Danish Ministry of the Environment
Environmental Protection Agency

Survey of molybdenum trioxide

Part of the LOUS-review

Environmental project No. 1716, 2015

Authors:

Survey of molybdenum trioxide

Authors:

Frans M. Christensen [1]
Marlies Warming [1]
Jesper Kjølholt [1]
Lars-Henrik Lau Heckmann [2]
Nils H. Nilsson [2]

[1] COWI A/S, Denmark
[2] Danish Technological Institute, Denmark

Published by:

The Danish Environmental Protection Agency
Strandgade 29
1401 Copenhagen K
Denmark
www.mst.dk/english

Year:

2015

ISBN no.

978-87-93352-29-2

Contents

Foreword

Background and objectives
The Danish Environmental Protection Agency's List of Undesirable Substances (LOUS) is intended as a guide for enterprises. It indicates substances of concern whose use should be reduced or eliminated completely. The first list was published in 1998 and updated versions have been published in 2000, 2004 and 2009. The latest version, LOUS 2009 (Danish EPA, 2011) includes 40 chemical substances and groups of substances which have been documented as dangerous or which have been identified as problematic using computer models. For inclusion in the list, substances must fulfil several specific criteria. Besides the risk of leading to serious and long-term adverse effects on health or the environment, only substances which are used in an industrial context in large quantities in Denmark, i.e. over 100 tonnes per year, are included in the list.

Over the period 2012-2015 all 40 substances and substance groups on the LOUS will be surveyed. The surveys include collection of available information on the use and occurrence of the substances, internationally and in Denmark, as well as information on environmental and health effects, alternatives to the substances, existing regulations, monitoring and exposure, and on-going activities under REACH, among others.

On the basis of the surveys, the Danish EPA will assess the need for any further information, regulation, substitution/phase out, classification and labelling, improved waste management or increased dissemination of information.

This survey concerns molybdenum trioxide.

The substance was included in LOUS due to "Properties of concern with regard to the List of hazardous substances"; specifically its classification with R40 "Limited evidence of a carcinogenic effect" in relation to the Dangerous Substance Directive (67/548/EEC).

The main objective of this study is, as mentioned, to provide background for the Danish EPA's consideration regarding the need for further risk management measures.

The process
The survey has been undertaken by COWI A/S (Denmark) in cooperation with Technological Institute (Denmark) from April to October 2014. The work has been followed by an advisory group consisting of:

- Louise Grave-Larsen, Danish EPA, Chemicals
- Lone Schou, Danish EPA, Waste
- Nikolai Stubkjær Nilsen, Confederation of Danish Industry
- Sigrídur Ingimarsdóttir, Haldor Topsøe A/S
- Frans Christensen, COWI A/S

Data collection
The survey and review is based on the available literature on the substances, information from databases and direct inquiries to trade organisations and key market actors.

The literature search included the following data sources:

- Legislation in force from Retsinformation (Danish legal information database) and EUR-Lex (EU legislation database);
- Ongoing regulatory activities under REACH and intentions listed on ECHA's website (incl. Registry of Intentions and Community Rolling Action Plan);
- Relevant documents regarding International agreements from HELCOM, OSPAR, the Stockholm Convention, the PIC Convention, and the Basel Convention;
- Data on harmonised classification (CLP) and self-classification from the C&L inventory database on ECHAs website;
- Pre-registered and registered substances from ECHA's website;
- Data on ecolabels from the Danish ecolabel secretariat (Nordic Swan and EU Flower);
- Production and external trade statistics from Eurostat's databases (Prodcom and Comext);
- Export of dangerous substances from the Edexim database;
- Data on production, import and export of substances in mixtures from the Danish Product Registry (confidential data, not searched via the Internet);
- Data on production, import and export of substances from the Nordic Product Registers as registered in the SPIN database;
- Information from Circa on risk management options (confidential, for internal use only, not searched via the Internet);
- Monitoring data from the National Centre for Environment and Energy (DCE), the Geological Survey for Denmark and Greenland (GEUS), the Danish Veterinary and Food Administration, and the European Food Safety Authority (EFSA);
- Waste statistics from the Danish EPA;
- Chemical information from the ICIS database;
- Reports, memorandums, etc. from the Danish EPA and other authorities in Denmark;
- Reports published at the websites of:
  - The Nordic Council of Ministers, ECHA, the EU Commission, OECD, IARC, IPCS, WHO, OSPAR, HELCOM, and the Basel Convention;
  - Environmental authorities in Norway (Klif), Sweden (KemI and Naturvårsverket), Germany (UBA), UK (DEFRA and Environment Agency), the Netherlands (VROM, RIVM), Austria (UBA). Information from other EU Member States was retrieved if quoted in identified literature;
  - US EPA, Agency for Toxic Substances and Disease Registry (USA) and Environment Canada;
  - PubMed and Toxnet databases for identification of relevant scientific literature.

Direct enquiries were also sent to Danish and European trade organisations and a few key market actors in Denmark.

Conclusion and summary

The substance
Molybdenum trioxide – MoO_3 – is an inorganic compound appearing in its pure form as a white-yellow, sometimes bluish powder at room temperature. The molybdenum content originates from molybdenum ores. Molybdenum is considered a commercially important metal.

Molybdenum trioxide is marketed in two grades:

- Pure grade molybdenum trioxide
- Technical grade molybdenum trioxide

It should be noted that most of the information sources reviewed in this project do not distinguish between the pure and technical grades, but generally simply refer to "molybdenum trioxide".

Molybdenum trioxide is a source of molybdate ions (MoO_4^{2-}). In the environmental and toxicological literature the word 'molybdenum' is used generically for molybdenum-containing species when what is being referred to is the molybdate ion (not the metal). This, if not explicitly stated, can be inferred from the context. In relation to legislation addressing waste, emissions and chemicals in environmental media, the review has therefore included legislation referencing "molybdenum".

Similarly, in addition to discussing data on molybdenum trioxide specifically, the chapters on health and environment refer also to molybdenum/the molybdate ion" as the species responsible for eco-toxicity and systemic human toxicity..

Regulatory framework
Pure grade molybdenum trioxide is subject to harmonised classification as a suspected carcinogen, with the potential for respiratory irritation and serious eye irritation properties, whereas the technical grade, in the absence of a harmonised classification, has been self-classified by industry. This self-classification is in line with the harmonised classification for the pure grade in relation to carcinogenicity classification. However, the technical grade has not been classified for respiratory irritation and serious eye irritation, as the REACH Molybdenum Consortium disagrees with this classification (see Section 6.1.1 for further details).

Molybdenum trioxide is neither subject to other REACH procedures nor in the pipeline for such procedures.

"Molybdenum" (including molybdenum trioxide) is subject to a range of waste and emission/environmental media legislation.

In addition to being subject to the general hazardous waste legislation, there are specific waste codes addressing the use of molybdenum compounds in catalysts. The EU legislation on shipment of waste (implementing the Basel Convention), has requirements for the transboundary movement of molybdenum waste, however e.g. molybdenum in scrap (as metal and metal alloy) and catalysts waste does not fall under the prohibition of export to non-OECD Decision counties. There are specific Danish provisions related to release of molybdenum from landfill percolate. EU legislation addresses emission to and presence of molybdenum in surface- and groundwater and Danish provisions set standards for the presence of molybdenum in drinking water and in the air. There are also Danish provisions for molybdenum content in Dredge/Spoil material, which is sediment removed from e.g. harbours or navigation channels and dumped again in designated areas of the sea. In addition to being subject to provisions in the Basel Convention, the Baltic Sea (HELCOM) and the Mediterranean Sea Conventions list molybdenum as a noxious substance and call for strict control of emissions from land-based sources.

Content and release of "molybdenum" (which could originate from molybdenum trioxide) is subject to the EU flower eco-labelling criteria for sanitary tapware.

