Chromium behavior in aquatic environments: a review

Josselin Gorny, Gabriel Billon, Catherine Noiriel, 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(II) 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 complexion 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 transposes 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 réactions 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,
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 (NO₃⁻-N), iron (Fe) hydroxides, sulfates (SO₄²⁻)) (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 Cr⁴⁺(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 (CO₃²⁻), chloride (Cl⁻), and humic acid, which can dramatically interfere with the chromatographic separation of Cr(III) (Seby et al. 2003; Xing 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).

### 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).

<table>
<thead>
<tr>
<th>Oxidation State</th>
<th>Formulas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(III)</td>
<td>Cr³⁺</td>
</tr>
<tr>
<td>Cr(IV)</td>
<td>Cr⁴⁺</td>
</tr>
<tr>
<td>Cr(VI)</td>
<td>Cr⁶⁺</td>
</tr>
</tbody>
</table>

In the environmental pH range (i.e., 5 < pH < 9), Cr³⁺(OH)₃, HCr⁴⁺O₄⁻, and Cr⁶⁺(OH)₂⁻ represent the main free aqueous Cr species (Rai et al. 1989; Kotas and Stasicka 2000). Contents of polynuclear complexes ([Cr(II)OH]₃⁺, Cr³⁺(OH)₂⁻, Cr⁶⁺(OH)₄⁻, [Cr³⁺(II)OH]₄⁻, and Cr⁶⁺O₂²⁻) and mixed ligand complexes (Cr³⁺(II)OHCr⁺, Cr³⁺SO₄²⁻) 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; Torapav 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).

\[
\text{(1) } \text{Cr}^{3+} + 3 \text{OH}^- \leftrightarrow \text{Cr(OH)}_3^+ \text{, with } K_f = 6.7 \times 10^{-31}
\]

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 (HCr⁵⁺O₄⁻ and Cr⁵⁺O₅²⁻), 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 (Ca²⁺), potassium (K⁺), sodium (Na⁺), ammonium (NH₄⁺)) (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: O₂/H₂O, Mn⁴⁺/Mn²⁺ (including the metastable Mn(III) species), NO₃⁻/NO₂⁻, NO₂⁻/NO₃⁻, Fe(III)/Fe(II), and SO₄²⁻/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.

\[
\text{(2) } 2 \text{Cr(OH)}_2^+ + 1.5 \text{O}_2 \text{aq} + \text{H}_2\text{O} \rightarrow 2 \text{CrO}_4^{2-} + 6 \text{H}^+
\]

Schroeder and Lee (1975) observed that, where the concentration range was 1.9–2.4 μmol 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. Early and Rai (1987) reported no redox reaction in −2 μg 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 g L⁻¹ (Namgung et al. 2014); while not

