Results from the Swedish Screening Programme 2006

Subreport 5:
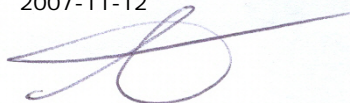## Hexavalent Chromium, Cr(VI)

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Summary

As an assignment from the Swedish Environmental Protection Agency, IVL has during 2006/2007 performed a "Screening Study" of hexavalent chromium, Cr(VI). Also the concentrations of total chromium, Cr(tot) (i.e. Cr(III) + Cr(VI)) and lead, Pb(tot) were measured in the study.

This report approved
2007-11-12

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Scientific Director

Sammanfattning

IVL har på uppdrag av Naturvårdsverket genomfört en screening av förekomsten av sexvärt krom, Cr(VI), i den svenska miljön. Utöver sexvärt krom inkluderades även totalhalten krom, Cr(tot) och totalhalten bly, Pb(tot). Då de enda i naturen stabila förekomstformerna av krom är Cr(VI) och Cr(III) kan vi sätta Cr(tot) = Cr(III) + Cr(VI). Sexvärt krom är giftigt, allergent och cancerogent och har förbjudits i en rad produkter inom EU (t ex elprodukter).

Att analysera halterna av krom i olika matriser på regelbunden basis genomförs i olika miljöövervakningsprogram, däremot är haltspeciering av krom (trevärt- respektive sexvärt krom) i olika matriser betydligt ovanligare. Ett skäl till detta är att krom med olika oxidationstal föreligger i redoxjämvikter med varandra och haltförhållandena är således inte statiska över tiden.

Det huvudsakliga syftet med föreliggande studie var att få en uppfattning om koncentrationer i olika matriser i miljön, att belysa tänkbara transportvägar samt bedöma huruvida uppmätta koncentrationer kan tänkas ha någon miljöpåverkan. Även eventuellt upptag i biota och människa undersöktes.

Screeningprogrammet innefattade mätningar i bakgrundsområden och i närheten av möjliga punktkällor. Mätningar gjordes också i urbana områden vilket avspeglar diffusa emissioner från samhället. Provtyperna var luft, nederbörd, sediment, jord, slam, biota (fisk) och human urin. Totalt analyserades 62 prover i programmet. Ingen provtagning i regional regi förekom i denna screening.

I tabellen nedan visas uppmätta halter av Cr(VI), Cr(tot) och Pb(tot).

Species	Luft (ng/m³) n=14	Regn-vatten (ng/l), n=7	Ytvatten (ng/l) n=7	Biota (µg/kg WW) n=7	Slam (µg/g DW) n=6	Sediment (µg/g DW) n=6	Jord (µg/g DW) n=9	Urin (µg/L) n=6
Cr(VI)	<0.016 -2.6	30-680	150-330	3-17	0.007- 0.016	<0.0012- 0.10	0.008- 0.13	<0.4- 0.6
Cr(tot)	0.3-63	<40-5300	150-340	2.5-39	0.26-14	0.85-25	1.5-210	<0.9
Pb(tot)	1.1-20	100-4300	20-110	<2.3-25	0.65-12	9.4-59	16-200	<1.3

Cr(VI) detekterades i samtliga i programmet ingående matriser. De högsta halterna i luft och jord uppmättes i närheten av en kromanvändande industri. Koncentrationerna var i de flesta fall högre i urban miljö än i bakgrundsområden vilket indikerar diffus spridning. Cr(VI) återfanns i alla analyserade prov av reningsverksslam. Även detta indikerar diffusa källor. Cr(VI) halten i fisk från det urbana området var oftast i samma nivå som i bakgrundsområdena; i ett fall var halten i ett bakgrunsprov högre.

Andelen Cr(VI) av Cr(tot) varierade mellan olika provtyper. Andelen var högst i fisk, vatten och nederbörd, lägre i luft och lägst i fasta provtyper.

Kromhalten i urin är en indikation på exponering av hexavalent krom, men enbart exponeringen under de sista 24 timmarna. Sex urinprov från friska individer analyserades. Låga koncentrationer Cr(VI) återfann i tre prov. I de återstående proven kunde Cr(VI) inte påvisas.

Riskbedömning baserad på de uppmätta halterna i ytvatten (MEC) och PNEC-värden från litteraturen resulterade i att de uppmätta koncentrationerna inte utgjorde någon miljörisk.

Eftersom krom oftast analyseras enbart som Cr(tot) men inte specieras är det svårt att jämföra dessa mätningar med tidigare data.

Koncentrationen av Cr(tot) följde samma huvudsakliga mönster som Cr(VI) d.v.s. högst nära punktkällan, lägre i urban miljö och lägst i bakgrundsområden.

Summary

As an assignment from the Swedish Environmental Protection Agency, IVL has during 2006/2007 performed a "Screening Study" of hexavalent chromium, Cr(VI). Also the concentrations of total chromium, Cr(tot) (i.e. Cr(III) + Cr(VI)) and lead, Pb(tot) were measured. Hexavalent chromium is toxic, allergenic and carcinogenic and has, despite a wide area of applications, been banned in several products within the EU, for instance in electronic devices. Chromium emission to the environment also occurs through combustion processes, for instance the combustion of oil.

The chemical analysis of chromium in various environmental matrices is common practice in many environmental monitoring programmes while the speciation of chromium is less frequent. A reason for this is that the concentrations of the chromium species are not stabile enough to persist in the environment. When environmental parameters such as redox potential and pH changes, a change in the Cr(III)/Cr(VI)-ratio takes place.

The overall objectives of the screening were to determine the concentrations of the metal in a variety of media in the Swedish environment, to highlight important transport pathways, and to assess the possibility of current emissions in Sweden. A further aim was to investigate the likelihood of atmospheric transport and uptake in biota and humans. The screening programme included measurements in background areas and in the vicinity of potential point sources. Measurements were also done in urban areas reflecting diffuse emission pathways from the society. The sample types were air, precipitation, sediment, soil, sludge, biota (fish), and human urine. A total of 62 samples were included in the national sampling programme. No regional sampling programme was pursued within this screening. In the table below the reported concentrations of Cr(VI), Cr(tot) and Pb(tot) in different matrices are summarised.

Species	Air (ng/m^3) n=14	Precipi- tation (ng/l), n=7	Surface water (ng/l) n=7	Biota (µg/kg WW) n=7	Sludge (µg/g DW) n=6	Sediment (µg/g DW) n=6	Soil (µg/g DW) n=9	Urine (µg/L) n=6
Cr(VI)	<0.016-2.6	30-680	150-330	3.1-17	0.007-0.016	<0.0012-0.10	0.008-0.13	<0.4-0.6
Cr(tot)	0.3-63	<40-5300	150-340	2.5-39	0.26-14	0.85-25	1.5-210	<0.9
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Cr(VI) was found in all analysed environmental sample types. The highest concentrations in air and soil were found in the vicinity of a chromium using industry. The concentrations were in most cases higher in urban than in background areas indicating diffusive spreading. Cr(VI) was found in all analyzed samples of STP sludge which is also and indication of diffusive sources. Cr(VI) concentrations in fish collected in the urban area was mostly in the same level as in fish from background lakes, occasionally the concentration in the background samples was higher.

The ratio Cr(VI) to Cr(tot) varied among the different sample types. The ratio was highest in fish, water and precipitation, lower in air and lowest in solid sample matrices.

Chromium measured in urine is an indication of exposure to hexavalent chromium, but only of the exposure over the last 24 hours. Six urine samples from healthy individuals were analyzed. Low

concentrations of Cr(VI) were found in three samples. In the remaining samples Cr(VI) was not detected.

Risk assessments based on the measured surface water concentrations (MECs) and PNEC-values from the literature indicated that the measured aqueous concentrations of Cr(tot) and Cr(VI) did not pose a risk to the environment. Even though one of the PNEC-values used seems highly arguable (Cr(III)) it was chosen since it maximises the MEC/PNEC-quotient, in consistency with the precautionary principle.

Although Cr(tot) is frequently analyzed in environmental investigations, speciation is seldom done. Thus it is not easy to compare our Cr(VI) measurements with earlier data.

Cr(tot) concentrations followed the same general pattern as Cr(VI), i. e. highest near the point source, lower in urban areas (diffusive sources) and lowest in background areas.

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1. Introduction

As an assignment from the Swedish Environmental Protection Agency, IVL has during 2006/2007 performed a "Screening Study" of phthalates, 1,5,9-cyclododecatriene, zinc pyrithione, pharmaceuticals and chromium(VI). These substances are emitted and distributed in the environment via a variety of sources, e.g. point sources and via use in consumer products. Pharmaceuticals in particular are frequently spread by domestic use.

The overall objectives of the screening were to determine the concentrations of the selected substances in a variety of media in the Swedish environment, to highlight important transport pathways, and to assess the possibility of current emissions in Sweden. A further aim was to investigate the likelihood of atmospheric transport (phthalates, 1,5,9-cyclododecatriene and chromium) and uptake in biota.

The results are reported in five sub-reports according to Table 1.

Table 1. Substances / substance groups included in the screening

Substance / Substance group	Sub-report #.

Phthalates:
        Di-isononyl phthalate (DINP)
        Di-isodecyl phthalate (DIDP)
	1

1,5,9-Cyclododecatriene (CDDT)	2
Zinc pyrithione	3

Pharmaceuticals:
        Fentanyl, Propofol, Dextropropxyphene,
        Bromocriptine, Thioridazine, Clozapine, Risperidone,
        Zolpidem, Sertraline, Fluoxetine, Flunitrazepam,
        Diazepam, Oxazepam
	4

Hexavalent chromium (Cr(VI))	5

This subreport considers the screening of hexavalent chromium, (Cr(VI)).

Total chromium (Cr(tot)), and total lead (Pb(tot)) were included in the screening as reference substances.

2. Chemical properties and toxicity

Chromium (Cr) is a metallic element of the transition metals group. The metal is steel-gray, lustrous and hard with a melting point of 1907 °C. Chromium has four stable isotopes of masses 50 (4.4%), 52 (84 %), 53 (9.5 %), and 54 (2.4 %) (Rotaru et al.,1992). It is odourless, tasteless and brittle. Chromium is passivated by oxygen, forming a thin protective oxide surface layer which prevents oxidation of the underlying metal. The most common oxidation states of chromium are +2, +3, and +6, with +3 being the most stable. Chromium compounds of oxidation state 6 are powerful oxidants and also very toxic (Grevatt P C, 1998).

Trivalent chromium (Cr(III)) is essential in the human body and is required in trace amounts for sugar metabolism. Lack of this species may result in a disease called chromium deficiency. In contrast, hexavalent chromium (Cr(VI)) is very toxic and mutagenic when inhaled, as popularized by the film "Erin Brockovich". In solution, Cr(VI) is well established as a cause of allergic contact dermatitis (ACD).

Chromium enters the body through inhalation, ingestion and dermal absorption. The general population is exposed to chromium through ingestion of chromium in food and water, while occupational exposure predominantly occurs through inhalation and dermal contact. Workers exposed to chromium are at risk of developing lung cancer as well as nasal, pharyngeal and gastrointestinal carcinomas.

