of Cr(VI) ranges from several hours to several hundred hours with increasing pH in the presence of POM, while Fe(II) and S(-II) completely reduce Cr(VI) over a period ranging from a few hours to a few days (Kim et al. 2001; Schlautman and Han 2001). Considering the natural pH range (5–9), it is unlikely that POM acts as a powerful reducing agent in sediments, even if clays (Deng et al. 2003), Fe(III) (Wittbrodt and Palmer 1996), or Mn(II) (Kabir ud et al. 2000; Tian et al. 2010) are able to catalyze the reduction. Surface-catalyzed Cr(VI) reduction has been studied by Deng and Stone (1996) using oxide minerals and low molecular weight organic compounds. However, the authors underlined the importance of studying larger molecular weight organic compounds (like humic and fulvic acids) to evaluate the environmental significance of such processes.

3.2.4. Bacterial activity

Biotic reduction of Cr(VI) to Cr(III) is observed either through detoxification or dissimilatory reduction (see Chen and Hao 1998, Fendorf et al. 2000, Cheung and Gu (2007), Barrera-Díaz et al. 2012). Numerous Cr(VI)-reducing bacteria have been identified in aerobic and (or) anaerobic environments: *Achromobacter* sp. Strain Ch1 (Ma et al. 2007), *Agrobacterium radiobacter* EPS-916 (Llovera et al. 1993), *Enterococcus gallinarum* (Sayel et al. 2012), *Escherichia coli* ATCC 33456 (Shen and Wang 1993), *Leucobacter* sp. CRB1 (Zhu et al. 2008), *Pannonibacter phragmitetus* LSSE-09 (Xu et al. 2011), and *Pseudomonas fluorescens* LB300 (DeLeo and Ehrlich 1994). Microbial reduction of Cr(VI) often produces both insoluble Cr^{III}(OH)₃ precipitates and soluble organo-Cr(III) complexes (Cheng et al. 2010). These complexes are relatively stable over time due to slow ligand exchange processes, conferring a better stability to Cr(III) in pore waters than what can be thermodynamically predicted (James and Bartlett 1983; Remoundaki et al. 2007; Beck et al. 2008). Factors affecting Cr(VI)-reducing bacteria are multiple: biomass concentration, initial Cr(VI) level, carbon source, pH, temperature, redox potential, the presence of inhibitors, etc. (Chen and Hao 1998). Rate comparisons for Cr(VI) reduction between Fe(II), S(-II), and bacteria suggests that biotic reductive pathways dominate in aerobic environments. Bacteria contribute partially to the reduction of Cr(VI) in anaerobic environments. Fe(II) is the main reducer in anaerobic environments at pH > 5, whereas the reduction of Cr(VI) by sulfides dominates at pH < 5 (Fendorf et al. 2000).

4. Dissolution/precipitation

The solubility of Cr in pore waters can be partly controlled by the formation of several precipitates, as pore waters can contain dissolved species in high proportions (sometimes > mg·L⁻¹). Precipitation/dissolution reactions of Cr have been studied extensively (see Rai et al. 1989; Richard and Bourg 1991; Fendorf 1995; Kimbrough et al. 1999).

Cr(VI) is generally soluble and rarely forms precipitates, but can be incorporated into some solid phases by substituting oxyanions—primarily sulfates and carbonates. (Baron and Palmer 1996; Baron et al. 1996; Kimbrough et al. 1999). Generally, only BaCr^{VI}O₄, KFe^{III}₃(Cr^{VI}O₄)₂(OH)₆, KFe^{III}(Cr^{VI}O₄)₂·2H₂O, Fe^{III}OHCr^{VI}O₄·2Fe^{III}(OH)₃, and (or) SrCr^{VI}O₄ may precipitate in sediments. Cr(VI) can also be incorporated in several precipitates, such as allophanes (Opiso et al. 2009), CaCO₃ (Hua et al. 2007; Tang et al. 2007), or barium sulfate (BaSO₄) (Meldrum et al. 1943), contributing to decreasing the solubility of Cr(VI) in sediment pore waters.

