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An Overview of Chromium in the Marine Environment

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Summary

Chromium concentrations in natural waters range from 2 to 5 nmol kg^{-1} in open ocean water up to 100 nmol kg^{-1} in freshwater. Its oceanic behavior is complicated by the occurrence of two important oxidation states with very different properties and possible organically bound species. Cr(III) has a significant affinity for suspended particulate matter and is readily adsorbed to it in the water column and in the sediment. Cr(VI), as the thermodynamically stable form in sea water, is the dominant species. It is also known to be of much higher toxicity than Cr(III), which is generally accepted as an essential trace element. Sources for chromium in the oceans are mineral weathering processes and riverine and atmospheric input. The possibility of conversion between different species impedes the determination and classification of chromium compounds particularly when preliminary separation and preconcentration steps are necessary to determine the very low levels of chromium in natural waters.

Chrom in der Meeresumwelt – Eine Übersicht – (Zusammenfassung)

Chrom-Konzentrationen in natürlichen Gewässern reichen von 2 bis 5 nmol · kg^{-1} im Wasser des offenen Ozeans bis zu 100 nmol · kg^{-1} in Süßwasser. Das Verhalten des Chroms im Ozean ist komplex, da es in zwei wichtigen Oxidationsstufen vorkommt, die sehr unterschiedliche Eigenschaften haben und außerdem noch organisch gebundene Formen des Chroms möglich sind. Cr(III) zeigt eine besonders starke Bindung an suspendierte Schwebstoffteilchen und wird leicht in der Wassersäule und im Sediment an diese adsorbiert.

Cr(VI) ist die thermodynamisch stabile Form im Meerwasser und deshalb die vorherrschende Bindungsform. Es ist bekannt, daß dieses eine wesentlich höhere Toxizität als Cr(III) hat, welches wiederum allgemein als ein essentielles Spurenelement angesehen wird. Quellen für Chrom in den Ozeanen sind Verwitterungsprozesse der Gesteine und Eintrag durch Flüsse und die Atmosphäre.

Die Möglichkeit der Umwandlung zwischen den verschiedenen Wertigkeitsstufen des Chroms erschwert die analytische Bestimmung der Chromverbindungen, vor allem wenn vorher Abtrennungs- und Anreicherungsschritte notwendig sind, um die sehr niedrigen Konzentrationen von Chrom in natürlichen Gewässern zu messen.

Introduction

The heavy metal chromium and its compounds affect man in three ways: as an important raw material, as a toxicant and as an essential trace element. In nature chromium occurs almost exclusively as chromite ($FeCr_2O_4$). The toxic properties mainly refer to Cr(VI) compounds, which are highly soluble and able to pass negatively charged cell membranes. Carcinogenic and mutagenic effects of chromates are also known. Chromium, as a constituent of the glucose tolerance factor (GTF), is essential in the maintenance of normal glucose tolerance.

Efforts to detect ng-amounts of chromium especially in open ocean waters have increased in the past years with development and improvement of analytical techniques with sufficient sensitivity and specifity.

Forms of Chromium in the marine environment

The main oxidation states of chromium in natural waters are +3 and +6. On the basis of thermodynamic properties and equilibrium data it has been predicted that Cr(VI) should be the only species of chromium existing in sea water. Experimental work has shown, however, a significant amount of Cr(III) (E l d e r f i e d [1970]; S i b l e y and M o r g a n [1975]; C r a n - s t o n and M u r r a y [1978]. The most probable species were claimed to be $Cr(OH)_2^+ 4 H_2O$ and CrO_4^{2-}.

Speciation studies in the North East Pacific by Cranston and Murray (C r a n s t o n and M u r r a y [1978]) showed Cr(VI) to be the dominant form. In anoxic zones with H_2S present Cr(III) is the major species (C r a n s t o n and M u r r a y [1978]).

The existence and relevance of organically bound species of chromium depend on the amount of organic matter in sea water as discussed by different authors. Humic acids and other organic acids are probable complexing agents for chromium, as for many other heavy metals (N a k a y a m a et al. [1981a]; see Tab. 2).