Depending on the type of target organism, chromium poses different toxicological modes of entry. Cr(III) does generally not readily cross cell membranes but is in many species able to bind to transferring type proteins and may thus be circulated within the body through the blood stream. It may also enter the cells via Cr(VI), which in some cases may be able to penetrate different kinds of nuclear membranes followed by enzymatic reduction to form Cr (III) and free radicals. Cr(VI) may also be reduced to Cr(III) by chemicals produced within the body such as ascorbic acid, thiols (i.e., glutathione, cysteine, cysteamine, lipoic acid coenzyme A and coenzyme M).

When inside the nucleus, Cr(III) can bind to DNA and to certain proteins (such as reproductive enzymes) and damage their functions, thus it is defined as mutagenic and carcinogenic (Zhitkovich, 2005 and Zhitkovich et al., 1996). Even though it is Cr(III) that causes the harmful effects, it can only cross the cell membrane as Cr(VI), which is why the latter is considered the toxic species.

The ecotoxic effects of chromium are primarily found at the lower trophic levels. The main potential ecological impacts result from direct exposure of algae, benthic invertebrates, embryos and fingerlings of freshwater fish and amphibians to chromium. Chromium may bioaccumulate in algae, other aquatic vegetation and invertebrates, but it does not biomagnify. Chromium inhibits growth in duckweed and algae, reduces fecundity and survival of benthic invertebrates, and reduces growth of freshwater fingerlings. It is cancer-causing, mutation-causing, and teratogenic (embryo-damaging) (Grevatt PC, 1998).

Table 2 lists available data on ecotoxicity of chromium. When interpreting the data, it is important to note that for some of the tests, the resulting toxicity may be regarded as the summed contribution of both Cr(III) and Cr(VI) since these species are inter-convertible both in the aqueous solution used to expose the test organisms, as well as within the test organism. Furthermore, little is known about the relation between concentrations of total chromium in a

given environment and biological effects on the organisms living there (Irwin et al, 1997). Depending on the physical and chemical state of chromium, the same elemental concentration has a wide variety of mobility and reactivity and thus has different effects (Irwin et al., 1997). Chromium toxicity to aquatic biota is significantly influenced by abiotic variables such as hardness, temperature, pH, and salinity of water; and biological factors such as species, life stage, and potential differences in sensitivities of local populations (Irwin et al., 1997).

Table 2. Ecotoxicological data on Chromium

Test organism	Toxic Effect	Duration	Value [μg/L]	Reference
C Indian Toad (*Bufo melanostictus*, Amphibian)	LC_{50}	96 h	4990	Anusuya et al., 1999
Eastern Narrow-Mouthed Toad (*Gastrophryne carolinensis*, Amphibian)	LC_{50}	7 days	30	Birge et al., 1979
Fathead minnow (*Pimephales promelas*, fish)	NOEC	7 days	3000	Pickering, Q.H., 1988
Goldfish (*Carassius auratus*, fish)	LC_{50}	7 days	660	Birge et al., 1979
Bryozoan (*Plumatella emarginata*, Benthic)	LC_{50}	96 h	650	Pardue et al., 1980
Mussel (*Anodonta imbecillis*, Mollusc)	LC_{50}	96 h	39	Keller et al., 1991
Green algae (*Selenastrum capricornutum*, Phytoplankton)	NR	2 h	320	Call et al., 1981
Dinoflagellate (*Gymnodinium splendens*, Phytoplankton)	EC_{50}	48 h	240	Wilson et al., 1980
Water flea (*Daphnia mangna*, Zooplankton)	EC_{50}	748 h	72	Dorn et al., 1993
Indian prawn (*Penaeus indicus*, Crustaceans)	LC50	48 h	1010	Govindarajan et al., 1993

3. Fate

The only forms of chromium stable enough to persist in the environment are Cr(III) and Cr(VI). The Cr(III)-form is the most stable and substantial energy is required to convert Cr(III) to lower or higher oxidation states. Cr(VI) exists as chromate (CrO_4^{2-}), its corresponding acid (bichromate, $HCrO_4^-$), and as dichromate ($Cr_2O_7^{2-}$). These anions form a variety of complexes that are rather water soluble and thus mobile in the environment.

The distribution of the various species of Cr as a function of redox conditions and pH can be visualised in a Pourbaix diagram (Pourbaix M, 1974). The Pourbaix diagram of chromium and water (Cr-O-H system) can be made rather complex but for the purposes of this report some simplifications can be made.
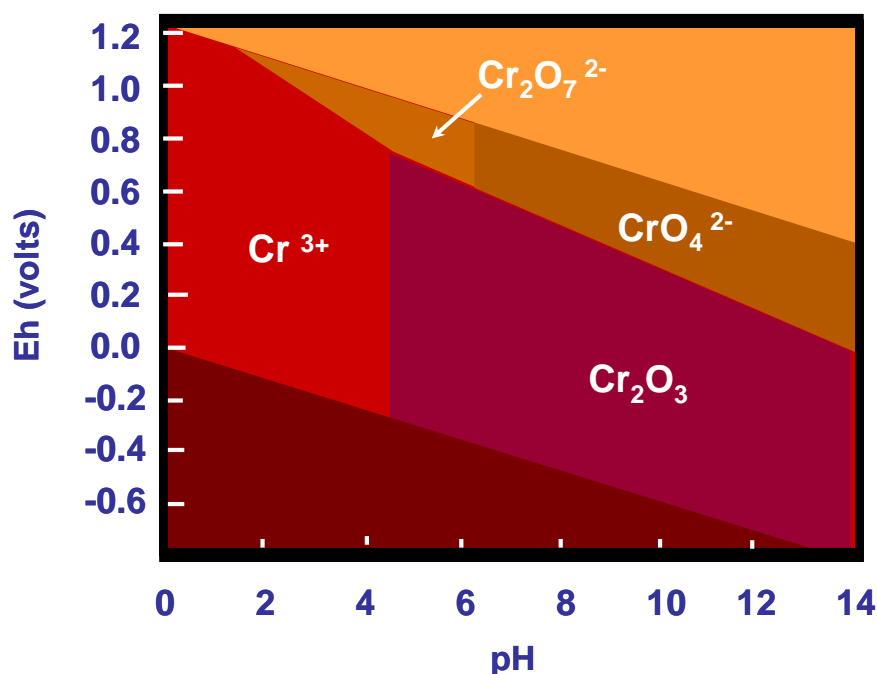

Figure 1. Simplified Pourbaix diagram for the system Cr-O-H (after Pourbaix M, 1974).

Explanation to Figure 1.
Uppermost line: Represents the equilibrium: $H_2O \leftrightarrow 2H^+ + \frac{1}{2} O_2 + 2e^-$.
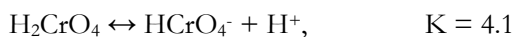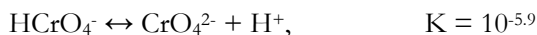*Water is unstable above this line, so natural solutions never go above it.*
Lowermost line: Represents the equilibrium: $H^+ + e^- \leftrightarrow \frac{1}{2} H_2$.
Water is unstable below this line, so natural solutions never go below it.
*Vertical lines: Gives the pH values for the crossover points for de-protonation reactions*
Diagonal lines: Gives the pH and Eh values for the crossover points for redox reactions.

CrO_4^{2-} is the dominant Cr(VI) species in alkaline solutions whereas in the pH-range 2-6 the equilibrium between $HCrO_4^-$ and $Cr_2O_7^{2-}$ is governing the fate;

$$HCrO_4^- \leftrightarrow CrO_4^{2-} + H^+, \qquad\qquad K = 10^{-5.9}$$

$$H_2CrO_4 \leftrightarrow HCrO_4^- + H^+, \qquad\qquad K = 4.1$$

$$Cr_2O_7^{2-} + H_2O \leftrightarrow 2\ HCrO_4^-, \qquad\qquad K = 10^{-2.2}$$

Acid solutions of dichromate are very strong oxidants;

$$Cr_2O_7^{2-} + 14\ H^+ + 6\ e^- \leftrightarrow 2Cr^{3+} + 7\ H_2O, \qquad\qquad E^0 = 1.33V$$
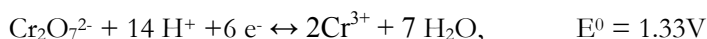
While chromate in alkaline solution is much less oxidizing;
$$CrO_4^{2-} + 4\ H_2O + 3\ e^- \leftrightarrow Cr(OH)_{3(s)} + 5OH^-, \qquad E^0 = -0.13V$$

Under oxidizing conditions, Cr is highly soluble and mobile as Cr(VI) anions of chromate (CrO_4^{2-}) and bichromate ($HCrO_4^-$). Under reducing conditions, Cr(VI) may convert to Cr(III), which is insoluble and strongly adsorbed onto solid surfaces (Loyaux-Lawniczak et al., 2001). Cr(VI) can be artificially removed from solution by in situ reduction (Blowes et al., 1997, and Lytle et al., 1998), or naturally by reductants such as aqueous Fe(II), dissolved humic acids, and Fe(II)-bearing minerals (Buerge et al., 1998 and Wittbrodt et al., 1996). For these reasons, knowledge of reduction rates is essential in many Cr(VI) contamination cases. For example, sufficient rates of natural reduction at a given site allow the use of the "monitored natural attenuation" approach, which is much less expensive and disruptive than active remediation.

Determining reduction rates can be difficult; multiple rounds of groundwater sampling and analysis over several years have been required in some contaminant plumes.

The lighter chromium isotope, [52]Cr, preferentially reacts during reduction of Cr(VI) to Cr (III) (Hoefs J, 1987), which leads to an enrichment of [52]Cr relative to [53]Cr in the resulting Cr (III) and a corresponding enrichment of [53]Cr in the residual Cr(VI) as reduction proceeds (Boettcher et al., 1990, Thode et al., 1965, Johnson et al., 1999). Thus, under reducing conditions in the environment, the isotope pattern of the Cr(III) fraction will be shifted to lighter isotopes while the isotope pattern of the remaining Cr(VI) fraction will be shifted to the higher isotopes.

Long-term reduction rates can be estimated using the extent of reduction of Cr(VI) to Cr (III) which is obtained from the change of the ratio of stable isotopes of chromium over time ([53]Cr/[52]Cr) (Ellis et al., 2002).

4. Sources, use, emissions and regulations

Chromium is mined as chromite ore ($FeCr_2O_4$). Roughly half the chromite ore in the world is produced in South Africa. Kazakhstan, India and Turkey are also substantial producers. Untapped chromite deposits are plentiful, but geographically concentrated in Kazakhstan and southern Africa.

Approximately 15 million tons of chromite ore were produced in 2000, and converted into approximately 4 million tons of ferro-chrome.

Chromium is frequently used in various metallurgy applications such as to impart corrosion resistance and a shiny finish. Stainless steel is for instance always alloyed with a small proportion of chromium. Also in surface metallurgy chromium is used as in the case of chrome plating. In the process of making anodised aluminium, chromium present in the electrolyte (as chromic acid), renders the aluminium surface thin, soft and ductile (type I anodisation). Chromium and chromium salts are important ingredients in dyes and paints. Chromium salts are for instance used to colour glass melts (emerald green glass bottles). It is also used in the production of synthetic rubies, as the presence of trace amounts of chromium is essentially what makes a ruby red. In most paints, the yellow colour is a result from addition of chromium salts. Chromium and its salts are also used as catalysts in the chemical industry. Chromite ($FeCr_2O_4$) has for instance been used to make moulds for the firing of bricks. Chromium salts are used in the tanning of leather.