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

<table>
<thead>
<tr>
<th>Environmental compartment</th>
<th>pH range</th>
<th>Total Cr (mg kg(^{-1}))</th>
<th>Exch (%)</th>
<th>Red (%)</th>
<th>Oxi (%)</th>
<th>Res (%)</th>
<th>Species detected</th>
<th>Where and why</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lake</td>
<td>8.1–9.6</td>
<td>&lt;85 10^3</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>Only Cr(III)</td>
<td>Conditions at the study site favor the reduction of Cr(VI) to Cr(III)</td>
<td>Burbridge et al. 2012</td>
</tr>
<tr>
<td>Aquifer</td>
<td>7–9</td>
<td>&lt;15 10^3</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>35–91 Cr(III and VI)</td>
<td>[Cr(VI)] &gt; [Cr(III)]</td>
<td>Dermatas et al. 2015</td>
</tr>
<tr>
<td>River</td>
<td>—</td>
<td>30–720</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>&lt;50 Cr(III and VI)</td>
<td>Mn(III,IV) (hydr)-oxide in SPM modify Cr speciation. [Cr(III)] ≥ [Cr(VI)]</td>
<td>Szalinska et al. 2010</td>
</tr>
<tr>
<td>Estuary</td>
<td>7.6–8.1</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>3.6 Cr(III), DOM-Cr(III)</td>
<td>DOM-Cr(III) is the main species</td>
<td>Walsh and O’Halloran 1996</td>
</tr>
<tr>
<td>River</td>
<td>7.9–8.5</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>&lt;90 Cr(III and VI)</td>
<td>[Cr(III)] ≥ [Cr(VI)]</td>
<td>Bobrowski et al. 2004</td>
</tr>
<tr>
<td>Sea</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>&lt;2 Cr(III and VI)</td>
<td>[Cr(III)] ≥ [Cr(VI)]</td>
<td>Sumida et al. 2005</td>
</tr>
<tr>
<td>River</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>&lt;1 Cr(III and VI)</td>
<td>Cr(III)/Cr(VI) ratios vary according to the origin of seawater samples</td>
<td>Abu-Saba and Flegal 1995</td>
</tr>
<tr>
<td>River</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>&lt;10 Cr(III and VI)</td>
<td>[Cr(III)] ≥ [Cr(VI)]</td>
<td>Wen et al. 2002</td>
</tr>
<tr>
<td>Sea</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>&lt;1 Cr(III and VI)</td>
<td>[Cr(VI)] &gt; [Cr(III)]; Cr(III) production through photoreduction?</td>
<td>Van Den Berg et al. 1994</td>
</tr>
<tr>
<td>Sea</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>&lt;1 Cr(III and VI)</td>
<td>[Cr(VI)] &gt; [Cr(III)]</td>
<td>Connelly et al. 2006</td>
</tr>
<tr>
<td>River</td>
<td>—</td>
<td>18 1 2 42 55</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>Davidson et al. 1994</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lake</td>
<td>—</td>
<td>18 0 0 43 57</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>Davidson et al. 1998</td>
<td></td>
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</tr>
<tr>
<td>River</td>
<td>—</td>
<td>2.5–25 0−5−10−20−65−80</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>Nemati et al. 2011</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sea</td>
<td>6–7</td>
<td>20–90 0−10−20−30−60−90</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>Yuan et al. 2004</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sea</td>
<td>7–8</td>
<td>35–110 0−15−20−30−60−80</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>Guevara-Riba et al. 2004</td>
<td></td>
<td></td>
</tr>
<tr>
<td>River</td>
<td>—</td>
<td>75–130 0−20−10−60−70−80</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>Filgueiras et al. 2004</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sea</td>
<td>—</td>
<td>74–124 0−15−15−70−80</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>Yu et al. 2010</td>
<td></td>
<td></td>
</tr>
<tr>
<td>River</td>
<td>—</td>
<td>7.5–8 30–110 0−15−30−40−70</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>Davutluoglu et al. 2011</td>
<td></td>
<td></td>
</tr>
<tr>
<td>River</td>
<td>—</td>
<td>7.5–8 7–5−15−40−40−70</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>Lesven et al. 2010</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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).

<table>
<thead>
<tr>
<th>Eh (V)</th>
<th>pe</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH = 7</td>
<td>1</td>
</tr>
</tbody>
</table>

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 CrIII to CrV (eq. 3) occurs only in harsh conditions (at high temperatures ranging from 200 to 300 °C). Temperature is therefore one of the limiting parameters for generating aerobic oxidation of CrIII in aquatic environments.

(3) 2 CrIII + 3 O2(g) → 4 CrIV

### 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 CrIII by various natural or synthetic Mn(III,IV) (hydr)-oxides. The latter can be birnessite [Na, K, Mg, Ca]MnIII,IV-OH2·nH2O], buserite [NaMnIII,IV-OH2·H2O], cryptomelane [(K)MnIII,IV-OH2], hausmanite [MnIII,IV-OH2], manganeite [MnIII,IV(OH)2], lithiophorite [Al3LiMnIII,IV(OH)2], pyrolusite [β-MnIII,IV-OH2], romanechite [Ba3H2O2MnIII,IV-OH2·3H2O], and todorokite [(Na)MnIII,IV-OH2·3H2O] (Eary and Rai 1987; Johnson and Xyla 1991; Silvester et al. 1995; Kim et al. 2002; Weaver et al. 2002; Feng et al. 2006).

(4) 1.5 MnIVO20 + CrIII(OH)2+ → 1.5 MnII + HCrIVO4-

(5) 3 MnIII(OH)2 + CrIII + 3 H+ → 3 MnII + 2 HCrIVO4- + 3 H2O

The oxidizing capacities of Mn(III,IV) (hydr)-oxides species differ according to their physico-chemical and surface properties, including pH, 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 CrIII species at initial concentrations of 0.4–0.8 g·L−1 and 200 μmol·L−1, respectively. The decrease of the CrIII-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 → romanecite > cryptomelane ≫ manganeseite → pyrolusite ≫ lithiophorite.