N a k a y a m a et al. [1981a] started the discussion about the extent of organically bound chromium. The nature of Cr-organic compounds was unknown since analytical techniques lacked sufficient selectivity to detect isolated species. The role of MnO_2 as catalysator in the reduction of Cr(VI) has been examined (N a k a y a m a et al. [1981a]; v. d. W e j d e n and R e i t h [1982]).

Recent work of Z i k a et al. [1985] on the photochemical production of H_2O_2 in surface sea water led to calculations of P e t t i n e and M i l l e r o [1990], which indicate that the levels of H_2O_2 in natural surface waters are 20 times more effective in oxidizing Cr(III) than is oxygen.

Redox reactions between Cr(III) and Cr(VI) are possible in the marine environment as well as during storage and analysis of samples. Conversion depends on pH, concentrations of Cr(VI) and the amount of dissolved organic matter (F r e i e r [1978]; P a v e l et al. [1985]).

Analytical methods and speciation

The measured concentrations of chromium in seawater, as shown in Tab. 1, indicate several analytical problems. In some of the early work authors did not specify the oxidation state. There is a development of increasing sensitivity in methods. Blank values have decreased with more efforts at purification of reagents and cleaning of apparatus. Modern techniques have not solved all the uncertainties related to contamination and change of composition of the sample.

a) S a m p l i n g   a n d   p r e s e r v a t i o n   o f   s a m p l e s

While sampling is not a chromium-specific problem, the sample preservation is. The established procedure of acidifying sea water will change the proportion of Cr(III)/Cr(VI) if there are reducing compounds in the water (P a v e l et al. [1985]; v. d. W e j d e n and R e i t h [1982]). To avoid changes of equilibrium both oxidation states should be stabilized against redox reactions caused by oxygen and reducing substances in the water sample. pH-values of 7 to 8 and complexation or precipitation of Cr(III) are needed if speciation is desired. To determine the total metal content an oxidation of Cr(III) or reduction of Cr(VI) is necessary. Among several possibilities are the oxidation of Cr(III) with $NH_4S_2O_8$ in acidic solution, with H_2O_2 and UV-irradiation (G e i s l e r [1992]) and the reduction of Cr(VI) with $NaSO_3$ or methanol in acid solution.

b) P r e c o n c e n t r a t i o n   a n d   d e t e c t i o n

A preconcentration procedure is required for nearly every detection method to enhance sensitivity. Combining electrothermal atomic absorption and coprecipitation of Cr(III) with ferric hydroxide, detection limits in the ng/kg-range are possible (C r a n s t o n and M u r r a y [1978]; see Tab. 1). Magnesium hydroxide (K o r o l e f f [1980]) and bismuth oxide

Table 1
Chromium concentrations in seawater (ng/kg)

Author	Year	Cr(III)	CR(VI)	Organic-bound	Area
Ishibashi, Shigematsu	1950	40–70			Japan Sea
Chuecas, Riley	1966	460	0		British Coast
Kuwamoto, Murai	1970	130–900		7–270	Pacific Ocean
Elderfield	1970	60–500	10–160		
Grimaud, Michard	1974	240–520	30–110		Pacific Ocean
v. d. Weijden et al.	1975	130–500	240–900		North Sea
Hiiro et al.	1976	400	1000		Japan Sea
Cranston, Murray	1978	5	150		Pacific Ocean
deJong, Brinkman	1978	50–1000	1000–1500		Dutch Coast
Campbell, Yeats	1981	170–270			Atlantic Ocean
Nakayama et al.	1981 c	60	140	260	Japan Sea
Murray et al.	1983	10	156		Japan Sea
Sunkay et al.	1985	150–1250	30–2000	300	Japan Sea
Ahern et al.	1985	250–430	190–310	0	
Golimowsky, et al.	1985	100–500		300	Pacific Ocean
Jeandel, Minster	1987	156			Atlantic Ocean
		135–234			Pacific Ocean
		135–177			Mediterranean Sea