Potassium dichromate ($K_2Cr_2O_7$) is a chemical reagent, also used as a fixing agent for dyes in fabric. Chromium(IV) oxide (CrO_2) is used to manufacture magnetic tape, where its higher coercivity than iron oxide tapes gives better performance. Chromium hexacarbonyl ($Cr(CO)_6$) is used as a gasoline additive. Chromium boride (CrB) is used as a high-temperature electrical conductor. Chromium (III) sulfate ($Cr_2(SO_4)_3$) is used as a green pigment in paints, in ceramics, varnishes and inks as well as in chrome plating.

According to the Swedish Chemicals Agency, about 755 tonnes of various chromium salts (inorganic) and metallic chromium raw materials were imported to Sweden in the year 2000. Six hundred tonnes of the imported amount were used by the Swedish industry and of these 326 tonnes of chromium were exported in products. The import of chromium in products to Sweden was 1326 tonnes. This yields a balance where roughly 2000 tonnes of chromium are imported while only some 330 tonnes were exported that particular year.

Chromium is released to the environment mainly via industrial products containing chromium, the burning and combustion of fossil fuels and by the release of production fluids from various chemical plants using chromic acid in their processes.

Specific sources associated with chromium emission are;
- cement-producing plants;
- exhaust emission from catalytic converters in automobiles;
- waste from electroplating, leather tanning and textile industries indiscriminately discharged into lakes and rivers;
- solid wastes from the manufacture of chromium compounds;

- consumer products such as inks, paints and papers; leather materials; stainless steel and a few other alloy metals; chrome-plated products; some toner powders used in copying machines.

Many chromium containing products release chromium to the environment through different leaching and weathering processes but these are slow. Annual emissions are likely to be related to the net import figures but of a different order of magnitude, as the leaching processes are very slow.

Chromium will also be emitted to the Swedish environment through the combustion of fossil fuels.

Globally, chromium is released in vast quantities to the environment in the volcanic eruptions of magma. For instance during a 48 hour eruption of the volcano Pinatubo (in the Philippines) approximately 10 billion tonnes of magma erupted containing some 550 000 tonnes of chromium.

Within the European Union, the use of hexavalent chromium in consumer gadgets is regulated by a directive concerning the use of certain hazardous substances in electrical and electronic equipment (EU-legislation, 2003). From 1 July 2006, new electrical and electronic equipment put on the market may not contain lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyls (PBB) or polybrominated diphenyl ethers (PBDE).

In Sweden, most chromium salts and organic chromium compounds are classified as CMR-compounds (class 1 or 2), thus they are considered carcinogenic. Furthermore, they are often classified within the groups of N;R50-53 or R53 (very toxic to aquatic organisms and/or may cause long-term adverse effects in the aquatic environment) (KEMI, 2007)

In Sweden the threshold value for chromium in drinking water is 50 μg/L (SLVFS, 2001), which is in accordance with the WHO-values of 50 μg/L for chromium(VI).

In the United States the dietary guidelines for daily chromium uptake are 35 μg (adult male) and 25 μg (adult female) (Vincent, 2004). Furthermore, in the US the EPA has set a limit of 100 μg chromium(III) and chromium(VI) per litre of drinking water.

5.Previous investigations in the environment

The background concentration of chromium (total) has previously been investigated by the Swedish EPA. In agricultural soil (the plough layer) the national average concentration was 20.5 mg/kg dw. The highest concentrations were found in the clay soil areas of the Mälar valley and in the region of Västernorrland in the North of Sweden (Figure 2). In the southern parts of Sweden, the chromium content in the soil decreases (Eriksson et al., 1997).

The regulatory threshold value for chromium (total) concerning the use of STP sludge on agricultural land is 30 mg/kg dw of soil (plough layer) prior to sludge addition. In 12 % of the agricultural land in Sweden, the natural occurring chromium content exceeds this value. In the Uppsala region 77 % of the soil exceeds the threshold (Klang & Eriksson, 1997).

Also the background concentration of chromium in Swedish surface waters has been monitored (Alm et al., 1999). In the southern parts of Sweden the chromium concentrations in surface waters could be as high as 0.3 µg/l or above (see Figure 3).

Chromium, among other elements, is regularly measured in precipitation within the (European Monitoring and Evaluation Programme (EMEP). During 2000 -2001 the average concentration of chromium (total, Cr(III) + Cr(VI)) in rain was 0.2-0.9 µg/l and the wet deposition rate was 33-235 µg/m²×year (Svensson A, 2003a,b).

In 2000 the Stockholm County Administrative Board sampled Schreber's feather moss (*Pleurozium Schreberi*) at 39 sites throughout the county, as a bioindicator of heavy metal deposition.

Most of the sites were located in the central part of the county. The concentrations in the moss samples were used to estimate the atmospheric deposition of heavy metals on a regional scale. The concentration of heavy metals in the moss was assumed to represent the mean deposition during the previous three years. The concentration of chromium (total) in the feather moss was 0.5-3.7 µg/g (median 1.1 µg/g) in the Stockholm region whereas the concentration in samples collected at background sites in southern Sweden was 0.8 µg/g (median). The overall median concentration in Sweden was 0.51 µg/g (Ljungqvist L, 2003).

Chromium (total) was measured in fish muscle in the vicinity of Landskrona in southern Sweden. The concentration in Flounder (*Platichthys flesus*) was 350 – 620 µg/kg ww (Landskrona, 1997). In a study from Luleå the concentrations of chromium (total) in Carp bream and Perch, ranged from <14 to 140 µg/kg ww (Byrsten et al., 2005). In a study from Gnosjö on the chromium concentration in Pike liver the levels reported were 58 - 190 µg/kg ww (Rossiter H, 2005)

According to the Swedish EPA , the background concentration of chromium (total) in ground water is 0.1 – 1 µg/l (Naturvårdsverket, 1990 and 1999).
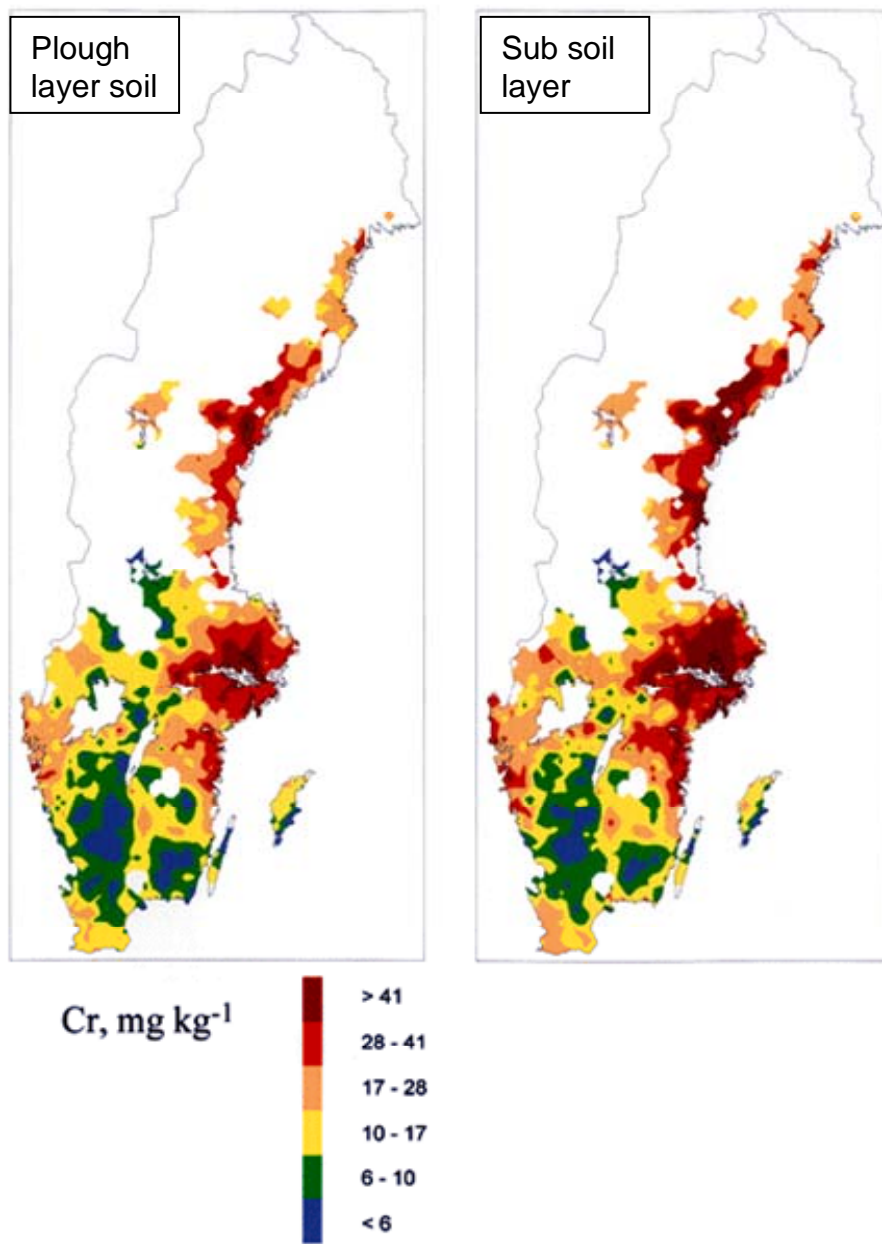
Figure 2. Chromium concentration in the plough- and subsoil layer (n = 1717). Only sites where subsoil samples were also taken are included in the plough layer map. Reprinted with kind permission of the author Jan Eriksson, SLU.
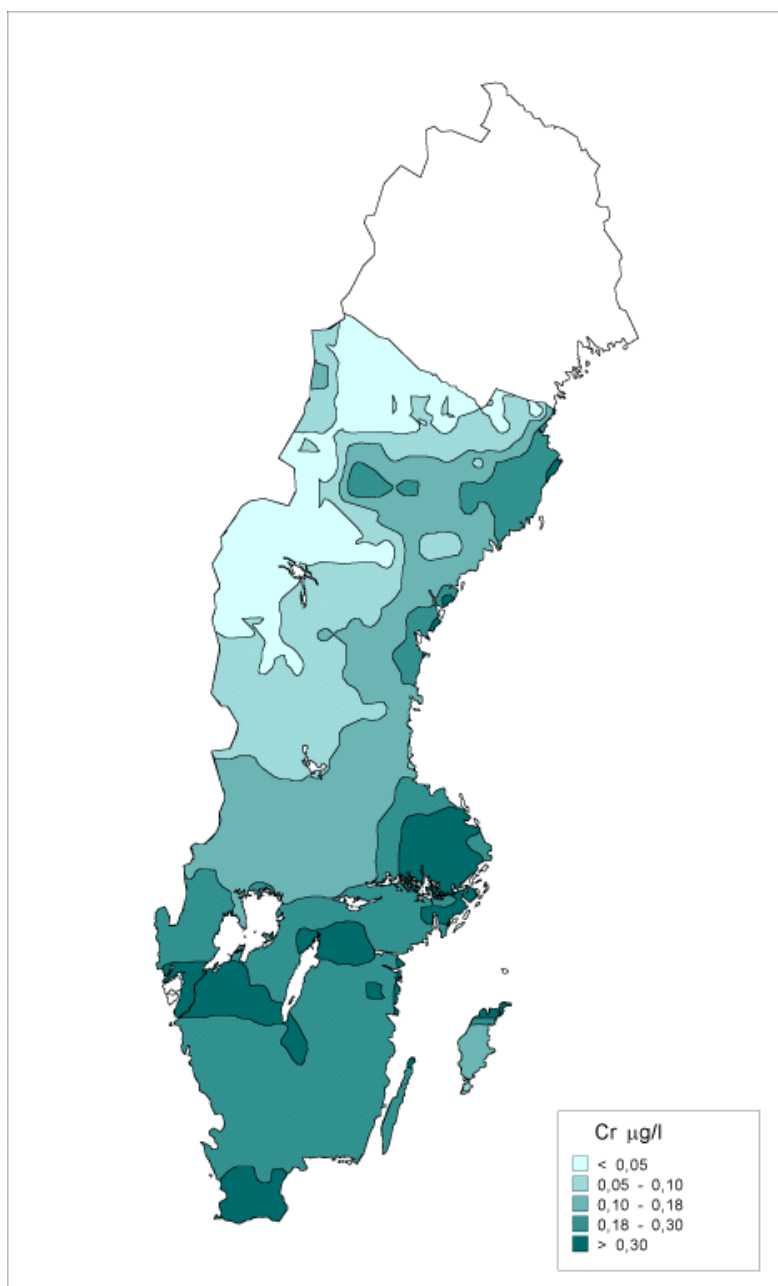
Figure 3. Background chromium concentrations in Swedish surface waters.