Manufacture and consumption
Molybdenum trioxide supplied to the market as pure grade molybdenum trioxide is manufactured at two EU sites and the technical grade in one or two EU sites. These sites are located outside Denmark. In addition, pure grade molybdenum trioxide can be manufactured directly into catalyst mixtures from other molybdenum starting materials. This process does not result in manufacture of molybdenum trioxide as a free substance. One such company is located in Denmark.

The following volumes (including import and manufacturing of pure molybdenum trioxide and import as part of mixtures) have been registered under REACH:
- Pure grade molybdenum trioxide: 10,000 – 100,000 tonnes/year
- Technical grade molybdenum trioxide: 100,000 – 1,000,000 tonnes/year.

However, based on data from the International Molybdenum Association (IMOA), supported by data from EUROSTAT and a 2010 report from the European Commission, total European use of about 48,000 tonnes molybdenum trioxide (both grades)/year can be estimated.

The reason for these discrepancies has not been identified, but might be due to REACH double-registrations.

Based on the available information, the following estimated shares between applications for the global and the EU levels have been estimated for molybdenum trioxide (Pure and Technical grades):
- Approx. 80-90% for various steel applications
- Approx. 10% for catalysts (mainly for refineries)
- Approx. 5% for super alloys
- Approx. 0.5% for other applications.

"Other applications" include use of molybdenum trioxide for formulating/producing the following mixtures/articles: Water treatment chemicals; ceramic additives/enamel frits; pigments; metal surface treatment, and sintered metal additives. These are uses for which molybdenum trioxide is converted to other molybdenum compounds/molybdates before possibly coming into contact with consumers. A rough estimate of "Other applications" amounts to approx. 240 tonnes molybdenum trioxide/year in the EU.

The pure grade molybdenum trioxide is used for catalysts (mainly for refineries) and the above "Other applications", whereas both grades can be used for steel and other alloy production. However, mainly the cheaper technical grade is used for the steel and alloy applications.

There might be some import to the EU of articles containing molybdenum trioxide as flame retardant (e.g. polyester based). Available data, however, do not allow confirmation or quantification of this.

To the knowledge of the authors, no steel or alloy production applying molybdenum trioxide takes place in Denmark, as confirmed by statistics showing a lack of registered import of technical grade molybdenum trioxide.

It is known that catalyst production takes place in Denmark, including using imported pure grade molybdenum trioxide, as well as other molybdenum compounds, for manufacturing molybdenum trioxide directly into the catalysts during the catalyst production process. More than 95% of these catalysts are exported. Data are too scarce or confidential to map other applications of molybdenum trioxide in Denmark. Overall, the Danish Product Registry indicates that about 400 – 450 tonnes pure grade molybdenum trioxide/year is imported to Denmark.

Generally, the use of molybdenum trioxide is expected to increase, due to increased demand for sulphur-reducing catalysts in the refinery industry (need for cleaner fuels based on fuel reserves containing more sulphur than in the past) and the need for high-strength steels, e.g. for lighter vehicles (requiring less fuel) and for coal-fired power stations which will need to run at higher temperatures in the future.

Waste management
The vast majority of molybdenum waste originating from molybdenum trioxide applications comes from using molybdenum trioxide for catalysts and alloys manufacturing. Most of the waste generated is recycled due to the economic incentive in reusing molybdenum. Molybdenum trioxide is likewise, although to a much lesser extent, an input material into different mixtures and articles (e.g. ceramics, pigments and water treatment chemicals). In most of these products, molybdenum trioxide is chemically transformed into other molybdenum compounds (e.g. in aqueous media it will be transformed into molybdate ions), entering the environment or various waste streams as these molybdenum compounds. There are no data available that estimate the level of molybdenum trioxide present in the different waste streams described in this chapter; however, it is reasonable to conclude that it is minimal because of the chemical transformation that molybdenum trioxide undergoes in various applications.

The release of molybdenum trioxide or molybdenum compounds originating from molybdenum trioxide to the environment from e.g. landfills and waste water is considered limited, particularly due to the largely closed recycling loop for its main applications.

Environment

Environmental fate and effects
Molybdenum is a naturally occurring element, present at an average concentration of 12 to 16 ppm in seawater and 1 ppm in the earth's crust. Oxidation state +6 is considered to be the most prominent in oxidised aquatic and terrestrial environments i.e. typically as the molybdate ion, MoO_4^{2-}. In the soil, environmental molybdenum is considered to be relatively immobile with a sorption constant of 150-2000 mg/kg depending on the soil's content of clay and organic material. In the atmospheric compartment molybdenum is likely present only in the oxidised form.

Effect data are available for a significant number of organisms in the aquatic environment (based on tests with the molybdate ion). Molybdenum (tested as molybdate) is not particularly toxic in the aquatic environment; the reported acute EC50/LC50 values are all above 100 mg Mo/l while the lowest chronic effect value is >17 mg Mo/l in freshwater and 4.4 mg Mo/l in saltwater.

Releases to the environment
In Denmark, the main emissions of molybdenum trioxide are considered to be emissions from coal power plants and waste incineration plants. At the EU level, the same sources of release are also relevant and, additionally, some of the other EU countries have significant metallurgical industries, which contribute further to releases of this element to the environment. No data on the amounts released have been identified.

Monitoring data – levels in the environment
The environmental monitoring data on molybdenum are rather few but do indicate that, generally speaking, the molybdenum concentrations in surface water, groundwater and soil are low and not exceeding the relevant threshold values or quality criteria.

Environmental impact
No assessments of environmental impact/risk of molybdenum have been identified but the identified environmental background concentrations are below the relevant threshold values/quality criteria.

Human health

Human health hazard
Molybdenum is an essential element via its involvement in various enzymes systems. Deficiency symptoms (tachycardia, severe bifrontal headache, night blindness, nausea, vomiting and periods of lethargy, disorientation and coma) in humans have been seen following diet intake of total parenteral nutrition (TPN) and in children/young adults with Crohn's disease and inborn metabolic disorders, but no "naturally occurring" molybdenum deficiency has been identified in "free living" humans or animal species.

The systemic toxicity of molybdenum compounds seems to be associated with the molybdate ion and thus with the solubility of the molybdenum compounds. Molybdenum trioxide is partially soluble, although to a lesser degree than molybdate salts. The toxic mode of action is often associated with the fact that molybdenum, copper and sulphate have a complex interrelationship in the body. The balance between molybdenum and copper in the body may be disrupted following exposure to molybdenum. This may lead to copper deficiency (especially when sulphate intake is high) with symptoms of severe copper-deficiency: anaemia, neutropenia and osteoporosis.

These systemic toxicity symptoms were, however, not observed in a two-year carcinogenicity study on molybdenum trioxide in mice and rats. Symptoms have been seen in human studies related to high exposures to molybdenum compounds, but it is generally not possible to draw firm conclusions based on those studies.

Molybdenum trioxide is thought to have some irritating potential due to the strong acidification during the dissolution/dissociation reaction with water. Indeed the above mentioned carcinogenicity study showed effects in the respiratory airways including alveolar/bronchiolar carcinoma, especially in mice, concluded to indicate some evidence of carcinogenicity. Thus molybdenum trioxide is subject to harmonised classification as a suspected carcinogen.

Molybdenum trioxide is also classified for eye and respiratory irritation. The data/reasoning behind these classifications is not available, but the REACH Molybdenum Consortium disagrees with these classifications based on available evidence from irritation studies and a recent acute inhalation study.

Some effects on reproduction have been seen at relatively high molybdate dose levels and indications of effects are seen in a non–conclusive human study. Available data have not led to classification for this endpoint.

