CHROMIUM VI

The HBM4EU Scoping document on cadmium and chromium VI (https://www.hbm4eu.eu/wp-content/uploads/2017/04/Scoping-document-on-cadmium-and-chromium-VI.pdf) provides background information on these substances, identifies relevant policy questions on the group of substances and outlines research activities under HBM4EU.

The lead authors of the scoping document were Milena Horvat of the Jožef Stefan Institute and Alessandro Alimonti of the Italian National Institute of Health. The document was produced in December 2017.

A short overview report (https://www.hbm4eu.eu/wp-content/uploads/2019/03/HBM4EU_AD5.2_Results-reported-for-Cadmium-and-Chromium_2019.pdf) was produced in 2019 to answer the main policy questions with the available data at the time.

These pages were last updated on January 2020

Uses of chromium(VI)

Chromium can exist in oxidation states ranging from -2 to +6, but is most frequently found in the environment in the trivalent (+3) and hexavalent (+6) oxidation states. The +3 and +6 forms are the most important as the +2, +4, and +5 forms are unstable and are rapidly converted to +3, which in turn is oxidized to +6 (Towill et al. 1978 (https://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=9100SI4L.TXT)). Hexavalent form – Cr(VI) – is more toxic than trivalent form – Cr(III) for its high oxidizing potential – and easily penetrates biological membranes.

The occurrence of Cr(VI) is rare naturally. Most of Cr(VI) compounds are man-made (products or by-products) and human-caused Cr(VI) contamination is a result of large industrial emissions (mainly from metallurgical, chemical, and refractory brick industries). Major uses of Cr(VI) compounds include metal plating, manufacture of pigments and dyes, corrosion inhibitors, chemical synthesis, refractory production, leather tanning, and wood preservation (Blade et al., 2007 (https://www.ncbi.nlm.nih.gov/pubmed/17577750)). Due to a lack of internal supply and to demand from the steel industry, the EU has been an importer of Cr ores. The main sources for EU imports in 2006 were South Africa (approximately 80%). Within the EU, Finland was the main producer of Cr in 2006, producing over 99% of the total EU Cr production (219,500 tonnes). A report on a critical raw material profile by the European Commision in 2014 revealed that the forecast average annual demand for Cr growth of 3%-4.5% per year (EC Report, 2014, Report on Critical raw materials for the EU (http://www.catalysiscluster.eu/wp/wp-content/uploads/2015/05/2014_Critical-raw-materials-for-the-EU-2014.pdf)).

Mobilisation of Cr occurs mainly through air, water and soil. For more detailed information on chromium concentrations in these environmental compartments, please consult the HBM4EU Scoping document on cadmium and chromium VI (https://www.hbm4eu.eu/wp-content/uploads/2017/04/Scoping-document-on-cadmium-and-chromium-VI.pdf).

Other sources of exposure to Cr(VI) need to be considered for general population, including the release of Cr, with Cr(VI) as the predominant species, from orthopedic implants made from stainless steel and cobalt-chromium alloys. Dermal exposure through leather articles and cosmetics, and oral exposure of children through toys have been reported.

Hazardous properties of chromium(VI)

Hexavalent chromium was classified by the International Agency for Research on Cancer (IARC) as a human carcinogen (Group 1) associated with increased lung cancer risk among workers in certain industries and also cancer of the nose and nasal sinuses.

In the European Union (EU), the estimated number of Cr(VI)-exposed workers in 2012 was ~786,000, with the largest numbers exposed to welding (IARC, 2012 (http://monographs.iarc.fr/ENG/Monographs/vol100C/mono100C-9.pdf)). In the EU Classification, Labelling and Packaging (CLP) Regulation (EC) No 1272/2008 (https://eur-lex.europa.eu/legal-content/en/TXT/PDF/?uri=CELEX:02008R1272-20180301&from=EN), Cr(VI) are classified as genotoxic (Muta. 1B) and as carcinogen (Carc. 1B or 1A).

