CHROMIUM IMPACT ON MARINE ECOSYSTEM

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Abstract: This study is an overview of chromium in marine environment. Chromium is a heavy metal with toxic potential for marine environment. Water contaminations occur by atmospheric pollution as major source. Chromium alloy and metal producing industry, cooling towers, industrial discharged into the water (electropainting and metal finishing industries being the major sources) and runoff from urban areas are the principal sources. In aquatic environment chromium is found as Cr (III) and Cr (VI) as water soluble complex anions. Information on the geochemical behavior of Cr in seawater is limited. Bioaccumulation occurs mostly in marine biota that utilize gill. Chromium, however, does not appear to be accumulated at higher trophic level in the marine food web. All available evidence suggests that Cr is not biomagnified in marine environments. However, K.R. Campbell study results (1995) suggest that biomagnification could be occurring.

Of all the metals, Cr has truly unique toxicological characteristics. Toxicological impact can result both from the action of Cr (VI) itself as an oxidizing agent and from Cr (III) which is capable of complexing with various organic compounds and thus may inhibit several metalloenzyme systems. It is concluded that Cr (VI) is more toxic to marine organisms. Oceans and seas are the ultimate receptacle for pollutants. Metals are continuously accumulating in marine environment, except for a minor portion that may be taken away along with marine food and other products (15).

1. SOURCES

1.1 Natural

Chromium, in the crystalline form, is a steel-gray, lustrous, hard metal characterized by an atomic weight of 51.996, an atomic number of 24, a density of 7.14 g/ml at 28ºC, a melting point of 1900ºC, a boiling point of 2642ºC, a vapor pressure point of 1 mm Hg at 1610ºC, and is insoluble in water (4, 5).

In nature chromium do not exists as elementary form Cr (0) but exists in Earth Crust in many oxidation states (4, 5, 15, 16). Chromium oxidation states range from -2 to +6, but is most frequently found in the environment in the trivalent (+3) and hexavalent (+6) oxidation states (4, 5, 7). The +3 and +6 forms are the most important because +2, +4 and +5 forms are unstable and are rapidly converted to +3, which in turn is oxidized to +6 (5). Chromite (FeOCr₂O₃ or FeCr₂O₄) is the primarily important ore mineral (4, 5, 6, 7, 15).

It also can be found as results of volcanic activities, from terrestrial or marine volcanoes (13).

1.2 Anthropogenic

Ferrochrome, dichromate production, and sodium chromate are used in different industrial processes or result from them (10, 11). Ferrochrome is used for the production of stainless steel. The major uses of sodium dichromate are for the production of chromate pigments; for the production of chromate salts used for tanning leather, mordant dying, and wood preservative; and as an anticorrosive. Chromates are produced by a smelting, roasting, and extraction process (7).
For aquatic environment are important Cr (III) and Cr (VI) (4, 5, 15). Cr (III), mostly found in nature, results from the watering of minerals while Cr (VI) in the environment is man-made, the results of contamination by industrial emissions or as by products (4, 8, 16).

2. AQUATIC ENVIRONMENT

In aquatic environment Chromium is found as Cr (III) and Cr (VI) as water soluble complex anions (5, 6, 15, 17).

Water contaminations occur by atmospheric pollution as major source (5, 6, 7). Chromium alloy and metal producing industry (5) or cooling towers (6), industrial discharged into the water (electropainting and metal finishing industries) and runoff from urban areas (5). Chromium is removed from air by atmospheric fallout and precipitations (6, 7).

2.1 Sediment is considered an ultimate sink for Cr in marine environments but if the ecological conditions are reversed, the sink can become a source by supplying Cr to the interstitial water and underlying seawater. Chromium is adsorbed on the sediment surface. Important adsorbing surfaces in the marine sediments are organic matter, oxides, hydroxides, carbonates, and clays (15). Adsorption of Cr by sediment is salinity dependent; adsorption is greatest at 0.1-1‰ (5).

The concentrations of Cr in sediments range between 1 and 1317 mg kg⁻¹, with about 20 mg kg⁻¹ as background Cr concentrations in uncontaminated sediments. In coastal marine area Cr concentration is higher then in open sea (15).

<table>
<thead>
<tr>
<th>Uncontaminated</th>
<th>Contaminated</th>
<th>Maximum value</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;20</td>
<td>&gt;20</td>
<td>1317</td>
<td>15</td>
</tr>
</tbody>
</table>

2.2 In seawater concentration of Cr may regulate its uptake, accumulation, and toxicity to marine organisms. Information on the geochemical behavior of Cr in seawater is limited. This situation is further complicated because Cr is affected by redox conditions of the water column.