Human exposure and biomonitoring
Consumer exposure and humans exposed via the environment to molybdenum trioxide or molybdenum compounds originating from molybdenum trioxide is generally assessed to be low. Environmental exposure data are scarce, but those available indicate low molybdenum levels; levels which integrate all molybdenum sources, including e.g. molybdenum/molybdenum trioxide emitted from coal power plants.

Relatively high inhalation exposures are seen in some occupational settings, as e.g. evidenced by measurement data from a molybdenum sulphide roasting process, possibly manufacturing technical grade molybdenum trioxide. Blood biomonitoring data from such studies are, however, not always consistent with exposure levels and clinical symptoms.

Available data are not robust enough to indicate any trends in exposure levels.

Human health impact
No authoritative risk assessments for molybdenum trioxide have been identified.

In relation to molybdenum trioxide, the main exposure and possible risks seem to be inhalation exposure in occupational settings.

Molybdenum trioxide is not expected to contribute significantly to human exposure to molybdenum via the environment, given the applications and recycling in place for the main uses and considering molybdenum occurring from natural sources and emitted from coal power plants.

A human study suggests some correlation between blood molybdenum levels and sub-normal sperm concentration and sperm morphology in individuals seeking treatment in fertility clinics. It is not clear whether these increased blood molybdenum levels originate from occupational or environmental sources.

Alternatives
There are alternatives to molybdenum trioxide; however, they are either significantly more expensive, not able to meet demands (e.g. platinum) or their performance is inferior as compared to molybdenum trioxide for the specific application. This is in regard to alternatives to molybdenum trioxide in the production of catalysts, steel and other alloys in particular.

The study does not elaborate on alternatives for a range of minor applications for producing mixtures and articles, as these applications are estimated to only account for approx. 0.5% of the volume and as molybdenum trioxide has been converted to other molybdenum compounds or molybdate before reaching the consumer.

In conclusion, molybdenum trioxide is currently the best candidate from an economic, performance and health and environmental perspective; in particular as regards applications that require materials with strong endurance such as catalysts, steel and other alloys.

Main data/information gaps
Within the scope of this project, the following issues are considered the main data/information gaps for molybdenum trioxide:

- The total volume of molybdenum trioxide used on the EU market
- The volume of the relatively minor amounts of molybdenum trioxide used for "other applications", i.e. other than for production of refinery catalysts and alloys
- Knowledge about occupational inhalation exposure levels in manufacturing sites and sites using molybdenum trioxide industrially, in particular in steels and alloy productions. It should be noted that such manufacturing/productions takes place outside Denmark.

- Correlation between molybdenum blood levels and impacts on reproduction. Indications of a correlation between molybdenum blood levels and sub-normal sperm concentration and sperm morphology in a human study could lead to consideration for further human and mechanistic studies for this endpoint.
- CLP classification. There are different views on the need to classify molybdenum trioxide for respiratory and eye irritation. The reasoning behind the harmonised classification for these endpoints might be revisited, including consideration of recent data.

Sammenfatning og konklusioner

Stoffet
Molybdæntrioxid – MoO_3 - er en uorganisk forbindelse, som i ren form er et hvidt-gult, undertiden blåligt pulver ved stuetemperatur. Molybdænindholdet stammer fra molybdæn malm. Molybdæn betragtes som et kommercielt vigtigt metal.

Molybdæntrioxid markedsføres i to kvaliteter:
- Ren kvalitet ("pure grade") molybdæntrioxid
- Teknisk kvalitet ("Technical grade") molybdæntrioxid

Det skal bemærkes, at de fleste af de informationskilder, som er gennemgået i dette projekt ikke skelner mellem den rene og den tekniske kvalitet, men generelt blot henviser til "molybdæntrioxid".

Molybdæntrioxid kan være en kilde til molybdæn (molybdat-ioner) i miljøet. Gennemgangen af lovgivning vedrørende affald, emissioner og forekomst i miljøet, omfatter derfor også lovgivning, som er rettet mod "molybdæn".

Endvidere, ud over at gennemgå viden om molybdæntrioxid, gennemgår kapitlerne vedr. sundhed og miljø også viden om "molybdæn/molybdat-ionen", som er den bestanddel, som er ansvarlig for molybdæntrioxids økotoksicitet og systemiske human toksicitet.

Lovgivning
Ren kvalitet molybdæntrioxid er klassificeret som muligt kræftfremkaldende og for luftvejs- og øjenirritation. Teknisk kvalitet er i mangel af en harmoniseret klassificering blevet selvklassificeret af industrien. Denne selvklassificering er i overensstemmelse med den harmoniserede klassificering for ren kvalitet i forhold til kræftfremkaldende egenskaber. Imidlertid er teknisk kvalitet ikke blevet selvklassificeret for respiratorisk irritation og alvorlig øjenirritation, da REACH Molybdænkonsortiet er uenig med denne klassifikation.

Molybdæntrioxid er ikke underlagt andre REACH procedurer eller i pipelinen for sådanne procedurer.

"Molybdæn" (herunder molybdæntrioxid) er underlagt en række regler vedr. affaldsbortskaffelse og udledning til miljøet.

Udover at være omfattet af den almindelige lovgivning vedr. farligt affald er der særlige affaldskoder, som adresserer anvendelsen af molybdænforbindelser i katalysatorer. EU lovgivningen om kontrol med grænseoverskridende transport af farligt affald og bortskaffelse (Basel-konventionen) har krav vedrørende molybdæn, men undtager f.eks. molybdæn i skrot (som metal og metallegering) og som katalysator-affald fra forbuddet mod eksport til lande, der ikke er omfattet af OECD-beslutningen. Der er særlige danske bestemmelser relateret til udledning af molybdæn med losseplads-perkolat. EU-lovgivningen omhandler udledninger til og forekomst af molybdæn i overflade- og grundvand og danske bestemmelser fastsætter standarder for tilstedeværelsen af molybdæn i drikkevandet og i luften. Der er også danske bestemmelser om indhold af molybdæn i klapmateriale, som er sedimentet, der fjernes fra f.eks. havne og sejlrender og dumpes i udpegede havområder.

Ud over at være omfattet af bestemmelserne i Basel-konventionen, er molybdæn underlagt konventionerne for Østersøen (HELCOM) og Middelhavet som et skadeligt ("engelsk: noxious") stof og med en opfordring til streng kontrol af emissioner fra landbaserede kilder.

Indhold og frigivelse af "molybdæn" (som kunne stamme fra molybdæntrioxid) er omfattet af EU blomstens miljømærkekriterier for sanitetsarmaturer.

Fremstilling og forbrug
Ren kvalitet molybdæntrioxid, som markedsføres til salg, fremstilles to steder i EU og teknisk kvalitet ét eller to steder i EU. Disse produktionssteder er beliggende uden for Danmark. Desuden kan ren kvalitet molybdæntrioxid fremstilles direkte i katalysatorblandinger fra andre udgangsmaterialer, som indeholder molybdæn. Denne proces resulterer ikke i fremstilling af molybdæntrioxid som et frit stof. En sådan produktion foregår i Danmark.

De følgende mængder (herunder import og fremstilling af molybdæntrioxid som stof og import som del af blandinger) er blevet registreret under REACH:
- Ren kvalitet molybdæntrioxid: 10.000 - 100.000 tons/år
- Teknisk kvalitet molybdæntrioxid: 100.000 - 1.000.000 tons/år.

Baseret på tal fra IMOA (International Molybdenum Association), som underbygges af tal fra Eurostat samt en 2010 rapport fra Europa-kommissionen, kan det samlede europæiske forbrug af molybdæntrioxid (ren og teknisk kvalitet) imidlertid estimeres til cirka 48.000 tons/år.

Årsagen til disse uoverensstemmelser er ikke blevet identificeret, men kan skyldes dobbeltregistreringer under REACH.

