HEALTH AND ENVIRONMENTAL EFFECTS OF HEXAVALENT CHROMIUM AND EVOLUTION OF RELEVANT LEGISLATION

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ABSTRACT

Chromium can be found in various oxidation states most importantly as Cr_{III} and Cr_{VI} Cr_{III}, the most abundant environmental form, while Hexavalent Chromium in the environment has generally been assumed to be caused by anthropogenic contamination, since it is used in a number of industrial applications. However, Chromium $_{VI}$ does also occur in nature due to geological conditions, such as the existence of ophiolite masses. Cr_{III} is an essential element that plays a role in glucose metabolism. Typically actual intake rates appear to match the recommended doses. However, even these higher than normal intake rates of Cr_{III} (e.g. 770 μg/day) are much lower than the doses that may create adverse effects. The situation is somewhat confusing and less informed in the case of the hexavalent form. In many of the studies there is no distinction between the two forms, on the basis of the rationale that Cr_{VI} is reduced to Cr_{III} in the gastrointestinal tract, thus only intakes that exceed the reducing capacity of the stomach will result in significant absorption of Cr_{VI} across the gastrointestinal mucosa. On the basis of this rationale, the widely adopted limit is for total chromium, usually set at 50 μg/L, in accordance with the provisional guidelines value of the World Health Organisation. Recently it has been realized that the complexity of the fate of Cr_{VI} during oral uptake requires further careful consideration, which may lead to much stricter tolerable doses than the reported so far. However, although there is growing evidence that hexavalent chromium may be carcinogenic even through the oral route, there is still no international standard regarding this form of chromium and potable water. As already mentioned, the widely adopted limit is for total chromium, usually set at 50 μg/L, in accordance with the provisional guidelines value of the World Health Organisation. However, recently the Californian Environmental Protection Agency has set in 2011 a "Public Health Goal (PHG)", for hexavalent chromium of 0,02 μg/L recognising its impact on young children and vulnerable people, particularly the risk of cancer in the event of early exposure. PHG was developed based on the best available toxicological data in the scientific literature. Using the criteria described above, PHGs are developed for use by the California Department of Public Health (DPH) in establishing primary drinking water standards (State Maximum Contaminant Levels, or MCLs). This indeed has happened and as from July 2014, a 10 μg/L drinking water standard for hexavalent chromium is effective in California.

Keywords: Hexavalent chromium, Legislation, Drinking water

1. Introduction

Approximately 170,000 tonnes of chromium (Cr) are released annually to the environment through a large number of industrial activities such as steelworks, petroleum refining, metal finishing, Cr electroplating, leather tanning, etc. It occurs mainly in two states, the trivalent: Cr_{III} and the less common hexavalent: Cr_{VI}, both of which are used in various industrial activities. Hexavalent chromium is plated onto metal surfaces to add resistance to impact, corrosion and oxidation, the development of pigments, chemicals and other processes. Owing to its many industrial uses and in some cases, the absence of a substitute (ex:Hard Chroming) hexavalent chromium will be present in the wastewaters of a large amount of industries and, if not contained, may contaminate urban water supplies.

Until recently, high levels of hexavalent Cr in the environment were attributed as a rule to anthropogenic pollution. However over the last 5-10 years there are reports in the literature (Fantoni *et al*. (2002); Gonzalez *et al*. (2005); Robles-Camacho *et al*. (2000); Oze *et al*. (2007)) demonstrating that relatively high levels of hexavalent Cr may be due to natural geogenic processes, especially in areas where there are relatively high levels of naturally occurring Cr_{III} or Cr_{VI} in the sediments, and natural processes that can convert Cr_{III} to Cr_{VI}. Such conditions are met in several populated areas in the Pacific (California (USA), Mexico) and in the Mediterranean (Greece, Italy) as well as in other parts of the world. According to these findings in ultramafic rocks and serpentinites of ophiolite complexes, Cr content may exceed values of 200 mg/L. These values are much higher than these of limestones (22 mg/L) and sandstones (35 mg/L). Although chromite [$FeCrIII_2O_4$} which is the primary form of Cr in ultramafic rocks, exhibits very low solubility in water, there are some naturally occurring oxidants of Cr_{III}, i.e. some Fe_{III} and Mn_{IV} compounds which can oxidize Cr_{III} to Cr_{VI} at pH less than 9.