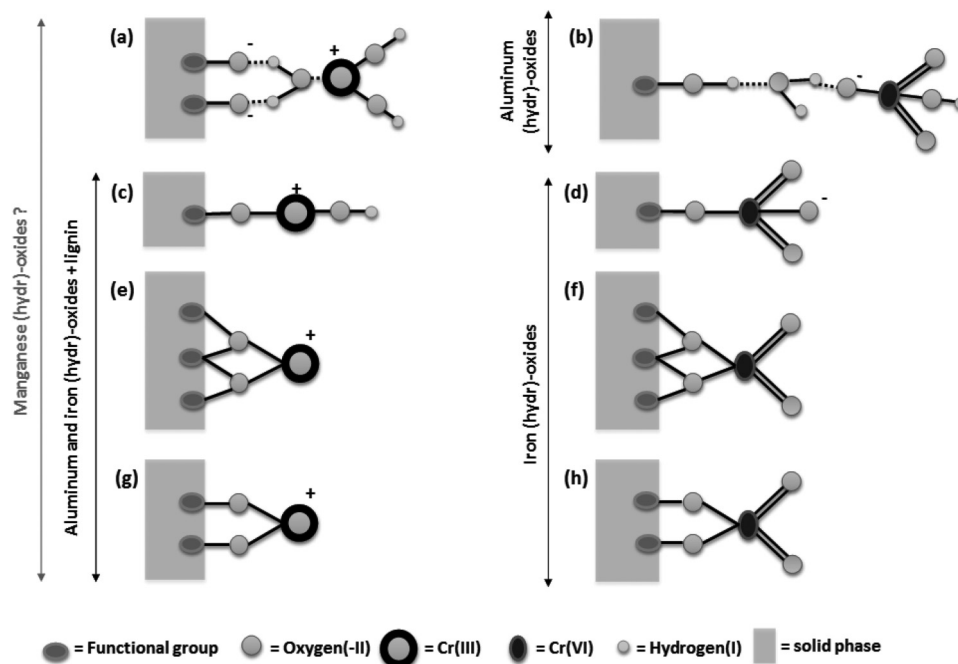
Amorphous Cr^{III}(OH)₃, crystalline Cr^{III}(OH)₃·H₂O, and esko-laite (Cr^{III}₂O₃) are the main Cr(III) precipitates in pore waters at pH values ranging from 5 to 12 (Rai et al. 1989). However, numer-

Table 2. Sorption mechanisms between inorganic chromium species and some solid phases.