På grundlag af de foreliggende oplysninger estimeres det, at såvel det globale forbrug som forbruget i EU af molybdæntrioxid (ren og teknisk kvalitet) fordeler sig som følger:
- Ca. 80-90% anvendes som legering i forskellige typer af stål
- Ca. 10% anvendes til katalysatorer (primært til raffinaderier)
- Ca. 5% anvendes til superlegeringer
- Ca. 0,5% har andre anvendelser

"Andre anvendelser" omfatter brug af molybdæntrioxid til formulering/produktion af følgende blandinger og artikler: Vandbehandlingskemikalier, keramiske tilsætningsstoffer/emalje fritter, pigmenter, overfladebehandlingsmidler til metal og sintrede metaltilsætningsstoffer. I disse anvendelser omdannes molybdæntrioxid til andre forbindelser af molybdæn/molybdater og en eventuel forbrugereksponering vil være til disse stoffer. Et groft skøn over mængden anvendt til "andre anvendelser" beløber sig til ca. 240 tons molybdæntrioxid/år i EU.

Ren kvalitet molybdæntrioxid anvendes til fremstilling af katalysatorer (primært til raffinaderier) samt til de ovennævnte "andre anvendelser", mens begge kvaliteter kan anvendes til produktion af stål og andre legeringer. Dog anvendes hovedsageligt den billigere tekniske kvalitet som molybdænkilde til stål og andre legeringer.

Der kan være nogen import til EU af varer, der indeholder molybdæntrioxid som flammehæmmer (f.eks. i polyester). Dette kan imidlertid hverken bekræftes eller kvantificeres på basis af de fundne oplysninger.

Så vidt forfatterne er orienteret, fremstilles der ikke stål eller andre legeringer, hvor der anvendes molybdæntrioxid, i Danmark. Dette bekræftes af statistikker, som viser at der ikke importeres teknisk kvalitet molybdæntrioxid til Danmark.

Det vides, at der produceres katalysatorer i Danmark, som anvender importeret ren kvalitet molybdæntrioxid og molybdæntrioxid som dannes ud fra andre molybdæn-forbindelser, som et integreret trin i produktionsprocessen. Mere end 95% af disse katalysatorer eksporteres. Data er for sparsomme eller fortrolige til at kunne identificere andre anvendelser af molybdæntrioxid i Danmark. Data fra det danske Produktregister viser, at der årligt importeres omkring 400-450 tons ren kvalitet molybdæntrioxid til Danmark.

Generelt forventes det, at anvendelsen af molybdæntrioxid vil stige i takt med øget efterspørgsel efter svovl-reducerende katalysatorer fra raffinaderier (behov for renere brændstoffer baseret på oliereserver, der indeholder mere svovl end tidligere) og behovet for højstyrke-stål f.eks. til lettere køretøjer (som kræver mindre brændstof) og til kulfyrede kraftværker, som bliver nødt til at anvende højere temperaturer i fremtiden.

Affaldshåndtering
Langt størstedelen af det molybdæn-affald, som stammer fra anvendelsen af molybdæntrioxid, kommer fra anvendelse af molybdæntrioxid til fremstilling af katalysatorer og legeringer. Det meste af affaldet bliver genvundet på grund af det økonomiske incitament til at genbruge molybdæn. Molybdæntrioxid er ligeledes, om end i langt mindre omfang, anvendt til fremstilling af forskellige blandinger og artikler (f.eks. keramik, pigmenter og kemikalier til vandbehandling). I de fleste af disse produkter er molybdæntrioxid kemisk omdannet til andre forbindelser af molybdæn (f.eks. vil det i vandige medier blive omdannet til molybdat-ioner) og ender i miljøet eller forskellige affaldsstrømme, som disse molybdænforbindelser. Der er ingen tilgængelige data, der estimerer niveauet af molybdæntrioxid i de forskellige affaldsstrømme, men det virker rimeligt at konkludere, at mængden er minimal på grund af den kemiske transformation, som molybdæntrioxid undergår i disse anvendelser.

Udledninger af molybdæntrioxid eller molybdænforbindelser til miljøet fra f.eks. lossepladser og spildevand, som skyldes den tilsigtede brug af molybdæntrioxid, anses for begrænset, da der sker en effektiv genvinding af molybdæntrioxid fra de vigtigste anvendelser.

Miljø

Miljømæssig skæbne og effekter
Molybdæn er et naturligt forekommende element med gennemsnitlige koncentrationer på 12 til 16 ppm i havvand og 1 ppm i jordskorpen. Oxidationstrin +6 anses for at være det mest fremtrædende i oxiderede akvatiske og terrestriske miljøer, dvs. typisk som molybdat-ionen, MoO_4^{2-}. I jord anses molybdæn for relativt immobil med en adsorptionskonstant på 150-2000 mg/kg afhængig af jordens indhold af ler og organisk materiale. I atmosfæren er molybdæn sandsynligvis kun til stede i den oxiderede form.

Der eksisterer effekt-data for et stort antal organismer i vandmiljøet (baseret på forsøg med molybdat-ionen). Molybdæn (testet som molybdat) er ikke særligt giftigt i vandmiljøet. De rapporterede akutte EC50 / LC50-værdier er alle over 100 mg Mo/l, mens den laveste kroniske effekt-værdi er > 17 mg Mo/l i ferskvand og 4,4 mg Mo/l i saltvand.

Udslip til miljøet
I Danmark anses de vigtigste emissioner af molybdæntrioxid at være emissioner fra kulfyrede kraftværker og affaldsforbrændingsanlæg. Disse kilder til udslip er også relevante på EU-plan. Nogle EU-lande har endvidere betydelig metalindustri, som bidrager yderligere til udledninger til miljøet.

Data for udslip til miljøet er ikke blevet identificeret.

Moniteringsdata for koncentrationer i miljøet
Moniteringsdata for molybdæn i miljøet er begrænsede, men viser generelt set, at koncentrationerne af molybdæn i overfladevand, grundvand og jord er lave, og at de ikke overstiger de relevante tærskelværdier eller kvalitetskriterier.

Miljøpåvirkning
Der er ikke identificeret vurderinger af påvirkning/risiko for miljøet, men de identificerede moniteringsdata er under de relevante tærskelværdier/kvalitetskriterier.

Sundhed

Sundhedsfare for mennesker
Molybdæn er livsnødvendigt grundet dets funktion i forskellige enzym-systemer. Mangelsymptomer i mennesker, resulterer i tachycardi (unormalt hurtigt hjerteslag), svær bifrontal hovedpine, natteblindhed, kvalme, opkastning og perioder med sløvhed, desorientering og koma. Mangelsymptomer er set efter indtag af TPN ("total parenteral nutrition"), og hos børn / unge med Crohns sygdom og medfødte stofskiftesygdomme. "Naturligt forekommende" molybdænmangel er ikke blevet identificeret i mennesker eller dyr.

Den systemiske toksicitet af molybdæn synes at være forbundet med molybdat-ionen og således med opløseligheden af molybdæn. Molybdæntrioxid er delvist opløseligt, om end i mindre grad end molybdatsalte. Den toksiske virkningsmekanisme er ofte forbundet med det faktum, at molybdæn, kobber og sulfat har et komplekst indbyrdes forhold i kroppen. Balancen mellem molybdæn og kobber i kroppen kan blive forstyrret efter forhøjet indtag af molybdæn. Dette kan føre til kobbermangel (især når indtaget af sulfat er utilstrækkeligt) med symptomer på svær kobber-mangel: anæmi, neutropeni (færre hvide blodlegemer, hvilket øger sårbarheden for infektion) og osteoporose/knogleskørhed.

Disse symptomer på systemisk toksicitet blev dog ikke observeret i et toårigt carcinogenicitetsstudie med molybdæntrioxid i mus og rotter. Symptomerne er blevet set i humane studier med høje doser af molybdænforbindelser, men det er generelt ikke muligt at drage endelige konklusioner på baggrund af disse studier.