6. Sampling programme

A sampling strategy was developed in order to determine concentrations of Cr(VI) and Cr (total) in different environmental matrices in Sweden. An additional aim of the sampling programme was to identify major emission sources as well as important transport pathways.

The sampling programme was based on identified possible emission sources and the behaviour of the metal in the environment. Air and precipitation were considered to be highly relevant matrices for characterising the emission and transport pathways of chromium.

In order to determine levels at background areas; air, precipitation, water, sediment and biota samples were collected. The sampling station Råö at the Swedish west coast, which is a station within the national monitoring programme for air pollutants as well as in the EMEP programme, was used for the air and precipitation measurements. From lake Gårdsjön, also at the Swedish west coast, water, sediment and fish were collected. Soil was sampled in the vicinity of the lake.

Fish were also collected at three background lakes used within the national monitoring programme of contaminants in biota. The samples were delivered by the Swedish Museum of Natural History.

In order to identify diffusive emissions from the society measurements were carried out in air, precipitation, surface water, sediment, fish and soil from the urban area Stockholm.

Sludge from municipal sewage treatment plants (STPs) are often used to indicate diffuse spreading of chemicals to the environment. Sludge samples were obtained from the Swedish Environmental Protection Agency's Monitoring Program for Environmental Pollutants in Sludge.

Hallstahammar, a town historically recognized as one of the most interesting places in Sweden with regard to the manufacture and production of metal goods and items was selected as a "point source". Also today, metal manufacturing is a very important branch of industry in the region. Air samples were collected at a production plant for chrome-plated metal goods for the construction industry. At the plant, huge tubs with chromic acid (H_2CrO_4) are utilized for the chrome-plating process.

A point source where the chromium emission is a mere result of combustion had also been desirable. However, no point source of this type could be identified since oil is rarely used as a fuel for neither large scale heat- nor large scale power production.

Finally, as an indication of human exposure urine from healthy individuals were analyzed.

Since covariance between the concentrations of Pb and Cr could indicate if the origin of the chromium in the samples is combustion of oil, petrol, bio fuels or coal, thus also the total content of Pb was determined in the samples.

The sampling programme is summarised in Table 3. Site information and sample characteristics of the samples collected within the national programme are given in Appendix 1.

Table 3.   Sampling programme

Category	Site	Air	Precipit ation	Surfac e water	Sedi- ment	Soil	Sludge	Fish	Urine	Total
Back- ground	Råö	3	3							**6**
	Gårdsjön			3	3	3		1		**10**
	Lake Tärnan			1				1		**2**
	Krageholmssjön							1		**1**
	Övre Skärsjön							1		**1**
Point Sources / Affected Areas	Hallstahammar	3				3				**6**
Diffusive Sources	Urban Stockholm	8	4	3	3	3		3		**24**
	Various STPs						6			**6**
Human exposure									6	**6**
Total		**14**	**7**	**7**	**6**	**9**	**6**	**7**	**6**	**62**

7. Sampling

The overall most important instructions regarding sampling within the chromium programme, was that all collected water samples were to be extracted immediately after being sampled. A detailed ion exchange extraction routine was developed and optimised for field applicability (see "Water"). During sampling of solid matrices, i.e., sediment and sludge, plastic tools rather than steel tools were used in order to avoid contact contamination.

7.1. Air

Air samples (particle phase) were collected using a low volume air sampler (LVS) with a flow of approximately 1 m³/hour. Particles were collected on a 2 μm PTFE filter (Zefluor, Pall Life Sciences). The sampling was carried out for one week on each filter. After sampling the filters were wrapped in aluminium foil and sent to the laboratory where they were stored in a freezer (-18°C) until analysis. An additional filter used as a field blank was sent back to the laboratory unexposed.

7.2. Precipitation

Samples of precipitation were collected using an inert funnel connected to a 5-liter bottle (cleaned with concentrated nitric acid and subsequently with distilled water). The samples were ion exchanged as described for water samples (see 7.3) and were stored frozen until analysis.

7.3. Water

Water samples were collected in pre-cleaned plastic bottles (cleaned with concentrated nitric acid and subsequently with distilled water). Immediately after the sampling, the samples were divided into two aliquots. One aliquot (~15 ml, first 5 ml was discarded) was filtered directly through a 45 μm Nylon syringe filter (Nalgene), acidified by a 100 μl addition of concentrated nitric acid and stored frozen until analysed. This constituted the Cr(tot)-water sample. The other aliquot was passed though an assembly of syringe filter and a 1.5 ml IC-H Maxi-clean cationic exchange column (Alltech). The first 5 ml of sample passing through was discarded. Only anionic Cr-species passes the exchange column ($Cr(VI)O_4^{2-}$/ $Cr(VI)_2O_7^{2-}$). Upon acid addition (100 μl concentrated nitric acid, converting Cr(VI) to Cr(III)) this aliquot constituted the Cr(VI)-water sample.

7.4. Sediment

Sediment samples from lakes were collected by means of a Kajak sampler. The sediment core was sliced and transferred into plastic jars and stored until analysed.

7.5. Sludge

The staff at the different treatment plants collected the sludge samples from the anaerobic chambers. The sludge was transferred into plastic jars and stored at 4°C or -18°C until analysed.

7.6. Soil

Soil samples were taken according to the composite sampling method, each sample analysed being made up of 20-30 sub-samples after thorough mixing.

7.7. Biota

Fish samples were collected by means of fishing net, hoop net or fishing rod. Samples of herring from background sites were supplied from The Environmental Specimen Bank and the Museum of Natural History (A. Bignert and colleagues). Fish samples were individually wrapped in aluminium foil and stored in a freezer (-20°C).

7.8. Urine

Urine samples were provided by the University Hospital of Lund, Department of Occupational and Environmental Medicine (Staffan Skerfving). The samples were collected from women (age 34-51) in connection to mammography.

8. Analysis

8.1. Extraction

Extraction of Cr(VI) from solid samples, air filters and urine
Up to 2 g of sample material or a half air filter was weighed into 50 ml polypropylene tubes and diluted to 50 ml using a 12.5 mM bi-carbonate buffer. The buffer was prepared from 1.05 g $NaHCO_3$ added to 1 l MilliQ water. The pH was adjusted to 6.4 using 192 µl HCl. The samples were placed in an ultrasonic bath for 30 minutes, followed by filtration through a 0.45 µm nylon syringe filter. Cr(VI) was extracted using a cation-exchange cartridge as described above. The samples were conserved, by adding HNO_3 to a final concentration of 1% vol/vol.

Extraction of Cr(tot) and Pb from solid samples, air filters and urine
Up to 1 g sample material or a half air filter was weighed into Teflon vessels, and 2 ml H_2O_2 and 3 ml HNO_3 was added. The Teflon vessels were closed and the sample material digested in a microwave oven. After digestion, the samples were diluted to 20 or 100 ml using MilliQ-water.

8.2. ICP-MS analysis

Water samples
Before analysis, 1 ppb Rhenium (Re), which served as internal standard, was added to the samples. Cr(VI) in the samples was determined by monitoring ^{52}Cr in medium and high resolution using a ICP-HR-MS. The measurements were conducted on a Thermo Element 2 ICP-HR-MS.

Solid samples, air samples and urine
Cr in the samples was determined by monitoring ^{53}Cr in medium and high resolution using a ICP-HR-MS while Pb was determined by monitoring ^{208}Pb in low resolution. The measurements were conducted on a Thermo Element 2 ICP-HR-MS.

9.Results and discussion

The concentrations of Cr(VI), Cr(tot) and Pb(tot) found in the different samples are given in tabular form in Appendix 1 together with detailed sample information.

9.1. Air

Air was sampled for consecutive periods of one week during the spring of 2007. The concentration of Cr(VI) in background air (Råö, three samples) varied between <0.016 and 0.047 ng/m^3. In urban air (Stockholm) the concentration in seven of the eight weekly samples varied between 0.019 and 0.055 ng/m^3, which are similar to Råö. However at one sampling occasion the levels in Stockholm reached 0.20 ng/m^3. Higher concentration of Cr(VI) were found close to a point source, a chromium using industry, where concentrations in the range 0.64 – 2.6 ng/m^3 were measured (Figure 4). The median concentrations found in air from background, urban and point source sites were 0.025, 0.039 and 0.97 ng/m^3 respectively.
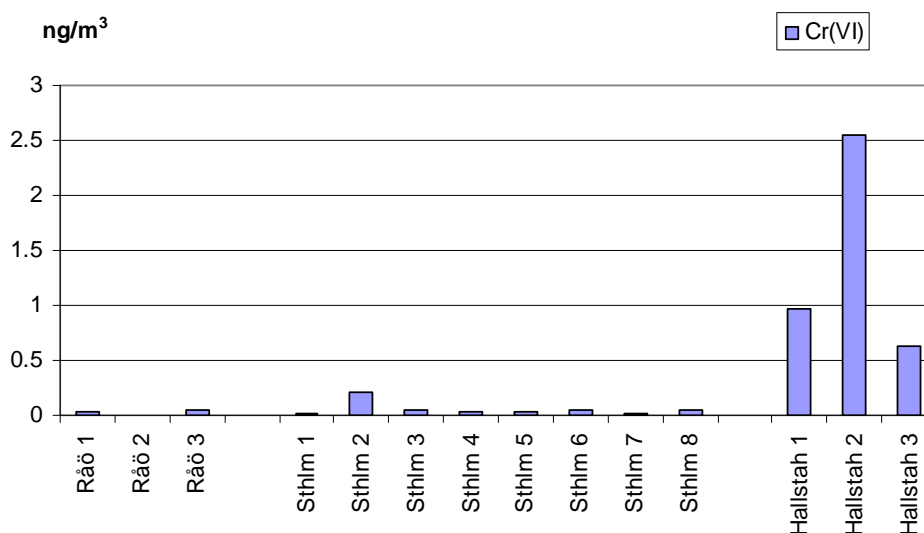

Figure 4.   Cr(VI) concentration in background air (Råö), urban air (Sthlm) and air near a chromium using industry (Hallstah).