Also the dermal exposure to Cr(VI) compounds can cause skin irritation, ulceration, sensitization, and allergic contact dermatitis (NIOSH, 2002 (http://www.cdc.gov/niosh/topics/hexchrom/pdfs/Cr(VI)_NIOSH_OSHA.pdf)). The toxicity of Cr(VI) in humans has been reviewed extensively (ATSDR, 2012 (http://www.atsdr.cdc.gov/toxprofiles/tp7.pdf); Costa and Klein, 2006 (https://www.tandfonline.com/doi/abs/10.1080/10408440500534032); U.S. EPA 1998 (https://cfpub.epa.gov/ncea/iris/iris_documents/documents/toxreviews/0144tr.pdf)). After absorption, mainly via inhalation for workers and/or via ingestion for the general population, Cr(VI) readily penetrates cell membranes. The details of Cr(VI) toxic activity assumed that genotoxicity, including a wide variety of effects such as DNA damage, gene mutation, sister chromatid exchange, chromosomal aberrations, cell transformation, and dominant lethal mutations, may be due to the reduced forms of intracellular origin, formed by the reduction of Cr(VI) to Cr(III) (Stearns et al., 1995 (https://pubs.acs.org/doi/abs/10.1021/bi00003a025)). The main protection mechanism against Cr(VI) activity in the lungs and the stomach is the extracellular reduction of Cr(VI) to Cr(III) by a NADPH-dependent mechanism involving ascorbate (De Flora et al., 2000 (https://academic.oup.com/carcin/article/21/4/533/2733644)). Animal trials show that glutathion plays an important role in Cr(VI) reduction in erythrocytes, also showing certain reduction activity in the lungs (Suzuki and Fukuda, 1990 (https://link.springer.com/article/10.1007/BF02010721)).

Human exposure to chromium(VI)

Breathing contaminated workplace air is the main source in occupational setting. For the general population, exposure to Cr occurs primarily by ingestion of Cr-contaminated soil, food, and water, but also through inhalation of ambient air. Cigarette smoking is another important source of Cr exposure, including the hexavalent state. When talking about total Cr, it is accepted that the contribution of drinking water to the total exposure is substantial only when levels are above 25 µg/L (WHO, 2003 (http://www.who.int/water_sanitation_health/dwq/chemicals/chromium.pdf)). However, the EFSA Panel on Contaminants in the Food Chain noted that the contribution of drinking water to total Cr refers to Cr(VI), whereas in food the trivalent form Cr(III) is the major form. Mean chronic exposure assessment for Cr(VI) across European dietary surveys through the consumption of drinking water ranged from 0.7 ng/kg b.w. per day to 159.1 ng/kg b.w. per day (EFSA, 2014 (https://efsa.onlinelibrary.wiley.com/doi/epdf/10.2903/j.efsa.2014.3595)).

Biological monitoring of exposure to Cr(VI) compounds is a practice in occupational settings. In workers, the distribution of inhaled Cr(VI) permits the biological monitoring of Cr in urine, whole blood, plasma, and blood cells. Relevant biological monitoring guidance values for occupational exposure to Cr have been reported on a national basis, but not at EU level. The Spanish authorities set a biological limit value (BLV) for total Cr concentration of10 µg/L in urine measured during a shift and 25 µg/L at the end of the workweek (INSHT, 2016 (http://www.insht.es/InshtWeb/Contenidos/Documentacion/LEP%20_VALORES%20LIMITE/Valores%20limite/Limites2016/LEP%202016.pdf)). In the UK, a biological monitoring guidance value (BMGV) of 10 µmol/mol creatinine in post shift urine was established (HSE, 2011 (http://www.hse.gov.uk/pUbns/priced/eh40.pdf)). In Germany, in order to help interpretation of occupational biomonitoring results, DFG did set a BAR (Biologischer Arbeitsstoff-Referenzwert) for the general not occupationally exposed population of working age of 0.6 µg/L urine for Cr(VI) compounds (inhalable fraction) (DFG, 2012 (http://onlinelibrary.wiley.com/doi/10.1002/3527600418.bb0ek1e0001/full)). DFG further established the DFG-EKA values (biological exposure equivalents for carcinogenic substances) for Cr(VI) that set the range of total Cr in urine (form 10 µg/L to 40 µg/L) and in erythrocyte fraction of whole-blood (form 9 µg/L to 35 µg/L) if soluble alkaline chromate of a certain concentration and/or hexavalent welding fumes (only for urine) were inhaled over a work shift (DFG, 2015 (http://onlinelibrary.wiley.com/doi/10.1002/9783527695539.ch2/pdf)).

No HBM survey have been performed at EU level on Cr(VI) exposure of the general population. Few human biomonitoring data come from individuals accidentally or intentionally ingesting Cr(VI) compounds.