Molybdæntrioxid menes at have potentiale for irritation på grund af den stærke forsuringsreaktion ved opløsning/dissociation i vand. Ovennævnte carcinogenicitets-studie viste effekter i luftvejene, herunder alveolær/bronchiolær karcinomer, især i mus, som blev fortolket til at indikere mulige kræftfremkaldende egenskaber. Derfor er molybdæntrioxid underlagt harmoniseret klassificering som muligt kræftfremkaldende.

Molybdæntrioxid er også klassificeret som irriterende ved inhalation og øjenkontakt. Ræsonnementet bag denne harmoniserede klassificering er ikke tilgængelig, men baseret på foreliggende data fra irritations-studier og et nyligt indåndingsstudie for akut toksicitet, er REACH Molybdænkonsortiet uenig med disse klassificeringer.

Nogle reproduktionseffekter er set ved relativt høje doser af molybdat og indikationer af effekter er set i et ikke-entydigt human studie. Tilgængelige data har ikke ført til klassificering for denne effekt.

Human eksponering og biomonitering
Forbrugereksponering og den generelle befolknings udsættelse for molybdæntrioxid eller molybdænforbindelser, som stammer fra molybdæntrioxid, vurderes til at være lav. Data for eksponering via miljøet er få, men de, der er til rådighed, indikerer lave molybdæn-niveauer; niveauer, som

integrerer alle molybdæn-kilder, herunder f.eks. molybdæn/molybdæntrioxid som udledes fra kulkraftværker.

Relativt høje inhalationseksponeringer er set i nogle arbejdsmæssige sammenhænge, f.eks. måledata fra en molybdænsulfid ristnings-proces, som sandsynligvis fremstiller teknisk kvalitet molybdæntrioxid. Biomoniteringsdata fra sådanne undersøgelser er imidlertid ikke altid i overensstemmelse med eksponeringsniveauer i indåndingsluften og observerede kliniske symptomer.

De tilgængelige data er ikke robuste nok til at vise eventuelle tidsmæssige udviklingstendenser i eksponeringsniveauer.

Sundhedspåvirkning
Der er ikke identificeret autoritative risikovurderinger af molybdæntrioxid.

Den vigtigste eksponering og mulige risiko forbundet med molybdæntrioxid synes at være via indånding i arbejdsmiljøet.

I betragtning af at molybdæn genanvendes i forbindelse med stoffets væsentligste anvendelser, at molybdæn er naturligt forekommende, og at stoffet udledes fra kulkraftværker, forventes molybdæntrioxid ikke at bidrage væsentligt til molybdæneksponering af mennesker via miljøet.

Et humant studie indikerer en vis sammenhæng mellem molybdæn-indhold i blodet og subnormale koncentrationer af sædceller og sædmorfologi i personer, der søger behandling i fertilitetsklinikker. Det er ikke klart, om disse øgede molybdæn-niveauer i blodet stammer fra arbejdsmiljøet eller miljømæssige kilder.

Alternativer
Der er alternativer til molybdæntrioxid, men de er enten betydeligt dyrere, ikke tilgængelige i væsentlige mængder (f.eks. platin) eller deres tekniske egenskaber er ringere i forhold til molybdæntrioxid for den specifikke anvendelse. Dette gælder især for alternativer til molybdæntrioxid anvendt til fremstilling af katalysatorer, stål og andre legeringer.

Nærværende studie går ikke i dybden med alternativer til en række mindre anvendelser til fremstilling af kemiske blandinger og artikler, da disse anvendelser kun vurderes at tegne sig for ca. 0,5% af det samlede forbrug, og da molybdæntrioxid tilmed er blevet omdannet til andre molybdænforbindelser eller molybdat før forbrugeren eksponeres.

Alt i alt, er molybdæntrioxid i øjeblikket den bedste løsning ud fra et økonomisk, teknisk, samt miljø- og sundhedsmæssigt perspektiv; navnlig med hensyn til anvendelser, som kræver materialer med stor holdbarhed, såsom katalysatorer, stål og andre legeringer.

Vigtigste informations- og datamangler
Inden for rammerne af dette projekt er de følgende forhold vurderet at være de væsentligste informations- og datamangler for molybdæntrioxid:

- Den samlede mængde molybdæntrioxid anvendt i EU.
- Mængden af molybdæntrioxid anvendt til de forholdsvis små anvendelser af stoffet, dvs. til andre anvendelser end produktion af raffinaderi-katalysatorer og legeringer.
- Viden om eksponeringsniveauer i arbejdsmiljøet i forbindelse med fremstilling og industriel anvendelse af molybdæntrioxid, især ved produktion af stål og legeringer. Det skal bemærkes, at sådan fremstilling/produktion finder sted uden for Danmark.
- Sammenhængen mellem molybdæn i blodet og reproduktionsvirkninger. Indikationer af en korrelation mellem molybdæn i blodet og sub-normale koncentrationer af sædceller og sæd-

morfologi i et humant studie kunne lede til overvejelser om behovet for yderligere humane studier og mekanistiske undersøgelser af dette.

- CLP klassificering. Der er forskellige synspunkter vedrørende behovet for den harmoniserede klassificering af molybdæntrioxid for inhalations- og øjeirritation. Ræsonnementet bag den harmoniserede klassificering for disse effekter kunne tages op til fornyet overvejelse, bl.a. på basis af nye data.

1. Introduction to the substance group

1.1 Definition of the substance group

Molybdenum trioxide – MoO_3 – is an inorganic compound appearing in its pure form as a white-yellow, sometimes bluish powder at room temperature. The molybdenum content originates from molybdenum ores. Molybdenum is considered a commercially important metal and has been subject to supply certainty investigations, e.g. by the European Commission (European Commission, 2010). Molybdenum is a transition metal belonging to group 6 of the periodic table.

Molybdenum trioxide is marketed in two grades:

- Pure grade molybdenum trioxide
- Technical grade molybdenum trioxide.

Table 1 shows the identifiers under which these two grades have been registered under REACH. It should be noted that technical grade molybdenum trioxide is registered as a so-called UVCB substance (Unknown or Variable Composition, Complex Reaction Products or Biological Materials) named after the manufacturing process and starting material. The Danish EPA's List of Undesirable Substances (LOUS) lists the CAS number for the pure grade; however, as the technical grade is marketed in higher volumes, both grades are included in this survey.

Table 1 also provides the registered tonnage under REACH and the hazard classification. Pure grade molybdenum trioxide is subject to harmonised classification as a suspected carcinogen, with a potential for respiratory irritation and serious eye irritation properties, whereas the technical grade, in the absence of a harmonised classification, has been self-classified by industry. This self-classification is in line with harmonised classification for the pure grade in relation to carcinogenicity classification. However, the technical grade has not been classified for respiratory irritation and serious eye irritation. This is because the Molybdenum Consortium disagrees with the harmonised classification for the pure grade and therefore decided to self-classify the technical grade differently (Carey, 2014; Molybdenum Consortium, 2010). The reasons for this disparity will be further addressed in Chapter 6.

TABLE 1
MOLYBDENUM TRIOXIDE - TONNAGE REGISTERED AND CLASSIFICATION

Grade / REACH name	CAS No	EC No	Registered, tonnage band, t/y	Pre-registered?	C&L*
Pure / Molybdenum trioxide	**1313-27-5**	**215-204-7**	10,000 – 100,000	Yes	Harmonised Carc. 2, H351 STOT SE 3, H335 Eye Irrit. 2 H319
Technical / Molybdenum sulphide (MoS2), roasted	**86089-09-0**	**289-178-0**	100,000 - 1,000,000	Yes	Self-classification Carc. 2, H351

* HAZARD STATEMENT CODES: H351: SUSPECTED OF CAUSING CANCER; H 335: MAY CAUSE RESPIRATORY IRRITATION; H319: CAUSES SERIOUS EYE IRRITATION

For the technical grade, the REACH Molybdenum Consortium has published the typical composition of technical grade molybdenum trioxide as reproduced in Table 2.