At higher concentrations of Cr(III) (4 mmol·L−1) and pH = 4.5, the CrIII-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 CrIII remains birnessite.

This difference in CrIII-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 CrIII by manganese, lithiophorite, and pyrolusite is observed, the surface sites of these Mn(III,IV) (hydr)-oxides are positive (i.e., pHPC > pH; see Section 6). From an electrostatic point of view, the complexion between the cationic CrIII 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 CrIII, while performing experiments in N2-sparged solutions (pH 3–6) with birnessite and dissolved CrIII at initial concentrations of 0.1 g·L−1 and 50 μmol·L−1, respectively. They have also shown that, at a concentration of 1 mmol·L−1, pyrophosphate (P₂O₇³⁻), a powerful complexing agent of Mn(III) [log $K$ = −29, (Klewicky and Morgan 1998)], inhibits the oxidation of CrIII by Mn(III) present on birnessite. The inhibition rate of CrIII oxidation due to the formation of MnII(PO₄)₂ 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 CrIII by (hydr)-oxides occurs following three main steps: (i) sorption of aqueous CrIII 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 CrVI and MnII) (Richard and Bourg 1991). However, there is still a lack of information on the reaction mechanisms, particularly concerning CrIII sorption (see Section 3.1.4) and forms a physical barrier between dissolved CrIII 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 Mn²⁺ in dissolved phase, and (or) generated during an oxidation reaction with CrIII. Several assumptions have been proposed to explain this process: (i) Mn²⁺ could occupy a surface site on Mn(III,IV) (hydr)-oxides, thereby limiting CrIII sorption; (ii) Mn²⁺ could reduce CrIV and Cr(V) (intermediate products of the oxidation reaction between CrIII and Mn(III,IV) (hydr)-oxides); or, (iii) incorporation of Mn²⁺ 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 CrIII to CrV: (i) competition between trace...
The redox transformations of Mn(III) to mixed valence Mn(II/III)–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 oxidant (Murray and Tebo 2007). 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)₃ₗ₀ 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 Mn³⁺ is divided into five steps: (i) sorption of dissolved Mn(II) onto the surface sites of Cr(III) hydroxides; (ii) surface oxidative sorption of Cr(VI) by Mn(III) species. 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(VI) (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)), calcium (Ca(II)), iron (Fe(III)), and strontium (Sr(II)) (Baron et al. 1996; Olazabal et al. 1997; Buerge and Hug 1999; Kimbrough et al. 1999).
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 μmol·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).

\[
\text{(10) } \frac{1}{2} \text{H}_2\text{CrO}_4^{2-} + 3 \text{Fe(OH)}_2^{2-} \rightarrow \text{Fe(OH)}_3^{3-m} + 3 \text{Fe}^{III}(\text{OH})_3^{3-k} + n \text{H}_2\text{O} + q \text{H}^+ 
\]

where the j, z, m, k, and q indexes denote the speciation of the possible hydrolyzed species, with j = 0 to 2, \( x = 0 \) to 3, m = 0 to 4, k = 0 to 4, n = 4 + 3z - (3k + m), and q = j + (3z - n) - (3k + m + 2n). The production of Fe(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.

\[
\text{(11) } x \text{Cr(OH)}_2^{2-} + (1-x) \text{Fe(OH)}_2^{2+} + 2 \text{H}_2\text{O} \rightarrow \left(\text{Fe}^{III}\text{Fe}^{II}_{1-x}\right)\text{(OH)}_3^{3+} + 2 \text{H}^+ 
\]

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 π-systems, resulting in a decrease of Fe(III)/Fe(II) redox potential values. Thus, the species Fe(H(OH))₂⁻ (with \( x = 1 \) or 2) appears to be a better reductant than hexaquo Fe²⁺ (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 (Fe₆II₇III₃O₁₄) (Peterson et al. 1997b), ilmetite (Fe₆II₈III₄O₁₉) (White and Peterson 1996), and siderite (Fe₆II₃CO₃) (Erdem et al. 2004). In addition, surface reactions of Fe(II)-bearing minerals such as CaCO₃ (Chakraborty et al. 2010), hematite (Fe₂O₃), (Buerge et al. 1999), goethite (Fe₆II(OH)₃) (Early and Ray 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 → ferrihydrite ≫ montmorillonite ≫ kaolinite → quartz ≫ aluminia. The enhanced reactivity of the adsorbed Fe(II) is commonly attributed to surface complexion 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.