Table 2
Stability constants of Cr(+3)-organic complexes

Ligand	Formula	Donor atom(s)	Log β_1	β_2	β_3
Oxalic acid	$C_2H_2O_4$	O	5.34	10.51	15.44
Glycine	$C_2H_5O_2N$	O,N	8.62	16.27	
α-Alanine	$C_3H_7O_2N$	O,N	8.53	15.97	
Serine	$C_3H_7O_3N$	O,N	8.0	14.2	19.4
Succinic acid	$C_4H_6O_4$	O	6.42	10.99	13.85
Phthalic acid	$C_8H_6O_4$	O,O	5.52	10.00	12.48
Aspargine	$C_4H_8O_3N_2$	O,N	7.7	13.6	18.5
Ethylenediamine	$C_2H_8N_2$	N,N	16.5	<30.5	
Sulfoxine	$C_9H_7O_4NS$	O,N,S	10.99	21.04	
Ethylenediamine tetra-acetic acid	$C_{10}H_{10}O_8N_2$	O,N	23.40		

Source: (from Moore [1982]; Sillén and Martell [1971]).

(N a k a y a m a et al. [1981c]) were also used for coprecipitation. Cr(VI) can be separated by ion exchange resin assuming that all Cr(VI)-species are anionic. Several authors, however, have discussed the possibility of additional anionic Cr(III)-species.

Preconcentration of Cr(III) can be achieved by the use of an immobilized diphenyl carbazone chelating agent (W i l l i e et al. [1983]) and by 8-hydroxy quinoline (W a t a n a b e et al. [1981]). Several other complexing agents like ammonium pyrrolidine dithiocarbamate (APDC) (S u b r a m a n i a n [1988]), diethyldithiocarbamate (DDTC) and alkylammonium salts (d e J o n g and B r i n k m a n n [1978]) will undergo complexing reactions with Cr(VI) only. The reaction mechanisms of many of these complexation reactions are not completely understood. It is assumed for example that Cr(III) produced by reduction processes is extraordinarily reactive and able to perform in-situ complexing reactions that "normal" Cr(III) would not, due to kinetic inhibitions (H a r z d o r f [1990]; H u l a n i c k i [1967]).

X-ray spectrometric determination of Cr(VI) is achieved by precipitation with dibenzyl dithiocarbamate (L e y d e n et al. [1985]; M o o r e [1982]; G e i s l e r [1992]) and coprecipitation with a cobalt pyrrolidine dithiocarbamate carrier complex (P i k et al. [1981]). Dithiocarbamate extraction was also used in combination with inductively-coupled plasma atomic emission spectometry to determine Cr in lake water (S u g i y a m a et al. [1986]).

If applied to sea water chromium concentrations, electrochemical methods, though very sensitive, also need a preconcentration. With cathodic stripping voltammetry chromate can be concentrated at the hanging mercury drop electrode as Hg_2CrO_4. Even more sensitivity is achieved by adsorption of anionic Cr(III)-complexes with diphenyl carbazide (DPC) or diethylene triamine pentaacetic acid (DTPA) at the hanging mercury drop and reduction to Cr(O) (G o l i m o w s k y et al. [1985]).

Sources and emissions of Chromium

The commercially important ore for the production of chromium alloys and chemicals is chromite, a spinel with Cr(III) in octahedral sites and Fe(II) in tetrahedral sites. Ferrochrome alloys are widely employed in the production of stainless steel and heat resisting steels. Chemicals are usually manufactured from pure sodium dichromate obtained from chemical-grade chromite. Chromium compounds are used as pigments, mordants and dyes in textile industry, tanning agents in leather industry, for chrome electroplating and as oxidants and catalysts. Total production of chromite from 1971 to 1980 was $86.2 \cdot 10^6$ metric tons (J a w o r s k y [1980]; M o o r e and R a m a m o o r t h y [1984]; see Fig. 1).

The natural background level of 10^{-6} mg/m^3 airborne chromium may rise to 1 mg/m^3 around chrome factories. The high boiling point of chromium causes rapid condensation and precipitation as oxide on the surface of the airborne particles (M o o r e and R a m a m o o r t h y [1984]).