The concentration of Cr(tot) in the same samples as presented in Figure 4 are illustrated in Figure 5. The median air concentrations at background, urban and point source sites were 0.38, 2.4 and 29 ng/m^3 respectively. Thus Cr(VI) constituted 1-10 % of Cr(tot) in all samples except one from the point source where Cr(VI) made up 39% of Cr(tot).

Median concentrations of Pb (tot) found in air collected at background, urban and point source sites were 1.2, 4.0 and 17 ng/m^3 respectively (Figure 5).
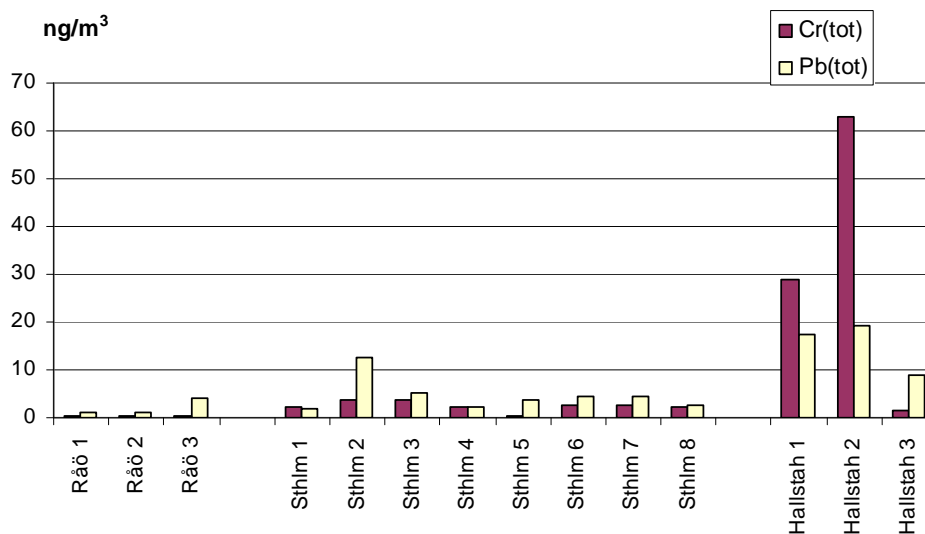
ng/m³

Figure 5. Cr(tot) and Pb(tot)) concentration in background air (Råö), urban air (Sthlm) and air near a chromium using industry (Hallstah).

The atmospheric concentrations of Cr(tot) in urban air (Stockholm) found in this screening (0.3-3.7; median 2.4 ng/m³) are in the same levels as previously have been measured in Stockholm 2003-2004, where the mean concentration of Cr(tot) at roof level was 2.3 ng/m³ (Johansson & Burman, 2006). They are also in agreement with measured levels at two roadside locations in Stockholm 2003 (median 1.9 and 3.0 ng/m³ respectively; Furusjö et al., 2007).

The concentration of Pb in urban air (1.9 – 12.7, median 4.0 ng/m³) is in accordance with the reported annual mean concentration at roof level in Stockholm which was 3.5 ng/m³ in 2004 (SLB, 2007). It is in the same order of magnitude as measured levels near a highway site outside Stockholm in 2003 (median 4.5 ng/m³) where the traffic is even and particle levels mainly influenced by long-range transport, and roughly 3 times lower than measured levels at a heavily trafficked street canyon in the centre of Stockholm (median 13 ng/m³; Furusjö et al., 2007), which is not surprising considering the dispersion effect in the atmosphere; concentrations can be expected to be higher near the traffic than at the roof top level. The mean concentration at roof top level in 2004 (which is similar to our median concentration) is 40% lower than 1996 and 90% lower than 1989, mostly due to the discontinued use of leaded petrol as car fuel (SLB, 2007).

9.2. Precipitation

The concentration range of Cr(VI) in three precipitation samples from the background station Råö was 30 - 90 ng/l with a median of 63 ng/l. In the urban area of Stockholm, a great variation among the four samples was found. The range was 67 - 680 ng/l with a median of 290 ng/l. At Råö, the concentration of Cr(tot) ranged from <40 to 250 ng/l with a median of 160 ng/l. Also the concentration of Cr(tot) showed a large variation in Stockholm (180 - 5 300 ng/l) with a median of 770 ng/l (Figure 6). The ratio Cr(VI) to Cr(tot) was 0.36 – 0.81 at Råö and 0.37 – 0.75 in Stockholm with the exception of the sample with the highest Cr(tot) where the ratio was only 0.04. Thus, the Cr(VI) to Cr(tot) ratio was usually higher in precipitation than in air.
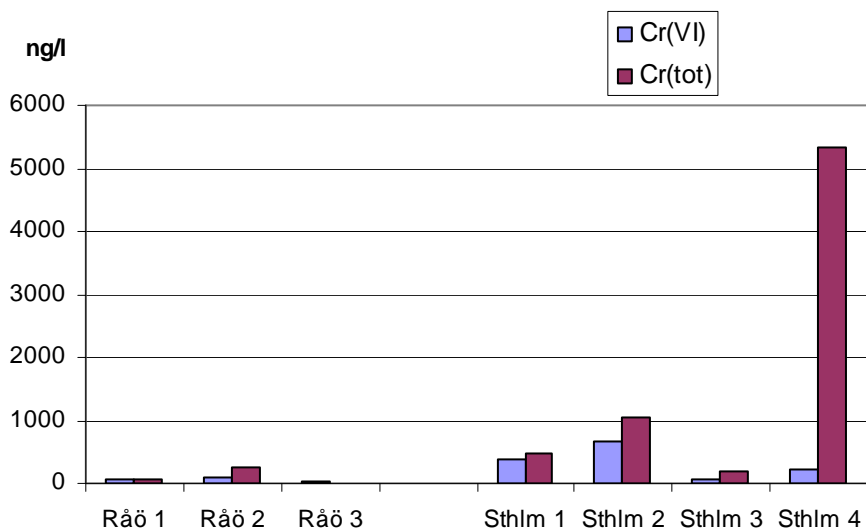
Figure 6. Cr(VI) and Cr(tot) in precipitation at Råö and Stockholm .

The concentration of Pb in precipitation is presented in Figure 7.
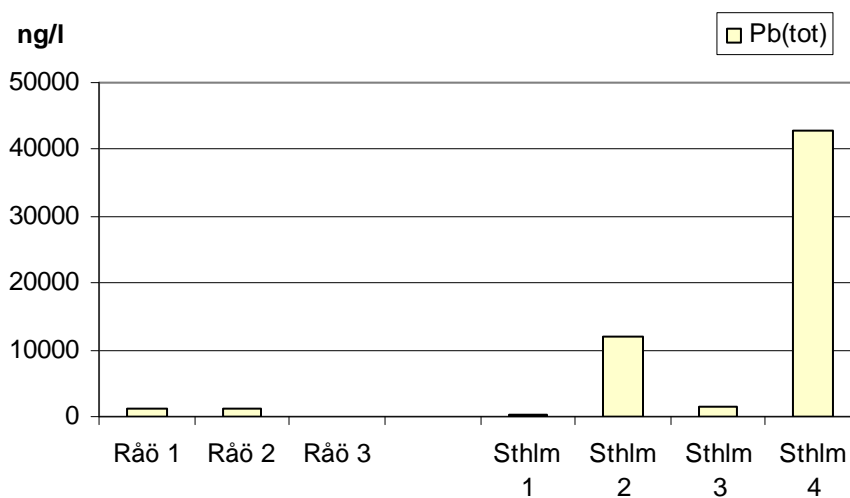

Figure 7. Pb(tot) in precipitation at Råö and Stockholm .

A previous study on the chromium concentration (no speciation) in precipitation from Stockholm indicated a weighted year-average concentration of 0.054 μg/l during the period 2003-2004 (Johansson & Burman, 2006). The corresponding lead concentration reported in that study was 0.9 μg/l (weighted year-average concentration). It should be noted that different sampling devices were used in the different studies, which may affect the deposition rates.

In the precipitation samples from Stockholm there seemed to be a correlation between the total chromium- and the total lead concentrations (Figure 8). Despite the low number of data points, it cannot be ruled out that this correlation may be an indication that the content of these two metals in the samples partly have the same origin.
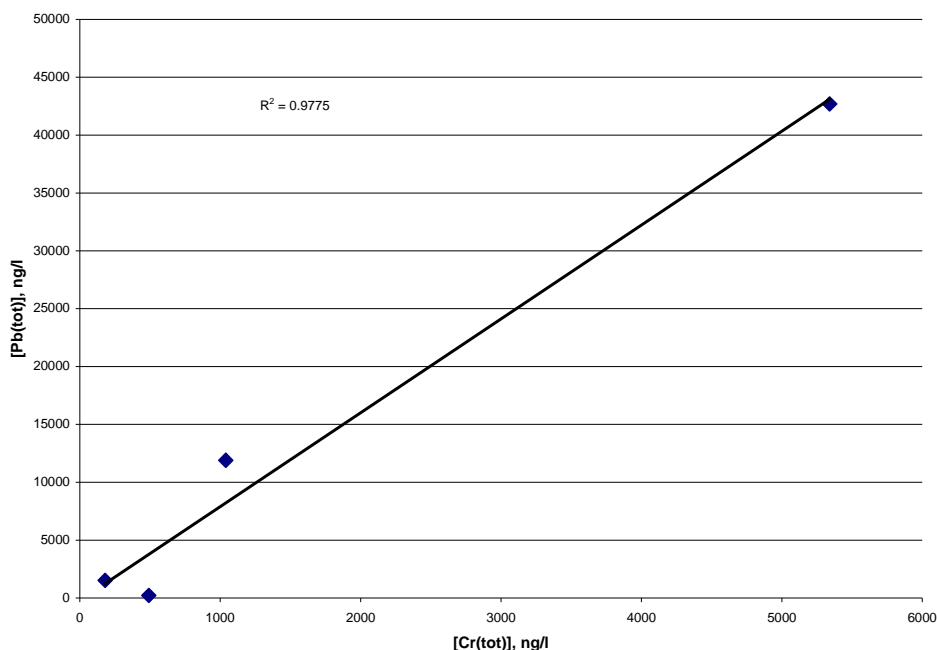

Figure 8. Concentration of Pb(tot) vs. Cr(tot) in precipitation from urban Stockholm.

9.3. Surface water

The Cr(VI) concentration in surface water samples collected in background lakes was 150 -160 ng/l. Surface water samples from the urban area showed slightly higher concentrations (210 - 270 ng/l) compared to the lakes from background areas (Figure 9). The corresponding Cr(tot) concentrations were similar in background and urban waters: 230 - 340 ng/l in background lakes and 230 - 350 ng/l in Stockholm. The ratio Cr(VI) to Cr(tot) was 0.46 - 1.

