Chromium, Nickel and Molybdenum In Society and the Environment

A Compilation of Facts on Flows, Quantities and Effects in Sweden

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Contents

1

Objective

Several proposals or demands have been raised by various authorities with a view to making radical changes in the use of metals in Sweden. At the same time, it has on various occasions been noted that the demand for knowledge of metals in society and the environment is still very great. For instance, the Commission for the Recycling of Materials (2) has, among other things noted that: *‘An increased knowledge of metals, of where metals are used, and of where diffused emissions of mainly toxic metals take place is needed’*.

Again, in the research programme for the project ‘Metals in town and country’ initiated by the Swedish Environmental Protection agency, it was remarked that:

‘The use of metals in goods and products has also increased, which has resulted in an increased accumulation of metals in the technosphere and in the urban environment. As the quantities of metals increase in those environments, the risks for the ecosystems and for human health also increase. Knowledge of how

fast this accumulation is taking place, and of present and future risks is, however, very scarce.'

By far the main use of chromium, nickel and molybdenum is in alloys of various kinds, mainly stainless steel. Existing surveys on these metals do not give any overall picture of their production, use, distribution or effects in the Swedish environment.

On the initiative of the Federation of Swedish Industries, a number of industrial organisations (the Association of Chemical Industries, the Ironmasters Association, the Mine Owners Association, the Scandinavian Copper Development Association and the Nordic Galvanising Association) and companies in the metal business agreed to form a 'Metals Information Task Force' (MITF), with the purpose, of compiling facts on some metals. The metals included in the project are zinc, copper and chromium/nickel/molybdenum.

The Environmental Research Group (MFG) has been detailed to collect and compile relevant material and to carry out a survey of facts in the form of three separate reports.

In June 1997, the Swedish Environmental Protection Agency and the MITF agreed to appoint a joint reference group, in which the National Chemicals Inspectorate was invited to participate. The purpose of the reference group was to discuss and scrutinise these three surveys before publication. The reference group also noted that the surveys are expected to be important bases for ongoing work in setting targets and actions regarding the use of metals in society.

In order to carry out a comprehensive, scientific evaluation of the surveys, the Reference Group appointed a panel consisting of five external specialists representing expert knowledge in the following areas: metals in the terrestrial environment, aquatic environment, human toxicology, as well as technical and energy-related aspects.

The Reference Group for Metals Surveys has had the following members:

Appointed by:

The Swedish Environmental Protection Agency	Staffan Lagergren, NV Husamuddin Ahmadzai, NV/Nefco Kjell Johansson, NV/SLU Hans Borg, ITM, University of Stockholm
National Chemicals Inspectorate	Ingela Andersson, KemI
MITF	Karl-Axel Waplan, Boliden AB Rolf Sundberg, SCDA/Outokumpu Birgitta Lindblad, Jernkontoret Hans Eriksson, Nordisk Zinkinfo
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Molybdenum-related extracts from the Swedish MITF Report
(compiled by IMOA)

1. Several proposals or demands have been raised by various authorities with a view to making radical changes in the use of metals in Sweden.

2.'An increased knowledge of metals, of where metals are used, and of where diffused emissions of mainly toxic metals take place is needed'.

3.'The use of metals in goods and products has also increased, which has resulted in an increased accumulation of metals in the technosphere and in the urban environment. As the quantities of metals increase in those environments, the risks for the ecosystems and for human health also increase. Knowledge of how fast this accumulation is taking place, and of present and future risks is, however, very scarce.'

4. The lack of data on the presence of molybdenum in various materials means that estimates of diffusion to the external environment have been made mainly for chromium and nickel.

5. The content of chromium and nickel in local authority waste water sludge clearly shows a decreasing trend during the last 15 years. The sludge contained about 7 t of chromium and 3 t of nickel during the 1990s. Of this quantity about one third is used in agriculture, corresponding to 2.5 t of chromium and 1.1 t of nickel respectively. The net inflow of chromium and nickel to farming land has been estimated at about 54 t of chromium and about 20 t of nickel respectively per year.

6. Total chromium, nickel and molybdenum emission from society, including agricultural land and waste tips, to air and water in Sweden can be totalled to about 90 t of chromium, 65 t of nickel, and about 19 t of molybdenum per year, of which about 49 t of chromium, about 61 t of nickel and about 11 t of molybdenum originate from point sources.

