Hexavalent chromium in drinking water and its sources – a literature study

KWR *Watercycle Research Institute*

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Annemarie van Wezel en Kees van Leeuwen

Authors
Cindy de Jongh, Roberta Hofman, Leo Puijker and Pieter Stuyfzand

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Summary

Chromium appears to be present worldwide in elevated concentrations in many natural or polluted groundwater sources which are used for public water supply. Many studies have shown that hexavalent chromium (Cr(VI)), which refers to compounds that contain chromium in the 6+ oxidation state, is much more toxic than trivalent chromium (Cr(III)). Based on studies showing genotoxic properties of Cr(VI), experts indicate that the drinking water standard for Cr(VI) should be lower than the current standard of 50 µg/L for total chromium. This study aims to describe what is known on chromium concentrations and its speciation in drinking water and its sources in the Netherlands, and to give an overview of the literature on developed techniques for chromium removal from water. We also aim to give an overview of literature on toxicity of Cr(VI) to determine the human health relevance of Cr(VI) in drinking water.

Chromium in Dutch waters

The most important sources of chromium in Dutch waters are related to industrial inputs, with minor natural background inputs from clayey sediments under specific conditions. The following dissolved chromium ions are most common and most important for equilibrium calculations, at the normal pH domain (4-9) in Dutch ground and surface waters: for Cr(III) they are $CrOH^{2+}$ and $Cr(OH)_3^0$; and for Cr(VI) they are $HCrO_4^-$ and CrO_4^{2-} (chromate). Cr(VI) only occurs in (sub)oxic environments, i.e. where oxygen is present or where nitrate and nitrite are (meta)stable. In (deeply) anoxic environments, Cr(VI) is reduced to the much less soluble Cr(III) especially by Fe^{2+}, organic material, pyrite and H_2S. In groundwater, Fe^{2+} and Cr(VI) appear to be antagonists, because Fe^{2+} reduces Cr(VI) to Cr(III). In general, Cr(III) will migrate under acidic conditions, while Cr(VI) generally migrates rapidly, but its mobility is inhibited when the Fe(II) and organic matter concentrations are high and when sorption processes are favoured (low pH). In studying dissolved chromium, it should be noted that filtration bias and bias by corrosion of stainless steel may strongly influence the analytical results.

All reported chromium concentrations in surface waters, infiltration waters and various groundwater types are well below the EU drinking water standard of 50 µg/L, with maximum values for total chromium of 12 µg/L. The only available Cr(VI) (chromate) data on raw and treated Dutch drinking water were published in 1998. These results were further elaborated by combination with data on the inorganic hydrochemical matrix (from different data sets). This yielded the following observations:
- Iron and chromium form antagonists: public supply well fields with Fe > 1 mg/L show total chromium ≤ 0.5 µg/L and Cr(VI) <0.2 µg/L, which is in agreement with previous findings;
- Chromate in raw water is only present when O_2 and NO_3 are > 1 mg/L;
- The maximum chromate concentration in 17 PSWFs was 2.1 µg/L;
- Concentrations in raw and treated water do not differ much in most cases, indicating that aeration and rapid sand filtration do not remove chromate; and
- In several cases where chromate was detected, the treated water contained a little more chromate than the raw water. Chromate formation during drinking water treatment steps cannot be excluded therefore.

Chromium removal

In literature several methods have been described to deal with the presence of chromium in ground water and waste water, mostly aimed at removal of chromium in high concentrations. Cr(III) is less mobile than Cr(VI) and often present in the form of a cation (Cr^{3+}). Cr(VI) is much more mobile and mostly present in the form of anions. This implies that different technologies have to be applied in order to remove Cr(III) or Cr(VI) e.g. by means of ion exchange or complexation. As it is relatively easy to reduce Cr(VI) to Cr(III), this reaction is often used in purification processes. The resulting Cr(III) can either be removed or be immobilized in the soil. Which technology will be most suitable for chromium removal strongly depends on the actual situation, e.g. relative low concentrations in ground water vs. relative high concentrations in waste water. Further, pH and presence of oxygen or salts can strongly affect the process.

Chromium toxicity

Toxicological studies showed that Cr(VI) is much more toxic than Cr(III). While Cr(VI) has long been recognized as a potent carcinogen through inhalation, recent studies clearly demonstrated that Cr(VI) is also carcinogenic by oral exposure. After oral absorption, Cr(VI) easily enters cells in various tissues. Within the cell, Cr(VI) is stepwise reduced to Cr(III), leading to the formation of reactive intermediates as well as DNA and protein adducts. These forms of DNA damage may cause mutations and chromosomal breaks and may finally lead to tumour formation.

Human exposure to Cr(VI) may be through inhalation of polluted air, drinking water or food. However, very little is reported on the magnitude of exposure to Cr(VI). RIVM recently derived a minimum risk level associated with a 10^{-6} cancer risk for Cr(VI) using their standard methodology. An excess lifetime cancer risk of 1 in 1 million is considered a generally accepted negligible risk. Based on this risk level, for the Netherlands a provisional guideline value for drinking water of 0.2 µg/L Cr(VI) may be derived. This provisional health-based target is based on state-of-the-art scientific publications. However, it is not an enforceable maximum contaminant level or drinking water standard.

The only available Cr(VI) (chromate) data on raw and treated Dutch drinking water were published in 1998. Raw water of six public supply well fields and treated drinking water of nine well fields exceeded the provisional health based target of 0.2 µg/L Cr(VI). As these observations are only based on one monitoring study and in view of the possible toxicological relevance, we suggest performing additional monitoring on Cr(VI) levels in raw and treated drinking water. When performing these analyses, the potential filtration bias should be taken into account.

Contents

1   Introduction

Groundwater is the major source of drinking water throughout the world. Chromium appears to be present worldwide in elevated concentrations in many groundwater sources which are used for public water supply. The name "chromium" is from the Greek word for colour. Chromium salts are characterized by a variety of colours, solubilities and other properties. The most important chromium salts are sodium and potassium chromates and dichromates, and the potassium and ammonium chrome alums. No taste or odour is associated with chromium compounds.

Hexavalent chromium (chromium VI or Cr(VI)) refers to chemical compounds that contain the element chromium in the 6+ oxidation state. The most common valences of chromium are 3+ and 6+, with Cr^{3+} as the dominant form. Cr(VI) can be reduced to the more stable Cr(III) in the presence of reducing agents (e.g. iron) or oxidizable organic matter. The metal chromium, which is the chromium(0) form, is used for making steel. Cr(VI) and Cr(III) are used e.g. for chrome plating, dyes and pigments, leather tanning, and wood preservation.

Toxicological studies showed that Cr(VI) is more toxic than Cr(III) (IARC, 2011). While Cr(VI) has long been recognized as a potent carcinogen via inhalation, recent studies clearly showed that Cr(VI) is also carcinogenic by oral exposure (IARC, 2011). Drinking water quality experts report that the drinking water standards for Cr(VI) should be lower than 50 µg/L, which is the current drinking water standard for total chromium in the EU (directive 98/83/EC) and by WHO. The California Environmental Protection Agency recently proposed a public health goal of 0.02 µg/L for Cr(VI) (California Environmental Protection Agency, 2011). In the United States, an environmental working group revealed the presence of Cr(VI) in drinking water in 31 of 35 cities tested. Of these cities, 25 had levels above 0.06 µg/L. The highest reported Cr(VI) levels were 2 µg/L in Honolulu, 12 µg/L in Norman Oklahoma and 580 µg/L in Hinckley, California (Eaton, 2011).

Not much is reported yet on the occurrence of Cr(VI) in drinking water and its sources in the Netherlands. The aim of the current literature study is to describe what is known on chromium concentrations and its speciation in resources for drinking water supply in the Netherlands, and to give an overview of the literature on developed techniques to remove chromium from wastewater and sources for drinking water. This literature study also gives an overview of literature on toxicity of Cr(VI) to determine the human health relevance of Cr(VI) in drinking water.

2 Chromium in resources for drinking water supply in the Netherlands

2.1 Hydrogeochemistry of chromium

Chromium is a heavy metal, lithophilic (accumulates in rock and is not well soluble in water), with atomic number 24, atomic weight 51.996 and a density of 7.19 kg/dm^3. In nature it occurs as a hexavalent (Cr^{6+}) and trivalent (Cr^{3+}) ion, of which Cr^{3+} is the predominant form. Specific chromium minerals are relatively rare and in the Netherlands they are practically lacking. Chromium frequently replaces Fe^{3+} and Al^{3+} in other minerals, which in the Netherlands yields the highest contents in sediments rich in clay minerals.

The various ionic species are shown in Figure 2.1 as a function of pH and Eh (redox potential). The following dissolved chromium ions are most common and most important for equilibrium calculations, at the normal pH domain (4-9) in Dutch ground and surface waters: for Cr(III) they are CrOH^{2+} and Cr(OH)$_3^0$; and for Cr(VI) HCrO$_4^-$ and CrO$_4^{2-}$ (chromate). Dichromate (Cr$_2$O$_7^{2-}$) only occurs at very low pH, it is a strong oxidant and therefore it is hardly observed in natural waters.

The better soluble and much more toxic chromate (Cr(VI)) only occurs in (sub)oxic environment, i.e. where oxygen is present or where nitrate and nitrite are (meta)stabile (Figure 2.1). Chromate is reduced to the much less soluble Cr(III) in (deeply) anoxic environments, especially by Fe^{2+}, pyrite, H$_2$S and organic material (Breit et al. 1992; Yao-Tung & Ching-Pao 2008). In groundwater Fe^{2+} and Cr(VI) appear to be antagonists, because Fe^{2+} reduces Cr(VI) to Cr(III) via the following reaction (modified after Richards & Bourg, 1991):

$$3\ Fe^{2+} + CrO_4^{2-} + 5\ H_2O \rightarrow 3\ Fe(OH)_3\ (s) + Cr^{3+} + H^+ \qquad (1)$$
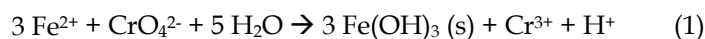
Precipitating ferrihydrite (Fe(OH)$_3$) is probably one of the most significant Cr^{3+} sinks, because of solid solution formation according to:

$$(1-x)\ Fe^{3+} + x\ Cr^{3+} + 3\ H_2O^- \rightarrow Fe_{1-x}Cr_X(OH)_3\ (s) + 3\ H^+ \qquad (2)$$
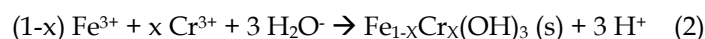
For typical natural conditions, the mole fraction (x) of chromium will be low (around 0.01), according to Richards & Bourg (1991). When the solution is free of dissolved iron, Cr(OH)$_3$ (s) is considered to be the solubility controlling phase. On the other hand, the oxidation of Cr^{3+} by O$_2$ is very slow, and catalysts are needed to speed up the reaction. Catalysts in nature, mentioned by Richards & Bourg (1991), are composed of bacteria and Mn-oxides. In the latter case the reaction may proceed as follows:

$$Cr^{3+} + 1.5\ MnO_2(s) + H_2O \rightarrow HCrO_4^- + 1.5\ Mn^{2+} + H^+ \qquad (3)$$

