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Reduction and Efflux of Chromate by Bacteria

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Abstract The widespread industrial use of chromium has caused this heavy metal to be considered as a serious environmental pollutant. The most common forms of chromium in nature are the relatively innocuous trivalent form, Cr(III), and the more toxic hexavalent species, Cr(VI). Cr(VI) is usually present as the oxyanion chromate. Toxic effects of chromate for bacteria are associated with the inhibition of sulfate transport and with oxidative damage to biomolecules. The best studied bacterial mechanisms of resistance to chromate include reduction of Cr(VI) to the Cr(III) species and efflux of chromate from cell cytoplasm. Several chromate reductases have been identified in diverse bacterial species. Most characterized enzymes belong to the NAD(P)H-dependent flavoprotein family of reductases. Efflux of chromate by the ChrA membrane transporter, a plasmid-encoded protein, has been demonstrated in *Pseudomonas* and *Cupriavidus* species. Chromate efflux by ChrA consists of an energy-dependent process driven by the membrane potential. The CHR protein family, which includes putative ChrA homologs, currently contains about 135 sequences from all three domains of life. Other mechanisms of bacterial resistance to chromate involve the expression of components of the machinery for repair of DNA damage as well as free-radical scavenging enzymes.

1
Introduction: Chromium in the Environment

Chromium (Cr) is a transition metal in group VI-B of the periodic table. Cr naturally occurs in rocks, soils, plants, animals, and volcanic emissions; it is the seventh most abundant element on earth. However, most Cr is in the earth's mantle which results in Cr being only the twenty-first most abundant element in the crust (McGrath and Smith 1990). The most stable and abundant forms are the trivalent Cr(III) and the hexavalent Cr(VI) species. Cr(VI) is commonly present in solution as the water-soluble chromate (CrO_4^{2-}) or dichromate ($Cr_2O_7^{2-}$) oxyanions. Cr(VI), a strong oxidizing agent, is rapidly reduced by organic matter and other reducing agents to yield Cr(III) in soil and aquatic settings (McGrath and Smith 1990). Cr(III) derivatives are much less mobile and exist in the environment mostly in the form of stable complexes with both organic and inorganic ligands. The widespread use of Cr in diverse industrial processes has converted it into a serious contaminant of air, soil, and water.

2
Chromium Transport and Accumulation

Active transport of chromate across membranes by means of the sulfate uptake pathway has been demonstrated in a variety of bacterial species (Cervantes et al. 2001). The chemical analogy of these oxyanions is emphasized by the fact that chromate is a competitive inhibitor of sulfate transport in all bacterial species where it has been tested. In contrast, most cells are impermeable to Cr(III), which forms insoluble compounds in non-acidic aqueous solutions (Cary 1982). Once inside the cells, Cr(VI) is readily reduced, nonenzymatically or by the action of various enzymes, to Cr(III), which then may exert diverse toxic effects in the cytoplasm (Cervantes et al. 2001).

3
Chromium Toxicity

The biological effects of Cr depend on its oxidation state. Cr(VI) is considered the most toxic form of chromium (Cervantes et al. 2001). At the extracellular level, Cr(VI) is highly toxic to most bacteria, whereas Cr(III) is relatively innocuous because of its insolubility and subsequent inability to traverse cell membranes (Katz and Salem 1993). In the cytoplasm, Cr toxicity is mainly related to the process of reduction of Cr(VI) to lower oxidation states [i.e., Cr(V) and Cr(III)] in which free radicals may be formed (Kadiiska et al.