7. Point sources for emission of the above metals and their compounds are mainly connected with various industrial activities, where metals are produced or handled. However, local authority waste water works and plants for the incineration of waste and other fuels (for instance oil, wood and peat) are also regarded as point sources.

Production of low and high alloy steel and iron-free or low-iron special alloys from primary or secondary metals (scrap).
Production of low or high alloy castings.
Production and use of metal chemicals.

8. Among the sources that can cause man-made diffusion to the environment are the following:

Transfer of chromium, nickel and molybdenum to farming land with fertilisers or manure and diffusion of waste water sludge from local authorities
Transfer from car workshops and car washes to the local authority waste water and/or surface water.

9. Table 6.4 Trace elements (mg/kg dry weight) in various slag types at Swedish iron works (from Fällman, 1995)

	Avesta Sheffield AB	Sandvik AB (AS)	Fundia AB Mo I Rana	Fundia AB Smedjeb.	Sandvik AB (OL)	Sandvik AB (LL)	SSAV Oxelö-sund H	SSAB Oxelö-sund LD
Cr	24400	22500	8600	7800	11900	13100	8	700
Cu	36	19	388	166	55	31	7	16
Ni	520	490	130	50	30	50	2	10
Mo	130	80	6	20	6	20	-	-

AS concentration slag (high alloy) OL non-alloy slag LL low alloy slag
H slag LD converter slag

10. An estimate of accumulated quantities cannot be made because of the lack of data on slag quantities and composition during various periods of production at Swedish steelworks. Investigations made so far regarding leaching of, chromium, nickel and molybdenum from tipped slag and from roads where slag has been used, shows that the leakage of metals is of minor importance (Waterson, 1997).

11. According to a smaller investigation made by Gryab in Gothenburg, the contents of chromium and nickel varied between <1 µg Cr/l and 50 µg Cr/l and between <2.3 µg Ni/l and 50 µg Ni/l respectively in the surface water from four areas (Matsson, 1998). Detectable contents of molybdenum in surface water (2.2 µg/l) were reported from a study (ref in Göthburg, 1993). On two other occasions the molybdenum content was below the detection limit.

12. No analytical results are available regarding molybdenum contents in the above material. Randahl et al (1997) reported that the largest concentration of molybdenum had been found in asphalt and crude oil. Reported chromium, nickel and molybdenum

contents in crude oil are 34 mg Cr/kg, 570 mg Ni/kg and 17 mg Mo/kg (Yen, 1975). The contents certainly varied depending on the origin of the crude oil.

13. Finally, there is a transfer of chromium, nickel and molybdenum to the external environment through, mainly, wear of railroad rails. The wear of rails has been estimated at approx 0.2 mm/year (Inexa Profile, 1997). The wear, however, varies considerably, depending on curve radius, load etc. Average chromium, nickel and molybdenum contents are 400 mg Cr/kg, 380 mg Ni/kg and 3 mg Mo/kg. The total railroad length is 25,000 km. Assuming that 5 cm rail width is exposed to wear, the total quantity of emitted chromium and nickel will be approx 1,000 kg each and about 100 kg of molybdenum per year. The emitted metal particles are probably found in some 20 or 30 metres of the railroad tracks.

14. Diffused emissions via local authority waste sludge

In 1992 a total of 230,000 t dry weight of sludge was produced in Sweden. The sludge contained slightly more than 7 t of chromium and about 3 t of nickel, according to chromium and nickel quantities presented in Fig 6.6. According to the above assumption (50% reduction of molybdenum in the treatment plant), about 1.2 t of molybdenum is transferred to sludge.

At the 25 largest treatment plants in Sweden, which includes about half of the connected population, the metal contents in the sludge were in most cases lower than the highest allowable contents for use of the sludge in agriculture. There is presently no limit value for the molybdenum content in the sludge. Most of the treatment plants did cope with the stricter limits that applied from 1988 (see Table 6.17).
Sweden has some of the world’s most stringent limits on the content of heavy metals in waste sludge. Public opinion strongly influences the use of sludge as soil fertiliser, which can cause difficulties for the use of sludge in the agricultural industry (Stockholm Water, 1996).