Rai et al. (1989) indicate that the solubility of Cr(VI) may be limited by formation of a Ba(S,Cr)O$_4$ solid solution, which controls the dissolved chromium concentrations in environments that contain barite (BaSO$_4$). The mobility of Cr(VI) in water considerably exceeds the mobility of Cr(III), because Cr(VI) exists as an anion and Cr(III) as a cation. At the predominating pH-values anions adsorb less and

cations much more to the negatively charged soil or aquifer. Richard & Bourg (1991) state that Cr(III) will migrate under acidic conditions and/or if present as dissolved organic matter complexes, while Cr(VI) generally migrates rapidly but its mobility is inhibited when the Fe(II) and organic matter concentrations are high and when sorption processes are favoured (low pH).
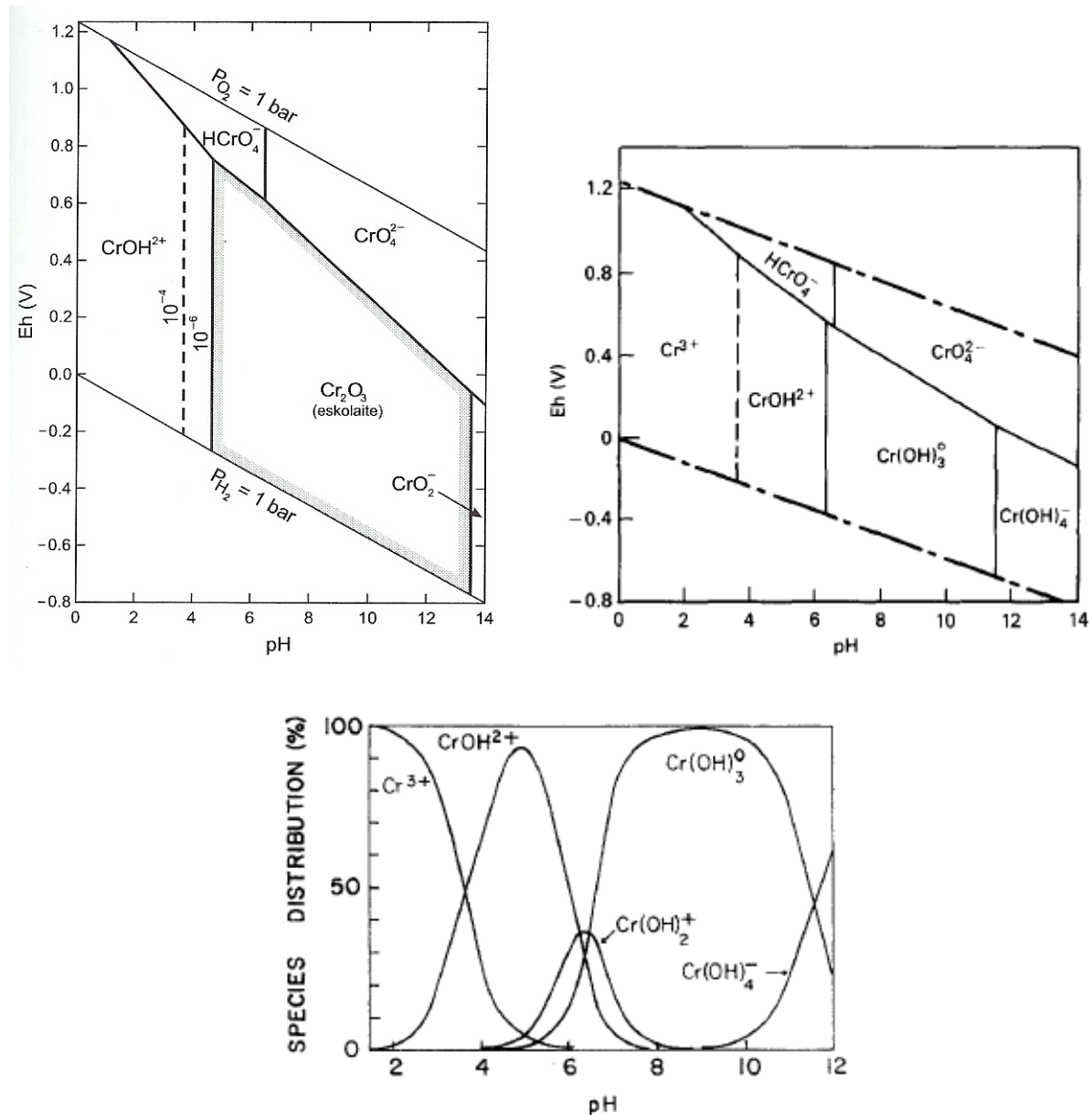
Figure 2.1. Stability diagrams of chromium dissolved in water with eskolaite (upper left; Brookins, 1988) and without solid phase (upper right; Rai et al., 1989), and inorganic Cr(III) speciation as a function of pH (below; Richard & Bourg, 1991). Chromium (upper left): the Cr-O-H system at 25 °C, 1 bar and dissolved Cr-activity = 10^{-6} mol/L = 52 µg/L. Chromium (upper right and below): dissolved species only, in equilibrium with solid Cr(OH)$_3$ at 25 °C and 1 bar.

2.2 Sources of chromium in water

Natural sources of chromium in water are composed of various iron and aluminium minerals, natural ores (practically absent in the Netherlands) like eskolaite (Cr_2O_3), chromite ($Fe(II)Cr_2O_4$) and crocoïte ($PbCrO_4$), and the sorption complex of clay minerals (Wedepohl, 1978). Chromium is hardly bound to sulfide minerals and organic material.

The most important human activities that raise the environmental concentrations of Cr (VI), are composed of industrial activities producing chemicals, leather and textile, electropaints and various other Cr(VI) applications in industry. Metallurgical industrial spills mainly discharge Cr(III) to surface and ground water. Chromium is used there, among others, to galvanize metal surfaces or to produce stainless steel, which contains 12-15% Cr(III).

Chromium is emitted to the atmosphere, according to RIVM (2008), especially by industry (46%), traffic (43%), refineries (5%), waste processing industries (3%) and the power supply sector (2%). RIVM (2008) states that soil emissions of chromium are mainly related to industry (65%) and consumers (30%, significant part by using wolmanized wood) and others (5%). Water is polluted by chromium (directly and indirectly) mainly via sewage (42%) and industrial effluents (37%), and in addition by the construction sector (3%), waste processing industries (3%), traffic (1%) and others (14%).

2.3 Total chromium in Dutch waters

2.3.1 Concentrations of total chromium

Table 2.1 offers an overview of chromium concentrations in various water types in the Netherlands. Chromium concentrations are differentiated into total unfiltered, total filtered over 0.45 µm (= total dissolved), dissolved Cr(III) and dissolved Cr(VI).

In rain and surface waters large differences exist between total unfiltered and total dissolved, due to the strong binding of chromium to suspended solids like iron flocks, clay and organic material. In rain water and even more in Rhine river water, chromium concentrations strongly declined during the past 20-30 years thanks to all kinds of sanitation measures. Recently reported chromium concentrations in Dutch surface waters range from <1 to 4.4 µg/L (Table 2.1).

Concentrations in pretreated infiltration waters for artificial recharge are very low (≤1 µg/L), and remain low (<1-2 µg/L) during and after aquifer passage (Stuyfzand, 1991c). Chromium concentrations in raw water of Dutch Public Supply Well Fields (PSWFs) varies between <0.5 and 7.9 µg/L (Table 2.1 and 2.2). The highest values are observed for semiconfined PSWFs (type B) and the lowest for PSWFs with artificial recharge (type I; Table 2.2). Regarding PSWFs little has changed during the past 20 years. Shallow, coastal dune groundwaters (<5 m below groundwater table) normally show low chromium concentrations (<1 µg/L), but in decalcified dunes with pH<6 and in calcareous dunes with Fe>10 mg/L chromium concentrations may rise up to 12 µg/L (Table 2.1). These values correspond with chromium concentrations observed in the national monitoring network of groundwater (Landelijk Meetnet Grondwaterkwaliteit, LMG) between 9 and 25 m below ground level (RIVM, 1992). According to Bouman and Fraters (1993) chromium concentrations in shallow groundwaters in the Netherlands show a positive correlation with land use by (intensive) agriculture,

mixed forests and grass lands, atmospheric SO_X deposition, total dissolved solids and concentrations of SO_4, DOC and Al, and a negative correlation with depth and pH.

All reported chromium concentrations in surface waters, infiltration waters and groundwater are well below the EU drinking water standard of 50 µg/L.

Table 2.1. Overview of chromium concentrations in various water types (ranges and averages).

Water type	year(s)	Cr-total [µg/L]		Cr(III) aq.	Cr(VI) aq.	Reference
Netherlands unless stated otherwise		unfiltered	filtered	[µg/L]		
Rain water (bulk)						
Petten, North Holland	1970s	3.7	1.2	-	-	Cambray et al. 1979
Coastal dunes N + S Holland	1979-1981	0.3-2.4				Stuyfzand, 1991a
Wijk a/z, Zandvoort, The Hague, Enschede	1995	0.3-1.3	-	-	-	Stuyfzand & Luers, 2000
Coastal dunes Bloemendaal	2010-2011	-	0.16	-	-	Stuyfzand & Arens, 2011
N. Carolina, USA	1999-2001	0.24	0.12	0.04	0.06	Kieber et al. 2002
Surface water						
Meuse River, Eijsden	2008	2.0	0.5	-	-	RIWA 2008
Meuse River, Heel	2009	<1	<1	-	-	RIWA 2009b
Meuse River, Keizersveer	2009	1.2	-	-	-	RIWA 2009b
Rhine River, Lobith	1970-1972	54	15	-	-	Stuyfzand, 1991b
Rhine River, Lobith	1987-1988	7.7	0.7	-	-	Stuyfzand, 1991b
Rhine River, Lobith	2009	2.1	<0.5	-	-	RIWA 2009a
Lek channel, Nieuwegein	2009	4.4	-	-	-	RIWA 2009a
Lake IJssel, Andijk	2009	1.5	-	-	-	RIWA 2009a
North Sea water, coastal	1980s	-	0.5	-	-	Stuyfzand, 1993
Standard Mean Ocean Water	1970s	-	0.2	-	-	Van der Sloot, 1979
Infiltration water for artifical recharge						
Lake Yssel, Andijk	1988-1995	0.4-1.2	-	-	-	St 1991c; St&L 2000 $
Rhine from Lek canal, Nieuwegein,	1988-1995	<1-1	-	-	-	St 1991c; St&L 2000 $
Meuse, from Afgedamde Maas, Brakel	1988-1995	<0.5	-	-	-	St 1991c; St&L 2000 $
Rhine / Meuse mix from Haringvliet	1988-1995	1	-	-	-	St 1991c; St&L 2000 $
Groundwater						
Fresh, shallow, in calcareous dune areas	-	-	<0.2-11.9	-	-	datafiles Stuyfzand
Fresh, young, in decalcified dune areas	-	-	0.6-7.9	-	-	datafiles Stuyfzand
Fresh, young, upper 25 m LMG $$	-	-	<1-8	-	-	RIVM, 1992
Fresh, raw water Public Supply Well Fields	2008	<0.2-2	<0.5-7.4	-	-	Tables 2.2/2.3, this publ.
Brackish	-	-	<0.5-18	-	-	datafiles Stuyfzand
Salt - hypersaline	-	-	1-450	-	-	datafiles Stuyfzand

#: AR = Artificial Recharge as applied for public drinking water supply $$: LMG = National Groundwater Monitoring Network
$: St 1991c = Stuyfzand 1991c; St&L 2000 = Suyfzand & Luers 2000

Table 2.2. Overview of total chromium concentrations in groundwater extracted by Dutch well fields for drinking water supply, in µg/l in 1989 and 2008.