Inorganic species	Adsorbent	[sorben]₀ (g·L ⁻¹)	[Cr]₀ M	pH	Experimental Method used	Complexation mode	Remarks	References
Cr(III)	Silica	10	4·10 ⁻⁵	3.5–6.3	ΔIS	Inner-sphere (outer-sphere)	Inner-sphere complexation requires time	Csobán et al. 1998
	Silica	—	5·10 ⁻⁶	5–6	XAS, DRIFT	Inner-sphere monodendate	Formation of γ-CrOOH	Fendorf and Sparks 1994
	Goethite	—	10 ⁻³ –10 ⁻⁷	4	XAS	Inner-sphere	Formation of α- and γ-MeOOH, with Me = Fe and (or) [Cr], precipitation or sorption as a function of [Cr]	Charlet and Manseau 1992
Cr(VI)	γ-Al ₂ O ₃	40	3·10 ⁻³	3–5	ΔIS, PJRE	Inner-sphere	—	Chang et al. 1994
	γ-Al ₂ O ₃	10	0.5–3·10 ⁻³	—	ESR	Inner-sphere	Slow dissociation of organic-Cr(III) complexes leading to inner-sphere complexes between Cr(III) and γ-Al ₂ O ₃	Karthein et al. 1991
	Lignin	5	5·10 ⁻⁵	—	ΔIS	Inner-sphere	—	Wu et al. 2008
	Hematite	4	10 ⁻⁴	2–10	ΔIS	Inner-sphere	—	Ajouyed et al. 2010
	Goethite	4	10 ⁻⁴	2–10	ΔIS	Inner-sphere	—	Ajouyed et al. 2010
	α-alumina	4	10 ⁻⁴	2–10	ΔIS	Outer-sphere	—	Ajouyed et al. 2010
	Al hydroxides	2	10 ⁻⁴ –0.2	6	ΔIS	Outer-sphere	—	Alvarez-Ayuso et al. 2007
	γ-Al ₂ O ₃	10	10 ⁻³	4–9	ΔIS	Outer-sphere	—	Elzinga et al. 2009
	Goethite	1.6	7·10 ⁻⁶	3–9	ΔIS	Inner-sphere	—	Weerasooriya and Tobschall 2000
	Goethite	10	2–5·10 ⁻³	5–6	XAS	Inner-sphere, mono-/bi-dendate	—	Fendorf et al. 1997
Goethite	10	0.5–2·10 ⁻³	6.5–8	PJRE	Inner-sphere, mono-/bi-dendate	—	Grossl et al. 1997	

Note: ΔIS, change in ionic strength; XAS, x-ray adsorption spectroscopy; DRIFT, diffuse reflectance infrared fourier transform; PJRE, pressure-jump relaxation technique; ESR, electron spin resonance and electron ppin-echo spectroscopies.

Fig. 2. Schematic representation of Cr(III) and Cr(VI) configurations on the surface of solids present in aquatic systems and surface sediments: (a, b) outer-sphere surface complexation; (c, d) mononuclear monodentate inner-sphere surface complexation; (d, e) mononuclear bidentate inner-sphere surface complexation; and, (g, h) binuclear bidentate inner-sphere surface complexation.



ous iron-containing Cr co-precipitates can form in sediments: amorphous hydroxides ($\text{Cr}^{\text{III}}_x\text{Fe}^{\text{III}}_{1-x}(\text{OH})_3$), goethite-bracewellite solid-solution ($\text{Cr}^{\text{III}}_x\text{Fe}^{\text{III}}_{1-x}\text{OOH}$), hematite-eskolaite solid-solution ($\text{Fe}^{\text{III}}_x\text{Cr}^{\text{III}}_{2-x}\text{O}_3$), donatite $[(\text{Fe}^{\text{II}}, \text{Mg}, \text{Zn})(\text{Cr}^{\text{III}}, \text{Fe}^{\text{III}}, \text{Al})\text{O}_4]$, ferrous chromite ($\text{Fe}^{\text{II}}\text{Cr}^{\text{III}}_2\text{O}_4$), and heideite $[(\text{Fe}^{\text{II}}, \text{Cr}^{\text{III}})_{1-x}(\text{Ti}, \text{Fe}^{\text{II}})_x\text{S}_4]$ (Richard and Palmer 1991; Charlet and Manceau, 1992; Nriagu et al. 1993; Peterson et al. 1997a). The occurrence of such co-precipitates mainly depends on redox conditions, with a prevalence of Cr(III)/Fe(II) compounds under reducing conditions. It is also worth mentioning that, during early diagenetic processes in surface sediments, the reductive dissolution of Fe plays a key role in the mobility of Cr(III). For example, Scholz and Neumann (2007) demonstrated that the reduction of Fe(III) hydroxides leads to a temporary increase of dissolved Cr(III) species. Complexation of Cr(III) with DOM during both the mineralization of particulate organic matter in sediments (Gustafsson et al. 2014; Saputro et al. 2014) and through bacterial activity itself (Puzon et al. 2008; Kantar et al. 2011) can also increase the solubility of Cr(III) in pore waters.