Underoxic 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 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. Sulfoxides

Dissolved sulfoxides 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 N₂-sparged phosphate buffer solutions (pH 6.6–7.3) containing Cr(VI) and S(-II) with initial concentrations of 20 μmol·L⁻¹ and 200–800 μmol·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 H₂S compared to HS⁻ (pKₐ = 7).

\[
\text{(12) } 2 \text{Cr}^{VII}O_4^{2-} + 3 \text{H}_2\text{S} + 4 \text{H}^+ \rightarrow 2 \text{Cr}^{III}(\text{OH})_{30} + 3 \text{S}^{0(n)} + 2 \text{H}_2\text{O} 
\]

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 ([Cr(VI)]₀ = 40 μmol·L⁻¹, [S(-II)]₀ = 800 μmol·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 ([Cr(VI)]₀ = 40 μmol·L⁻¹) at pH 7.6 decreased from more than 32 min to 12 min when 80 μmol·L⁻¹ of elemental sulfur was initially added into the system.

Cr(VI) complexation by divalent cations (Me₆Cr⁴VIO₄) can change its own redox reactivity towards sulfoxides. Pettine et al. (1998a) observed an increase in Cr(II) 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 mmol·L⁻¹) also have significant effects on the reduction of Cr(VI) by sulfoxides. Oxygen affects the reaction by mainly oxidizing S₀ and to a lesser extent S(-II): the half-time of Cr(VI) reduction is 25 min in anaerobic conditions ([Cr(VI)]₀ = 40 μmol·L⁻¹, [S(-II)]₀ = 800 μmol·L⁻¹, pH 7.6), whereas reduction is attained in 35 min inoxic conditions with [O₂(0)] = 63 μmol·L⁻¹ (Pettine et al. 1998a). These results show that the reduction of Cr(VI) still occurs inoxic conditions, even if it is slightly limited.

Various sulfoxide minerals naturally present in sediments are reported to be reductant agents for Cr(VI), for example, amorphous Fe and Mn sulfoxides (Patterson et al. 1997; Wadhawan et al. 2015), mackinawite (Fe₇S₈) (Mullet et al. 2004), and pyrite (FeS₂) (Doyle et al. 2004). At pH > 5, Fe sulfoxides 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 sulfoxide minerals by forming new surface sites, depending on the nature of the FeL₂⁺ 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 ≥ oxalate → tartarate > EDTA > salicylate → no organic ligands.

\[
\text{(13) } \text{Fe}^{II} - \text{S} - \text{S} + \text{FeL}²⁺ \rightarrow \text{Fe}^{II} - \text{S} - \text{S} - \text{Fe}³\text{II} 
\]

\[
\text{(14) } 3\text{Fe}^{II} - \text{S} - \text{S} - \text{Fe}^{II} + \text{HCrO}_4^{2-} + 7 \text{H}^+ + 2 \text{L}²⁻ \rightarrow 3\text{Fe}^{II} - \text{S} - \text{S} - \text{Fe}^{III}\text{L}³⁺ + \text{Cr}^{III}\text{L}²⁺ + 4 \text{H}_2\text{O} 
\]
### 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 for reductive 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 for 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 dissipatiatory 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), *Enterobacter gallinarum* (Sayel et al. 2012), *Escherichia coli* ATCC 33456 (Shen and Wang 1993), *Leuconostoc sp.* CRB1 (Zhu et al. 2008), *Pannibacter phragmitetus* LSE-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) 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). Generally, only BaCrO₄, K₂Fe₃(CrO₄)₂(OH)₄, FePO₄·Cr₂O₇·2Fe(OH)₃, and (or) SrCrO₄ 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)₂·H₂O, and eskolaite (Cr₁₂O₃) are the main Cr(III) precipitates in pore waters at pH values ranging from 5 to 12 (Rai et al. 1989). However, number...
ous iron-containing Cr co-precipitates can form in sediments: amorphous hydroxides \(\text{[Cr}^{III},\text{Fe}^{II},\text{OH}]_3\), goethite–bracewellite solid-solution \(\text{[Cr}^{III},\text{Fe}^{II},\text{OH}]_3\text{(OH)}_2\), hematite–eskolaité solid-solution \(\text{[Fe}^{III},\text{Cr}^{III},\text{O}]_2\), donatite \([\text{Fe}^{III},\text{Mg},\text{Zn}][\text{Cr}^{III},\text{Fe}^{III},\text{Al}]_4\), ferrous chromite \(\text{[Fe}^{III}\text{Cr}^{II},\text{O}]_2\), and heideite \([\text{Fe}^{III},\text{Cr}^{III}]_3\text{(Ti},\text{Fe}^{III})_2\text{S}_4]\) (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 \(\text{Cr}^{III}/\text{Fe}^{II}\) 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 \(\text{Cr}^{III}\). For example, Scholz and Neumann (2007) demonstrated that the reduction of \(\text{Fe}^{III}\) hydroxides leads to a temporary increase of dissolved \(\text{Cr}^{III}\) species. Complexation of \(\text{Cr}^{III}\) 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 \(\text{Cr}^{III}\) in pore waters.