Public Supply Well Field type	A	B	I	K	U	All
Cr-total µg/L (Vogelaar, 1993)						
Minimum	0.05	0.25	0.5	0.25	0.25	0.05
Average	1.1	0.7	0.5	0.4	0.6	0.8
Maximum	2.5	8	0.5	1.7	2.5	8
Number	88	81	6	15	13	203
Cr-total µg/L (Datafiles Stuyfzand)						
Minimum	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Average	0.6	0.5	<0.5	0.4	1.1	1.3
Maximum	2.2	7.4	<0.5	0.9	1.9	7.4
Number	70	119	13	9	30	241

A = phreatic (often shallow and (sub)oxic, i.e. NO3 > 1 mg/L);   B = semiconfined (often deep and (deeply) anoxic, i.e. NO3 = O2 = 0 mg/L);   I = artificially recharged surface water;
K = groundwater from limestone aquifer Limburg;   U = river bank filtrate.

2.3.2 Bias

Stuyfzand (1987) observed that dissolved chromium is very susceptible to filtration bias. When water samples are preserved for later analysis by acidification, suspended material has not always been sufficiently eliminated by filtration over a 0.45 μm membrane filter. Filtration bias is easily identified by raised dissolved Al concentrations in samples that otherwise should have a very low Al concentration (<10 μg/L), as is normally the case with pH 6-8. Elevated levels of Ni and Cr should be mistrusted in case of stainless steel wells due to corrosion effects (Oakley & Korte, 1996).

2.4   Hexavalent chromium in Dutch waters

Chromate (Cr(VI)) data on the raw and treated water for drinking water in the Netherlands were published by RIVM by Jonker et al. (1998). Their results are shown in Table 2.3, with distinction between water abstracted by public supply well fields (PSWFs) and surface water. Data were added on the main constituents, total dissolved Cr, Al and Ni. However, the data come from different data sets. The following trends can be observed in Table 2.3:

1. Iron and Cr form antagonists indeed: PSWFs with Fe > ca. 1 mg/L show Cr-total ≤ 0.5 and Cr(VI) < 0.2 μg/L.
2. Chromate (Cr(VI)) in raw water is only present when O_2 and NO_3 are >1 mg/L, which is in line with the previous conclusion.
3. The maximum chromate concentration encountered in the 17 PSWFs was 2.1 μg/L;
4. Chromate (Cr(VI)) and total chromium do not differ much either in most samples, indicating that chromate is the principal species there.
5. Concentrations in raw and treated water do not differ much in most cases, indicating that aeration and rapid sand filtration do not remove chromate.
6. In several cases where chromate (Cr(VI)) was detected, the treated water contained a little more than the raw water. Further study is needed to determine whether this results from bias or that chromate concentrations increase during drinking water treatment steps.
7. Surface water (only 2 samples) showed lower chromate (Cr(VI)) contents than groundwater.
8. PSWF Hoenderloo showed an anomaly in Cr and Ni in 2008, probably due to dissolution of stainless steel.
9. The data set does not show a relation between pH and Cr, nor with depth and Cr.

No other data on Cr(VI) in drinking water and its sources in the Netherlands were found in literature. Further Cr(VI) data from other countries are given in paragraph 4.2.

Table 2.3. Overview of total dissolved chromium (Cr-tot) and chromate (Cr(VI)) concentrations in the raw water of 17 public supply well fields and 2 surface water intake points, and some further chemical characteristics. Data are based on one single measurement. Chromate data are derived from Jonker et al. (1998), the other data from datafiles of Stuyfzand at KWR Watercycle Research Institute (from 1998 or 2008).

Raw waters for drinking water supply				Well screen		Cr(VI) µg/L		Raw (black = 2008; red = 1998)									
Name	Company 1998	Type	LS m ASL	From	To	Raw 1998	Treated 1998	Cr-tot µg/L	pH	O2	NO3	SO4	Cl	HCO3	Fe	Al µg/L	Ni
				m ALS								mg/L				µg/L	
Public Supply Well Field																	
Arnhem, La Cabine	NUON	B	30	80	120	2,0	1.3	1.5	7.0	5.5	<0.06	14.8	16	87	0.04	1	0.4
Baarn-van Reenenlaan	WMN	A	6	24	48	0.3	0.6	0.7	7.6	2.6	7.3	16.5	27	122	0.3	1	0.5
Bilthoven	WMN	A	6	23	100	0.4	< 0.2	<0.5	7.2	<1	2.3	18.3	20	78	0.76	12	0.8
Boxmeer	WOB	A	15	9	15	< 0.2	< 0.2	0.5	6.7	-	0.5	101.3	40	241	8.94	2	1.7
Driebergen mix	WMN	B	7	41	172	1.8	1.5	1.2	7.3	1.9	7.2	18.3	37	49	0.01	<1	0.2
Grubbenvorst conv	WML	B	20	25	45	< 0.2	< 0.2	<0.5	6.6	0.1	<0.06	15.3	34	126	5.95	<1	2.1
Herkenbosch	WML	B	49	60	170	< 0.2	< 0.2		-	6.8	<0.5	<0.5	<5	15	251	3.6	9	-
Hoenderloo ondiep	NUON	A	60	40	70	< 0.2	0.3	35.4	6.7	3.2	14.8	15.4	15	49	0.13	1	22.8
Laren Mix	WMN	A	10.5	15	67	<0.2	< 0.2	<0.5	7.3	1.6	0.1	12.7	31	185	3.34	2	4.1
Leersum	WMN	B	10	42	68	< 0.2	2.1	0.7	6.9	2.6	8.0	17.2	14	39	0.53	1	0.7
Lichtenvoorde	WG	A	19	25	35	< 0.2	< 0.2	0.5	7.1	0.5	0.9	83.0	45.3	431	11.2	<5	<5
Montferland, Galgenberg	WG	A	50	50	62	0.9	0.6	0.6	7.0	6.7	38.1	36.4	19	101	0.22	1	<0.2
Oosterbeek	NUON	B	10	55	75	< 0.2	1.1	1.1	7.3	2.0	<0.06	12.0	12	111	0.04	3	<0.2
Soestduinen	WMN	A	7.5	33	93	0.4	0.6	1.3	7.1	2.2	4.2	21.1	17	88	-0.01	8	0.5
Susteren diep	WML	B	30	95	230	< 0.2	<0.2	<0.5	6.3	0.2	<0.06	5.1	4	90	3.94	<1	<0.2
Vierlingsbeek	WOB	A	20	8	28	< 0.2	< 0.2	<0.5	5.9	2.0	15.5	154.6	28.9	25	9.18	920	90.0
Zeist	WMN	B	6	60	76	<0.2	1.6	2.5	7.5	<1	3.8	21.4	20	90	0.36	1	1.6
Surface water																	
WRK III (Prinses Juliana)	WRK	O				0.3	-	-	-	-	-	-	-	-	-	-	-
A'dam-Weesperkarspel	GWA	O	-1.1	-2	-2	<0.2	< 0.2	-	-	-	-	-	-	-	-	-	-

ASL = Above Sea Level; ALS = Above Land Surface; LS = Land Surface

Limit of quantification (LOQ) of Cr(VI): < 0.2 µg/L. Cell colouring for chromium and iron only: green = chromate close to LOQ; yellow = chromate significant but <1 µg/L; red brown (Cr) = chromate >1 µg/L; red brown (Fe) = Fe > 1 mg/L.

2.5   Analytical techniques

ATSDR (2008) described several analytical methods to determine total chromium and Cr(III) and Cr(VI) in environmental samples, including drinking water. Measurements of low levels of chromium concentrations in water have been made by specific methods, such as inductively coupled plasma mass spectrometry (ICP-MS), capillary column gas chromatography (HRGC) of chelated chromium with electron capture detection (ECD), and electrothermal vaporization inductively coupled plasma mass spectrometry. A method using high performance liquid chromatography (HPLC) interfaced with direct current plasma emission spectrometer has also been used. The quantification of soluble and insoluble chromium is done by determining chromium concentrations in aqueous filtered and unfiltered samples. However, soluble Cr(VI) may be reduced to Cr(III) on filtering media, particularly at low concentrations, and under acidic conditions. Teflon® filter and alkaline solution are most suitable to prevent this reduction (ATSDR, 2008). The HPLC-method used by US EPA (Method 7199) allows the detection of Cr(VI) in drinking water at 0.3 µg/L (ATSDR, 2008). US EPA advises to perform sample analysis using a modified version of EPA Method 218.6, "Determination of Dissolved Hexavalent Chromium in Drinking Water, Groundwater and Industrial Wastewater Effluents by Ion Chromatography"[1]. These modifications allow for improved low concentration measurement. With these modifications, laboratories are capable of attaining a detection limit as low as 0.02 µg/L. US EPA states that any equivalent ion chromatographic system from any manufacturer with comparable hardware can generate this performance and meet the quality control requirements of EPA Method 218.6.

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[1] Rev. 3.3, 1994; www.nemi.gov. Application Update 144 "Determination of Hexavalent Chromium in Drinking Water by Ion Chromatography" found at www.dionex.com/en-us/webdocs/4242-AU144_V18.pdf.

3   Chromium removal from water

The presence of chromium in the environment can be a problem for the drinking water production. The toxicity of chromium strongly depends on the form in which it is present: Cr(III) or Cr(VI). Several methods have been developed for the removal of chromium from (ground)water, depending on the type of chromium ions and/or complexes present. This chapter gives an overview of the various methods that have been developed to remove chromium from wastewater and sources for drinking water (like ground water).

As already described in the previous chapter, chromium can be present in the environment either as Cr(III) or Cr(VI). The dominant Cr(III) species occurring in water depend on pH, and include $Cr(OH)^{2+}$, $Cr(OH)_2^+$, $Cr(OH)_3$ (aq) and $Cr(OH)_4^-$ (Sharma, 2008). $Cr(OH)_2^+$ is the dominant species in natural groundwater with a pH between 6 and 8. Under slightly acidic to alkaline conditions Cr(III) can precipitate as amorphous chromium hydroxide, $Cr(OH)_3$ (s). Cr(III), being a positively charged ion, has a strong tendency to form very stable complexes with negatively charged organic or inorganic ligands. Hence, it is normally found in the form of complexes. The mobility of Cr(III) in the aquatic environment is expected to be low because of the low solubility of Cr(OH)3(s) and (Cr,Fe)(OH)3(s) precipitates and their strong adsorption onto solids under slightly acidic to basic conditions. Cr(III) attains its minimum solubility in the pH range of natural waters (i.e. pH = 7.5–8.5). Cr(VI) exists in solution as monomeric species/ions: $H_2CrO_4^0$, $HCrO_4^-$ (hydrogen chromate) and CrO_4^{2-} (chromate); or as the dimeric ion $Cr_2O_7^{2-}$ (dichromate, which only exists in very strongly acidic solution). In the pH range (1–10) and at low concentrations, chromium is present in groundwater as either monovalent $HCrO_4^-$ or divalent chromate CrO_4^{2-}. The monovalent form predominates in acidic water while the divalent form predominates at neutral pH or above. In dilute solutions (<1 mg/L), the predominant form is CrO_4^-, which, being negatively charged, does not complex with negatively charged surfaces. However, Cr(VI) anions are adsorbed onto positively charged surfaces, such as the oxides and hydroxides of Fe, Mn and Al. Adsorption of Cr(VI) is usually limited, and decreases with increasing pH. Hence, Cr(VI) is more mobile than Cr(III).

3.1   Treatment methods

Treatment methods available for the removal of chromium from water can be classified into the following main groups: coagulation and precipitation, adsorption onto different media, ion exchange, membrane technology, electrodialysis, biological removal and solvent extraction (Sharma, 2008; Lv, 2011). The latter technique is not applied on a large scale and is not discussed in this report.