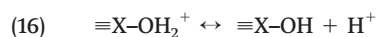
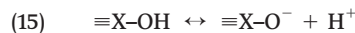
5. Adsorption reaction

Adsorption reactions depend heavily on the Cr oxidation state, since the charge of Cr(III) and Cr(VI) species can be opposite depending on the pH values encountered in sediments. Sorption mechanisms are usually described as nonspecific (outer-sphere surface complexation) and specific adsorption (inner-sphere surface complexation). Note that the sphere of hydration is only maintained for the nonspecific adsorption. Outer-sphere complexes are characterized by electrostatic interactions, which are less stable than the covalent bindings of inner-sphere surface complexes (Bradl 2004). As presented in Table 2, Cr(III) forms inner-sphere surface complexes whatever the solid phase involved. The complexation mechanism is probably divided into two main steps: (i) an outer-sphere surface complexation between Cr(III) and the adsorbent; and (ii) the evolution over time of the binding to an inner-sphere surface complex (Csobán et al. 1998). Sorption mechanisms of Cr(VI) differ according to the mineral

surface. For instance, iron (hydr)-oxides involve inner-sphere surface complexation, whereas aluminum (hydr)-oxides involve outer-sphere surface complexation (Grossl et al. 1997; Ajouyed et al. 2010). The whole set of these processes are summarized in Fig. 2.

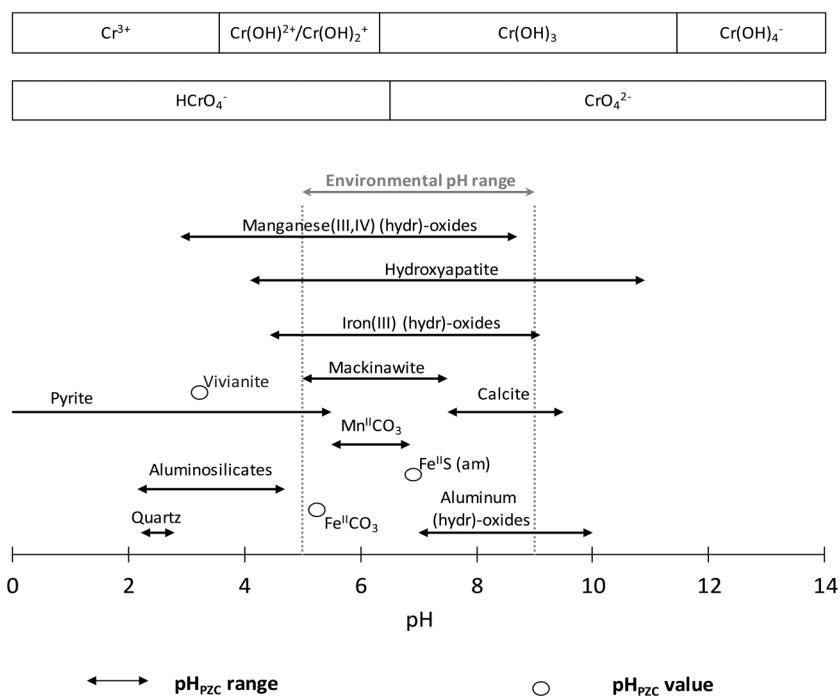
5.1. Sorption onto mineral surfaces

The characteristics of minerals, such as their nature, degree of crystallinity, and surface charge, as well as pH and competing ions, can change the distribution of Cr(III) and Cr(VI) between the liquid and solid phases. Mineral surfaces are considered amphoteric with the existence of a point of zero charge (PZC). For instance, the surface of hydroxyl groups is positively charged when pH values are below pH_{PZC} , and negatively charged when pH values are above pH_{PZC} . This surface reaction is described by eqs. 15 and 16, where $\equiv\text{X}$ corresponds to an active surface site:



pH_{PZC} values of minerals commonly found in sediments (see Fig. 3) allow us to define the surface charge of these minerals as a function of pH. Note that hydrogen (H^+) and hydroxide (OH^-) are not the sole ions determining the PZC for carbonate, phosphate, and sulfide minerals. In these latter cases, PZC values also depend on concentrations of Fe^{2+} , Mn^{2+} , CO_3^{2-} , phosphate (PO_4^{3-}), etc. Two separate groups of minerals are observed: (i) minerals with negative surface charges including aluminosilicates, quartz, pyrite, and vivianite; and (ii) minerals with mixed surface charges like amorphous Fe sulfides, CaCO_3 , hydroxyapatite, (hydr)-oxides, mackinawite, rhodocrosite, and siderite. Cationic Cr(III) species, especially $\text{Cr}^{\text{III}}(\text{OH})^{2+}$ and $\text{Cr}^{\text{III}}(\text{OH})_2^+$, adsorb better onto anionic sites of minerals belonging to the first group, such as aluminosilicates (Khan et al. 1995; Abollino et al. 2003; Álvarez-Ayuso and García-Sánchez 2003).

Fig. 3. Evolution of pH_{PZC} (values in supplementary data¹) for mineral phases present in aquatic systems and surface sediments, including the predominance diagram of Cr speciation.



Cr(III) sorption efficiency on kaolinite and silica decreases with the formation of organo-Cr(III) complexes (Takahashi et al. 1999). For example, Abollino et al. (2003) showed up to a 70% decrease in sorption of Cr(III) on Na-montmorillonite after addition of organic ligands (ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), tartaric acid, oxalic acid) under the following conditions: pH 5.5; $[\text{Cr(III)}]_0 = 10^{-4}$ M; $[\text{ligand}]_0 = 10^{-3}$ M. Puzon et al. (2008) also observed that the elution of Cr(III) was enhanced during leaching experiments on soil column systems because of the formation of complexes with organic ligands in the following order: citrate-Cr(III) > malate-Cr(III) \gg histidine-Cr(III) \gg Cr(III) (pH 6.8; $[\text{organo-Cr(III)}]_0 = [\text{Cr(III)}]_0 = 2$ mmol·L⁻¹). The sorption mechanisms of dissolved Cr^{III}(OH)₃ remain unclear, but precipitation likely controls the fate of this neutral species.

Adsorption processes between the ionic Cr species and minerals with mixed surface charge are, however, more difficult to assess in a natural pH range (Fig. 3). In surface sediments containing a significant fraction of amorphous minerals, positive surface sites can promote the sorption of anionic species of Cr(VI) (i.e., $\text{HCr}^{\text{VI}}\text{O}_4^-$ and $\text{Cr}^{\text{VI}}\text{O}_4^{2-}$) (Bradl 2004). Rai et al. (1988) have studied the sorption capacity of these species by various precipitates as a function of pH. The sorption capacity for Cr(VI) tends to decrease as a function of pH and also according to the nature of the minerals in the following order: Fe (hydr)-oxides \geq Al₂O₃ \gg kaolinite > montmorillonite. In addition, the sorption of Cr(VI) tends to increase with decreasing pH. Above pH \geq 9, Cr(VI) species desorb quantitatively and turn into soluble anions. Obviously, the adsorption of Cr(VI) is favored in minerals holding high pH_{PZC} values, so that early diagenetic processes involving a decrease in pH (up to 2 units (Lesven et al. 2008)), contribute to the decline in mobility of Cr(VI) in sediments.