Technical challenges in biomonitoring chromium(VI) in humans

An important consideration in biological testing for Cr(VI) is the reduction of Cr(VI) to Cr(III) throughout the body. Basically, inhalation is the primary route of concern for occupational Cr(VI) exposure. Inhaled Cr(VI) enters the respiratory system, where it may remain, be reduced, or enter the bloodstream. Cr(VI) may be reduced to Cr(III) in the lungs or plasma and excreted as Cr(III) in the urine. Cr(VI) that is not reduced in the plasma may enter erythrocytes and lymphocytes. This distribution of absorbed Cr(VI) permits the biological monitoring of Cr in urine, whole blood, plasma, and red blood cells (RBCs) in occupational settings.

‣ Cr in urine: urinary Cr levels are a measure of total Cr exposure as Cr(VI) is reduced within the body to Cr(III). The average urinary excretion half-life of Cr(VI) is about 39 h.

‣ Cr measurements in blood and plasma: plasma or whole blood Cr levels are indicative of total Cr exposure because Cr(VI) may be reduced to Cr(III) in the plasma. Moreover many variables can affect Cr levels in the blood, including diet, varying rates in gastrointestinal absorption, and individual capacity to reduce Cr(VI).

‣ Cr measurements in red blood cells (RBCs): intracellular Cr levels are indicative of Cr(VI) exposure because Cr(VI) passes through cell membranes, while Cr(III) does not. The Cr concentration inside erythrocytes indicates exposure to Cr(VI) sometime during the approximate 120-day lifespan of the cells. There are two advantages to the monitoring of Cr levels in RBCs versus urine: i), the sampling time may be relatively independent of the time of exposure, and, ii), it permits the determination of Cr(VI), rather than only total chromium, absorption.

Thus, in principle, erythrocyte Cr concentration was recommended for its specificity but limited by its low sensitivity. Plasma Cr concentration was recommended as a sensitive parameter, limited by its lack of specificity.

‣ Cr measurements in exhaled breath condensate (EBC): in the last years also the exhaled breath condensate (EBC) is depicted as a very good biomarker of occupational exposure. This could potential be a non-invasive alternative to measure exposure to Cr(VI) compounds long after exposure.

The above biomarkers of exposure are not sufficiently validated and great efforts could be made in this sense. In addition, while biomonitoring of occupationally exposed workers has been used to assess high-level inhalation exposures in the workplace, evaluating low-level environmental exposure to Cr(VI) has to be still addressed. Moreover, the inter- and intrapersonal variability in background levels of Cr is known to be significant and influenced by food and beverage intake, smoking, exercise, habits. Thus, the role of each factor must be carefully understood.

Overview of the biomoritoring methods is available for total Cr in occupational setting. The DFG proposed two regulatory methods: the first for total Cr in urine, the second for total Cr in whole blood as well as in plasma and in erythrocytes.

Because Cr(VI) is largely reduced to Cr(III) in the body, speciation of Cr could not be useful in HBM programmes. However, several methods aiming at direct or indirect measurement of Cr(VI) have been published in literature. They are usually based on separation of Cr(III) and Cr(VI) (i.e., micro liquid chromatography (µLC) system or ion chromatography), followed by ICP-MS quantification (detection limits ranging from 0.1 to 1.0 µg/L).

However, none of these methods have obtained the status of regulatory method yet nor have they undergone a validation.

Legislative status in the European Union

Following on the Advisory Board's advice to strengthen the science-policy interface, HBM4EU developed a strategic and systematic approach to outreach and align science and policy. A legislative mapping exercise was done by RPA Consultants, providing relevant public policy processes that may benefit from the knowledge generated under HBM4EU. The documents are available for consultation here (https://www.hbm4eu.eu/wp-content/uploads/2019/03/Chromium-VI-3101020.pdf), with the tables presented here (https://www.hbm4eu.eu/wp-content/uploads/2019/03/Chromium-results.xlsx).

In the case of Cr(VI) compounds, an oral minimal risk level (MRL) of 0.005 mg/kg b.w. per day was derived for intermediate (15-364 days) exposure based on haematological effects in rats, while reported in a chronic drinking water study (> 1 year) an oral MRL of 0.001 mg/kg b.w. per day was derived selecting as critical effect non-neoplastic lesions of the duodenum (ATSDR, 2012 (http://www.atsdr.cdc.gov/toxprofiles/tp7.pdf)). The WHO derived an oral tolerable daily intake (TDI) for non-cancer effects of 0.9 µg CrVI/kg b.w. per day taking into account the data relative to outcome observed in female mice after exposure to sodium dichromate dehydrate in drinking-water (WHO/IPCS, 2013 (http://www.who.int/ipcs/publications/cicad/cicad_78.pdf)). In a recent document, EFSA provided information on benchmark doses, margin of exposure (MOE) and TDI for the European population (EFSA, 2014 (https://efsa.onlinelibrary.wiley.com/doi/epdf/10.2903/j.efsa.2014.3595)).