An estimate of chromium inputs into the North Sea as an example of waters surrounded by highly industrialized countries was made by K e r s t e n et al. [1988]:

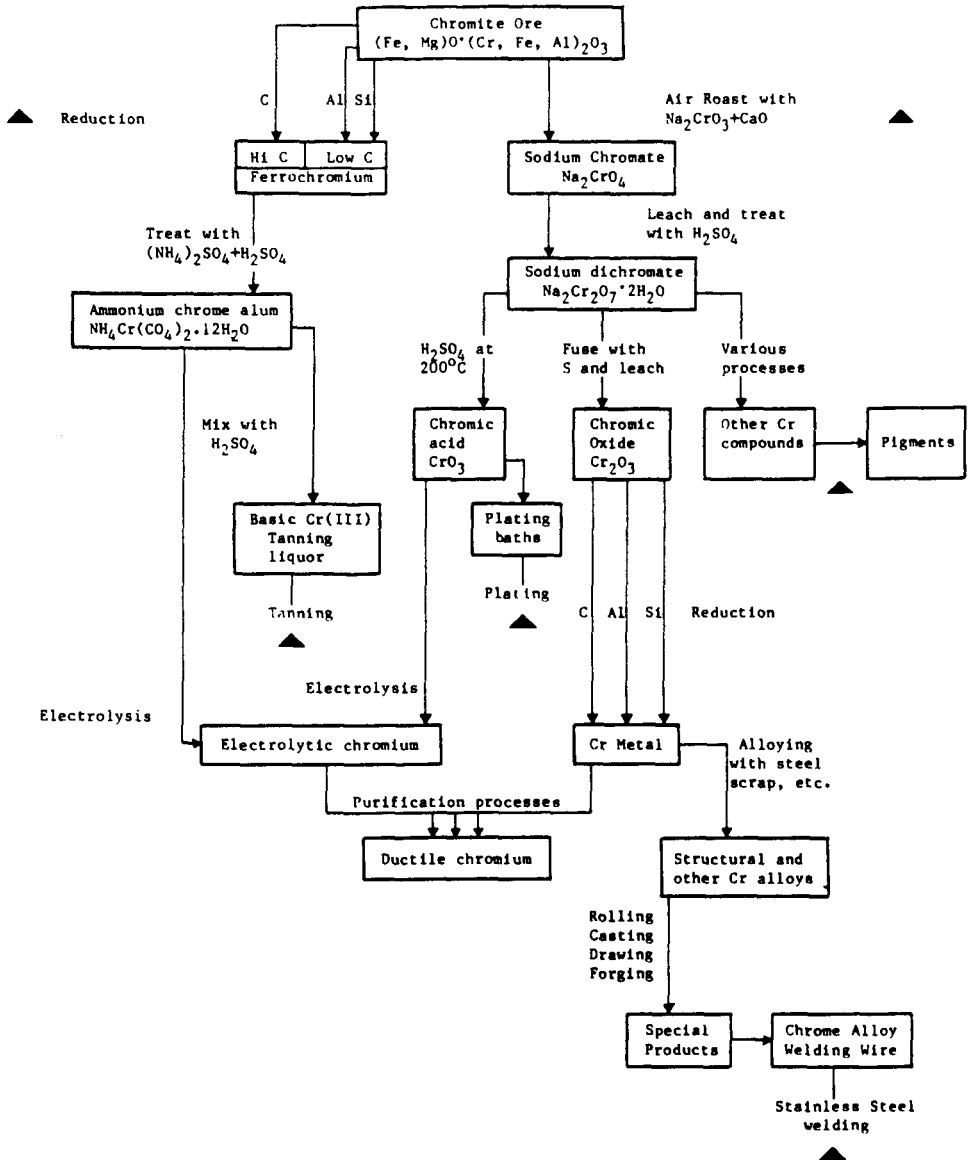| C h r o m i u m I n p u t s	M i n.		M a x.
	(tonnes per annum)		
River Inputs	590	–	630
Direct discharges		< 500	
Atmosphere	100	–	530
Dredgings		2500	
Sewage Sludge		40	
Industrial Waste		350	
Total t/a	4200	–	5000

Fig. 1   Production of chromium metal alloys and compounds from chromite ore.