Most of these methods are suitable for the removal of chromium in high concentrations. An overview is given below. Traditional methods of chromium removal from (waste)water are specially aimed at recovery and reuse of chromium. However, in groundwater environments, the chromium concentration levels are much lower and the aim is to remove them to below the level specified by the drinking water quality standards and guidelines. This requires a different technological approach.

3.2 Coagulation and precipitation

Metals can be removed by precipitation as metal oxides/hydroxides, sulfides, carbonates, and phosphates (Blas, 2008). In general, the removal of Cr(III) from water is relatively easier than removal of Cr(VI). Cr^{3+}, which mostly is present as a cation, forms complexes with chlorides, fluorides, sulfates, ammonium salt, cyanides, sulfocyanides, oxalates and citrates. Coagulation using alum and ferric (Fe(III)) coagulants has been used for Cr(III) removal in conventional treatments. In these processes removal is due to precipitation as $Cr(OH)_3$ and co-precipitation with $Al(OH)_3$ or $Fe(OH)_3$, resulting in the formation of for example $Fe_xCr_{1-x}(OH)_3$ (Sharma, 2008; Hashim, 2011). This removal strongly depends on pH, and thus it sometimes is possible to achieve precipitation of Cr(III) just by adding NaOH or $Ca(OH)_2$. Cr(VI) in aqueous solution is present in different ionic forms, depending on the pH. In general, Cr(VI) appears to be present in anionic complexes. As a result of this, the coagulants which are used for Cr(III), are ineffective for Cr(VI) removal. Two types of chemical treatment are currently used for Cr(VI) removal: the first type removes Cr(VI) anions directly while the second type relies on the reduction of Cr(VI) to the less mobile and less toxic Cr(III) (followed by immobilization or removal of Cr(III)). An overview of the available literature is presented below.

- Hashim et al. (2011) describe the injection of chelating agents in contaminated soil to form stable water soluble metal-chelate complexes, which can be used to remove the metal from a solid phase. Chelating agents like EDTA, NTA and DTPA appeared not to be suitable for removal of Cr(III).
- Zero or divalent iron ($FeSO_4$), sulfur dioxide, sulfides and sodium bisulfite are applicable only for reduction. Often, a reducing agent can act as a sorbent for the resultant Cr(III) ion, resulting in an effective removal of the chromium by conventional solid-liquid phase separation treatment (Sharma, 2008; Hashim, 2011). This especially is true for reduction by means of Fe(II), which is oxidized to Fe(III), an excellent coagulating agent for Cr(III). The reduction of Cr(VI) to Cr(III) is fast (minutes to hours) and effective over the pH range of 5.0-9.0. Required Fe(II) dosage is 3-5 times the Cr(VI) concentration. Fe(II) can also be added electrochemically to Cr(VI) containing water (Sharma, 2008). From a pure iron electrode, Fe^{2+} ions are released into the solution.
- Hashim et al. (2011) describe the reduction of Cr(VI) to Cr(III) by soil organic matter, S^{2-} and Fe^{2+} ions under anaerobic conditions.
- Cequiera et al. (2012) describe the reduction of Cr(VI) by means of tropical peat and humin. Peat is formed in natural wetlands containing high levels of organic matter, such as marshes and swamps, due to the inhibition of microbial decomposition of plant materials in flooded environments. Depending on the state of the redox-active functional groups present, humic substances can either take up electrons (by oxidized functional groups with electron accepting capacities), or alternatively, release electrons (from reduced functional groups with electron donor capacities) to an electron acceptor with a more positive redox potential, such as Cr(VI). Reduction of Cr(VI) by humic acids is due to the presence of hydroxyquinone-quinone redox couples, and increases at lower pH due to lowering of the redox potential of the $HCrO_4$.. Phenol groups, present in humic substances, were shown to be excellent chelants for metal ions such as Cr(III). Groundwater contaminants are often dispersed in plumes over large areas, deep below the surface, making conventional types of remediation technologies difficult to apply. When groundwater is passed through a reductive zone or a purpose-built barrier, metal reduction may occur. The sub-surface redox conditions can be

manipulated by injection of liquid reductants, gaseous reductions or reduced colloids. Soluble reductants, such as sulfite, thiosulphate, hydroxylamine, dithionite, hydrogen sulphide and also colloidal reductants like Fe(0) and Fe(II) can be used in clays for soil remediation purposes. Dithionites, for example, can be injected just downstream of the contaminant plume to create a reduced treatment zone within the clay minerals of the aquifer sediments. Although delivery of H_2S gas to a contaminated zone can be difficult, it has been successfully applied for Cr(VI) reduction, by using nitrogen as a carrier gas, both for delivery and control of the H_2S during treatment and for removal of any unreacted agent from the soil after treatment. This principle was also tested on a laboratory scale, using a column filled with soil and a 100 ppm aqueous solution of H_2S.

- A technique which is becoming more and more important is the use of zerovalent iron (ZVI) particles. According to Sharma et al. (2009), nanoparticles are the most efficient for this purpose. Hashim et al. (2011) describe the injection of colloidal ZVI nanoparticles into natural aquifers. Corrosion of the particles resulted in the formation of ferrous sulphides, various Fe oxides, hydroxides and oxyhydroxides. Thus, no excavation of contaminated soil was needed, and human exposure to hazardous materials was minimized. Injection wells could be installed much deeper than tranches. Furthermore, the treatment barrier created this way could be renewed with minimal costs or disturbance to above-ground areas. A problem regarding the use of ZVI as reactive medium in permeable reactive barriers (PRB) is the accumulation of precipitates of hydroxides, iron corrosion products and different salts like carbonates, which may clog the pores of the PRB (Hashim, 2011; Gupta, 2011). Furthermore, toxic byproducts may be formed, making this process mainly suitable for sub-surface regions in stead of for aquifers. Sanchez et al. (2011) not only describe ZVI nanoparticles, but also cerium oxide nanoparticles for this purpose.

- Lv et al. (2011) report on the application of porous materials like chitosan, zeolite and bentonite to support nano ZVI particles. They also describe the use of nanocomposites, consisting of ZVI nanoparticles and multiwalled carbon nanotube nanocomposites. Anions, such as SO_4^{2-}, NO_3^-, and HCO_3^- exhibited negative effects on the removal of Cr(VI), while the effects of PO_4^{3-} and SiO_3^{2-} were insignificant.

3.3   Adsorption onto different media

The use of activated carbon for water purification has been described extensively in literature. Also for the removal of heavy metals, activated carbon can be applied. It is known that the removal of e.g. Cr(VI) by means of activated carbon depends very much on factors such as pH, temperature, contact time, initial concentration and adsorbent amount (Anupam, 2011). An overview on absorption onto different media obtained from the available literature is presented below.

- Based on its size and shape, activated carbon is classified into four types: powder (PAC), granular (GAC), fibrous (ACF) and clothe (ACC). Activated carbon can be made from various sources: wood and various agricultural waste materials (coconut shells, rice husk etc.). There also are several ways to activate the carbon, for example physical methods and chemical methods based on treatment with sulfuric acid or zinc chloride (Babel, 2003; Hashim, 2011). Due to the different sources of raw materials, the extent of chemical activation and the physicochemical characteristics, each type of activated carbon has its specific applications as well as inherent advantages and disadvantages in (waste)water treatment (Babel, 2003). Besides, operating conditions (pH, presence of other

compounds, loading of the carbon) play an important role. Anupam et al. (2011) found that with PAC the maximum adsorption could be obtained with high PAC dose and at a low pH. According to Babel and Kurniawan, the highest removal performance was obtained using an activated carbon prepared by physical activation. Treating the GAC with an oxidizing agent such as nitric acid increased the amount of chemisorbed oxygen on the carbon surface, resulting in a larger negative charge at the surface. This enhanced the adsorption of Cr^{3+} ions. The introduction of Cu^{2+} on ACFs increased the surface basicity resulting in an increased adsorption of Cr^{6+}. Other chemical modifications (using tetrabutyl ammonium iodide and sodium diethyl dithiocarbamate) also affected the adsorption of chromium. The authors found, that the adsorption of chromium essentially depended on surface properties, rather than on surface area and porosity. This is in accordance with the findings of Özdemir et al. (2011).

- Cho et al. (2011) describe the use of GAC modified with a cationic polymer to enhance its adsorption capacity for Cr(VI) from aqueous solutions. The adsorption capacity increased with increasing temperature. According to Gupta and Bhattacharyya (2011), GAC can be regenerated by phosphate extraction and acid washing.

- Jing et al. (2011) studied the effect of ultrasound on the adsorption and desorption of Cr(VI) on activated carbon. The ultrasound only slightly enhanced the adsorption rate in the initial stage of adsorption. The addition of NaOH tot the system caused an enhancement of Cr(VI) desorption, especially on activated carbon in the presence of ultrasound. After acid treatment, the ultrasonic regenerated activated carbon had a good re-adsorption capacity.

As activated carbon is a relatively expensive material, many authors have been studying alternative, low-cost adsorbents. Examples are shown below.

- Low-cost adsorbents were derived from tyres and sawdust (Babel, 2003), hazelnut shell and soy bean hull (Kurniawan, 2006), powdered pistachio (Moussavi, 2011) and walnut hull for Cr(VI) and sepiolite for Cr(III) (Gupta, 2011). A polymeric resin was applied by Jing et al. (Jing, 2011) and by Kurniawan et al (Kurniawan, 2006), who used a long alkyl quaternized poly-4-vinylpyridine for Cr(VI) removal. The performance of chitosan was improved, by reducing its particle size (increasing the surface area).

- Zeolites are naturally occurring crystalline aluminosilicates, consisting of a framework of tetrahedral molecules, linked with each other by shared oxygen atoms (Gupta, 2011). Kurniawan et al. (2006) concluded that NaCl treated zeolite had better removal capacities for Cr(VI) ions than as-received zeolites. On a laboratory scale, zeolites were studied by applying column experiments.

- The adsorption by clays (Babel, 2003; Favas, 2011) strongly was affected by the pH. It was found that Cr6+ strongly binds to the organic matter present in clay. Gupta and Bhattacharyya (2011) describe the adsorption of Cr(III) on kaolinite, sepiolite, illite, (dodecyl sulfate or hydroxyl-alumino-silicate modified) Na-monmorillonite, and hydrotalcite. The adsorption of Cr(VI) on organic modified rectorite (modified with dodecyl benzyl dimethyl ammonium, hexadecyl trimethyl ammonium or octadecyl trimethyl ammonium) was partially explained on the basis of very fast pore diffusion at the start, followed by a slow diffusion process filling up the pores. The rate of adsorption increased under acidic conditions (positively charged surface in combination with anionic Cr(VI)). Uncalcined and calcined $Mg-Al-CO_3$ hydrotalcite (a double-layered mixed metal hydroxide belonging to the family of

anionic clays) was also used for chromium adsorption. The adsorption of Cr^{6+} on bentonite (Babel, 2003) was favoured by increasing the temperature, and at low pH (pH = 2).

- Peat moss is a complex soil material, containing lignin and cellulose as major constituents. Its adsorption capacity for Cr^{6+} increased with decreasing pH. Peat was used to adsorb both Cr(III) and Cr(VI) (Kurniawan, 2006). Since the acidic functional groups including carboxylic, hydroxyl, and carbonyl groups are present on the surface of peat, the physicochemical interactions that might occur during Cr(VI) removal were expressed by: $M^{n+} + n(-COOH)X(-COO)_nM + nH^+$. Where (-COOH) represents the surface functional group of peat and n is the coefficient of the reaction component, depending on the oxidation state of metal ions, while M^{n+} and H^+ are Cr(III) and hydrogen ions respectively.