Sources	Total to the environment			Direct to the aquatic environment			Note
	Cr	Ni	Mo	Cr	Ni	Mo	
Point Sources							
Industries and incineration to Air	<24	26	>0.5				A
Industries and local authorities to water (incl. 150 connected deposits and 20 % day-water from combined system)	<23	<33	10.5	<23	<33	10.5	B
Leakage from process waste	<2	<2		<1	<1		C
Sum of Point Sources	49	61	11	24	34	10.5	
Diffuse Point Sources							
Emissions from unconnected households	0.4	1.5	0.2				D
Local authorities, separate surface-water ducts (80 %)	2.4	2.4	0.4-0.6	2.4	2.4	0.4-0.6	E
Domestic waste (leakage from unconnected and closed tips)	1.4	4.2		<1.4	<4.2		F
Agricultural sector	1.7	9.4		<1.7	<9.4		G
Road traffic, road wear	61	33					H
d:o brake linings	(2)	(6)					I
d:o car tyres	1.8	1.7					J
d:o fuels	0.5	0.5					K
d:o wear of rails	1	1	0.1				L
Road traffic (subtotal) (abt.)	67	44					
Stainless steel	2.9	1.7					M
Surface coated surfaces	0.8	1.2					N
Paints/pigments	0.3						O
Wood impregnation agents	12.5						P
Concrete / cement	<1	<1					R
Sum of diffused sources (c.)	90	65	>0.7-0.9				
Total from human activities	206	126	>14	30	50	>11	
Natural flow							
d:o air (avge)	44	30	3				S
d:o water (avge)	>26	>79	>18	>26	>79	>18	T
Sum of Natural Flow (c.)	>70	>109	>21	>26	>79	>18	

15. At Avesta Sheffield, moss samples were taken in 1971 and in 1993. Compared to the investigation of 1971 (which did not include nickel), the contents of chromium and molybdenum were considerably lower in 1990. In the more exposed areas, the contents were reduced to less than 1/10 of the previous values (Rühling, 1993).

The contents of chromium, molybdenum and nickel in the moss decreased rapidly with distance from the steelworks. The increased precipitation in the 1993 investigation can be seen up to about 15 km from the plant (see Fig 7.4).

16.

7.2.4 Actual Content in Humus in Forested and Open land in Areas Close to Major Emission Sources

Steelworks

The contents of chromium, nickel and molybdenum in the ground have been investigated around some major emission sources.

An investigation was made at Sandvik AB in 1991 (Walterson, 1992). Total and 'bio-accessible' contents of chromium, nickel and molybdenum in the humus layer in forested land around the steelworks is shown in Fig 7.6. In this investigation, the easily-accessible fraction was determined by leaching of the new humus sample buffered with ammonium-acetate solution for four hours to the same pH as was measured in the original samples.

At sites with low pH values, the accessible proportion of chromium and nickel in absolute numbers was larger than at the sampling sites with the highest measured pH values in the new humus. Despite the total quantities being lower, the percentage 'bio-accessible' proportion of molybdenum is, however, higher at the place with the highest accessible pH value (1.2% at pH = 5.39) and lowest at the lowest pH value (0% at pH = 3.08).

In connection with studies of the effects of metals on the decomposition processes in forested land at the end of the 1970s, chromium, nickel and molybdenum in the humus layer have been surveyed in the environment of Ferrolegeringar in Trollhättan and the steelworks in Avesta (Rühling & Tyler, 1979). The investigated area at Avesta is mainly located in a sector north-west/north-east from the town centre. The investigated area at Trollhättan is situated mainly in a sector west/south-west from the northern part of the town, ie in an area where the deposition from Vargön Alloys AB also contributes to the metal contents in the new humus. The results from these investigations are shown in Table 7.5.

Ferrolegeringar in Trollhättan was closed down in 1991. A new investigation of metal contents in new humus took place in 1991, east of Vänersborg, ie in the neighbourhood of Vargön Alloys AB and north-east of Trollhättan (Rühling, 1992). The highest metal contents were measured in an area near to Vargön Alloys AB and near Trollhättan. The chromium, nickel and molybdenum contents varied between 15 and 330 mg Cr/kg dry weight, 9.3 and 15 mg Ni/kg dry weight, and 8.3 and 23 mg Mo/kg dry weight near Vargön. The highest molybdenum content of 28 mg Mo/kg dry weight was measured near Trollhättan.