Simplified flow chart for the production of metallic chromium, chromium compounds and selected products, from chromite ore. Processes for which occupational exposure level to chromium are known are indicated (▲).

Source: R. M. Stern. In: Langard [1982] with kind permission of Elsevier Biomedical Press

There are still great uncertainties in the case of atmospheric input. The enrichment factor of chromium in marine atmospheric particulates relative to earth's crust indicates that most chromium in the atmosphere results from normal crustal erosion (F ö r s t n e r and W i t t m a n n [1979]). Cr(III) pollution of surface waters by liquid waste discharges with up to several thousand mg/1 Cr result from tanning industry and textile dyeing. The more toxic Cr(VI)-discharges result mainly from electroplating, pickling and bright dipping when emitted uncontrolled (J a w o r s k y [1980]). In freshwaters, anthropogenically introduced soluble Cr(IV) is removed by reduction to Cr(III) and subsequent sorption to particulates and sediments (P f e i f f e r et al. [1980]; J a n and Y o u n g [1976]).

Distribution of Chromium in the marine environment

a) Open ocean waters

C a m p b e l l and Y e a t s [1984] calculated a residence time of chromium in ocean water of 25000 to 40000 years. An estimation of chromium inputs into the ocean was made by Mayer (N r i a g u and N i e b o e r [1988]) with data from several authors (see Fig. 2). In the Atlantic and Pacific Oceans concentrations of total chromium around 3 nmol/kg were found between depths of 800 and 2500 m. Surface values are slightly less (2,8 nmol/kg). Concentrations increase in deep waters: 3.5 to 4.4 nmol/kg in the Atlantic Ocean and 4.5 to 6 nmol/kg in the Pacific Ocean (J e a n d e l and M i n s t e r [1987]). Values for Cr(III) in the North Atlantic Ocean are 0.2 nmol/kg at the surface, 0.5 nmol/kg in deep waters and as a maximum 1.7 nmol/ kg at 800 m (J e a n d e l and M i n s t e r [1987]).

C r a n s t o n and M u r r a y [1978] found an increase in Cr(VI) with depth which correlates with dissolved silica, while Cr(III) values show a maximum at 75 m in the North East Pacific Ocean. Fig. 3 shows profiles of chromium concentrations for different locations in the deep sea. It reveals the existence of comparable data though obtained by very different analytical techniques.

N a k a y a m a et al. [1981 c] differentiated between inorganic Cr(III), inorganic Cr(VI) and organically bound chromium and found that sea water contains an average of 9nmol/l of dissolved chromium consisting of 45 to 60 % organic chromium species, which had not been considered properly in the past (see Tab. 1) (N a k a y a m a et al. [1981 c]). These data have not been reproduced by other authors.
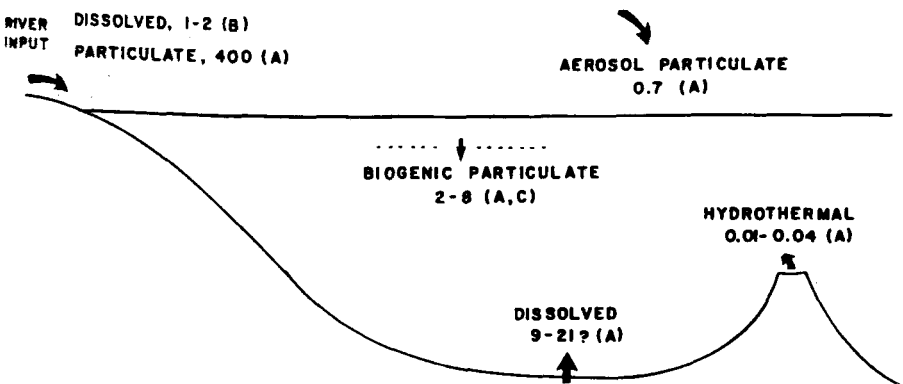

Fig. 2   Fluxes of chromium in the ocean.