- Fly ash, waste of thermal power plants, showed good affinity for chromium (Babel 2003, Gupta 2011). It was also applied in combination with coal. Natural oxides (Al_2O_3 or iron oxide coated with sand) also were successfully applied for chromium removal (Sharma, 2008 and 2009). Hydrous TiO_2, ZrO2.nH2O and mixed magnetite/maghematite nanoparticles were studied by Gupta and Bhattacharyya (2011). Pyrite showed good Cr(VI) removal in a pH range of 5.5-6.5 (Kurniawan, 2006). Sharma et al. (2008) describe laboratory experiments with column filled with pyrite fines, calcined Mg-AlCO3 hydrotalcite, coal, bone charcoal and manganese-oxide coated sand. These adsorbents, however, have not yet been applied in practice.

- Fe(III) hydroxide, a waste material from fertilizer industries, also can be used to adsorb $HCrO_4^-$ at pH 8.5. Red mud, a by-product of the aluminium industry is mainly composed of silica, aluminium, iron and titanium oxides, and can also show good adsorption of Cr(VI), depending on temperature and the presence of other anions. Here too, higher adsorption was observed at low pH (5.2), whereas at a pH of 7.06 the adsorption became negligible (Babel, 2003; Wang, 2008).

In these studies, it is not always clear whether Cr^{6+} cations are meant, or Cr(VI) anions. Therefore, care has to be taken into interpretation of the results.

3.4 Ion exchange and membrane filtration

Cation exchangers are effective for Cr(III), while anion exchangers are appropriate for Cr(VI) removal (as Cr(VI) normally is present in the form of anions). For the removal of Cr(VI) strong basis anion exchangers, with an exchangeable counter ion of Cl^- are commonly used (Sharma, 2008). In case both Cr(III) and Cr(IV) have to be removed, a two-step ion exchange process will be required, using a cation resin for Cr(III) removal, followed by an anion resin for Cr(VI) ions. For removal of chromates from water under acidic pH values, weak-base anion exchange resins can be used. These can be regenerated with a concentrated (5-8%) sodium chloride solution. The efficiency of the regeneration process can be improved by adding sodium hydroxide. The main limitations of this method are the requirements for regular regeneration and concentrate disposal, potential fouling of the resins, and the effect on removal efficiency of other ions present in the water.

Reverse osmosis has been used for the removal of chromium and other heavy metals from different wastewater effluents. There is little literature available on nanofiltration techniques (Sharma,

2008). Different modifications of membrane technology have been examined for their effectiveness in chromium removal:

- Micellar-enhanced ultrafiltration using cationic surfactants
- Use of polymer inclusion membranes
- Ion-exchange membranes

In their review article, Hashim et al. (2011) describe cation and anion-exchange membrane barriers in an electrokinetic method to remove chromium from soils. If the soil has a high buffer capacity, then soil acidification is prevented resulting in a poor performance of the electrokinetic extraction of toxic metals. In those cases, chelating agents such as EDTA can be added to the soil to enhance the process. Liquid membranes, employing metal complexing ligands were applied to isolate metal ions like Cr(VI) from groundwater in the presence of calcium and magnesium ions. Ultrafiltration techniques were applied, where the aqueous phase was pretreated with a functionalized polymer, like polyethylene imine or polyacrylic acid, which formed complexes with the metal ions.

An important issue in applying membrane technology for chromium removal is to prevent foiling and corrosion of well casings and entrapment of air that could cause oxidation of iron and sulfur compounds (which also causes severe fouling of membranes). Therefore, non-corrosive materials such as stainless steel, polyvinyl chloride and fibreglass should be used for piping. In addition, vertical turbine pumps with mechanical seals or submersible pumps should be used, so that an airtight system is ensured (Sharma, 2008).

3.5   Biological systems

Several techniques have been described for chromium removal by biological systems. An overview is presented below.

- Hashim et al. (2011) describe the accumulation of heavy metals by natural vegetation (like willow and poplar trees) over a long period of time. Carbon sources, such as molasses, lactate, acetate and composts can be injected into aquifers, where they undergo fermentation and trap the metal ions in an organic matrix. However, the stability of the metal precipitates remains to be a questionable issue.
- Water containing metals can also be treated in biological systems in which metals are precipitated by the action of microorganisms. These systems also include passive systems of constructed wetlands, or of the biological reactors comprising specifically sulfate reducing microorganisms (Blais, 2008). An example is the removal of chromium by adsorption in non-living *Rhizopus arrhizus* biomass at pH = 2 in a stirred tank or fluidized bed reactor (Hashim, 2011). Srivastava and Mjumder (2008) used microorganisms fixed to a porous medium. They grow in a biofilm on the surface of the medium or are suspended in the water phase surrounding the medium particles. The filter bed medium consisted of relatively inert substances which ensure large surface attachment areas and additional nutrient supply. The overall effectiveness of a biofilter as largely governed by the properties and characteristics of the support medium, which include porosity, degree of compaction, water retention capabilities and the ability to host microbial populations. Critical biofilter operational and performance parameters include the microbial inoculation, medium pH, temperature, medium moisture and nutrient content. For chromium, *Thauera selenatis*, *Pseudomonas fluorescens* LB300, *Enterobacter cloaceae* HO1, *Bacillus* sp (bacterial species), *Aspergillis niger* (fungal species), brown algea, *Scenedesmus genus*, and *Sargassum* sp. (algal species) were proven to be suitable. The suitability of

Pseudomonas putida was improved by genetic modification. According to Sharma et al. (2008), there is little information available on the biological removal of chromium from water sources used for the production of drinking water. Furthermore, the biological removal methods in general are more effective at lower pH, which may not be suitable for drinking water treatment applications (although the same problem is encountered with most other techniques too).

- Bank filtration is a well established and proven natural water treatment technology, where surface water is infiltrated to an aquifer through river or lake banks (Sprenger, 2011). The water quality is improved by a series of chemical, biological and physical processes during subsurface passage. The removal process for chromium involves sorption and precipitation and ion exchange processes. However, the system is highly affected by drought and flood, and thus the overall removal efficiency is inconsistent. Bank filtration systems comprising an anoxic redox sequence ensure maximum removal efficiency, due to the redox dependant degradation rate of many contaminants. Dune filtration has not been described in recent literature. As bank filtration is successful, it can be expected that dune filtration also will be applicable. Besides, it has the advantage that it is less dependent on drought and flood.

3.6   (Advanced) oxidation processes

This paragraph gives an overview on the effect of (advanced) oxidation process on valence state and removal of chromium.

Cr(III) complexes can be very stable, making it difficult to analyze the amount of chromium present in e.g. solutions. For this purpose, Rodman et al. (2006) used UV/H_2O_2 as an advanced oxidation process (AOP), not only to degrade the organic part of the complex, but also to completely oxidize Cr(III) to Cr(VI). The latter then could be analyzed. Another AOP, based on TiO_2, has been described by Pandikumar and Ramaraj (2012), who used titanium dioxide-gold nanocomposite materials for the photodegradation of Cr(VI) and methylene blue. Under irradiation, TiO_2 can form electron-hole pairs, which are very reactive. The Cr(VI) was reduced to Cr(III) at the TiO_2 surface (where the "holes" are formed), while simultaneously the methylene blue was oxidized by the electron formed during this process.

Durante et al. (2010, 2011) have studied the removal of stable Cr(III) complexes from water for purification purposes by means of AOPs and electrocoagulation. They found that AOPs are completely inefficient owing to the formation of Cr(VI), which is more soluble than Cr(III). However, by using first ozonation or electrochemical oxidation (using a boron doped diamond electrode), followed by electrocoagulation, they were able to remove the major part of the chromium. In the first step, the organic complex was degraded and the Cr(III) was (completely) oxidized to Cr(VI), but in the second step Fe(II) was formed, which could effectively reduce the Cr(VI) back to Cr(III), although a small concentration of Cr(VI) stayed present. This rather easy reduction and oxidation of chromium was applied by Bokare and Choi (2010, 2011) to form an AOP, based on the dual role of H_2O_2 as an oxidant of Cr(III) and a reductant of Cr(VI). This process, however, is very dependent on pH, and does not remove chromium from the water.

In general, it can be concluded that AOPs are very effective in oxidizing Cr(III) to Cr(VI), but as Cr(VI) is much more difficult to remove than Cr(III), these will not be suitable processes for water treatment.

Aeration is a process often applied in groundwater treatment processes. Although oxygen (in air) can oxidize Cr(III) to Cr(VI), it is not very likely that this will cause severe problems, as Cr(III) easily complexes with several compounds, immobilizing the chromium. Besides, according to Apte et al, (Apte, 2006), this reaction with oxygen in air takes place at elevated temperatures (Cr_2O_3 was readily converted to Cr(VI) at a temperature range of 200-300 $^{\circ}$C, which is not an ambient temperature for water treatment processes).

3.7   Conclusions on chromium removal from water

In literature several methods have been described to deal with the presence of chromium in (ground) and waste water under different circumstances. Methods for treatment of waste water often aim at the recovery of the chromium, and are applicable for water with a relatively high chromium concentration. These methods cannot always be applied to (ground) water, with a lower chromium concentration.

Cr(III) is less mobile than Cr(VI) and often present in the form of a cation (Cr^{3+}). Cr(VI), on the contrary, is much more mobile, and mostly present in the form of anionic complexes. This implies that other technologies have to be applied in order to remove Cr(III) or Cr(VI) (e.g. by means of ion exchange or complexation). As it is relatively easy to reduce Cr(VI) to Cr(III), this reaction often is used in purification processes. The resulting Cr(III) can either be removed or be immobilized in the soil.

Which type of process will be the most suitable strongly depends on the actual situation: pH and the presence of oxygen or salts can strongly affect the process. Dune filtration has not been described in recent literature for chromium removal, but there is some literature on the successful application of bank filtration. Thus, dune filtration probably also will be applicable (with the advantage, that it will not be dependent on external parameters like flood and drought).

In literature also some biological systems have been described to remove chromium from the environment, e.g. by accumulation of the metal by natural vegetation. Such methods, however, require a very long period of time. Further, little information is available on the biological removal of chromium from water sources used for the production of drinking water.

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Aeration is a process often applied in groundwater treatment processes. Although oxygen (in air) can oxidize Cr(III) to Cr(VI), it is not expected that large amounts will be formed as Cr(III) easily complexes with several compounds, immobilizing the chromium. Further, literature data show that this reaction takes place at temperatures of 200-300 $^{\circ}$C, which is not an ambient temperature for water treatment processes.

4 Human exposure to hexavalent chromium

Very little information is available on the human environmental exposure to Cr(VI). Below we give an overview as presented by ATSDR (2008), IARC (2011), California EPA (2011) and other publications.

4.1 Air

Chromium is present in the atmosphere in small particles. Sources for chromium in ambient air are anthropogenic point sources such as smelters, windblown soil, road dust or seawater. In the USA, reported total chromium levels in the air are typically <0.01 $\mu g/m^3$ in rural areas, and between 0.01 – 0.03 $\mu g/m^3$ in urban areas (ATSDR, 2008). Tobacco smoke contains Cr(VI), and indoor air polluted by cigarette smoke can contain hundred of times the amount of Cr(VI) found in outdoor air (IARC, 2011). However, no reference is cited by IARC.