17
. Steelworks

In recent years apprehension has been expressed that metal leakage from slagtips at Swedish steelworks has contributed to a pronounced burden of the external environment. For this reason, a relatively large number of laboratory tests have taken place during the 1990s in order to find out how large the metal leakage from various types of slag is. At some steelworks the metal contents in leach and groundwater beneath the slagtips have also been measured in the field. One example of results from measurements in the field and various leach tests on slag from Sandvik AB are shown in Table 7.7.

Table 7.7 Contents of chromium, nickel and molybdenum (µg/l) in leach/groundwater samples beneath slag tip in May 1990 and 1993 and in leach liquor from laboratory tests 1993 at Sandvik AB (From: Walterson, 1993[1]; Elander & Fällman, 1993[2])

	Excavated pit in the centre	Well for pumping of leach/groundwater from tip		Shake test[1] L/S2	Column 1 L/S 1.95	Column 2 L/S 2.05	Shake test[2] L/S 5 (regulated pH)
	1993	1990	1993				
Cr	7.6	<10	0.5	41	420	420	610
Ni	10.5	<10	9.7	2.3	<0.20	<0.20	22
Mo	240	-	210	280	180	180	-
pH	12.2	11.9	12.2	-	12.4	12.5	12

18.
8.1 Essential and Non Essential Metals

The potential of metals to cause harmful effects upon organisms is dependent on their ability to influence and react with biological systems. However, many various metals are contained in enzymes, proteins and vitamins of living organisms and therefore play a key role to maintain and control various vital functions.

There seems to be a certain correlation between the occurrence of a substance in nature and its ‘usefulness’. The more common a substance is in the earth’s crust, the higher the probability that by developing during millions of years in one way or another, it is utilised by living organisms in their tissue and/or metabolisms. There are, however, exceptions from this 'rule', for example for aluminium, silicon and titanium.

The essential metals include, among others, iron, manganese, magnesium, copper, zinc, molybdenum, chromium, selenium and cobalt. In the literature there are several references regarding the essential characters of nickel, but at the moment nickel is classified as 'probably essential'.

Molybdenum is required for the catalytic function of the enzymes xanthine-oxidase and aldehyde-oxidase (see also chapter 10). In plants and bacteria molybdenum is contained in several important enzyme systems, among others nitrogenase and nitrate-reductase. Nitrogenase regulates all biological fixing by action on various micro-organisms and nitrate reductors allow plants to use the nitrogen in nitrates. Molybdenum is therefore of crucial importance for all nitrogen metabolisms in nature (Tyler, 1981). Molybdenum has shown itself to be an essential trace element for normal growth of phytoplankton in freshwater environments (USEPA, 1972).

Too large doses of these essential metals can damage organisms of plants and animals in terrestrial and aquatic environments. The situation can be illustrated by the diagram in Fig 8.1, where it is seen that the state of health of the test organisms deteriorates at both very low and very high metal contents in the environment, ie in both cases the organism can be injured or die.

19.
Molybdenum

The occurrence of molybdenum in the ground has been studied to a large extent since the element has a rather unique position among the other trace elements because of its low solubility in acid soils. In alkaline soils molybdenum is, however, quite mobile (see Fig 8.2).

Molybdenum in the ground is mainly associated with iron oxides, probably in the adsorbed phase. Molybdenum adsorbed on freshly precipitated iron hydroxide, is easily exchangeable, but in precipitated phase molybdenum is less soluble and ferrite-molybdite ($Fe_2(MoO_4)_3.8H_2O$) or other slightly soluble Fe-Mo semi-crystalinic forms can occur in alkaline soils. Molybdenum is easily bio-accessible because of high activity on molybdate (MoO_4^{2-}) and under reducing conditions by formation of soluble thio-molybdates, eg MoS_4^{2-} and $MoO_2S_2^{2-}$ (Kabata-Pendisa & Kabata, 1984).

Liming of acid soils increases the bio-accessibility of molybdenum. As an approximation it can be stated that the molybdenum content in crops can increase two to three times if the soil is limed from pH5 to pH6. If the lime addition is increased to pH7, the molybdenum content in the growth is increased several times (Swedish Environmental Protection Agency, 1997). At high lime additions the solubility can, however, decrease because of adsorption to calcium carbonate. Use of molybdenum salts is preferred to liming of soils where pH increase to raise the bio-accessibility of molybdenum is not wanted (Kabata-Pendias & Pendias, 1984).