Each of the Cr oxidation states has very different biological and chemical properties. Trivalent Cr is more stable, nearly immobile, has relatively low toxicity and is an essential nutrient that is present in many types of food. Chromium deficiency may be associated with a number of disorders (Anderson, 1993, 1995). Several recommendations for daily oral intakes of chromium have been reported, an indicative number of them presented in Figure 1.

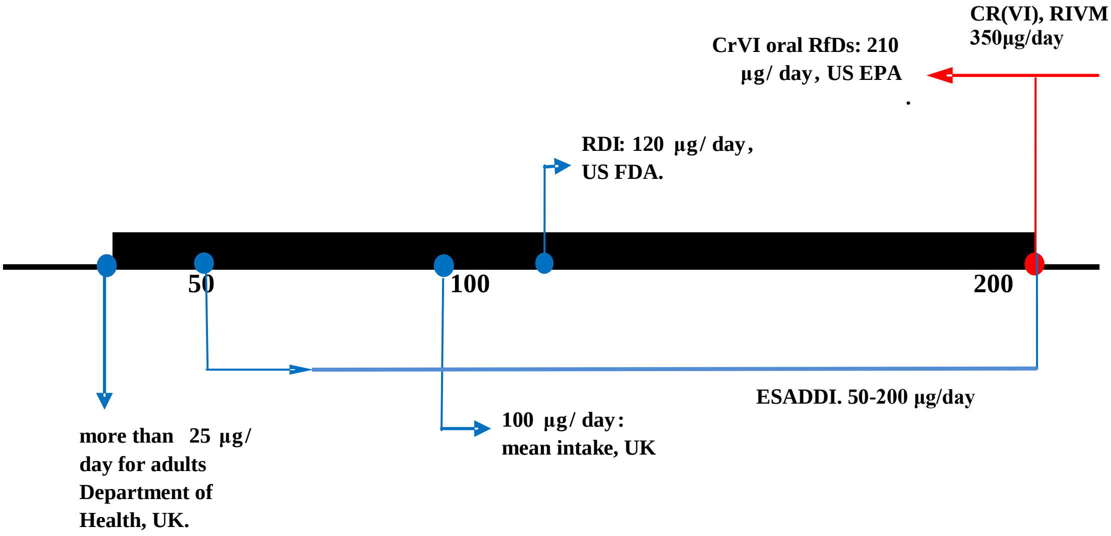

Figure 1: Regulatory assessment of intakes of Cr

Typically actual intake rates appear to match the recommended doses. Data from 2003 on the estimated dietary intakes of chromium from all foods sources in the UK indicate that chromium intakes from food range up to 170 μg/day, with mean consumption levels of 100 μg/day. Data from other EU countries suggest that chromium intake from foods ranges from 61- 160 μg/day for mean intakes, although an intake of up to 580-770 μg/day may occur (FSA 2003). The high (higher than 170-200 μg/l) intake rates are usually associated with food supplements, which may contain trivalent Cr at levels up to 0.6 mg. In these cases Cr_{III} intake from supplements may account for as much as 70% of the daily intake. Even these higher than normal intake rates of Cr_{III} (e.g. 770 μg/day) are much lower (by orders of magnitude) than the doses that may create adverse effects.

2. The hexavalent cromium controversy

Contrary to trivalent Cr, hexavalent Cr is very soluble and thus highly mobile in the environment and presents high toxicity, being acutely toxic, mutagenic, teratogenic and carcinogenic.