All numbers are units of 10^8 mol/year.

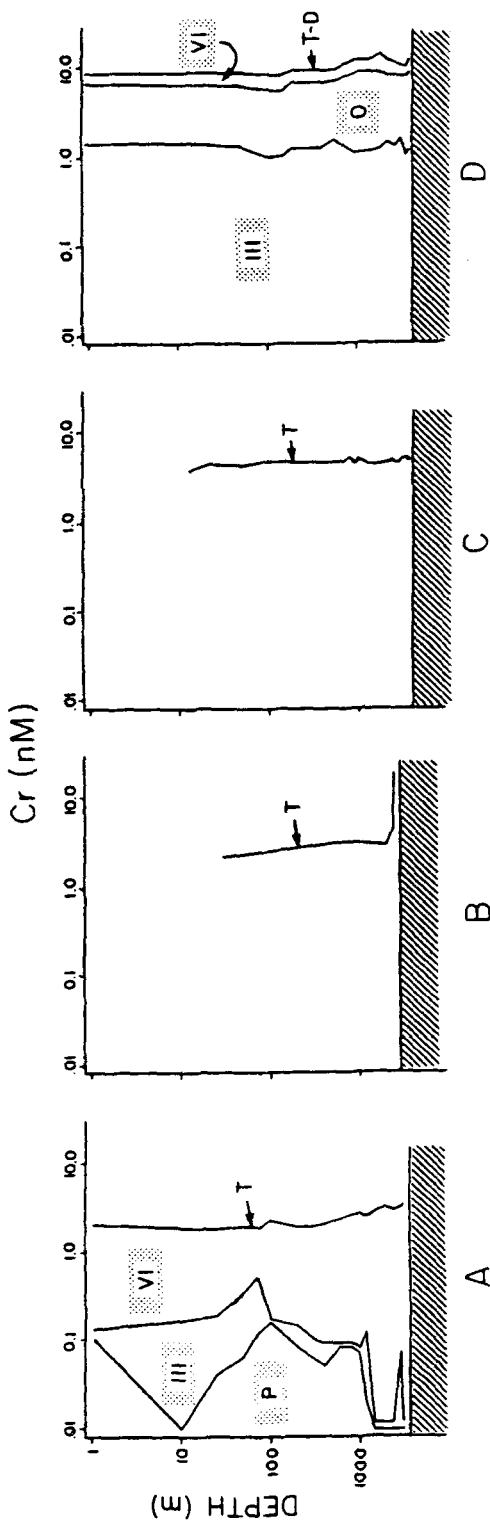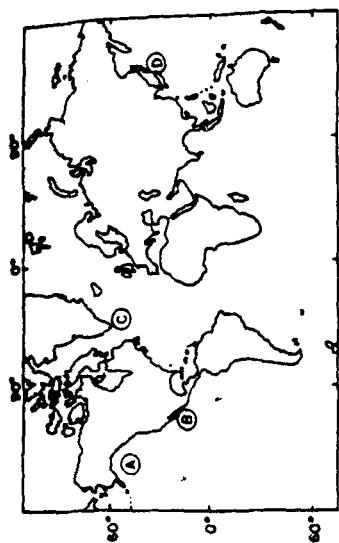Source: L. M. Mayer. In: Nriagu et al. [1988] with kind permission of J. Wiley and Sons

Fig. 3   Chromium concentrations versus depth in the deep sea

Chromium concentrations versus depth for four locations in the deep sea. Lines represent cumulative
concentrations in plots A and D. P., particulate; III, dissolved, free, trivalent; VI, dissolved hexavalent;
O, organic; T, total; T-D, total dissolved. These definitions are the operational descriptors used by
the original authors.

b) Coastal Waters

Median concentrations of Cr(III) and Cr(VI) in "clean" coastal waters are 0.045 and 0.14 µg/kg respectively (M o o r e and R a m a m o o r t h y [1984]). In the St. Lawrence estuary and Columbia river estuary average concentrations of 0.3 µg/l and 0.13 µg/l for dissolved chromium were found (C a m p b e l l and Y e a t s [1984]; C r a n s t o n and M u r r a y [1980]).