20.

There are no significant differences between the nickel contents of herring and perch caught in the Baltic. The nickel contents in the livers of herring and sea mussels were about 2.5 times higher in the Kattegat (Fladen) than in the Skagerrak (Väderö Islands). All comparisons must, however, be taken very cautiously since there is no suitable material available from other years. Variation between years occurs without doubt (Bignert, 1997a).

Apart from this, relatively little data on chromium and nickel contents (and also other metals) in fish exists for the sea areas around Sweden. The uncertainty for older analytical data also limits the possibility to comparisons back in time. An investigation of the metal contents in flounder in recent years in the Oxelösund area can be presented here as an example of chromium contents in the neighbourhood of industrial activities and at a 'reference site' (site 6 in Fig 8.9). Flounder feeds on stationary organisms like bivalves in which increased metal contents have been seen. Samples from liver and muscle were taken from three individuals in each group (Walterson, 1991).

From the figures it can be seen that the highest chromium contents, both in liver and muscle, were measured at the 'reference site' (station 6), at the largest difference from the two metal emitters SSAB and C-pipes. The enrichment of chromium in these organs is low. The contents in liver are in some cases lower than in the muscle, which underlines the fact that the flounder has a well developed controlling system for this metal.

21.
Table 9.2 Proposed and/or existing limit values for chromium and nickel (mg/kg soil) in arable land (agricultural) in several European countries.
(From: Witter, 1992)

	Chromium	Nickel
Sweden, proposed MAC value	-	50
UK proposed in 1990, based on toxicity to microbiological activity	120	70
CEC, 1986\	100-150	30-75
Denmark, Ministry of Environment, 1989	30	15
Germany 1990, soils with pH>6	100	30
The Netherlands, 1998	100	35
Switzerland, proposal 1987, based on toxicity to macro microbes	40	-
Switzerland (VSBo, 1992)	75	50

21.
Table 9.3 Estimated total chromium, nickel and molybdenum contents in land which is regarded as toxic to plants according to various authors.
(Source: Kabata-Pendias & Pendias, 1984)

Metal	mg/kg dry weight
Chromium	75-100
Nickel	100
Molybdenum	2-10

Considerable differences between species can be noted when it concerns the metal content that gives toxic effects. Table 9.4 shows chromium, nickel and molybdenum contents (intervals) in parts above ground which, according to various investigations in field and experimentally, has appeared to be toxic, normal or essential for various plants.

Table 9.4 Approximate content levels for chromium, nickel and molybdenum (mg/kg) in tissue of ripe leaves from various plants. (Source: Kabata-Pendias & Pendias, 1984)

Metal	Essential content	Sufficient or normal contents	Exceeding or toxic contents
Chromium		0.1-0.5	5-30
Nickel		0.1-5	10-100
Molybdenum	0.1-0.3	0.2-1	10-50

Remark: Content levels for very sensitive and very tolerant plants are not included in the table.

22.

Molybdenum

Problems with toxic effects on molybdenum for higher animals depend, to a large extent, on the intake not only of molybdenum, but mainly on copper and sulphate. Toxic effects of molybdenum on vertebrates thus vary with species, age, quantity and form of occurrence of molybdenum and copper status and copper intake, inorganic sulphate and total sulphur content in the diet.

Molybdenum acts as an antagonist against copper absorption and retention in the body. This effect is noted in ruminants when the molybdenum content in the forage exceeds 1 mg/kg dry weight (Swedish Environmental Protection Agency, 1997). Among sheep that were grazing on land containing 2.5 times more molybdenum than copper, pathological changes had been seen for 15 -39% of the animals (Friberg & Lenner, 1986).

The tolerance for molybdenum varies to a large extent between various species. Cows and sheep are the most sensitive domestic animals, followed by horses and pigs. Pigs have a very high tolerance to molybdenum. An intake of 1000 mg Mo/kg for three months gave no illness symptoms. This is about 10 - 20 times more than what can be tolerated by other domestic animals. The high tolerance of pigs does not depend on the fact that molybdenum is a bad assimilator, but higher inner tolerance (Swedish Environmental Protection Agency, 1997).