TABLE 2
TYPICAL COMPOSITION OF TECHNICAL GRADE MOLYBDENUM TRIOXIDE (MOLYBDENUM CONSORTIUM, 2010)

Constituent	Typical concentration	Concentration range	Remarks
MoO_3 EC No.: 215-204-7 CAS No: 1313-27-5	80 %(w/w)	≥ 45 — ≤ 96 % (w/w)	Constituent relevant for hazard classification
SiO2 (quartz) EC No: 238-878-4 CAS No: 14808-60-7	3 %(w/w)	≥1% — ≤ 15 % (w/w)	< 1% present as respirable crystalline silica
Mo Suboxides	6 %(w/w)	≥ 2 — ≤ 30 % (w/w)	According to XRD analysis, mainly MoO_2, Mo_4O_{11}, Mo_8O_{23}, Mo_9O_{26} (Mo_4O_{11} can individually be present in concentration ≥ 10%)
Iron molybdates	4 %(w/w)	≥ 1 — ≤ 15 % (w/w)	Based on expert judgement and/or XRDanalysis, expected to be present as FeMoO4, Fe2(MoO4)3, Fe3Mo3O12
Lead compounds	0.03% (w/w) Pb	< 0.25 % Pb (w/w)	Based on expert judgement, expected to be present as lead oxide (EINECS No. 215-267-0/CAS No 1317-36-8)
Arsenic compounds	0.012 % (w/w) As	≤ 0.075 % (w/w) As	Based on expert

			judgement, expected to be present as diarsenic trioxide (EINECS No. 215-481-4/CAS No. 1327-53-3)
Copper compounds	0.45 % (w/w) Cu	≤ 4 % (w/w) Cu	Based on XRD analysis and expert judgement, copper is present as CuO (EINECS No. 215-269-1/CAS No. 1317-38-0), copper molybdates and copper silicates; and is not present as Cu2O. The compounds in which copper is present have no impact on the classification.
Calcium molybdate EC No: 232-192-9 CAS No: 7789-82-4	1 % (w/w)	0 — 5 % (w/w)	
Ammonium molybdates	Powder: 0% (w/w) Briquettes: 10% (w/w)	0 — 15 % (w/w)	Based on expert judgement and/or XRD analysis, expected to be present as $(NH_4)_6.Mo_7O_{24}{\cdot}4H_2O$, $(NH_4)_6.Mo_9O_{30}{\cdot}5H_2O$; $(NH_4)_2Mo_4O_{13}$; $NH_3(MoO_3)_3$

The Molybdenum Consortium (2010) specifically notes that the self-classification for the technical grade (see Table 1) should differ if:

- the levels of lead or arsenic exceed those indicated in the 'concentration range' column of Table 2, and/or
- the level of respirable crystalline silica is > 1%, and/or
- other hazardous constituents are present in classifiable quantities.

Searches in the C&L inventory on the ECHA website do not reveal any self-classifications for the technical grade CAS number 86089-09-0 differing from the one listed in Table 1. It must therefore be inferred that technical grade molybdenum trioxide is not marketed with impurities/constituents exceeding those listed above. Furthermore, it is considered outside the scope of this project to investigate the influence on health and environment of the constituents/impurities listed in Table 2. Therefore, Chapter 5 and 6 will address molybdenum trioxide in these terms.

It should be noted that most of the information sources reviewed do not distinguish between the pure and technical grades, but generally simply refer to "molybdenum trioxide". Unless the opposite is explicitly specified or can be inferred from the context, we assume that such references refer to both grades.

Molybdenum trioxide might be a source of molybdenum (molybdate ions) in the environment. In relation to legislation addressing waste, emissions and presence of chemicals in environmental media, the review will therefore include "molybdenum" as a search term. Further, the chapters on health and environment will address to what extent "molybdenum/the molybdate ion" as such is the toxic moiety of molybdenum trioxide. The report will not address all environmental sources of molybdenum metal, ions, or other compounds, nor fully review the (eco) toxicity of all molybdenum forms.

1.2 Physical and chemical properties of molybdenum trioxide

Physical and chemical properties of the two grades of molybdenum trioxide are shown in Table 3.

TABLE 3
PHYSICAL AND CHEMICAL PROPERTIES OF MOLYBDENUM TRIOXIDE (PURE AND TECHNICAL GRADE)

Property	Value (pure grade)	Value (technical grade)	Reference
EC number	215-204-7	289-178-0	ECHA (2014a, b)
CAS number	1313-27-5	86089-09-0	ECHA (2014 a, b)
IUPAC name	Molybdenum trioxide	Molybdenum sulphide (MoS_2), roasted	ECHA (2014a, b)
Synonyms	Molybdena, molybdenum(6+) oxide, Molybdenum anhydride, molybdenum oxide, Molybdenum peroxide, Molybdenum (VI) oxide, Molybdic acid anhydride, Molybdic anhydride, Molybdic oxide, Molybdic trioxide, MoO_3, trik ide, MoO_3, triketomolybdenum, trioxomolybdenum	Tech oxide, Moly oxide, Technical Molybdic oxide, Technical grade Molybdenum oxide, Molybdenum oxide PCF, Roasted Molybdenite concentrates (RMC)	Pure grade: Chemind. website [1] Technical grade: ECHA (2014b)
Molecular formula	MoO_3	MoO_3 (main constituent)	ECHA (2014 a, b)
Physical state and appearance	white-yellow, sometime bluish powder	grey to slightly yellow powder or briquettes	ECHA (2014 a, b)
Melting point (°C)	802	ca. 801	ECHA (2014 a, b)
Boiling point (°C)	1155	1150	ECHA (2014 a, b)
Flash point (closed cup) (°C)	NA	NA	-

[1] http://www.chemindustry.com/chemicals/0389918.html

Property	Value (pure grade)	Value (technical grade)	Reference
Relative density	4.66 (20 °C)	4.48 (23.8 °C)	ECHA (2014 a, b)
Vapour pressure (at 40°C)	NA	NA	-
Surface tension	NA	NA	-
Water solubility (mg/l)	1000	ca. 560	ECHA (2014 a, b)
Log P (octanol/water)	NA	NA	-
Molecular weight	144	Varies	Chemind. web-site[1]

1.3 Function of the substances for main application areas

A main function of pure grade molybdenum trioxide is associated with its property as an oxidation catalyst; it is thus used as a precursor for the preparation of molybdenum-based catalysts. It can also be used as a source of pure molybdenum metal or as alloying element in steel and other alloys. However, technical grade molybdenum trioxide is mainly used as the molybdenum source for these metal applications.

Chapter 3 will further outline additional minor applications of molybdenum trioxide.

Molybdenum is an essential mineral and certain highly soluble molybdenum salts and molybdates may be added as food and feed supplements. Molybdenum trioxide is, however, not included in regulatory positive lists for such applications.

2. Regulatory framework

2.1 Legislation

This section first lists existing legislation addressing molybdenum trioxide and subsequently provides an overview of on-going regulatory activities, focusing on substances in the pipeline in relation to various REACH provisions. Finally, the chapter addresses to what extent the substance is addressed by eco-labelling criteria and international conventions. Some background information on the different instruments and agreements is provided in Appendix 2.

2.1.1 Existing legislation

Table 4 provides an overview of existing legislation addressing molybdenum trioxide. For each area of legislation, the table first lists the EU legislation (if applicable) and then (as concerns directives) existing transposition into Danish law and/or other national rules. The latter will only be elaborated upon in cases where Danish provisions differ from EU provisions.