All surface water samples were within the range specified by the Swedish EPA regarding background concentrations Cr(tot) in ground water (0.1 – 1 μg/l). The concentrations of Cr(tot) were like precipitation in the same levels as previously reported from Swedish measurements (see Figure 3 and Figure 9).
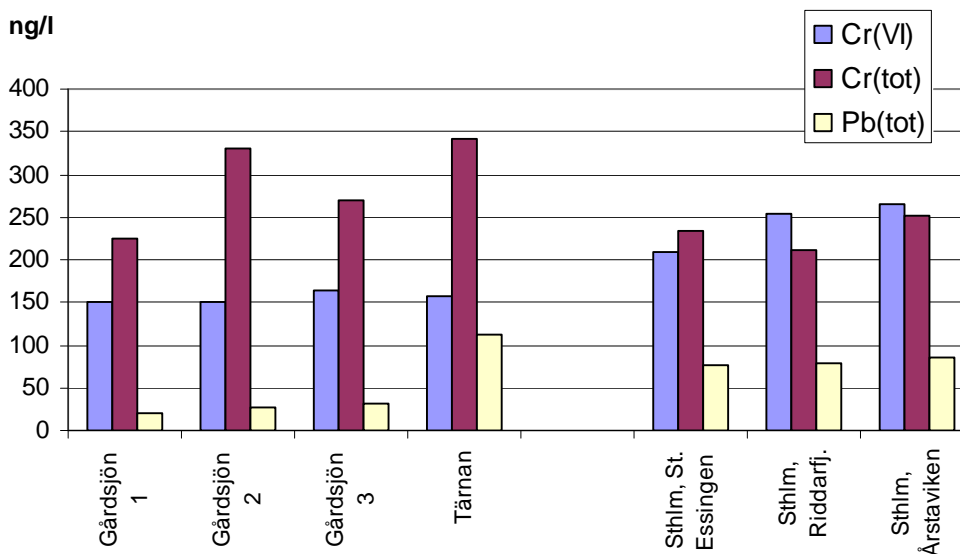
Figure 9. Cr(VI), Cr(tot) and Pb(tot)- concentrations in surface water.

9.4. Sediment

Cr(VI) was not detected in sediment samples from lake Gårdsjön (<0.0012 μg/g dw), a reference lake at the Swedish west coast. The sediment sample from Riddarfjärden in Stockholm contained higher concentrations (0.10 μg/g dw) compared to the other urban sites (0.002 - 0.003 μg/g dw) (Figure 10).
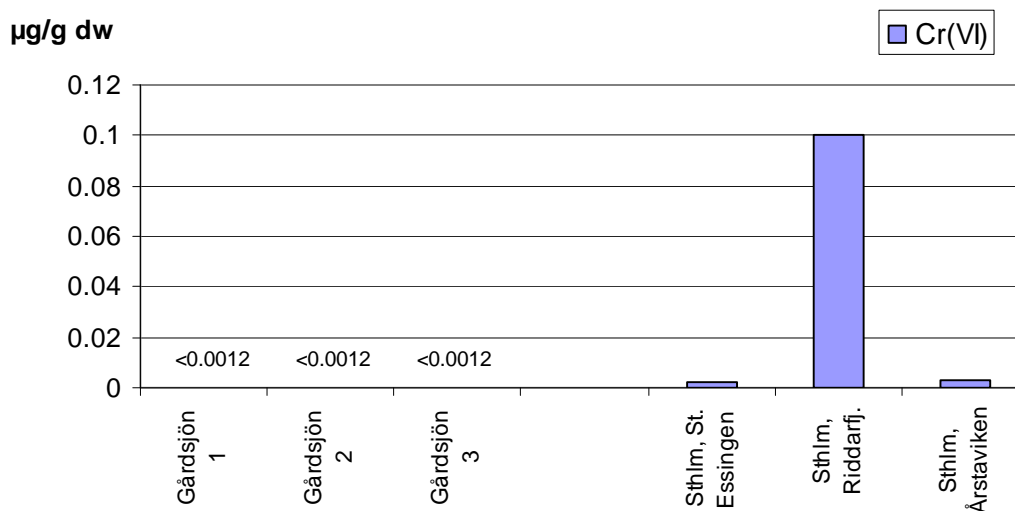

Figure 10. Cr(VI) in sediment from a background lake and urban Stockholm.

The concentrations of Cr(tot) in the same sediments are illustrated in Figure 11. Cr(tot) ranged between 0.85 and 5.6 μg/g dw in Gårdsjön and between 10 and 25 μg/g dw in Stockholm. Thus,

Cr(VI) constituted only a very small fraction of Cr(tot) in the Stockholm samples, corresponding to 0.01 - 0.5 %.

The sediment concentrations of Cr(tot) in Lake Gårdsjön are "very low" and in Stockholm "low" to "moderately high" according to the Swedish EPA (Naturvårdsverket, 2000). It can also be noted that surface sediments from the same area in Stockholm sampled 1996 showed considerably higher concentrations: Cr(tot) 53 - 93 µg/g dw, Pb(tot) 120 - 360 µg/g dw (Östlund et al , 1998).
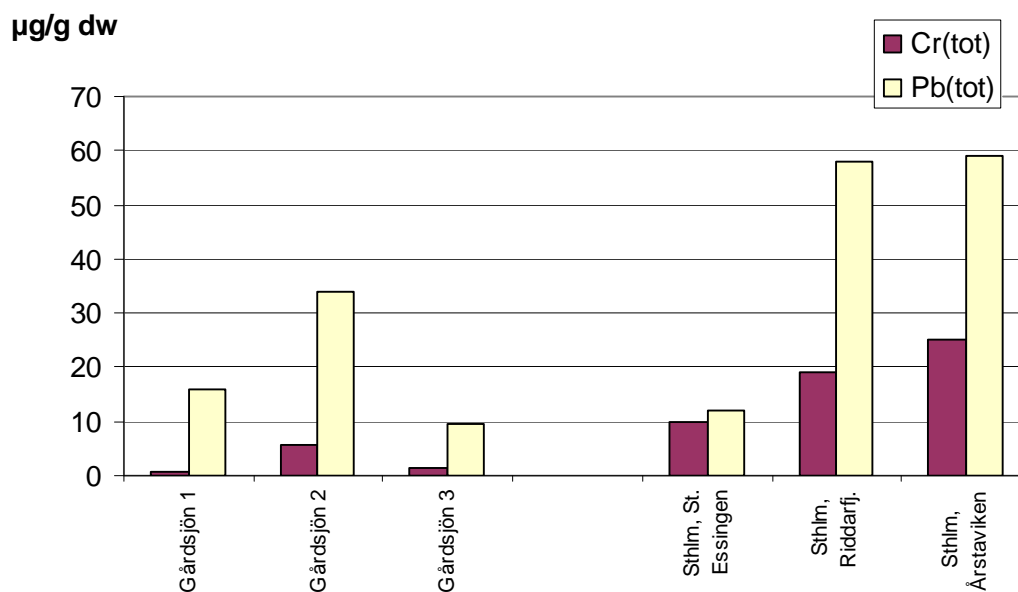
Figure 11. Cr(tot) and Pb(tot) in sediment from a background lake and urban Stockholm.

9.5. Soil

The Cr(VI) concentration in soil in the area close to lake Gårdsjön (background) varied between 0.0079 and 0.022 µg/g dw. In the Humlegården park in the centre of Stockholm, the concentration in soil was 0.056 µg/g dw. Additional samples from the Stockhom area, which were collected 5 km (Årstafältet) and 17 km (Vårberg) from the centre, showed concentrations of 0.033 and 0.042 µg/g dw respectively. In three soil samples collected at the point source area a greater variation was found: 0.0023 - 0.13 µg/g dw (Figure 12).

Figure 12.   Cr(VI) in soil from background station, urban Stockholm and point source.

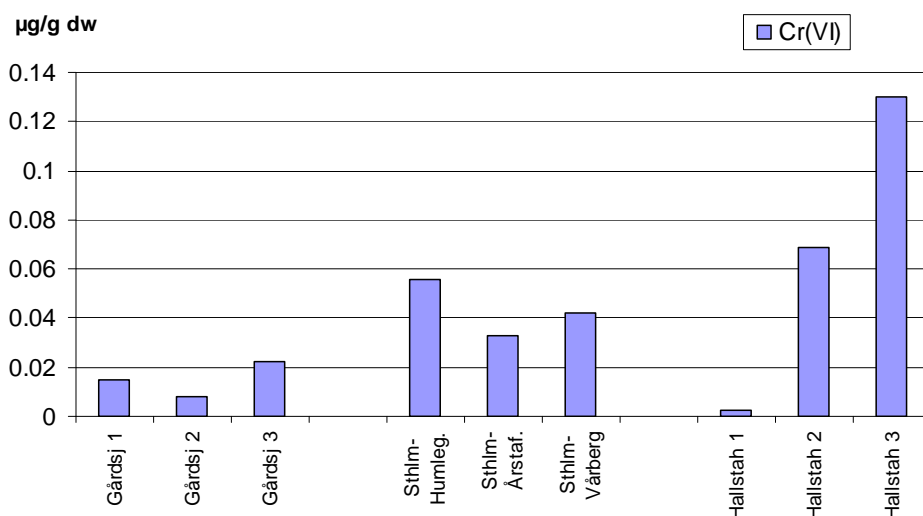The concentrations of Cr(tot) in the soil samples are illustrated in Figure 13. Cr(VI) constituted 0.33 - 1.5 % of Cr(tot) in the background soil, 0.024 - 0.031 % in urban soil and 0.001 - 0.16 % at the point source.
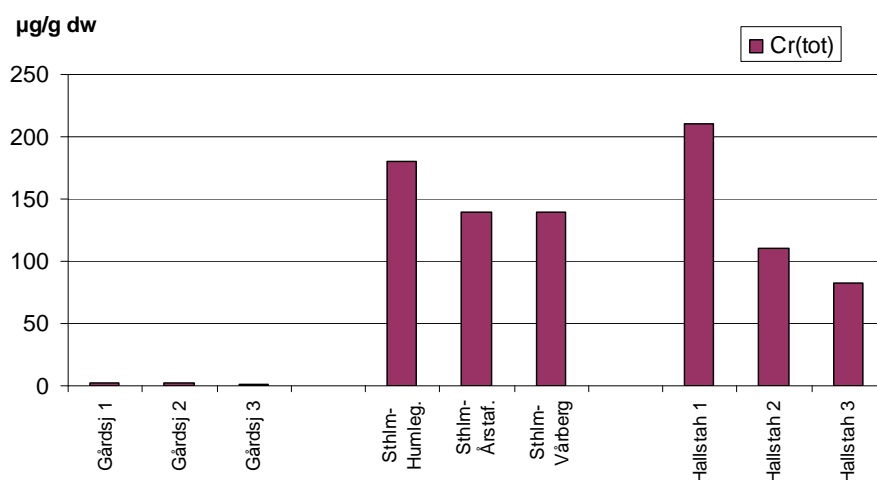
Figure 13.   Cr(tot) in soil from background station, urban Stockholm and point source.