Cattle that were grazing on contaminated land (26 mg Mo/kg) showed the symptoms such as diarrhoea, dehydration, weakness, spinal problems, and high mortality. The molybdenum content in forage varied between 32 and 40 mg Mo/kg. The copper content in the blood of the sick animals was lower than normal (0.28 - 0.38 mg/l) compared with normal concentrations of 0.75 - 1.5 mg Cu/l). In the liver the copper content was measured to <30 mg/kg and the molybdenum content was between 5 and 10 mg/kg wet weight (Randahl et al, 1997).

Animal studies have shown that the effect of a high intake of molybdenum is also affected by the intake of sulphate and copper. Sulphur generally increases the suppression of molybdenum via the kidneys which can increase the toxic effects of molybdenum. There is also information that the biological not accessible contents between molybdenum, copper and sulphur can be formed already in the stomach intestinal canal (Randahl et al, 1997).

23.

Molybdenum

In neutral or alkaline solutions, molybdenum occurs in soluble form. A pronounced positive correlation between the molybdenum contents in water and the hardness of the water has been reported (Randahl et al, 1998).

The basis for assessment of the toxicity of molybdenum to water organisms has for a long time been insufficient. Recently published acute toxic data, according to the EU and OECD recommended 'Base Set for the initial evaluation of new and existing chemicals' for the most common molybdenum compounds are shown in Table 9.5.

Table 9.5 Acute toxicity of molybdenum (mg/l) according to standardised text methods.
(Source: International Molybdenum Association)

Compound	Fish LC_{50}, 96hrs	Daphnia EC_{50}, 48hrs	Alga Growth IC_{50}, 72hrs
Molybdenum trioxide MoO_3	130	150	>100
Molybdenum trioxide, roasted molybdenum concentrate	77	88	>100
Ammonium molybdate $(NH_4)_2Mo_2O_7$	420	140	41
Sodium molybdate $Na_2MoO_4.2H_2O$	7600	330	100

Also organisms living in sea water are less sensitive to molybdenum. Two types of shrimps (Penaeus duorarum and Musidopsis bahisa), one fish species (Cyprinodon variegatus) and oyster (Crassostrea virginica) were exposed to sodium molybdate. The LC_{50}- value amounted for the shrimps and the fish to 1900 and 3000 mg Mo/l respectively. The shell growth for the oysters decreased with 18% at 500 mg Mo/l and with 98% at exposure to 4000 mg Mo/l (Randahl et al, 1998).

Reported values for chronic effects (‘Lowest test EC_{20}, Daphnia) is 360 µg Mo/l (Suter II, 1996).

24.
For molybdenum, USEPA has in its water quality criteria for large lakes proposed a ‘secondary acute value’ of 10,100 µg Mo/l and ‘secondary chronic value’ of 239 µg Mo/l (hardness: 100 mg $CaCO_3$/l), (USEPA, 1993).

25.

10

Effects of Chromium, Nickel and Molybdenum on Humans

Today, very large sections of the population experience low-dosage exposure to the general diffusion of metals and other chemical substances in most environmental media and products.

Exposure via inhalation of chromium, nickel and molybdenum in the urban environment is probably of secondary importance for humans in comparison with other exposure routes (via the food intake and other exposures like cigarette smoke, etc.).

In longer-term skin contacts with chromium compounds or with materials where chromium is contained allergic reactions can occur. People who have developed a chromium allergy have a tendency to be over sensitive to other metals, main to nickel and cobalt. Nickel is the most commonly occurring contact allergy. No information on allergic inconvenience because of skin contact with molybdenum has been given in available literature.

Provisions are the main source of metal exposure to human beings in general. The contents of chromium, nickel and molybdenum in various foodstuffs in Sweden and in other countries are low. One contribution to the oral intake of chromium and nickel is also received by the emission from stainless vessels and vessels of other materials at cooking of food. Various investigations have, however, shown that in comparison with the daily intake of chromium and nickel the contribution from the cooking utensils are negligible.

Another exposure to chromium and nickel can for instance occur by emissions of chromium and nickel from implants of various stainless alloys in the body; the contributions are very low compared to the daily average intake.

The importance of chromium as trace nutrient in humans and animals has been known for about 40 years. Chromium is necessary for an optimal metabolism. Chromium deficiency has been described for humans, apes, rats and mice. The daily need for chromium in humans should be around 50 µg.

The properties of nickel as necessary trace element to human beings are not completely known. Illness caused by nickel deficiency has been observed with chickens, goats, rats and pigs.