Several anionic or neutral competing species found in pore waters with concentrations ranging between μM and mM can enhance the mobility of Cr(VI). Experiments performed on $\gamma\text{-Al}_2\text{O}_3$ showed that Cr(VI) adsorption drastically decreases in the

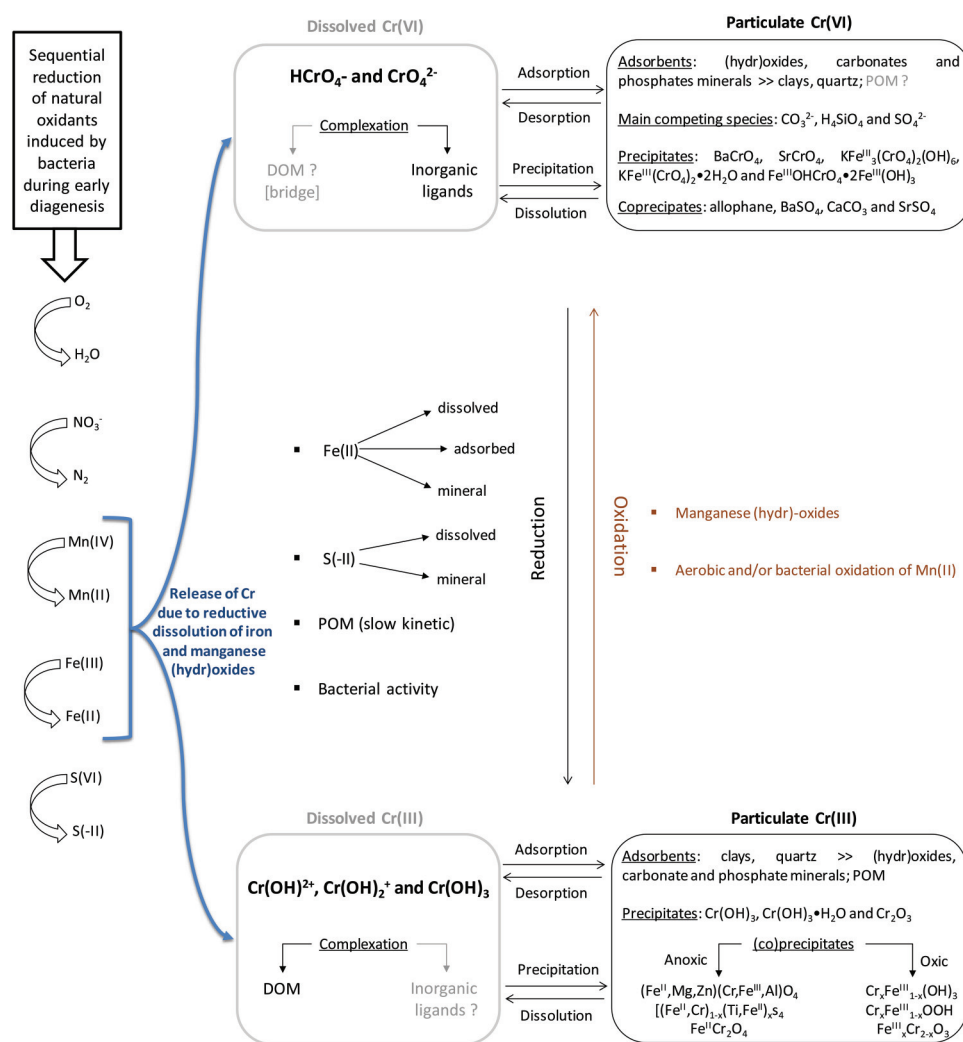
presence of competing anions in the following order: $\text{Mo}^{\text{VI}}\text{O}_4^{2-} > \text{Se}^{\text{VI}}\text{O}_3^{2-} > \text{Se}^{\text{VI}}\text{O}_4^{2-} > \text{SO}_4^{2-}$ (Wu et al. 2000). Adsorption on iron hydroxides can even be suppressed in the presence of CO_3^{2-} , SO_4^{2-} , and H_4SiO_4 (Zachara et al. 1987; Villalobos et al. 2001). Finally, the presence of these competing species, which are inherent in pore waters, increases the mobility of Cr(VI) in sediments.