The total chromium contents in soil samples from the Hallstahammar point source and from Stockholm were between 83 and 210 mg/kg DW (20-54 mg/kg WW). This can be regarded as elevated concentrations compared to the plough soil contents of chromium in Sweden, see Figure 2. The mapped plogh- and sub soil concentrations previously reported by Eriksson et al for these regions (Figure 2) are reported as "concentrations > 41 mg/kg DW", which in theory could mean any value above 41 mg/kg DW (and thus could potentially be as high as our measured levels). However, considering that the limit value recommended by the Swedish EPA regarding polluted land (Sv. *riktvärde Cr för klassningen förorenad mark*), is 120 mg/kg DW (Naturvårdsverket, 1999b), it does not seem unlikely that the soil concentrations of Hallstahammar and Stockholm reported herein are the result of human activities and industrial emissions.

9.6. STP sludge

Sludge samples from six municipal sewage treatment plants were included in the screening. The STPs varied in size from 644 000 to 2 200 p e. The Cr(VI) concentration found in the sludge samples from the different STPs was fairly constant (0.0071 - 0.016 µg/g dw) and independent of STP size (Figure 14).

µg/g dw
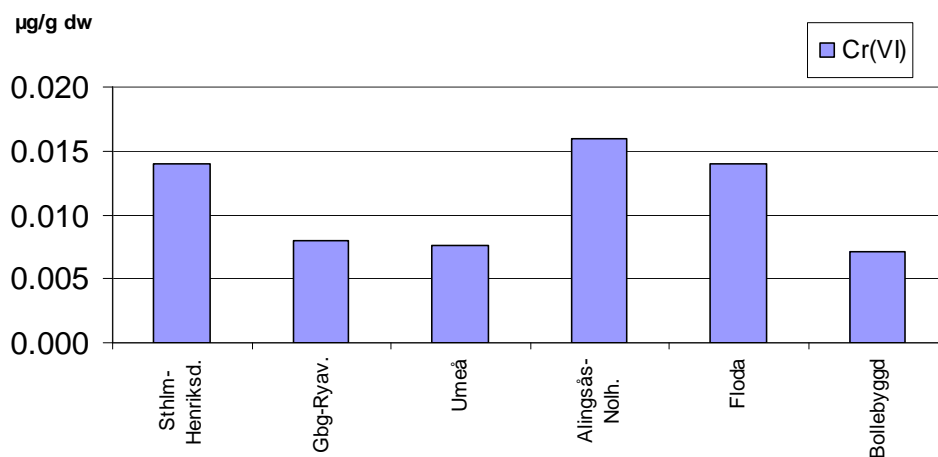
Figure 14. Concentration of Cr(VI) in STP sludge. The STPs are ordered according to decreasing size.

The Cr(tot) concentration was considerably lower in the sludge from the two smallest STPs (0.26 - 1.4 µg/g dw) than in the larger ones (9.6 - 14 µg/g dw) (Figure 15). Thus the ratio Cr(VI) to Cr(tot) was 0.01 – 0.027 in the small STPs but 0.0007 - 0.0015 in the larger ones.
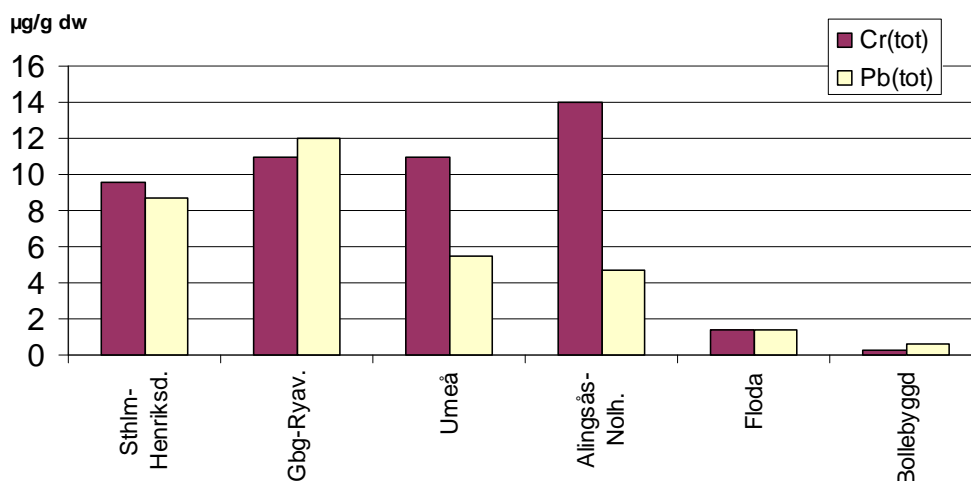
µg/g dw

Figure 15. Concentration of Cr(tot) and Pb(tot) in STP sludge. The STPs are ordered according to decreasing size.

The national mean concentrations of Cr and Pb in STP sludge in 2002 were 29.7 and 30.7 ug/g dw respectively. There was no large difference between small and large STPs (SCB, 2004).

9.7. Biota

The Cr(VI) concentration in fish muscle (perch) from three of the four background lakes and from the three sites within the Stockholm area was between 3.1 and 5.2 µg/kg ww, while the concentration in fish from the fourth background lake was higher: 17 µg/kg ww (Figure 16).

µg/kg ww
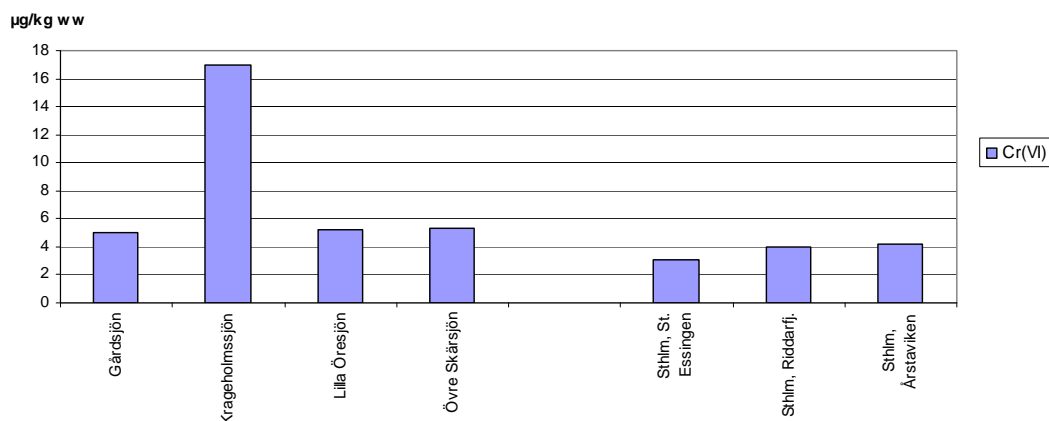
Figure 16. Cr(VI) content in fish from the background lakes and urban Stockholm

The concentrations of Cr(tot) and Pb(tot) in fish are illustrated in Figure 17. The variation in Cr(tot) concentrations was high (2.5 - 39 µg/g dw) with the highest concentration found in fish from background lakes. Pb(tot) was not detected in the fish samples collected in the Stockholm area (<2 µg/kg ww) while the background fish samples contained Pb concentrations between 4 and 25 µg/kg ww. The redox potential and pH of the water systems where fish has been sampled may influence the bioavailability of these metals and could possibly explain these results. The Cr(VI) / Cr(tot) ratio also varied a lot: 14 - 100 %. The fish sample from Lake Gårdsjön showed a ratio of 200 % which could be explained by analytical uncertainty close to the detection limit which was 2 µg/kg ww for both Cr(VI) and Cr(tot).
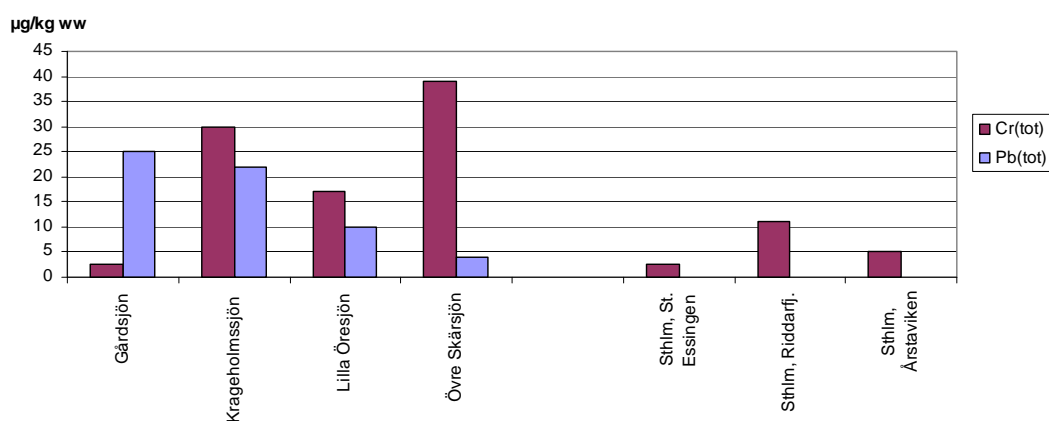
µg/kg ww

Figure 17. Cr(tot) and Pb(tot) content in fish from the background lakes and urban Stockholm

Cr has been reported to only rarely bioaccumulate in fish and in previous studies concentrations in muscle tissue from limnic fish species seldom exceeded 250 µg/kg (probably WW-units, Åhgren et

al., 1996). A extensive study of the metal concentrations in fish (carp bream and perch) and water from Luleå in Sweden indicated average concentrations of Cr(tot) (no speciation) of 46 μg/kg WW (Persöfjärden) and 146 μg/kg WW (Gussön), for muscle tissue of perch. Liver samples of perch and carp bream showed slightly higher concentrations (Byrsten & Sandberg, 2005). When comparing the results from this study with the data reported by Åhgren et al. and by Byrsten & Sandberg, the concentrations of chromium in biota found in the current study appear to be rather low. The reference value for chromium recommended by the Swedish EPA regarding perch (liver) is 100 μg/kg DW, and not easily comparable with the data presented herein as it is based on dry weight (Naturvårdsverket, 1996a-b).

9.8. Human exposure – urine

Out of the six human urine samples Cr(VI) was detected in three (LOD < 0.4 ng/l), in concentrations of 0.4, 0.5 and 0.6 ng/l. None of the other metal parameters (Cr(tot) and Pb(tot)) were detected in urine (LOD Cr(tot) < 0.9 ng/l, LOD Pb(tot) < 1.3 ng/l). Thus, Cr(VI) could be found in human urine, any other conclusions from the chromium content of the urine samples is difficult to draw . Internationally, metals are mostly measured in urine as μg/mg of creatinine. A normal value regarding chromium (Cr(tot) would be 0.01-0.15 μg /mg creatinine and a "normal" creatinine content in urine is 350 - 2250 mg/l (http://www.doctorsdata.com/). If the creatinine concentration, for simplicity, is assumed to be 1000 mg/l in the urine sample, that would correspond to a "normal" chromium concentration of 0.01-0.15 μg/l in urine, thus the urine samples analysed within this study contain low levels of chromium.

10. Risk assessment (MEC/PNEC)

In order to assess whether the concentrations of Cr(VI) and Cr(tot) reported for surface waters in this study pose any risk to the biodiversity of aquatic species a MEC/PNEC-evaluation has been performed. The Health & Consumer Protection Directorate of the European Commission have proposed the following PNEC-values for Cr(III) and Cr(VI) when performing risk assessment of various Cr-salts (CSTEE, 2003);

PNEC$_{WATER}$ (Cr(III)); 4.6 μg/l

PNEC$_{WATER}$ (Cr(VI)); 3.4 μg/l

Data on species endpoints were taken from Crommentuijn et al., 1997.