Molybdenum is needed for the catalytic function of several enzymes. The recommended daily intake of molybdenum for adults is 75 - 250 µg. Molybdenum deficiency in humans has, however, rarely been noted.

Most frequently occurring damages at increased uptake of chromium are damages to skin and mucus membranes. WHO, International Agency for Research on Cancer (IARC) has assessed that there is sufficient evidence that chromium (VI) compounds are carcinogenic to humans.

The most common effect of exposure to nickel is allergic contact eczema. Acute poisonings are very rare, as for chromium. The most toxic nickel compound is nickel carbonyl. Observed effects are various damages to the respiratory system. IARC has assessed that nickel compounds are carcinogenic while nickel, nickel alloys and welding fumes are possible carcinogens to humans.

High intake of molybdenum via food has been reported to give gout-like symptoms. Excess of molybdenum can lead to disturbances of the copper metabolism, particularly well documented for certain domestic animals. Molybdenum is not included among the substances that IARC has studied with regard to carcinogenic effects.

26.
10.1.2 Exposure via Skin Contact With Products

Molybdenum

No information on allergic disturbances caused by contact with molybdenum, molybdenum compounds and/or molybdenum alloys exists in available literature
27.

10.2.1 Absorption and Secretion
Molybdenum

Hexavalent molybdenum is absorbed in the gastro-intestinal canal. Of water insoluble molybdenum compounds, molybdenum trioxide (MoO_3) is absorbed, but molybdenum disulphide (MoS_2) is not (Browning, 1969). The absorption in the gastro-intestinal canal of man has been reported to be about 50%. The secretion mainly takes place with urine. Some 24 - 29% of injected radio-active molybdenum was secreted with urine in 10 days, while 1 - 6.8% was secreted with faeces (Odell & Cambell, 1972). A 30 day balance study on human beings showed a daily intake of about 100 µg molybdenum, of which 75 µg was secreted in urine. The daily secretion (urine and faeces) was in this test larger than the daily intake (SEPA, 1976).

The quantity of secreted molybdenum in urine is dependent on the sulphate content in the diet. A high sulphate content gives a significantly higher molybdenum secretion by forcing out molybdenum from, for instance, carrier proteins in the body (Odell & Cambell, 1972; SEPA, 1998).

28.

10.2.2 Distribution and Contents in Various Organs in Man

Molybdenum

The content of molybdenum in man, like in mammals, varies considerably and depends, on the intake of molybdenum in food. The daily intake for humans has been estimated at 0.1 - 0.5 mg. Molybdenum is, above all, found in liver, kidney and blood. In the liver half of the molybdenum is found to be outer membranes of the mitochondria. New born children have a low molybdenum content which then increases up to 20 years of age (Friberg et ,1986, etc). In Table 10.6 normal contents of various organs in humans and mammals are shown.

Table 10.6 Normal molybdenum contents (mg/kg dry weight) in various organs. (From Randahl et al, 1998)

Organ	Man	Rat	Chicken
Liver	3.2	1.8	3.6
Kidney	1.6	1.0	4.4
Spleen	0.2	0.52	-
Lung	0.15	0.37	-
Brain	0.14	0.24	-
Muscle	0.14	0.06	0.14

29.

10.4 Effects of Increased Chromium, Nickel and Molybdenum Uptake; Toxic Symptoms

Molybdenum.

Industrial exposure to molybdenum can cause effects on lungs (black lung) and cause pain in joints and the back and headaches.

Excess of molybdenum can cause disturbances of the copper metabolism, which is particularly well documented for certain domestic animals. Excess of molybdenum increases the copper emission from tissues so that copper deficiency can occur and can cause copper deficiency anaemia (ref.). For humans an intake of a diet with high molybdenum content results in a considerable increase of the copper secretion via urine and increased copper content in plasma (Landner, 1998).

Gout-like symptoms have been reported among the population groups in areas with high molybdenum contents in soil (Friberg et al, 1986). In Armenia, where the molybdenum contents in the ground in certain areas was measured at 77 mg/kg soil and the copper contents at 3 mg/kg soil, the inhabitants have shown various illness symptoms (joint pains, liver enlargement, stomach intestinal complaints and kidney diseases).

In this area more than 50% of the food consists of vegetables. The daily intake of the population was between 10 and 15 mg molybdenum and between 5 and 10 mg copper, while in the controlled area the daily intake of molybdenum was estimated at 1 – 2 mg and the copper intake at 10 – 15 mg.