Geochemical behavior of Cr is closely related to that of silica in seawater, and it was found a correlation between the distribution of Cr and silica in seawater.

It may be mentioned that Cr has no major known biochemical function, and it is therefore not surprising that many species of plankton do not concentrate Cr to any greater extent.

In the general sense, total dissolved Cr may be shown as:

\[ \text{[Dissolved Cr]} = [\text{inorganic-Cr}] + [\text{organic-Cr}] \]

Inorganic Chromium is found mainly in two oxidation states that can interchange in marine environments Cr (III) and Cr (VI).

At the present, it is difficult to comment the importance of organic Cr in marine system.

Concentrations of total Cr range between 0.04 and 10.8 ng ml⁻¹ seawater, with a reference value of the total dissolved Cr of 0.5 ng ml⁻¹ as background concentration in relatively uncontaminated seawaters. In general, costal waters contained more Cr than open seawater (15).
The removal of Cr from the seawater is rapid for Cr (III) because it is adsorbed on Fe oxide surfaces or forms complexes with organics. These reactions will certainly decrease the bioavailability of Cr (III). It is therefore speculated that Cr (VI) will accumulate more if present in Cr (VI) form (15). Other authors consider precipitation of chromium hydroxide to be the dominant removal mechanism of Cr (III) from water (17).

3. BIOACCUMULATION

Information on bioaccumulation of Cr in marine biota is lacking. Marine biota that utilizes gill tissue for active absorption is more affected by concentration and the chemical forms of metals in the external medium. Gill functions as the major route for absorption by marine organism (15).

Chromium bioaccumulation is influenced by the chemical form and the redox conditions of marine system. Oxidation increases Cr (VI) whereas Cr (III) is enhanced if the marine system is anoxic. As stated earlier, Cr (III) forms strong complexes and adsorbed on solid surfaces (4, 15) whereas Cr (VI) prefers to stay dissolved in seawater (4, 5, 15).

It seems that Cr bioaccumulation is size-dependent. The concentration of Cr in soft tissue and shell decreased significantly with an increase in size.

Chromium may accumulate differentially in different types of tissue. In fish gill, kidney and liver have been found to contain the highest Cr concentrations while muscle has been found to have very little capacity for Cr accumulation.

Chromium, however, does not appear to be accumulated at higher trophic level in the marine food web (15).

4. BIOMAGNIFICATION

All available evidence suggests that Cr is not biomagnified in marine environments (15). However, K.R. Campbell study results (1995) suggest that biomagnification could be occurring (1).

5. TOXICITY AND EFFECTS

Of all the metals, Cr has truly unique toxicological characteristics. Chromium should be in hexavalent form and not in trivalent form to readily cross the biological membrane (5, 15). Chromate (Cr VI) resembles phosphate and sulphate, and can be transported into the cells by anion carrier (14). Hexavalent Cr is a strong oxidant and once inside a biological system is generally reduced to Cr (III). Thus toxicological impact can result both from the action of Cr (VI) itself as an oxidizing agent and from Cr (III) which is capable of complexing with various organic compounds and thus may inhibit several metalloenzyme systems (15).

It is concluded that Cr (VI) is more toxic to marine organisms (15).

Any abiotic or biotic factor which enhances Cr (VI) form in seawater will increase Cr toxicity (15).
**Abiotic factors**

Chromium toxicity increased with the increase of concentration and temperature but decrease with an increase of salinity and sulfate concentration \((15, 17)\). Chromium toxicity to three species of marine animals increased as temperature increased from 5 to 15°C, but appears that temperature is of a minor importance as a modifying factor of Cr toxicity to aquatic organism \((15)\).

The pH of the media is known to affect Cr toxicity. Seawater pH is indeed well buffered around 8.1. However, interstitial waters and estuarine environments may experience fluctuation in pH. The toxicity of Cr (VI) is dependent on its aqueous chemical speciation. The hydrochromate \((\text{HCrO}_4^-)\), chromate \((\text{CrO}_4^{2-})\) \((15)\) and dichromate \((\text{Cr}_2\text{O}_7^{2-})\) are the basis of Cr toxicity \((4, 5, 15)\).

**Biotic factors**

Generally, smaller species and early life stages were most sensitive to Cr toxicity \((5, 15)\).

Concentration tends to increase with the age of organism, but uptake is significantly inhibited at high salinity \((5)\).