Cr_{VI} is a well known carcinogen via inhalation. However, the health effects of its liquid from have been widely disputed. In many of the relevant studies there is no distinction between the two forms, on the basis of the rationale that Cr_{VI} is reduced to Cr_{III} in the gastrointestinal tract, thus only intakes that exceed the reducing capacity of the stomach will result in significant absorption of Cr_{VI} across the gastrointestinal mucosa (Fleter and Dourson, 1997). However it has been reported that Cr_{VI} toxicity can result from the generation of reactive intermediates and free radicals during reduction to Cr_{V}, Cr_{IV} and ultimately Cr_{III}. Clearly it has been recently realized that the complexity of the fate of Cr_{VI} during oral uptake requires further careful consideration, which may lead to much stricter tolerable doses than the reported so far.

3. Potable water standards for chromium

Although, as mentioned, there is growing evidence that hexavalent chromium may be carcinogenic even through the oral route, there is still no international standard regarding this form of chromium and potable water. The widely adopted limit is for total chromium, usually set at 50 μg/L in accordance with the provisional guidelines value of the World Health Organisation. Total chromium was selected partly because of difficulties during the analysis of the hexavalent form. According to the U.S. EPA there was inadequate data to demonstrate that Cr_{VI} has oncogenic potential via ingestion (U.S. EPA, 1989). Thus the U.S. EPA does not have separate drinking water standards for Cr_{III} and Cr_{VI}, but only for total Cr. The MCLG (maximum contaminant level goal), based on the absence of observed toxic effects in the relatively old study of MacKenzie *et al*. (1958), is set at 100 μg/L. At the European Union level, the Drinking Water Directive (DWD), or Council Directive 98/83/EC adopts the WHO recommendation of 50 μg/L for total chromium. The European Commission commenced in 2007 a review of the Directive and the relevant study conducted by the DHI was published in 2007. According to the study, possible limit or indication values of chromium lies within 50-100 μg/L, and the standard was proposed to be retained at 50 μg/L.

However, it is well established by now that hexavalent chromium is much more dangerous to human health than trivalent chromium when inhaled, and there is growing concern related to ingestion as well (ECSR, 2011; WHO, 2011). The potential adverse health effects of hexavalent chromium where brought to the public's attention with the Hinkley case that was later dramatized in the movie *Erin Brockovich* (2000). The town of Hinkley, California, located in the Mojave Desert, had its groundwater contaminated with hexavalent chromium starting in 1952, resulting in a legal case against Pacific Gas & Electric (PG&E) and a multi-million-dollar settlement in 1996. An apparent elevated cluster of illnesses in the community where thought to be linked to hexavalent chromium. Though the case didn't provide undisputable evidence of Cr_{VI} toxicity via ingestion, the press and political attention raised public awarene about hexavalent chromium and initiated an extensive survey by the Califo authorities.

Following an 11 year effort, in 2011 the Californian Environmental Protection Agency set a final "Public Health Goal (PHG)"[1], for hexavalent chromium of 0,02 μg/L recognising its impact on young children and vulnerable people, particularly the risk of cancer in the event of early exposure (CDPH, 2012). This PHG was developed based on the best available toxicological data in the scientific literature. It is clearly stated in the supporting document that PHGs are not regulatory requirements, but instead represent non-mandatory goals. Using the criteria described above, PHGs are developed for use by the California Department of Public Health (DPH) in establishing primary drinking water standards (State Maximum Contaminant Levels, or MCLs). Thus, PHGs are not developed as target levels for clean-up of ground or ambient surface water contamination, and may not be applicable for such purposes, given the regulatory mandates of other environmental programs. Whereas PHGs are to be based solely on scientific

[1] A PHG is a level of a contaminant in drinking water that does not pose a significant health risk and reflects the risk from long-term exposure to a contaminant and should not be used to estimate risks from short-term or acute exposure. PHGs are not regulatory requirements, but instead represent non-mandatory goals (CDPH, 2012).

and public health considerations, drinking water standards adopted by DPH are to consider economic factors and technical feasibility. Each primary drinking standard adopted by DPH is required to be set at a level that is as close as feasible to the corresponding PHG, with emphasis on the protection of public health. MCLs established by DPH must be at least as stringent as the federal MCL, if one exists (OEHHA, California EPA, 2011).