Table 4 illustrates that no legislation addressing the content of molybdenum trioxide in products has been identified. Molybdenum (including molybdenum trioxide) is subject to a range of waste and emission/environmental media legislation. In addition to being subject to the general hazardous waste legislation, there are specific waste codes addressing the use of molybdenum compounds in catalysts. The EU legislation on shipment of waste (implementing the Basel Convention), has requirements for the transboundary movement of molybdenum waste, however e.g. molybdenum in scrap (as metal and metal alloy) and catalysts waste does not fall under the prohibition of export to non-OECD Decision counties. Chapter 4 further elaborates that such waste is normally recycled as molybdenum is a valuable resource. Chapter 3 outlines that application of molybdenum trioxide as precursors for catalysts and alloys are the main application areas. There are specific Danish provisions related to release of molybdenum from landfill percolate. EU legislation addresses emission to and presence of molybdenum in surface- and groundwater and Danish standards for the presence of molybdenum in drinking water and in the air. There are also Danish provisions for molybdenum content in dredge/spoil material, i.e. sediment removed from e.g. harbours or navigation channels and dumped again in designated areas of the sea.

TABLE 4
EU AND DANISH LEGISLATION ADDRESSING MOLYBDENUM TRIOXIDE (AS OF APRIL 2014)

Legal instrument *1	EU/ National	Substances (as indicated in the instrument)	Requirements as concerns molybdenum trioxide
Legislation addressing products			
Legislation addressing waste			
DIRECTIVE 2008/98/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 19 November 2008 on waste and repealing	EU	Molybdenum trioxide (although not specifically mentioned)	Molybdenum trioxide is generally subject to the general EU waste legislation. Specific legislation where molybdenum trioxide could be the source of molybdenum or molybdenum compounds in waste is listed further down.

Legal instrument *1	EU/ National	Substances (as indicated in the instrument)	Requirements as concerns molybdenum trioxide
certain Directives **COMMISSION DECISION of 3 May 2000 replacing Decision 94/3/EC establishing a list of wastes pursuant to Article 1(a) of Council Directive 75/442/EEC on waste and Council Decision 94/904/EC establishing a list of hazardous waste pursuant to Article 1(4) of Council Directive 91/689/EEC on hazardous waste**	EU	Transition metals and transition metal compounds (including specifying molybdenum as transition metal)	Specifies the following waste codes: - 16 08 02: spent catalysts containing dangerous transition metals (3) or dangerous transition metal compounds - 16 08 03: spent catalysts containing transition metals or transition metal compounds not otherwise specified and specifies: "... transition metals are: scandium, vanadium, manganese, cobalt, copper, yttrium, niobium, hafnium, tungsten, titanium, chromium, iron, nickel, zinc, zirconium, molybdenum and tantalum. These metals or their compounds are dangerous if they are classified as dangerous substances. The classification of dangerous substances shall determine which among those transition metals and which transition metal compounds are hazardous."
Bekendtgørelse om affald BEK nr. 1309 af 18/12/2012 [Statutory order on waste] *	DK	As above	Transposes above Directive and decision into Danish law.
REGULATION (EC) No 1013/2006 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 14 June 2006 on shipments of waste **NB! EU implementation of the Basel convention**	EU	 Molybdenum scrap Molybdenum Molybdenum	Included in Annex V, Part1, List B (Annex IX to the Basel Convention); i.e. wastes which are not covered by Article 1(1) (a) of the Basel Convention, and therefore not covered by the export prohibition. Metal and metal-alloy wastes in metallic, non-dispersible form Refractory metals containing residues Spent catalysts, transition metals
Bekendtgørelse om deponeringsanlæg BEK nr. 1049 af 28/08/2013 [Statutory order on facilities for landfilling] *	DK	Molybdenum	Included in Table 2.3 specifying maximum concentration of 20 µg molybdenum per litre groundwater following percolate leaching from landfills. Limits for maximum molybdenum content also included in various criteria for classifying inert, mineral and hazardous wastes.
Legislation addressing emissions and presence in environmental media			
DIRECTIVE 2006/11/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUN-	EU	Molybdenum and its compounds (i.e. implicitly molybdenum	Included in List II of Annex I for which Member States shall take steps to reduce pollution of the following waters:

Legal instrument *1	EU/ National	Substances (as indicated in the instrument)	Requirements as concerns molybdenum trioxide
CIL of 15 February 2006 on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community		trioxide)	(a) inland surface water; (b) territorial waters; (c) internal coastal waters.
Bekendtgørelse om miljøkvalitetskrav for vandområder og krav til udledning af forurenende stoffer til vandløb, søer eller havet BEK nr 1022 af 25/08/2010 [Statutory order on environmental quality criteria for water bodies and provisions for emissions of polluting substances to streams, lakes and the sea] *	DK	Molybdenum	Defines national Danish environmental quality criteria for water: - freshwater general: 67 µg molybdenum/l - marine water general: 6.7 µg molybdenum/l - fresh water short term: 587 µg molybdenum/l - marine water short term: 587 µg molybdenum/l
COUNCIL DIRECTIVE of 17 December 1979 on the protection of groundwater against pollution caused by certain dangerous substances (80/68/EEC)	EU	Molybdenum and its compounds (i.e. implicitly molybdenum trioxide)	Included in List II of the Annex for which Member States shall take the necessary steps to limit the introduction into groundwater
Bekendtgørelse af lov om beskyttelse af havmiljøet LBK nr 963 af 03/07/2013 [Law on protection of the marine environment] *	DK	Molybdenum	Listed in Annex 2 with substances and materials, which may only occur in negligible amounts or concentrations in dredge material/dredge spoil (in Danish: "klapmateriale")
Bekendtgørelse om vandkvalitet og tilsyn med vandforsyningsanlæg BEK nr 292 af 26/03/2014 [Statutory Order on water quality and inspection of water supply facilities] *	DK	Molybdenum (where molybdenum trioxide could be a molybdenum source)	Defines the following quality criteria for drinking water: - upon entry to a property: 20 µg molybdenum/l - at the consumer tap: 20 µg molybdenum/l
Bekendtgørelse om kvalitetskrav til miljømålinger BEK nr. 231 af 05/03/2014 [Statutory order on demands to quality of environmental measurements] *	DK	Molybdenum (where molybdenum trioxide could be a molybdenum source)	Specifies quality demands for measurements of molybdenum in a range of environmental media.
Supplement til B-værdivejledningen 2008 VEJ nr. 10702 af 19/11/2008 [Supplement to the B-value	DK	Molybdenum compounds in inorganic dust	Establishes a "B-value" for molybdenum compounds in inorganic dust: of 0.005 mg/m³ (measured as Mo)

Legal instrument *1	EU/ National	Substances (as indicated in the instrument)	Requirements as concerns molybdenum trioxide
guideline of 2008] *			
Legislation addressing occupational exposures			
Council Directive 98/24/EC of 7 April 1998 on the protection of the health and safety of workers from the risks related to chemical agents at work	EU	Hazardous chemical agents, thus including molybdenum trioxide	See below
Bekendtgørelse om arbejde med stoffer og materialer (kemiske agenser) BEK nr. 292 af 26/04/2001 med senere ændringer [Statutory Order on Working with Substances and Materials (chemical agents)]*	DK	As above	The Danish transposition of 98/24/EC obliges the employer to: - plan the work, in order to reduce any risk to the safety and health of workers arising from the presence of hazardous chemical agents, - replace hazardous substances, materials and work processes by less hazardous substances, materials and work processes, and - develop workplace guidelines for the use of hazardous substances and materials.
	DK	Molybdenum compounds	Soluble molybdenum compounds: 5 mg molybdenum/m³ Insoluble molybdenum compounds: 10 mg molybdenum/m³ NB! Dialogue with the Danish Occupational authorities has led to the interpretation that molybdenum trioxide in this context should be considered soluble

* Unofficial translation of the titles of Danish instruments.