<table>
<thead>
<tr>
<th>Species</th>
<th>LC(_{50}) 96h for Cr (III)</th>
<th>LC(_{50}) 96h for Cr (VI)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Juvenile mullets</td>
<td>53</td>
<td>24</td>
<td>15</td>
</tr>
<tr>
<td>Different species</td>
<td>3,300-7,500 ppb</td>
<td>445-2,000 ppb</td>
<td>5</td>
</tr>
<tr>
<td>Rats</td>
<td>-</td>
<td>54 mg/kg</td>
<td>14</td>
</tr>
</tbody>
</table>

Maximum acceptable toxicant concentration (MATC) of chromium to aquatic life were derived from life cycle or partial life cycle exposure, and expressed as the highest concentration tested having no significant adverse effect on the characteristics measured – usually survival, growth, and reproduction – and the lowest concentration at which these effects were observed. The most sensitive seawater organism tested was a polychete worm with a MATC range of 17 to 38 ppb for Cr (VI) \((5)\).

The current analytical quantitation limit (PQL) for both Cr (III) and Cr (VI) is 5 µg/l in both fresh and marine waters \((17)\).

Under laboratory conditions, chromium is mutagenic, carcinogenic and teratogenic to a wide variety of organism, and Cr (VI) has the greatest biological activity \((5)\).

Among marine organisms for Cr (VI), algal growth was reduced at 10 µg/l, measurable accumulation were recorded in oyster and worms at 5 µg/l, and reproduction of polychete annelids worm was inhibited at 12.5 µg/l. At higher concentrations, Cr (VI) is associated with abnormal enzyme activities, altered blood chemistry, lowered resistance to pathogenic organisms, behavioral modifications, disrupted feeding, histopathology, osmoregulatory upset, alterations in population structure and species diversity indices.

The significance of Cr residues is unclear, but available evidence suggests that organs and tissues of fish and wildlife that contain 4.0 mg total Cr/kg dry weight (=ppm) should be viewed as presumptive evidence of Cr contamination \((5)\).

6. **MARINE FOOD WEB Cr (VI) CONCENTRATION**

**ALGAE AND MACROPHYTES** 25 – 60 mg/kg dry weight

**MOLLUSCS** 0.1 – 0.6 mg/kg fresh weight

3.4 – 5.8 mg/kg fresh weight in oyster and clam
CRUSTACEANS 0.3 mg/kg fresh weight
ANNELIDS 0.03 – 0.10 mg/kg fresh weight
ECHINODERMS 1.0 mg/kg dry weight
FISH 0.1 -0.6 mg/kg fresh weight GENERALLY, BUT 97.0 mg/kg dry weight was recorded in some sp (5).

7. MARINE MAMMALS

7.1 Uptake
There are three major routes of uptake
- across the placenta before birth
- in milk during the suckling period (13)
- food (2, 13).

Still remain the possibility of some slight intake from ingested seawater, by absorption through skin, or from atmosphere via the lungs (13).

N. Cardellicchio et al. (2000) agree that dolphins assimilate metals both through water and food. Metal assimilation from water occurs mainly through passive diffusion of the metal as soluble compounds. The odontocetes assimilate a water quantity equal to 77 ml/kg of body weight per day. 18% (14 ml) is drunk directly, 51% (39 ml) is assimilated with food and the remaining 31% (24ml) is assimilated through the skin. Cetacean skin is sensitive and vulnerable because is not protected by mucous or scales, or any keratin layer as in other mammals. Food, however, is the main source of contamination (2, 9).

7.2 Bioaccumulation
The metal accumulation is influenced by many factors. Biotic factors are age, length, weight, sex, and the sea area where dolphins live.

The liver accumulated the highest concentrations of metals, except for cadmium and chromium. There were no preferential accumulation of Cr in any organ but the highest concentrations were found mainly in the blubber and in the lung. Other data, according to Viale (1978) the maximum levels were reached in the brain (2).

Table 4 Cr concentrations in dolphin organs and tissues (2, 13)

<table>
<thead>
<tr>
<th>Organ</th>
<th>Tissue Levels (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liver</td>
<td>0.03 - 1.8</td>
</tr>
<tr>
<td>Kidney</td>
<td>0.05 - 0.77</td>
</tr>
<tr>
<td>Blubber</td>
<td>0.4 – 0.8</td>
</tr>
<tr>
<td>Lung</td>
<td>0.12 – 0.15</td>
</tr>
</tbody>
</table>

7.3 Toxicity
Although dolphins may be able to tolerate high metal concentrations, there is no information on the long-term or sublethal impact of contaminants (2).

7.4 Effects
While the synergic effects of the various pollutants are not well understood, the accumulation of toxic compounds could lead to a stress condition in an organism (2). Chromium as a metal could have an immunotoxic effect on marine mammal health (9).

Epidemiologic studies implicate quite strongly the involvement of Cr (VI) in human cancer but are not relevant in marine mammals (3, 4, 6, 7, 10, 12, 13, 16).
REFERENCES