4.2 Water

Literature data on Cr(VI) levels in drinking water are mainly available from polluted areas. In the United States, an environmental working group revealed the presence of Cr(VI) in drinking water in 31 of 35 cities tested. Of these cities, 25 had levels above 0.06 $\mu g/L$. The highest reported Cr(VI) levels were 2 $\mu g/L$ in Honolulu, Hawaii, 12 $\mu g/L$ in Norman, Oklahoma and 580 $\mu g/L$ in Hinckley, California (Eaton, 2011). The Cr(VI)-contaminated drinking water in Hinckley lead in the mid-1990's to a legal fight by environmental activist's with Pacific Gas and Electric. In 2000, the movie Erin Brockovich, starring Julia Roberts, was released telling this true story (Eaton, 2011). In a 10-year monitoring period in California, 68.5% of drinking water samples contained less than 1 $\mu g/L$ Cr(VI), 27% between 1 and 10 $\mu g/L$, 4.4% between 10 and 50 $\mu g/L$ and 0.1% higher than 50 $\mu g/L$ (Eaton, 2011). In the Oinofita region of Greece, very high Cr(VI) levels in drinking water were reported between 1999 and 2009, with the five highest concentrations being 44, 48, 51, 53, 54, and 156 $\mu g/L$ (Linos et al., 2011).

In the Netherlands, the highest Cr(VI) chromate concentration observed in 17 PSWFs was 2.1 $\mu g/L$. See chapter 2 for more details.

4.3 Food and consumer products

Virtually all foods contain some chromium, ranging from 20 to 590 $\mu g/kg$, as reviewed by California EPA (2011). Most of the chromium ingested with food is Cr(III) (IARC, 2011). Foods with highest chromium levels are meats, molluscs, crustaceans, vegetables, and refined sugar. There is little information available on Cr(VI) in food. One study analysed 152 samples of Portuguese bread and showed total chromium contents of 47.3 ± 20.0 and 50.9 ± 22.2 $\mu g/kg$ of dry weight for white and whole bread samples, respectively. Those for Cr(VI) were 5.65 ± 5.44 and 6.82 ± 4.88 $\mu g/kg$ of

dry weight (Soares et al., 2010). The authors estimated mean daily intakes of Cr(VI) from bread of 0.6 and 0.7 µg/day. Measurements were performed after selective extraction of hexavalent chromium and quantification of this species and total chromium by electrothermal atomization atomic absorption spectrometry. No other studies on Cr(VI) in food were found in literature.

Surveys by the German Federal Ministry of Food, Agriculture and Consumer Protection undertaken in 2008 and 2009 found that many leather goods like gloves, shoes or watch straps, that come directly in contact with skin, contained high levels of Cr(VI). The highest Cr(VI) concentrations found were 141 mg/kg in work wear, 137 mg/kg in footwear and 112 mg/kg in gloves (BVL, 2011).

5 Toxicity of chromium

5.1 Toxicokinetics

Most dietary Cr is not absorbed and is excreted via the faeces. Intestinal absorption of Cr(III) is low (up to 2%) in both humans and animals. Cr(III) is considered to be an essential element for human health, essentially non-toxic. In the acidic environment of the stomach, the majority of Cr(VI) is converted to Cr(III) (Sedman et al., 2006). Human bio-availability of oral doses up to 10 mg Cr(VI) averaged up to 5.7% (Kerger et al., 1997). Small amounts of assimilated Cr (up to 0.5 µg/day) are excreted via the urine (Kerger et al., 1997).

The Cr(VI) anions in aqueous solution are in pH-dependent equilibrium. At pH>6 (i.e. physiological pH), Cr(VI) forms the chromate ion CrO_4^{2-}, which is structurally similar to phosphate and sulphate and readily enters all cells via the general anion channel protein. Cr(VI) is readily absorbed by all tissues, with the highest concentrations found in kidney, liver, and bone (ATSDR, 2008). In blood, Cr(VI) is taken up into red blood cells, is reduced, and then bound to proteins (ATSDR, 2008). The higher redox potential and the greater ability of Cr(VI) to enter cells contributes to the greater toxic and carcinogenic potency of Cr(VI) relative to Cr(III).

5.2 Acute toxicity

The lethal oral dose of soluble chromates in humans is 50-70 mg/kg body weight (bw) with target organs being the liver, kidney and haematopoietic system. The mechanism of action of Cr(VI) is thought to be by oxidation of biological tissues to form a variety of radical species including alkyl and oxygen radicals (ATSDR, 2008). In animal studies using rats, the oral LD50-doses[2] for Cr(VI) ranged from 13 to 28 mg/kg bw (California Environmental Protection Agency, 2011).

5.3 Subchronic and chronic toxicity (non-carcinogenic effects)

The California Environmental Protection Agency (2011) reviewed the available studies on repeated dose toxicity (subchronic and chronic). The data quality varied considerable between the studies and only six studies were identified which allowed an assessment of the non-carcinogenic effects of Cr(VI). These studies indicated adverse effects in the liver and blood forming tissues. The critical non-carcinogenic endpoint for risk assessment of Cr(VI) by the oral route is considered to be liver damage (mild chronic inflammation, fatty changes). A LOAEL of 0.2 mg/kg/day was derived, which is the lowest dose where toxicity was detected (obtained in a two-year oral exposure study in rats performed by NTP in 2008). No NOAEL below the LOAELs could be identified from the available studies (California Environmental Protection Agency, 2011).

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[2] LD50 is the amount of a substance, given all at once, which causes the death of 50% of a group of test animals. The LD50 is a way to measure the short-term poisoning potential (acute toxicity) of a material.

5.4 Developmental and reproductive effects

The California Environmental Protection Agency (2011) reviewed the available studies on developmental and reproductive effects of Cr(VI). Embryotoxic and fetotoxic effects have been observed in rodents at very high oral doses of Cr(VI) (up to 300 mg/kg bw/day). At lower doses effects are less clear (e.g. up to 10 mg Cr(VI)/kg bw/day). One study with rats and mice observed reduced sperm counts and/or increased abnormalities, whereas another study observed no effects under similar conditions.

5.5 Genotoxicity and carcinogenicity

Cr(VI), but not Cr(III) compounds have been shown to exert genotoxicity both *in vitro* and *in vivo* (ATSDR, 2008; IARC, 2011). Based on the available toxicity studies, IARC considered Cr(III) to be not classifiable as to its carcinogenicity to humans (Group 3), and Cr(VI) to be carcinogenic to humans (Group 1) (IARC, 2011). The available data is insufficient to evaluate the carcinogenic properties of metallic chromium (Health Council of the Netherlands, 2011). As several comprehensive literature reviews are available (Sedman et al., 2006; ATSDR, 2008; California Environmental Protection Agency, 2011; IARC, 2011; Zhitkovich, 2011), below we present a short overview.

5.5.1 In vitro studies
Soluble Cr(VI) compounds are mutagenic in *in vitro* bacterial and mammalian cell systems (ATSDR, 2008; IARC, 2011).

5.5.2 Animal studies
Several authorities extensively reviewed the available animal carcinogenicity studies on Cr(VI) (ATSDR, 2008; California Environmental Protection Agency, 2011; IARC, 2011; Zhitkovich, 2011). As summarized by IARC, the administration of chromate (calcium chromate, zinc chromate, strontium chromate, sodium dichromate) by inhalation or by intratracheal instillation caused lung cancer in mice and rats. Several chromium compounds by intramuscular injection (calcium chromate, lead chromate, zinc chromate, strontium chromate) caused local sarcomas. Oral administration of sodium dichromate to rats and mice caused cancer of the oral cavity and of the gastrointestinal tract. Potassium chromate given orally, although not given alone, enhanced UV-induced skin carcinogenesis, indicating tumour systemic effects (IARC, 2011).

In animal studies, Cr(VI) exposure by intratracheal instillation in rats and by intraperitoneal injection in mice induced DNA strand breaks in lymphocytes and micronuclei in bone marrow, respectively. However, after oral administration no micronuclei were observed in the latter study, indicating that Cr(VI) does not reach the target cells to a high extent by this exposure route. Another study showed the induction of dominant lethal mutations in male mice (IARC, 2011).

A summary of a good quality two year oral exposure study performed by NTP in 2008 is shown in the Supplementary Information (par 8.1).

5.5.3 Human studies

Several studies observed genotoxic effects of workers exposed to dusts of Cr(VI). They showed elevated frequencies of DNA strand breaks, sister chromatid exchange and micronuclei in lymphocytes of these workers (IARC, 2011).

The large majority of cohort studies on chromium indicate that there is an excess risk of lung cancer among workers exposed to Cr(VI), particularly in chromate production, chromate pigment production, and chromium electroplating (ATSDR, 2008; Zhitkovich, 2011). The IARC comments that it is unlikely that any biases or chance can explain these findings.

One study linked exposure to Cr(VI) through contaminated drinking water to stomach cancer, but due to major shortcomings this study is not suitable for risk assessment purposes (Sedman et al. (2006). More recently, citizens of the Oinofita municipality of Greece exposed to Cr(VI) through drinking water (five highest concentrations ranged from 44 to 156 µg/L) exhibited a statistically significant increase in primary liver cancer mortality compared to the population of the surrounding prefecture (Linos et al., 2011).

5.5.4 Genotoxic mechanism

The lower toxicity and carcinogenicity of Cr(III) may be due to a decreased penetration of chromium into the cells. The process of extracellular reduction of Cr(VI) is considered a detoxicification process, generating poorly cell-permeable Cr(III) (Figure 5.1). Within the cell, Cr(VI) is reduced stepwise to the thermodynamically stable Cr(III) resulting in reactive intermediates as well as DNA and protein adducts (ATSDR, 2008; Zhitkovich, 2011) (Figure 5.1).
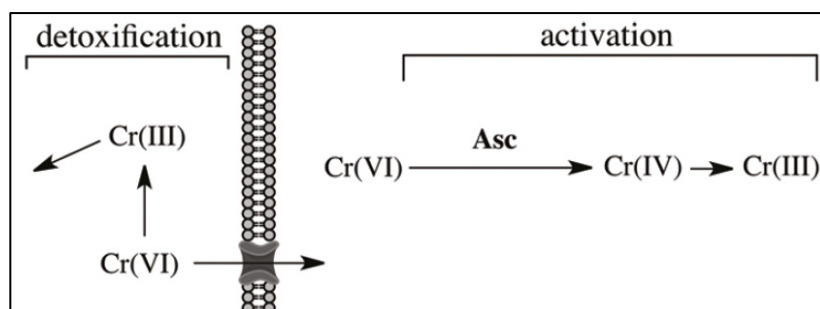

Figure 5.1. Intra- and extracellular reduction of Cr(VI) (reproduced from (Zhitkovich, 2011)).

