

Chromium(VI) is More Toxic than Chromium(III): Reality or Myth ?

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The two most common oxidation states of chromium occurring in the environment, (Cr^{VI} and Cr^{III}), have markedly different geochemical and (eco)toxicological properties. Chromium (VI) is considered of most concern because of its adverse effects on human and environmental health, while Cr^{III} is putatively much less (eco)toxic. Remedial or management actions at Cr contaminated sites therefore usually focus on how to effectively reduce Cr^{VI} to Cr^{III} . The ecotoxicity of Cr^{VI} is unquestionable and the sustained study of different remediation options fully justified. However, many primary literature sources dealing with the ecotoxic effects of Cr^{III} suffer from major and overlooked methodological drawbacks that cast doubt on their reliability.

The Cr^{III} concentrations reported to affect 50% of the organisms during ecotoxicological tests range from 0.05 to over 50 mg L^{-1} depending on the organism and biological endpoint of choice [1 and references therein]. Thermodynamic equilibrium calculations suggest that $\text{Cr}(\text{OH})_3$ almost certainly formed during most experiments. Considering the ISO medium for the freshwater crustacean *Daphnia magna* as an example, the formation of $\text{Cr}(\text{OH})_3$ would limit the solubility of Cr^{III} to 0.1–16 $\mu\text{g L}^{-1}$ in the pH range 6–8 units (Figure 1). Work from our group on the freshwater alga *Raphidocelis subcapitata* [1] also suggests that the kinetics of $\text{Cr}(\text{OH})_3$ formation is very rapid and causes ionic Cr^{III} to disappear from the test medium within 5 hours (i.e., less than 10% of the total test duration — 72 h) (Figure 2). Neglecting such changes in Cr speciation may result in underestimating the actual Cr^{III} ecotoxicity although the freshly formed $\text{Cr}(\text{OH})_3$ may actually contribute to ecotoxic effects via adsorption onto cell walls/membranes and even via ingestion in the case of filter feeder organisms. We acknowledge that the presence of colloidal carrier phases (organic matter, Fe oxi-hydroxides, Mn oxides) in natural waters may increase Cr^{III} solubility compared with laboratory ecotoxicological media. Overall, more studies properly characterizing Cr speciation during laboratory tests are needed to determine the real ecotoxicological potential of Cr^{III} toward freshwater organisms and, possibly, human tissues.

[1] Aharchaou, Py, Cambier, Loizeau, Cornelis, Rousselle, Battaglia & Vignati (2018), Environmental Toxicology and Chemistry 37, 983-992.

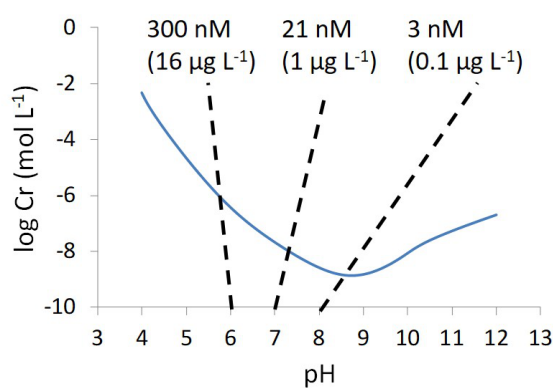


Figure 1. Theoretical Cr^{III} solubility in ecotoxicological test medium ISO6341 for the crustacean *Daphnia magna*.

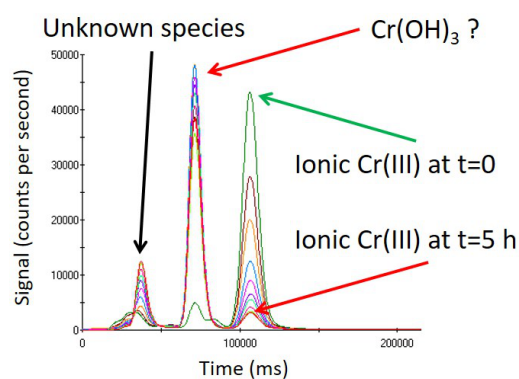


Figure 2. IC-ICP-MS chromatograms of Cr^{III} spiked test medium for *R. subcapitata* between 0 and 5 hours from the beginning of the test.