### 5. Adsorption reaction

Adsorption reactions depend heavily on the \(\text{Cr}\) oxidation state, since the charge of \(\text{Cr}^{III}\) and \(\text{Cr}^{VI}\) 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 surface complexation (Csobán et al. 1998). Sorption mechanisms of \(\text{Cr}^{VI}\) 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 \(\text{Cr}^{III}\) and \(\text{Cr}^{VI}\) 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 pHPZC, and negatively charged when pH values are above pHPZC. This surface reaction is described by:

\[
\begin{align*}
\text{X–OH} & \leftrightarrow \text{X–OH}^+ + \text{H}^- \\
\text{X–OH}^- & \leftrightarrow \text{X–OH} + \text{H}^+ \\
\end{align*}
\]

pH\text{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\(^{II}\), Mn\(^{II}\), 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 \(\text{Cr}^{III}\) species, especially \(\text{Cr}^{III}\text{(OH)}^{2+}\) and \(\text{Cr}^{III}\text{(OH)}_2^{3+}\), 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).
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; [Cr(III)]_0 = 10^{-4} M; [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) > histidine–Cr(III) (pH 6.8; [organo–Cr(III)]_0 = [Cr(III)]_0 = 2 mmol·L^{-1}). The sorption mechanisms of dissolved Cr(III) 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., Cr(VI) as HCrO_4^- and Cr(VI) as CrO_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 ≥ Al_2O_3 > kaolinite > montmorillonite. In addition, the sorption of Cr(VI) tends to increase with decreasing pH. Above pH ≥ 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 γ-Al_2O_3 showed that Cr(VI) adsorption drastically decreases in the presence of competing anions in the following order: MoO_4^{2-} > SeO_3^{2-} > SeO_4^{2-} > 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_2SiO_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 Cr(III)(OH)_3 for pH ≥ 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, –C_6H_4OH, –COOH, –NH_2, and –SH) is 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).

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

<table>
<thead>
<tr>
<th>pH_{PZC} range</th>
<th>pH_{PZC} value</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCrO_4^-</td>
<td>CrO_4^{2-}</td>
</tr>
<tr>
<td>Manganese(III,IV) (hydr)-oxides</td>
<td>Hydroxyapatite</td>
</tr>
<tr>
<td>Iron(III) (hydr)-oxides</td>
<td>Mackinawite</td>
</tr>
<tr>
<td>Pyrite</td>
<td>Calcite</td>
</tr>
<tr>
<td>Aluminosilicates</td>
<td>Quartz</td>
</tr>
<tr>
<td>Fe(III) (am)</td>
<td>Al(III) (hydr)-oxides</td>
</tr>
</tbody>
</table>

1Supplementary data are available with the article through the journal Web site at http://nrcresearchpress.com/doi/suppl/10.1139/er-2016-0012.
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 (Cr$_{\text{III}}$O$_2$, Fe$_{\text{II}}$Cr$_{\text{III}}$O$_2$, MgCr$_{\text{III}}$O$_4$, Cr$_{\text{III}}$PO$_4$, Fe$_{\text{III}}$Cr$_{\text{III}}$(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 Me$^{3+}$Cr$^{3+}$O$_4$ species during reductive processes.

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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.]

![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.)](image-url)