Only a few papers exist on chromium speciation in natural waters that contain data on total dissolved chromium together with data on Cr(III) and Cr(VI). Cr(III) compounds are known to have a strong affinity to suspended particulate matter and colloidal substrates like humic substances. Especially hydroxo complexes of Cr(III) are readily adsorbed to particulate matter (S i l l e n and M a r t e l l [1971]; Y a m a s a k i [1980]; N a k a y a m a et al. [1981 b]; M a y e r et al. [1984]). The colloidal material present in river waters can flocculate upon mixing with sea water, which results in the conversion of dissolved riverine trace metals to a particulate form in the estuarine zone (M a y e r et al. [1984]). The labels "bound chromium" and "labile" or "free" chromium are often used when there is a combination of the analytical technique with a pretreatment procedure by ultraviolet irradiation to destroy organic material. Many uncertainties in literature result from inexact description of analytical methods and nomenclature.

c) Sediments

Cr(VI) and, in particular, Cr(III) ions show a strong tendency to sorbing on the minerals which constitute the bottom sediments. Cr(VI) is adsorbed very quickly on both sediments and minerals, but is desorbed to a greater extent as well (S z p o n a r and P r z e w o c k a [1988]; M u s i c et al. [1986]; N a k a y a m a et al. [1981 b]). These processes are highly pH-dependent which cause the differences in sediments of the oceans and freshwater.

Typical chromium concentrations in sediments of 60 to 100 mg/kg are similar to those of crustal rocks (100 mg/kg) (N r i a g u and N i e b o e r [1988]). Elevated chromium levels, up to several hundred mg/kg, from anthropogenic sources are detectable in sediments of rivers and estuaries near industrial areas (L a n g a r d [1982]). The general range for chromium concentrations in Baltic Sea sediments was reported to be several mg/kg up to 130 mg/kg (S z p o n a r and P r z e w o c k a [1988]). Remobilisation of chromium from the sediments to the water column is frequently discussed in literature. Bottom water enrichments are possible by dissolution of biogenic material and catalytic oxidation at the sediment water interface (N a k a y a m a et al. [1981 b]; v. d. W e i j d e n and R e i t h [1982]).

Uptake of Chromium by aquatic plants, invertebrates and fish

Chromium is not a significant contaminant of plant tissues although concentrations in marine plants are usually higher than those in freshwater plants. Sorption by marine grass occurs almost exclusively through the roots, reflecting direct uptake from sediments (M o n t g o - m e r y and P r i c e [1979]). To invertebrates and fish, chromium is mainly transferred through food, however there is no evidence for bioaccumulation in any species. Concentrations in the muscle of freshwater fish are below 0.25 mg/kg wet weight. In marine species there are higher values (around 0.5 mg/kg) when collected in industrial areas (M o o r e and R a m a m o o r t h y [1984]).

Toxicity

Compared to Hg, Cd, Cu, Pb, Ni and Zn, toxicity of chromium for aquatic organisms is generally low due to the hard acid character of chromium ions. Significant growth inhibition of aquatic plants occurs at elevated chromium levels (0.5 to 5 mg Cr(VI)/l).
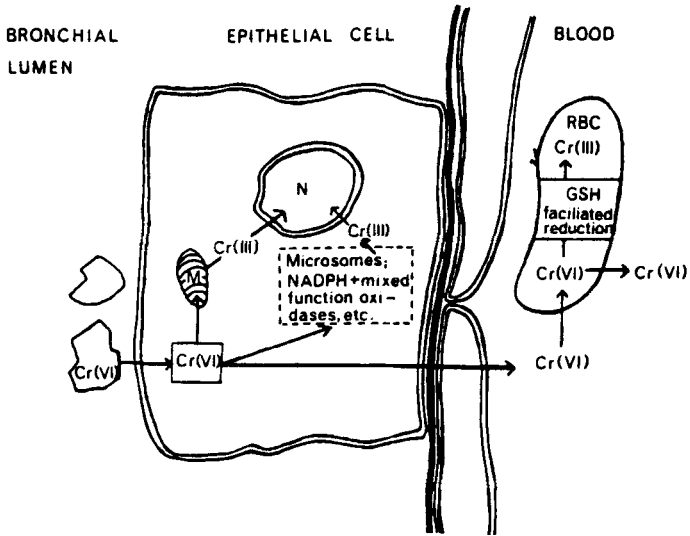
Fig. 4 Suggested model of Cr(VI) uptake in the lungs and in the GI-tract