In the aftermath of the PHG of 2011, a number of significant events and decisions associated with development of a maximum contaminant level (MCL) for hexavalent chromium in drinking water took place, which cn be outlined as follows :

- August 2013: CDPH proposes an MCL for hexavalent chromium.
- April 2014: CDPH submits the regulations package to the Office of Administrative Law (OAL) for review for compliance with the Administrative Procedure Act.
- May 2014: OAL approves the regulations.
- July 2014: The MCL=10 μg/L for hexavalent chromium effective.

4. Discussion - the case of Greece

Due to the geographical position of the country, authorities, public bodies and citizens in Greece (especially in vulnerable areas such as the Asopos basin) are particularly worried about a possible deficiency of the relevant to Cr existing legislation, both at national and EU levels. A typical example is the concern expressed by the Technical Chamber of Greece (TCG, 2009). In response to these concerns in January 2011 the Ministry of Environment, Energy and Climate Change in collaboration with the Ministry of Health organised an international workshop, attended by experts from the EU, WHO, EPA and California EPA and other countries with the objective to address the issue. The purpose of the workshop was to bring together leading international experts and top administrators from the European Union and the United States to:

- Present the most recent scientific evidence
- Share the regulatory experiences from the United States and the European Union
- Discuss with the Greek authorities and scientists the issues related to the presence of Cr (VI) in drinking water.

The main conclusions, reported after the workshop to the Greek and EU competent authorities, can be summarized as follows:

- There is sufficient scientific evidence for human toxicity of chromium VI, even through digestion. All experts (various scientific backgrounds) agreed on that.
- There was a general consensus amongst the experts of the doubtful validity of a regulatory value for total chromium in drinking water. The current value (EPA 100 ug/l) and (EC 50 ug/l) for chromium appears to be too high to ensure human health.
- Greece would welcome a stricter value for chromium VI in the DWD. Greece is considering the possibility of setting a lower national value for chromium VI and might seek support from other countries with similar problems e.g. Italy, Germany.
- An initiative was by Greece undertaken to raise the issue with the EU. However at the time in response it was made clear by the EU that at the moment there was no intention to revise the parameter lists in the DWD.

At the same time, it was recognized that there are considerable practical implications from lowering the standard to a figure significantly lower than 50 μg/L.

- The limit of quantification at some peripheral Greek labs (may be as high as 10 μg/L)
- The implications for many water supplies. Do they have to be shut down and alternative sources provided ?
- According to the Greek authorities the problem has not been systematically investigated in the small water supplies that are not reported to the EC (< 5000 persons or < 1000 m3/day). Significantly, the USA experts mentioned that the problem may be worse in small water supplies, as it happens in their country.

ACKNOWLEDMENTS

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REFERENCES

1. D. Andreadakis (2014), Hexavalent chromium: origin, impact and control methods, University of Patras Thesis (in Greek)
2. CDPH (2012), California Department of Public Health, Fact Sheet: Chromium-6 in drinking water, (http://www.cdph.ca.gov/certlic/ drinkingwater/Pages/Chromium6.aspx**).**
3. CEPA (2011), California Environmental Protection Agency, PETB, (Pesticide and Environmental Toxicology Branch), OEHHA, (Office of Environmental Health Hazard Assessment), Public Health goals for chemicals in drinking water: Hexavalent Chromium (CrVI).
4. NTUA (2012), The presence and impact of chromium to the aquatic environment, in "Chromium in Asopos groundwater system: remediation technologies and measures" Life Project-Charm