The cellular Cr(VI) reduction is an activation process, giving rise to redox-active intermediates (Figure 5.2). The antioxidant ascorbate (Asc) forms the dominant reducer of Cr(VI) in cells, other reducing agents are glutathione and cysteine. The intermediates Cr(V/IV) and stable Cr(III) may form mutagenic Cr-DNA adducts. Further, the reduction of Cr(VI) to Cr(III) generates potentially toxic intermediates such as oxygen radicals, sulphur radicals, and chromium radicals which may cause oxidative stress-induced DNA damage (Zhitkovich, 2011). Three mechanism are postulated to be involved in the carcinogenesis

induced by Cr(VI): 1) indirect free radical DNA damage, 2) direct metal-mediated oxidative DNA damage and 3) direct metal-DNA binding. These processes may lead to mutations, aneuploidy[3], or alteration of gene transcription (Sedman et al., 2006; Zhitkovich, 2011). With respect to DNA damage, the spectrum of induced lesions appears to depend strongly on the cellular reductant involved. Under physiological conditions the ascorbate-DNA adducts appears to be of major relevance, which may be linked to the increased number of mismatch-repair-resistant cells observed in chromate-induced lung tumours (IARC, 2011; Zhitkovich, 2011). The DNA-reactive mutagenic mechanism in Cr(VI) carcinogenicity supports a linear low-dose extrapolation of cancer risks in humans (Figure 5.2). Studies on gastric deactivation indicate that at (low) environmental Cr(VI) levels of exposure still 10-20% of Cr(VI) is bioavailable and enters the small intestine (Figure 5.2) (Zhitkovich, 2011). Currently, ongoing studies are trying to find out whether this gastric deactivation is higher in laboratory animals compared to humans.
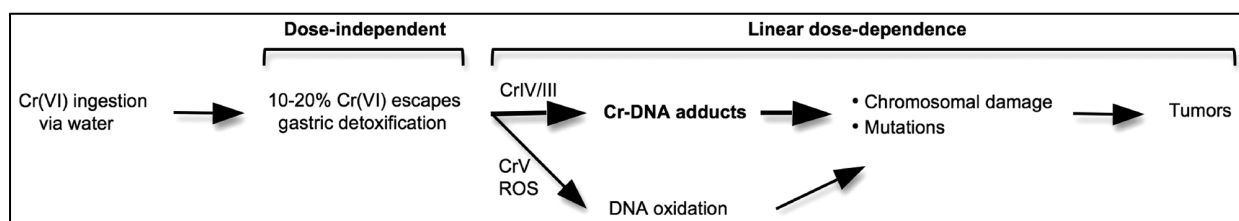

Figure 5.2. Genotoxic mechanism of ingested Cr(VI) (reproduced from (Zhitkovich, 2011)).

5.6   Health based targets for drinking water

5.6.1 Drinking water standards for chromium
Table 5.1 presents the drinking water standards from total chromium from the EU, WHO, US EPA and California EPA. These current standards do not distinguish between the presence of toxic Cr(VI) and non-toxic Cr(III).

Table 5.1. Drinking water standards for chromium

Authority	Total chromium (µg/L)
EU (Drinking water directive 98/83/EC)	50
WHO (Guidelines for drinking water quality)	50
U.S. Environmental Protection Agency (EPA; Max contaminant level)	100
California EPA (Maximum Contaminant Levels)	50

5.6.2 Health protective level for Cr(VI) derived by California EPA
While Cr(VI) has long been recognized as a potent carcinogen via inhalation, recent studies clearly showed that Cr(VI) is also carcinogenic by oral exposure. Triggered by these findings, in July 2011 the California EPA released a Public Health Goal for Cr(VI) in drinking water of 0.02 µg/L (20 ng/L) based

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[3] Abnormal number of chromosomes

on carcinogenic effects. This Public Health Goal is intended to guide the California Department of Public Health in developing a Maximum Contaminant Level for Cr(VI) in drinking water, as defined in the Safe Drinking Water Act (California Environmental Protection Agency, 2011). In addition, California EPA also derived a health-protective level of 2 µg/L for non-carcinogenic effects. In the Supplementary Information (par 8.2), the derivation of their Public Health Goal and health-protective level are summarized.

5.6.3 Health-based targets for Cr(VI) by US EPA
US EPA derived an oral reference dose for Cr(VI) of 0.003 mg/kg bw/day. A reference dose is the maximum acceptable oral dose of a toxic substance and is defined as a daily oral exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime (US EPA, 2011). This US EPA reference dose for Cr(VI) is currently under review.

5.6.4 Health-based targets for Cr(VI) by RIVM
RIVM recently performed a risk assessment concluding that use of wood treated with copper-chromium salts in playground structures and home projects is safe for children at play and for do-it-yourself use (Wolterink et al., 2011). This risk assessment was based on recent toxicity data for Cr(VI). The derivation of their health-based risk levels for carcinogenic and non-carcinogenic effects is summarized below.

For carcinogenic effects, the RIVM used data derived by the California EPA using Benchmark dose modelling (Wolterink et al., 2011). As the mouse appeared to be the most sensitive species, data from the NTP study were subjected to eight models in the US EPA Benchmark Dose Software to determine the mean (ED10)[4] and the lower-bound BMDL10 estimate[5] of the dose associated with a 10% increase in tumours. The California EPA calculated a lowest BMDL10 of 0.8 mg/kg bw/day for tumour incidence in male mice based on the NTP study. As described by Wolterink et al. (2011), RIVM uses low dose linear extrapolation to for risk assessment of genotoxic carcinogens, which has been the accepted approach since the early 1980's in the Netherlands. This approach assumes that there is no threshold for the mechanism of genotoxicity. Using a standard calculation formula, risk-specific doses are calculated for lifetime excess cancer risk levels. The calculation is based on the lowest tumorigenic dose as observed in the relevant animal bioassay (or in the relevant human epidemiology study). Using the BMDL10 of 0.8 mg/kg bw/day for a quantitative cancer risk assessment yields a lifetime risk-specific dose 0.0076 µg/kg bw/day as associated with a 10^{-6} cancer risk for Cr(VI) (Wolterink et al., 2011).

For non-carcinogenic effects, RIVM derived a minimum risk level (MRL) based on the 2-year drinking-water study in rats and mice by NTP in 2008 (same study as used by California EPA). To determine the point of departure for derivation of a chronic oral MRL, data from that NTP study were analysed with the US EPA Benchmark Dose Software. The lowest BMDL10-value of 0.09 mg Cr(VI)/kg bw/day was obtained for diffuse epithelial hyperplasia of the duodenum in female mice. Based on this value a chronic MRL of 1 µg Cr(VI)/kg bw/day was derived, using an assessment factor of 100 (for inter- and intraspecies variability) (Wolterink et al., 2011). This chronic MRL is a factor five higher than

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[4] Estimated benchmark dose corresponding to a 10% tumour incidence
[5] The lower bound of a 95th confidence interval on a benchmark dose (BMD) corresponding to a 10% effect incidence

the acceptable daily dose of 0.0002 mg/kg bw/day (0.2 µg/kg bw/day) as derived by California EPA (California Environmental Protection Agency, 2011). This difference may be explained by slightly different principles and methods used in risk assessment between California EPA and RIVM.

5.6.5 *Provisional drinking water guideline values based on RIVM methodology*

The lifetime risk-specific dose associated with a 10^{-6} cancer risk and the chronic MRL for non-carcinogenic effects derived by RIVM may be converted to provisional drinking water guideline values. The lifetime risk-specific dose of 0.0076 µg/kg bw/day as associated with a 10^{-6} cancer risk for Cr(VI) may be directly converted to a provisional drinking water guideline value by assuming an average drinking water consumption of 2 L per day and an average weight of 60 kg. This results in a provisional drinking water concentration of **0.2 µg/L** for Cr(VI) associated with a 10^{-6} excess lifetime cancer risk. This is a factor 10 higher than the health-protective drinking water value of 0.02 µg/L Cr(VI) as derived by California EPA (2011). As already mentioned, this difference may be explained by different principles and methods used in risk assessment between California EPA and RIVM. The chronic MRL for non-carcinogenic effects of 1 µg Cr(VI)/kg bw/day may be converted to a provisional drinking water guideline value by using the standard assumptions as regularly used by RIVM, i.e. an average drinking water consumption of 2 L per day, an average bodyweight of 60 kg and a drinking water allocation factor of 10%. This results in a provisional drinking water guideline value of (1 x 60 x 0.1) / 2 = **3 µg/L**. When applying a drinking water allocation factor of 80%, as also applied by California EPA, a provisional drinking water guideline of 24 µg/L may be derived.

Based on the state-of-the-art scientific publications and the generally accepted risk assessment methodologies used by RIVM, a provisional health-based target for Cr(VI) in drinking water may be set at the lowest value of 0.2 µg/L. However, it should be noted that this is not an enforceable drinking water standard.

5.7   Provisional drinking water guideline value and Cr(VI) levels in water

Table 5.2 shows the number of public supply well fields and surface waters that exceeded the provisional health-based target of 0.2 µg/L in raw water and in treated drinking water.

Table 5.2. Number of samples above the provisional health-based target of Cr(VI) for raw and treated water (based on data of Table 2.3).

Provisional health based target	Raw water		Treated water	
	Groundwater n = 17	Surface Water n = 2	Groundwater n = 17	Surface Water n = 1
0.2 µg/L	6	1	9	0

6 Conclusion and discussion

6.1 Chromium in resources for drinking water supply in the Netherlands

The most important chromium species at the normal pH domain (4-9) in Dutch ground and surface waters are $CrOH^{2+}$ and $Cr(OH)_3^0$ for Cr(III), and $HCrO_4^-$ and CrO_4^{2-} for Cr(VI). Cr(VI) only occurs in (sub)oxic environment, i.e. where oxygen is present or where nitrate and nitrite are (meta)stable. Oxygenation of aquifers, by declining water tables, raised nitrate inputs via agriculture and infiltration of river water with an increased oxidation capacity thanks to better treatment of sewage effluents, may therefore raise the chromate contribution to total dissolved chromium in groundwater. This deserves to be investigated.

In (deeply) anoxic environments, Cr(VI) is reduced to the much less soluble Cr(III) especially by Fe^{2+}, organic material, pyrite and H_2S. In groundwater Fe^{2+} and Cr(VI) appear to be antagonists indeed, because Fe^{2+} reduces Cr(VI) to Cr(III). This makes it easy to indicate those public supply well fields (PSWFs) where chromate may be or become significant.

In studying dissolved chromium, it should be noted that filtration bias and bias by corrosion of stainless steel may strongly influence the analytical results. This calls for research into (a) effects of different membrane pore diameters on results of chromium analysis, and (b) the impact of wells, pumps, transport mains and water distribution materials on chromium concentrations.

All reported chromium concentrations in surface waters, infiltration waters and various groundwater types (incl. data from all PSWFs in the Netherlands) are well below the EU drinking water standard of 50 µg/L, with maximum values for total chromium in filtrated samples not exceeding 12 µg/L. Cr(VI) chromate data on raw and treated water for drinking water in the Netherlands are very scarce; some were published by RIVM (Jonker et al., 1998). Their results have been further elaborated here by combination with data on the inorganic hydrochemical matrix (from other data sets) leading to the following observations:

1. Iron and chromium form antagonists indeed: PSWFs with iron > ca. 1 mg/L show total chromium ≤ 0.5 and Cr(VI) <0.2 µg/L;
2. Cr(VI) in raw water is only present when O_2 and NO_3 are >1 mg/L;
3. The maximum Cr(VI) concentration encountered in the 17 investigated PSWFs was 2.1 µg/L. This is far above the desirable but not yet established drinking water limit of ca. 0.02 - 0.2 µg/L Cr(VI);
5. Concentrations in raw and treated water do not differ much in most cases, indicating that aeration and rapid sand filtration do not remove Cr(VI); and
6. In several cases where chromate was detected, the treated water contained a little more than the raw water. Cr(VI) formation during drinking water treatment steps cannot be excluded therefore, and calls for further research.

Scarcity of chromate data call for future inclusion in monitoring schemes.

6.2 Chromium removal from water

In literature several methods have been described to deal with the presence of chromium in ground water and waste water, mostly aimed at removal of chromium in high concentrations. Cr(III) is less mobile than Cr(VI) and often present in the form of a cation (Cr3+). Cr(VI), on the contrary, is much more mobile and mostly present in the form of anions. This implies that different technologies have to be applied in order to remove Cr(III) or Cr(VI) (e.g. by means of ion exchange or complexation). As it is relatively easy to reduce Cr(VI) to Cr(III), this reaction often is used in purification processes. The resulting Cr(III) can either be removed or be immobilized in the soil. Which technology will be most suitable for chromium removal will strongly depend on the actual situation e.g. relative low concentrations in ground water vs. relative high concentrations in waste water. Further, pH and presence of oxygen or salts can strongly affect the process. Whether Cr(VI) might be formed during the aeration process of Cr(III) containing ground water requires further study as literature data is conflicting with our observation of higher Cr(VI) contact after drinking water treatment.