M   = mitochondria
N   = nucleus
RBC = red blood cell

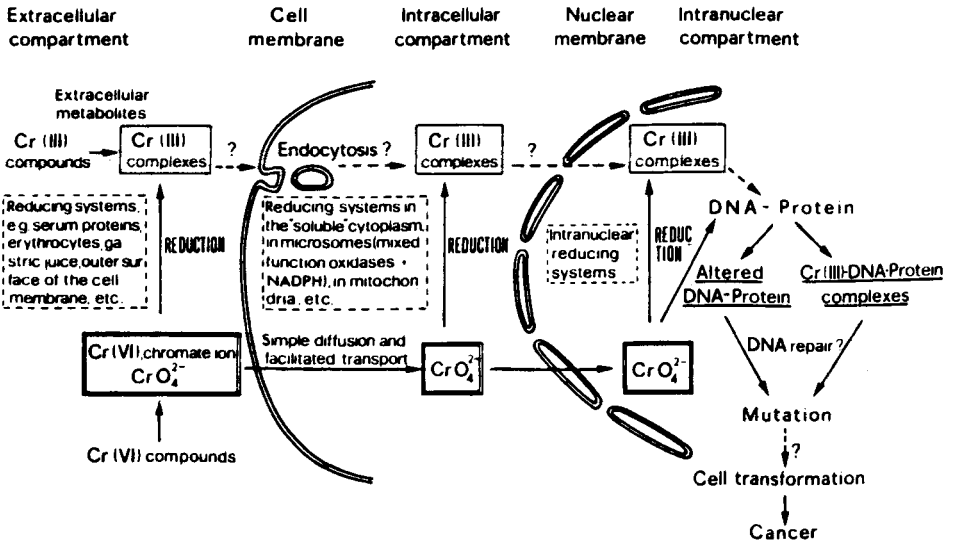Source: Langard [1982, p. 156] with kind permission of Elsevier Biomedical Press

Fig. 5 Possible mechanism of chromium mutagenic activity

Source: A. G. Lewis, V. Bianchi. In: Langard [1982] with kind permission of Elsevier
Biomedical Press

The 96h LC_{50} – value for blue crab ranges from 31 to 106 mg/l (F r a n k and R o b e r t s o n [1979]). Fish are considered to be less susceptible to the toxic effects of chromium than invertebrates. All processes are influenced by pH to a high degree.

For man chromium is an essential trace element (M e r t z [1979, 1981]). Cr(III) is able to co-ordinate several amino acid ligands. The complete structure of the glucose tolerance factor is yet uncertain as is the exact relationship between chromium deficiencies, diabetes and cardiovascular diseases.

Characteristic for the essential elements are adverse effects in the case of deficiencies as well as in case of oversupply. Typical chromium concentrations in human whole blood samples range from 0.04 to 0.3 µg/kg.

Cr(VI) compounds are approximately a hundred times more toxic than Cr(III) salts. Stomach acidity reduces Cr(VI) to the less toxic Cr(III) whose gastrointestinal absorption is less than 1% (F ö r s t n e r and W i t t m a n n [1979]). Cr(VI) is capable to permeate cell membranes (Fig. 4). It is assessed that Cr(VI) is a powerful mutagen for humans and a potential carcinogen (S i t t i g [1980], see Fig. 5). Also known are effects on the skin by direct contact like chrome ulcers of the hand and allergic contact dermatitis. Perforation of the cartilagenous septum of the nose occurs by exposure to ulcerogenous amounts mainly in chrome production, electropla- ting and chemical industries. Cement workers are the largest occupational group suffering from chromate allergy (L a n g a r d [1982]).

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