In two various villages that were chosen for a study, 57 people out of 284 and 14 people out of 78 respectively showed one or several of the above symptoms (SEPA, 1997).

An increased intake of molybdenum can theoretically mean increased activity of xanthine-oxidase, with an increased production of uric acid as a consequence, which may be the explanation for the observed gout-like symptoms (Friberg et al 1986).

It is stated in the RTECS database that molybdenum can be carcinogenic. This information is based upon an investigation by Soner (1976) with mice, which were exposed to extremely high doses of molybdenum. The author has, drawn the conclusion that molybdenum trioxide should be regarded as a weak carcinogenic for lung tumours in this type of test on mice. In 1981 USEPA questioned the value of the above investigation regarding molybdenum, after having found that the immune defence had been weakened at the test conditions (Wallén, 1995).

Molybdenum is not included among the substances which IARC has evaluated for carcinogenic effects.

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11.3 Environmental and Human Exposure and Effects of Chromium, Nickel and Molybdenum in Sweden

11.3.1 Risks of Effects on the Environment

Since chromium and molybdenum but also nickel are essential trace elements to number of organisms, plants, animals and humans have developed systems to control the assimilation and secretion of these. The uptake of metals in the organisms is besides controlled to a high extent by a series of environmental factors, which ultimately determine the mobility and bio-accessibility of the trace metals.

The survey of available information material has shown that the contents of chromium, nickel and molybdenum in the ground, water, plants and animals in Sweden generally are at such a level that there is no risk of negative effects. Exceptions to this general picture are the areas near the largest emission sources for metals , where at times high contents can be a risk of toxic effects.

There is extensive data material which indicates that in natural systems, usually higher or considerably higher metal contents are required to cause toxic effects compared with the metal contents that have been shown in laboratory tests with single metals to possibly develop toxic effects.

One of the reasons for reduced toxic effect in the nature is that a series of environmental factors reduce the bio accessibility of the metals and, with that, their toxicity. In the environment of Swedish steelworks with high chromium, nickel and molybdenum contents, it is above all iron, manganese and calcium that are emitted at the same time in large quantities which, mainly by co-precipitation/complex formation, decrease the bio-accessibility of the metals, both in the terrestrial and aquatic environment. Also the presence of other trace metals which always exist in the metal burden areas contributes to the decrease of the toxicity by interactions.

Another reason is that plants and animals have an ability to acquire tolerance against metals and therefore afterwards stand increased exposure without being injured. Many such examples exist among others from areas with naturally occurring high contents because of mineralisations.

There are no scientifically documented observations on the negative effects of high concentrations of the metals in question in Swedish environment, except at an investigation of microbiological ground activity around one of the largest emission sources. In the environment there was a significant but vaguely negative correlation between metal burden and the ground respiration, and a more outspoken negative correlation for the phosphotase activity. The contents of chromium, nickel and molybdenum were several hundred times higher than what was indicated as ‘critical concentrations’. In the other investigations, despite the recorded high metal contents no effects on the microbiological activity have been seen.

There are no indications that cattle in Sweden are likely to be exposed to excessive levels of chromium, nickel or molybdenum.

In many water recipients in the neighbourhood of the steelworks, disturbances in the bottom fauna society has been noted and the conditions are still strained despite improvements in recent years. In recipients that receive waste water from steelworks there is however an accumulation of metals other than chromium, nickel and molybdenum, as well as large quantities of oil. For that reason it is difficult to assess which substances that caused the observed effects. Certain older investigations indicate that acute toxicity is mainly caused by the oil.

This does not mean that effects of chromium, nickel and molybdenum on terrestrial and aquatic organisms have not taken place or occurred.

11.3.2 Risk of Effects on Human Beings

No indications exist that people in Sweden are being exposed to excessive levels of chromium, nickel and molybdenum via inhalation of ambient air, via intake of mains water or other foodstuffs, or other exposure for instance steel implants.

Chromium and nickel are, however, known contact allergens. The use of chromium plated and nickel plated products have decreased sharply in society. There are, however, products of low alloy steel which emission chromium and nickel and can cause chromium and nickel allergy with oversensitive people. Change to higher alloy steels should diminish this problem since the emission of these metals considerably decreases with higher alloying extent.