Location	[Cr(VI)], μg/l	[Cr(tot)], μg/l	MEC/PNEC (Cr(VI))	MEC/PNEC (Cr(tot))
Gårdsjön 1	0.15	0.23	0.04	0.05
Gårdsjön 2	0.15	0.33	0.04	0.07
Gårdsjön 3	0.16	0.27	0.05	0.06
Tärnan	0.16	0.34	0.05	0.07
Sthlm - St. Essingen	0.21	0.23	0.06	0.05
Sthlm - Riddarfjärden	0.25	0.21	0.08	0.05
Sthlm - Årstaviken	0.26	0.25	0.08	0.06

Since no risk quotient (MEC/PNEC) > 1, the assessment does not indicate any imminent environmental risk associated with the concentrations detected in the surface water samples.

The PNEC-data proposed by the European Commission have been subject to some criticism within the European industry due to uncertainties regarding especially the PNEC-value for Cr(III). Ecotoxicity data from Suter are also commonplace in risk assessments of chromium (Suter GW, 1996a-b). However these data suggest higher PNEC-values (algae, Daphnids and fish) and have thus not been used for the risk assessment herein.

The results reported herein regarding chromium in soil samples indicate substantially elevated concentrations of Cr in urban Stockholm and in the vicinity of a chromium-plating industry, compared to the average background plough layer soil concentration. However, it is very difficult to assess whether these concentrations pose any risk to the biodiversity of the soil since no generally accepted model incorporates soil as a matrix for risk assessment even though the concentrations measured exceed the recommended limit value for polluted land (120 mg/kg DW).

Regarding human exposure to chromium (Cr(VI)), risk assessment methods have been developed based on DNA-protein cross-links as biomarkers of chromium exposure (Chromium-induced DNA-protein crosslinks, DPC). Generally, cross linking of DNA occurs when various exogenous or endogenous agents react with two different positions in the DNA. This can either occur in the same strand (intrastrand crosslink) or in the opposite strands of the DNA (interstrand crosslink), or as a crosslink between DNA and protein. The cross linking agent may not necessary be Cr(VI), also

acrolein and crotonaldehyde are possible agents (Rudd et al., 1995). The methods of assessing risks associated with human chromium exposure using DNA-protein cross-links biomarkers have been evaluated for several professional groups working with metals; welders, subway workers, chrome-platers etc (Zhitkovich et al., 1998). Chromium itself also possess the ability to bind directly to the DNA, Cr(III), form stable Cr(III)-DNA(Cr-DNA) monoadduct which can be used as biomarkers for chromium exposure (Snow ET, 1992). The urine analysis performed within this study may thus not be optimal in estimating the human exposure level.

11. Conclusions

Cr(VI) was found in all analysed environmental sample types. The highest concentrations in air and soil were found in the vicinity of a chromium using industry. The concentrations were in most cases higher in urban than in background areas indicating diffusive spreading. Cr(VI) was found in all analyzed samples of STP sludge which is also and indication of diffusive sources. The ratio Cr(VI) to Cr(tot) varied among the different sample types. The ratio was highest in fish, water and precipitation, lower in air and lowest in solid sample matrices.

Although Cr(tot) is frequently analyzed in environmental investigations, speciation is seldom done. Thus it is not easy to compare our Cr(VI) measurements with earlier data.

Cr(tot) concentrations followed the same general pattern as Cr(VI), i. e. highest near the point source, lower in urban areas (diffusive sources) and lowest in background areas.

Cr(VI) concentrations in fish collected in the urban area was mostly in the same level as in fish from background lakes, occasionally the concentration in the background samples was higher.

Chromium measured in urine is an indication of exposure to hexavalent chromium, but only of the exposure over the last 24 hours. Six urine samples from healthy individuals were analyzed. Low concentrations of Cr(VI) was found in three samples. In the remaining samples Cr(VI) was not detected.

Risk assessments based on the measured surface water concentrations (MECs) and PNEC-values from the literature indicated that the measured aqueous concentrations of Cr(tot) and Cr(VI) did not pose a risk to the environment. Even though one of the PNEC-values used seems highly arguable (Cr(III)) it was chosen since it maximises the MEC/PNEC-quotinent, in consistency with the precautionary principle.

12. Acknowledgement

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Appendix 1. List of samples

MR-nr	Type	Matrix	Site	Information	Unit	Cr(VI)	Cr(tot)	Pb(tot)
5654	Background	Fish	Gårdsjön	perch, 2005 nov.	µg/kg WW	5.0	2.5	25
5243	Background	Fish	Krageholmssjön	perch, 2005 nov.	µg/kg WW	17	30	22
5244	Background	Fish	Lilla Öresjön	perch, 2005 nov.	µg/kg WW	5.2	17	10
5245	Background	Fish	Övre Skärsjön	perch, 2005 nov.	µg/kg WW	5.3	39	4.0
5527	Urban	Fish	St. Essingen	perch, 2005 nov.	µg/kg WW	3.1	2.7	<2.3
5528	Urban	Fish	Årstaviken	perch, 2005 nov.	µg/kg WW	4.2	5.1	<2.3
5526	Urban	Fish	Riddarfjärden	perch, 2005 nov.	µg/kg WW	4.0	11	<2.3
5224	Diffuse	Sludge	Henriksdal-Sthlm	644 000 p e	µg/g DW	0.014	9.659	8.74
5221	Diffuse	Sludge	Ryaverket-Gbg	605 000 p e	µg/g DW	0.008	110.9	12.3
5220	Diffuse	Sludge	Umeå	98 000 p e	µg/g DW	0.0076	110.6	5.548
5223	Diffuse	Sludge	Nolhaga-Allingsås	24 000 p e	µg/g DW	0.016	143.7	4.766
5222	Diffuse	Sludge	Floda	9 800 p e	µg/g DW	0.014	1.44	1.439
5225	Diffuse	Sludge	Bollebyggd	2 200 p e	µg/g DW	0.0071	0.26	0.6545
5296	Urban	Sediment	Riddarfjärden	061205	µg/g DW	0.10	19	58
5287	Urban	Sediment	St. Essingen	061205	µg/g DW	0.0021	10	12
5288	Urban	Sediment	Årstaviken	061205	µg/g DW	0.0028	25	59
5206	Background	Sediment	Gårdssjön1	061026	µg/g DW	<0.0012	0.85	16
5207	Background	Sediment	Gårdssjön2	061026	µg/g DW	<0.0012	5.6	34
5205	Background	Sediment	Gårdssjön3	061026	µg/g DW	<0.0012	1.4	9.4
5373a	Background	Soil	Gårdssjön1	06-dec	µg/g DW	0.015	2.7	16
5373b	Background	Soil	Gårdssjön2	06-dec	µg/g DW	0.0079	2.4	20
5373c	Background	Soil	Gårdssjön3	06-dec	µg/g DW	0.022	1.5	19
5553a	Point Source	Soil	Hallstahammar1	070320	µg/g DW	0.0023	210	910
5553b	Point Source	Soil	Hallstahammar2	070320	µg/g DW	0.069	110	45
5553c	Point Source	Soil	Hallstahammar3	070320	µg/g DW	0.13	83	82
5555	Urban	Soil	Vårberg-Sthlm	070327	µg/g DW	0.042	140	190
5561	Urban	Soil	Humlegården-Sthlm	070629	µg/g DW	0.056	180	110
5574	Urban	Soil	Årstafältet-Sthlm	07-april	µg/g DW	0.033	140	200
5202	Background	Surface water	Gårdsjön1	06-nov	ng/l	150	230	20
5203	Background	Surface water	Gårdsjön2	06-nov	ng/l	150	330	27
5204	Background	Surface water	Gårdsjön3	06-nov	ng/l	160	270	31
5563	Background	Surface water	Tärnan	070324	ng/l	160	340	110
5290	Urban	Surface water	Sthlm, St. Essingen	06-dec	ng/l	210	230	76

MR-nr	Type	Matrix	Site	Information	Unit	Cr(VI)	Cr(tot)	Pb(tot)
5293	Urban	Surface water	Sthlm, Riddarfjärden	06-dec	ng/l	250	210	80
5291	Urban	Surface water	Sthlm, Årstaviken	061205	ng/l	270	250	85
5582	Background	Precipitation	Råö1	070219-0305	ng/l	63	78	1100
5583	Background	Precipitation	Råö2	070305-12	ng/l	90	250	1300
5584	Background	Precipitation	Råö3	070312-19	ng/l	30	<40	110
5399	Urban	Precipitation	Stockholm1	070112-19	ng/l	370	490	230
5420	Urban	Precipitation	Stockholm2	070119-29	ng/l	680	1000	12000
5479	Urban	Precipitation	Stockholm3	070216-23	ng/l	67	180	1500
5576	Urban	Precipitation	Stockholm4	070406-13	ng/l	220	5300	43000
5644	Background	Air-particles	Råö 1	070410-0416	ng/m^3	0.025	0.38	1.2
5645	Background	Air-particles	Råö 2	070416-0423	ng/m^3	<0.016	0.30	1.1
5646	Background	Air-particles	Råö 3	070423-0430	ng/m^3	0.047	0.54	4.2
5650	Point Source	Air-particles	Hallstahammar 1	070320-0326	ng/m^3	0.97	29	17
5651	Point Source	Air-particles	Hallstahammar 2	070327-0403	ng/m^3	2.6	63	19
5652	Point Source	Air-particles	Hallstahammar 3	070403-0411	ng/m^3	0.64	1.7	9.0
5554	Urban	Air-particles	Stockholm 1, roof top	070316-0323	ng/m^3	0.019	2.2	1.9
5562	Urban	Air-particles	Stockholm 2, roof top	070323-0330	ng/m^3	0.20	3.7	13
5573	Urban	Air-particles	Stockholm 3, roof top	070330-0406	ng/m^3	0.047	3.6	5.2
5575	Urban	Air-particles	Stockholm 4, roof top	070406-0413	ng/m^3	0.026	2.1	2.2
5639	Urban	Air-particles	Stockholm 5, roof top	070413-0420	ng/m^3	0.030	0.32	3.6
5648	Urban	Air-particles	Stockholm 6, roof top	070420-0427	ng/m^3	0.054	2.6	4.4
5649	Urban	Air-particles	Stockholm 7, roof top	070427-0504	ng/m^3	0.023	2.5	4.4
5730	Urban	Air-particles	Stockholm 8, roof top	070504-0511	ng/m^3	0.055	2.2	2.6
5383	Human exps.	Urine	woman, age 51	06-dec	ng/l	<0.4	<0.9	<1.3
5382	Human exps.	Urine	woman, age 34	06-dec	ng/l	0.60	<0.9	<1.3
5385	Human exps.	Urine	woman, age 44	06-dec	ng/l	<0.4	<0.9	<1.3
5386	Human exps.	Urine	woman, age 39	06-dec	ng/l	<0.4	<0.9	<1.3
5384	Human exps.	Urine	woman, age 39	06-dec	ng/l	0.49	<0.9	<1.3
5387	Human exps.	Urine	woman, age 51	06-dec	ng/l	0.44	<0.9	<1.3