6.3 Health implications

Human exposure to Cr(VI) may be through inhalation of air, drinking water or food. Toxicological studies showed that Cr(VI) is much more toxic than Cr(III). The lower toxicity and carcinogenicity of Cr(III) may be due to a decreased penetration of chromium into the cells. While Cr(VI) has long been recognized as a potent carcinogen through inhalation, recent studies clearly showed that Cr(VI) is also carcinogenic by oral exposure. Cr(VI) compounds were positive in the majority of *in vitro* and *in vivo* tests. In occupational exposure studies in humans also evidence of Cr(VI)-induced genotoxicity was found. Animal studies have shown carcinogenic effects of Cr(VI) compounds after inhalation and oral exposure. Occupational exposure studies have shown increased incidences of cancer after inhalation exposure. Epidemiological support for increased cancer incidences after oral exposure is weak due to a lack of well-conducted studies.

After oral absorption, Cr(VI) easily enters cells in various tissues. Within the cell, Cr(VI) is stepwise reduced to Cr(III), leading to the formation of reactive intermediates as well as DNA and protein adducts. These forms of DNA damage may cause mutations and chromosomal breaks and may finally lead to tumour formation. A key issue might be to what extent Cr(VI) ingested through the oral route converts to Cr(III) in humans and how this compares to laboratory animals. Currently studies are ongoing on whether the gastric deactivation process of Cr(VI) is higher in humans compared to animals and expert judgement is needed on what this means for risk assessment.

As human epidemiological data on oral exposure is limited, calculations of cancer risks from Cr(VI) ingestion must rely on the extrapolation of results from high-dose animal studies to low-dose human exposures. For risk assessment purposes, a linear extrapolation of cancer risk to low environmental doses is a default regulatory approach for carcinogens with a mutagenic mode of action via DNA-reactive mechanisms. Based on carcinogenicity studies of Cr(VI), the California EPA recently released a Public Health Goal for Cr(VI) in drinking water of 0.02 µg/L. RIVM also recently derived a minimum risk level associated with a 10^{-6} cancer risk for Cr(VI) using their standard methodology. An excess lifetime cancer risk of 1 in 1 million is considered a generally accepted negligible risk. Based on this risk level, for the Netherlands a provisional guideline value of 0.2 µg/L Cr(VI) may be derived. This

provisional health-based target is based on state-of-the-art scientific publications. However, it should be noted that this target is not an enforceable maximum contaminant level or drinking water standard. The difference between the public health goal and the provisional health-based target may be explained by different principles and methods used for risk assessment between California EPA and RIVM. The latter uses a method which is generally accepted among regulators within the Netherlands.

The only available Cr(VI) (chromate) data on raw and treated Dutch drinking water were published by RIVM in 1998. Cr(VI) levels were above the health-based target of 0.2 µg/L at six public supply well fields for raw water and at nine for treated drinking water. As these observations are only based on one monitoring study, we suggest performing additional monitoring on chromate levels in raw and treated drinking water. When performing these analyses, the potential filtration bias should be taken into account.

6.4 Other elements

This report showed that toxic properties of chromium are mainly related to Cr(VI), and not to Cr(III). The question may arise whether this also might be the case for difference valence states of other elements. For example, arsenic 3+ is more toxic and bio-active than arsenic 5+. However, as reviewed by IARC, elemental arsenic and inorganic arsenic species share the same metabolic pathway: arsenate^v > arsenite^{III} > methylarsonate^v > dimethylarsenite^v (IARC, 2011). For arsenic, independent of the carcinogenic mechanisms of action, and independent of which of the metabolites is the actual ultimate carcinogen, different inorganic species should all be considered as carcinogenic (IARC, 2011). As the current WHO standard for arsenic is more a practical level than a health protective level, future studies should focus on setting a health-based target for arsenic based on a risk level associated with a 10^{-6} cancer risk.

To conclude on toxic properties of different valence states of other elements, additional literature studies are needed.

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8 Supplementary information

8.1 Summary of a two year oral exposure study

This study was published in 2008 by NTP, summary taken from (California Environmental Protection Agency, 2011).

Groups of 50 male and female rats (F-344) and mice (B6C3F1) were administered sodium dichromate in drinking water (male and female rats and female mice: 14.3, 57.3, 172 or 516 mg/L; male mice: 14.3, 28.6, 85.7 or 257.4 mg/L) for two-years (NTP, 2008). Based on measured water consumption rates and body weights, male rats received a time weighted average dose of 0.21, 0.77, 2.1, or 5.9 mg/kg-day of Cr VI, while female rats received 0.24, 0.94, 2.4 or 7.0 mg/kg-day of Cr VI (NTP, 2008). Based on measured amounts of water consumption, male mice received an average dose of 0.38, 0.91, 2.4, or 5.9 mg/kg-day of Cr VI, while female mice received 0.38, 1.4, 3.1 or 8.7 mg/kg-day of Cr VI (NTP, 2008).

Survival of male and female rats was good. Significant reductions in mean weight gains were observed in the high dose group, in both male and female rats. Reduced water consumption due to poor palatability of high concentrations of Cr VI probably accounts, in part, for the decreases in weight gain in the high dose groups (NTP, 2008).

Similar to what has been observed in other studies (NTP, 1996, 2007), erythrocyte microcytosis was observed in male rats receiving 57.3, 172 and 516 mg/L. Decreased red blood cell volume was observed on day 4, day 22, and at 3 and 6 months. Mean cell volume appeared to increase with time indicating the rats were adapting to the insult. Anemia that appeared to be compound-related was observed at day 22 in male rats exposed to 57.3, 172 and 516 mg/L as evidenced by decreased hematocrit, hemoglobin and erythrocyte counts. The animals appeared to be recovering from the anemia by 12 months.

No treatment related non-neoplastic lesions were observed in the male rat. No adverse effects were reported in oral mucosa, forestomach, glandular stomach, small intestine or liver. Interestingly, irritation/ulcers observed in the stomach in the 3 month study were not observed in the rats after 2 years of exposure. However, the high dose in the two-year study (516 mg/L) was substantially lower than the high dose in the three month study (1,000 mg/L).

Administration of Cr VI to female rats for two years resulted in a dose-related increase in liver toxicity as shown by increased fatty changes and chronic inflammation. Statistically significant increases in the number of rats exhibiting chronic inflammation were observed in all dose groups. The chronic inflammation in females also exhibited increased severity at the two highest drinking water concentrations. The incidences of increased fatty changes were significantly increased at the three highest concentrations, while the increase at the lowest dose level was not statistically significant. Another possible indication of liver damage was that of increased serum alanine aminotransferase (ALT at > 57.3 mg/L) in males at day 4, day 22, month 3, month 6 and month 12; however, this may have been

due to enzyme induction rather than liver damage, since no other serum markers of liver damage were observed. NTP noted that Cr VI appeared to increase the incidence of chronic liver inflammation, commonly observed in aged rats. No treatment related non-neoplasm toxicity was observed in the oral mucosa, forestomach, glandular stomach or duodenum. Hematology, considered a special study and not routinely performed in two-year NTP studies, was not done in the female rat. A LOAEL of 14.3 mg/L was identified in the female rat, based on chronic inflammation, which is below exposure levels associated with hematological effects in the male rat.

The survival of both male and female mice was good. There was no evidence of reduced survival in animals receiving Cr VI. Body weight gains were largely unaffected by Cr VI in the mouse except in the high dose groups. As in the rat, water consumption was reduced in mice in the high dose groups and the reduced body weight was partly attributed (by NTP) to the reduced water consumption.

Comparable to the male rat, female mice exhibited a compound-related microcytosis (decreased cell volume), although the mouse appeared to be less affected than the rat. Mean cell hemoglobin levels and erythrocyte counts were significantly decreased at 12 months in female mice that received 172 or 516 mg/L Cr VI. No hematology was performed in male mice.

No notable exposure related adverse effects were reported in oral mucosa, forestomach, glandular stomach, small intestine or liver in male or female mice. A dose-related increase in diffuse hyperplasia of the epithelium was observed in the duodenum in female and male mice.

8.2 Derivation of California EPA public health goals for Cr(VI)

Carcinogenic effects
A health-protective concentration for carcinogenic effects was derived using available toxicity data and exposure through ingestion and through inhalation during showering for children and adults (California Environmental Protection Agency, 2011). Exposure to Cr(VI) through the dermal route (e.g. through showering) was not taken into account as this is considered to be very low. The default risk level used in this calculation is one extra case of cancer in a million lifetime exposed persons (10^{-6} risk level). For the oral route, an oral slope factor[6] of 0.5 (mg/kg/day)$^{-1}$ was used based on data obtained from the NTP 2008 study. For the inhalation route, the human cancer slope factor of 510 (mg/kg/day)$^{-1}$ was used as derived from the available studies (see report for details (California Environmental Protection Agency, 2011)). To calculate a health-protective drinking water level representing an excess lifetime cancer risk of 1 in 1 million, estimations were made of the drinking water exposures through ingestion and showering corrected by age sensitivity factors and adjustments for duration for different life stages. This calculation resulted in a health-protective drinking water level of **0.02 μg/L**. The proportion of the total cancer risk

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[6] Cancer slope factors are used to estimate the risk of cancer associated with exposure to a carcinogenic substance. A slope factor is an upper bound, approximating a 95% confidence limit, on the increased cancer risk from a lifetime exposure to a substance. This estimate is usually expressed in units of proportion of a population affected per mg of substance/kg body weight-day.

contributed by inhalation appeared to be very small (~ 0.6%), despite the high cancer potency by the inhalation route (California Environmental Protection Agency, 2011).

Non-carcinogenic effects

According to standard procedures, also a health-protective level for non-carcinogenic effects was derived by California EPA. The results of six (sub)chronic exposure studies (paragraph 5.3) were evaluated by the California Environmental Protection Agency (2011) to derive a health protective concentration for Cr(VI) for non-carcinogenic effects. From these studies, a lowest LOAEL of 0.2 mg/kg/day was obtained for the critical non-carcinogenic endpoint liver damage (mild chronic inflammation, fatty changes). This LOAEL was the point of departure to derive an acceptable daily dose. Using an uncertainty factor of 1000 (10 for using a LOAEL, 100 for inter- and intraspecies variation), an acceptable daily intake of 0.2 / 1000 = 0.0002 mg/kg/day was derived. Subsequently, the public health-protective drinking water concentration was calculated from this acceptable daily intake as follows: (acceptable daily dose x relative source contribution) / upper 95th percentile water intake. A maximum default relative source contribution of 0.8 (80%) was used for Cr(VI), based upon the assumption that the major source of Cr(VI) is likely to be from drinking water. According to California EPA little or no Cr(VI) exposure is expected from air, food, incidental inhalation, dermal and oral exposure to soil and dust. However, they do not provide data on actual Cr(VI) exposure. The upper 95th percentile water intakes for a child (0 to 11 years) and adults (16 to 70 years) were calculated by U.S. EPA and were 0.067 and 0.039 L/kg bw/day, respectively. Using time weighted intake averages for children and adults (as weight changes over time), health protective levels of 0.0024 mg/L and 0.0041 mg/L were derived for children and adults, respectively. Based on the lowest value, a health-protective level of Cr(VI) in drinking water of **2 μg/L** for non-carcinogenic effects was derived (California Environmental Protection Agency, 2011).