To date, no EU regulation regarding maximum levels of total Cr in food has been established.

A maximum value of 50 µg Cr/L for total Cr both in water intended for human consumption and in natural mineral waters are reported by the Council Directive 98/83/EC (https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A31998L0083) and the Commission Directive 2003/40/EC (https://www.fsai.ie/uploadedFiles/Legislation/Food_Legisation_Links/Water/Commission_Directive_2003_40_EC.pdf), but no level is available specifically for Cr(VI).

Hexavalent Cr is included in the revised Annex XIV of the EU REACH Regulation (https://ec.europa.eu/info/law/better-regulation/initiatives/ares-2016-5404950_en); inclusion in this Annex means that in order to continue to use chromium trioxide and other hexavalent chromium compounds after 21 September 2017, an authorisation will be required.

In addition, since 1 May 2015 a restriction on Cr(VI) in leather is in place (EU Regulation 301/2014 (https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=uriserv:OJ.L_.2014.090.01.0001.01.ENG)) and applicable at EU level (limit of 3 ppm). That threshold is expected to be 80 % effective in reducing the occurrence of new Cr(VI)-related allergic dermatitis cases due to Cr(VI) in leather articles.

Current migration limits for Cr(VI) are laid down in the Toy Safety Directive 2009/48/EC (https://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2009:170:0001:0037:en:PDF) for ensuring the safety of toys. The current migration limits for Cr(VI) from toys are: 0.2 mg/kg toy for scraped-off toy materials, 0.02 mg/kg toy material for dry (powder-like or pliable) toy materials and 0.005 mg/kg toy material for liquid or sticky toy materials, respectively.

Regarding cosmetics, because of its allergenic character, the presence of Cr(VI) is prohibited in cosmetics by a German cosmetics regulation and also by the corresponding new EU Cosmetics Directive 76/768/EEC (https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=LEGISSUM:l21191); the only allowable green colorants are those based on the trivalent form of Cr (chromium hydroxide green ($Cr_2O(OH)_4$) and chromium oxide green (Cr_2O_3)).

Occupational exposure limits

Inhalation is the primary route of concern for occupational Cr(VI) exposure.

In air, the EU proposed an OEL (Occupational Exposure Limit) for the hazardous Cr(VI) of 25 µg/m^3; the number of future cancer cases can be most substantially decreased through full compliance with the OEL (https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:52016SC0152&from=EN). In addition, the Occupational Safety and Health Administration (OSHA) has established a permissible exposure limit (PEL) of 5 µg/m^3 and an action level (AL) of 2.5 µg/m^3; both for a 8-hour time-weighted average (TWA) exposure to Cr(VI) (OSHA, 2006 (https://www.osha.gov/laws-regs/federalregister/2006-02-28-0)). The National Institute for Occupational Safety and Health (NIOSH) has recommended a 10-hour TWA exposure limit for all Cr(VI) compounds of 1 µg Cr(VI)/m^3 (NIOSH, 2013 (https://www.cdc.gov/niosh/docs/2013-128/pdfs/2013_128.pdf)).

Policy questions on chromium(VI)

The exposure to chromium(VI) is mainly occupational. Hence, the policy questions reflect that but not only in order to have a wider picture of the exposure of the EU population.

1. What are the current exposure levels to Cr(VI) at workplaces in Europe?
2. What is the impact of authorisation and established limits of chromates on exposure levels (e.g. in surface treatment activities or in market products)?
3. What is the current exposure of the EU population to Cr(VI)?
4. Does exposure differ between countries? Why?
5. Is the limit of 50 µg Cr/L for total chromium in water intended for human consumption and natural mineral waters sufficiently protective?
6. To review the impact of the limit of 3 ppm of Cr(VI) in leather articles imposed in May 2015 on consumer exposure.
7. Feed into the discussion on whether to tighten controls of levels of Cr(VI) in toys, following the recommendation of the Scientific Committee on Health and Environmental Risks.

Stakeholder comments on the scoping documents

In the interest of transparency and accountability, HBM4EU invites interested stakeholders to submit comments on the scoping document.

All submitted comments will be made available for download on this webpage and will be taken into consideration by the HBM4EU consortium, where possible.

Please click here to submit your comments (https://www.hbm4eu.eu/surveys/stakeholder-comments-on-scoping-documents/).