5.2. Sorption involving particulate organic matter

POM represents an important fraction of sediments. Its chemical and structural composition is highly variable and only partially characterized via aromaticity, elemental composition, nature and content of functional groups, or molecular size (Kim et al. 1990; Sutton and Sposito 2005). The role of POM in the immobilization of Cr is non-negligible since it represents the second adsorbent phase (10%–40%) in sediments after aluminosilicates (Table 1). However, studies examining the sorption of Cr onto organic solid phases are very limited because of the precipitation of Cr(III) under $\text{Cr}^{\text{III}}(\text{OH})_3$ for pH \geq 5, and (or) the redox instability of Cr(VI) in acidic solutions (experimental pH value <5) (Parsons et al. 2002; Park et al. 2008). The existence of direct interactions between Cr(III) and some functional groups (-OH, -C₆H₄OH, -COOH, -NH₂, and -SH) are evidenced in numerous studies (Nakayama et al. 1981; Fukushima et al. 1995; Takahashi et al. 1999; Brown et al. 2000; Santosa et al. 2008; Batista et al. 2009), although the type of bindings have not yet been established. Few studies have examined the Cr(VI) sorption on POM. Two mechanisms of sorption can ultimately be considered: (i) indirect sorption via a cationic bridge (formed, for example, with Al, Fe, or Mn) between anionic Cr(VI) species and the negative surface charge of POM (Redman et al. 2002); and (ii) direct sorption between anionic Cr(VI) species and positively charged surface groups of the organic solid phase (e.g., protonated amino groups) (Park et al. 2008).

¹Supplementary data are available with the article through the journal Web site at <http://nrcresearchpress.com/doi/suppl/10.1139/er-2016-0012>.

Fig. 4. Summary of chromium reactions in aquatic systems and surface sediments during early diagenetic processes. Abbreviations: DOM, dissolved organic matter; POM, particulate organic matter. [Colour online.]



Conclusion

In aquatic systems and surface sediments, the behavior of Cr depends on both abiotic and biotic reactions, including complexation/decomplexation, sorption, precipitation/dissolution, redox, and respiration reactions. The main mechanisms, which happen during early diagenesis, are summarized in Fig. 4. It has been clearly shown that changes in Mn speciation, Cr(VI)-reducing phases (ferrous and sulfide minerals, and also Fe(II)-bearing minerals), and bacterial activity are the key points for the speciation and dynamics of Cr in surface sediment.

Although the preservation of inorganic Cr species is difficult due to precipitation of Cr(III) or redox instability of Cr(VI), analytical and experimental efforts are still needed to clarify certain mechanisms affecting Cr speciation in surface sediments. These include resolving Cr speciation linked to other parameters (Fe, Mn, S, etc.), identifying Cr(III)- and Cr(VI)-complexing functional groups of natural organic matter, and elucidating the sorption (outer- or inner-sphere complexation) and oxidative mechanisms (repeated comparison of redox reactivity in the presence of Mn(III) at different concentrations) of Cr(III) with Mn(III,IV) (hydr)-oxides. The oxidative dissolution mechanisms of Cr(III) should be consolidated by additional studies focusing on: (i) the nature of the precipitates ($\text{Cr}^{III}_2\text{O}_3$, $\text{Fe}^{III}\text{Cr}^{III}_2\text{O}_4$, $\text{MgCr}^{III}_2\text{O}_4$, $\text{Cr}^{III}\text{PO}_4$, $\text{Fe}^{III}_{1-x}\text{Cr}^{III}_x(\text{OH})_3$, with $0 < x < 1$); (ii) the ageing effect of Cr(III) minerals; (iii) the impact of anionic ligands on the dissolution kinetic rate of Cr(III);

(iv) the impact of competing cations towards Cr^{3+} and Mn^{2+} possibly present in pore waters; and (v) attaining a better understanding of the oxidative bacterial pathways. Complementary experiments should also be carried out on the redox reactivity of $\text{Me}^{II}\text{Cr}^{\text{VI}}\text{O}_4$ species during reductive processes.

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