(https://www.hbm4eu.eu/)

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CALENDAR I SEP 2020

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31 (https://www.hbm4eu.eu/events/2020-08-31/?limit)	1 (https://www.hbm4eu.eu/events/2020-09-01/?limit)	2 (https://www.hbm4eu.eu/events/2020-09-02/?limit)	3 (https://www.hbm4eu.eu/events/2020-09-03/?limit)	4 (https://www.hbm4eu.eu/events/2020-09-04/?limit)	5 (https://www.hbm4eu.eu/events/2020-09-05/?limit)
7 (https://www.hbm4eu.eu/events/2020-09-07/?limit)	8 (https://www.hbm4eu.eu/events/2020-09-08/?limit)	9 (https://www.hbm4eu.eu/events/2020-09-09/?limit)	10 (https://www.hbm4eu.eu/events/2020-09-10/?limit)	11 (https://www.hbm4eu.eu/events/2020-09-11/?limit)	12 (https://www.hbm4eu.eu/events/2020-09-12/?limit)
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28	29	30	1	2 (https://www.hbm4eu.eu/events/hbm-conference/)	3

HIGHLIGHTS

(https://www.hbm4eu.eu/)

Institute of Environmental Medicine, Karolinska Institutet offers the following **course** in autumn 2020:
Health risk assessment of endocrine disruptors, October 12-16, 2020.
The course is intended for PhD students and other participants from academia as well as participants from authorities and industry.
The course will be given as an **on-line course**.
Application deadline: **September 11, 2020**.
Application and further information:
https://ki.se/en/imm/international-training-in-health-risk-assessment (https://eur02.safelinks.protection.outlook.com/?url=https%3A%2F%2Fki.se%2Fen%2Fimm%2Finternational-training-in-health-risk-assessment&data=02%7C01%7CCatherine.Brytygier%40eea.europa.eu%7C54408ad418114e056cc408d82259d89d%7Cbe2e7beab4934de5bbc58b4a6a235600%7C1%7C0%7C637297116569491749&sdata=akgYGaROpc5oR0daP6%2BsK%2BCW8T4ynu40mz1dhivmYTg%3D&reserved=0)

Upcoming conference:
International Conference *"Human Biomonitoring for science and chemical policy"* under the German EU presidency on 2nd October 2020.
Registration and further information:
www.hbmc2020.com (https://eur02.safelinks.protection.outlook.com/?url=http%3A%2F%2Fwww.hbmc2020.com%2F&data=02%7C01%7CCatherine.Brytygier%40eea.europa.eu%7C8bd4f517572a4e04504c08d854cef410%7Cbe2e7beab4934de5bbc58b4a6a235600%7C1%7C0%7C637352595125114167&sdata=IEL0UhNYTaU2GrdDlwhynRY3%2FE87a68%2By80WxuGr4Vo%3D&reserved=0)

An Open letter was sent to the European Commission expressing support for the forthcoming chemical strategy and pointing to key elements. See more in the *Science to Policy* (https://www.hbm4eu.eu/the-project/science-to-policy/) section.

INFO:
3 **factsheets** on bisphenols, phthalates and chromium VI have been translated in all languages of the project and can be found here (https://eur02.safelinks.protection.outlook.com/?url=https%3A%2F%2Fwww.hbm4eu.eu%2Fresult%2Ffactsheets%2F&data=02%7C01%7CCatherine.Brytygier%40eea.europa.eu%7C9104707e5de54483eb1008d837ca6ba9%7Cbe2e7beab4934de5bbc58b4a6a235600%7C1%7C0%7C637320689820587159&sdata=M8g%2BP%2Bp4lXjqG0vfyR77U%2FncSxcVS5N2lAeRhml4dUU%3D&reserved=0). The factsheets will be sent for consultation, after having been revised.
A **research brief** of biomarkers of effect has also been prepared in collaboration with WP14 and is currently available in English and in Spanish, here (https://eur02.safelinks.protection.outlook.com/?url=https%3A%2F%2Fwww.hbm4eu.eu%2Fpolicy-briefs-and-reports%2F&data=02%7C01%7CCatherine.Brytygier%40eea.europa.eu%7C9104707e5de54483eb1008d837ca6ba9%7Cbe2e7beab4934de5bbc58b4a6a235600%7C1%7C0%7C637320689820597143&sdata=hQfWITshVgor8iQuXLqhabmjUk4celyA4KNPbUK9Xpw%3D&reserved=0).

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LINKS

FAQs

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