Standard conditions for industrial installations or activities
None of the standard conditions for industrial installations or activities listed in Annex II to the Danish Order on Environmental permitting (Godkendelsesbekendtgørelsen, BEK No 1454 of 20/12/2012) specifically address molybdenum trioxide (cf. Annex 5 to BEK No 486 of 25/05/2012).

Classification and labelling
Molybdenum trioxide (as such, i.e. applicable for the pure grade) is subject to harmonised classification. The technical grade has been self-classified by all registrants. Classifications are provided in Table 5 and Table 6. Classification of the two grades and why they differ is addressed in Section 1.1 and 6.1.1.

TABLE 5
HARMONISED CLASSIFICATION ACCORDING TO ANNEX VI OF REGULATION (EC) NO 1272/2008 (CLP REGULATION)

Index No	International Chemical Identification	CAS No	Classification	
			Hazard Class and Category Code(s)	Hazard statement Code(s) *
042-001-00-9	Molybdenum trioxide (pure grade molybdenum trioxide)	1313-27-5	Carc. 2 STOT SE 3 Eye Irrit. 2	H351 H335 H319

* Hazard statement codes: H351: Suspected of causing cancer; H 335: May cause respiratory irritation; H319: Causes serious eye irritation.

TABLE 6
SELF-CLASSIFICAITON ACCORDING TO THE C&L INVENTORY ON THE ECHA WEB-SITE

Index No	International Chemical Identification	CAS No	Classification	
			Hazard Class and Category Code(s)	Hazard statement Code(s) *
-	Molybdenum sulphide (MoS2), roasted (technical grade molybdenum triox-ide)	86089-09-0	Carc. 2	H351

* Hazard statement codes: H351: Suspected of causing cancer; H 335: May cause respiratory irritation; H319: Causes serious eye irritation.

2.1.2 REACH

Community rolling action plan (CORAP)
Molybdenum trioxide is not listed in CORAP.

Registry of Intentions
There is no registry of intentions for molybdenum trioxide.

Candidate list
Molybdenum trioxide is not listed on the candidate list. It should be noted that the current harmonised classification does not fulfil the CMR criteria and PBT criteria are considered not to apply to inorganic substances; see also Section 5.3.

Annex XIV recommendations
Molybdenum trioxide is not listed in Annex XIV (it would first have to be included in the candidate list).

2.1.3 Other legislation or initiatives

No other legislative initiatives have been identified.

2.2 International agreements

Table 7 provides an overview of contexts in which molybdenum compounds (including molybdenum trioxide) are addressed by international conventions. As already addressed in Table 4, molybdenum compounds are addressed by the Basel Convention. Furthermore, the Baltic Sea (HELCOM) and the Mediterranean Sea Conventions list molybdenum as a noxious substance and call for strict control of emissions from land-based sources.

TABLE 7
INTERNATIONAL AGREEMENTS ADDRESSING MOLYBDENUM TRIOXIDE

Agreement	Substances	How molybdenum (trioxide) is addressed
HELCOM (Helsinki Convention)	Molybdenum (introduced as waterborne into the marine environment)	Listed in Annex II (Noxious substances and materials) of the original convention for which the purposes of Article 6 (Principles and obligations concerning land-based pollution) apply, including: - "... the Contracting Parties shall take all appropriate measures to control and strictly limit pollution by noxious substances and materials in accordance with Annex II of the present Convention..." Requirements are further specified in Helcom recommendation 11/6 providing basic principles in waste water management in chemical industry: **General principles** a) low waste technology should be applied wherever possible; b) the chemicals listed in the Appendix 2 which may reach the environment should be substituted by less harmful chemicals or subjected to requirements which will provide at least as good a result from an environmental standpoint; c) water management in chemical factories should aim at closed water systems or at high circulating rate in order to avoid wastewater production wherever possible, **Principles for wastewater handling** d) wastewaters containing substances listed in the Appendix 2 should before 1995 be separately treated before mixing with diluting waters (cooling water and low polluted wastewater). Furthermore, the treatment of the hazardous substances should be continuously improved by using best available technology for different streams with regard to the total result; e) chemical factories producing wastewaters which contain hazardous substances should be equipped with a segregated sewerage system; one drainage system for polluted process water which must enter a suitable central treatment plant before it is mixed with non-polluted water for final discharge, and another drainage system which receives cooling water, non-polluted storm water and possibly very low polluted wastewater. This should be applied to all plants the construction of which starts after 1990. In existing plants segregating of process water from cooling water should start before the year 2000.
Basel Convention	Molybdenum and its compounds (i.e. including molybdenum trioxide)	See EU implementation in Table 4.
PROTOCOL for the protection of the Mediterranean Sea against pollution from land-based sources	Molybdenum and its compounds (i.e. including molybdenum trioxide)	Included in Annex II for which "The Parties shall strictly limit pollution from land-based sources in the Protocol area b - substances or sources listed in Annex II to this Protocol"

Agreement	Substances	How molybdenum (trioxide) is addressed
PROTOCOL for the Protection of the Mediterranean Sea against pollution resulting from exploration and exploitation of the continental shelf and the seabed and its subsoil	Molybdenum and its compounds (i.e. including molybdenum trioxide)	Included in Annex II for which "The disposal into the Protocol Area of harmful or noxious substances and materials resulting from the activities covered by this Protocol and listed in Annex II to this Protocol requires, in each case, a prior special permit from the competent authority."

2.3 Eco-labels

Table 8 shows that the content of molybdenum (not molybdenum trioxide) in materials to be used for sanitary tapware is subject to European eco-label criteria.

TABLE 8
ECO-LABELS SPECIFICALLY TARGETING MOLYBDENUM TRIOXIDE

Eco-label	Articles	Criteria relevant for molybdenum trioxide (beyond general EU restrictions)	Document title/number
EU flower	Sanitary tapware	In relation to constituents and impurities of materials used for sanitary tap ware, a value of ≤ 1% molybdenum is specified and a reference value of 20 µg molybdenum/l drinking water is specified. NB! The molybdenum content in materials for sanitary tapware would be metallic molybdenum in alloys rather than molybdenum trioxide, but molybdenum trioxide may likely have been used as the molybdenum source for such alloys; see Chapter 3.	COMMISSION DECISION of 21 May 2013 establishing the ecological criteria for the award of the EU Ecolabel for sanitary tapware

2.4 Summary and conclusions

Pure grade molybdenum trioxide is subject to harmonised classification as a suspected carcinogen, with the potential for respiratory irritation and serious eye irritation properties, whereas the technical grade, in the absence of a harmonised classification, has been self-classified by industry. This self-classification is in line with the harmonised classification for the pure grade in relation to carcinogenicity classification. However, the technical grade has not been classified for respiratory irritation and serious eye irritation, as the Molybdenum Consortium disagrees with this classification.

Molybdenum trioxide is neither subject to other REACH procedures nor in the pipeline for such procedures.

"Molybdenum" (including molybdenum trioxide) is subject to a range of waste and emission/environmental media legislation.

In addition to being subject to the general hazardous waste legislation, there are specific waste codes addressing the use of molybdenum compounds in catalysts. The EU legislation on shipment of waste (implementing the Basel Convention), has requirements for the transboundary movement of molybdenum waste, however e.g. molybdenum in scrap (as metal and metal alloy) and catalysts waste does not fall under the prohibition of export to non-OECD Decision counties. There are specific Danish provisions related to release of molybdenum from landfill percolate. EU legislation addresses emission to and presence of molybdenum in surface- and groundwater and Danish provisions set standards for the presence of molybdenum in drinking water and in the air. There are also Danish provisions for molybdenum content in Dredge/Spoil material, which is sediment removed from e.g. harbours or navigation channels and dumped again in designated areas of the sea.

In addition to being subject to provisions in the Basel Convention, the Baltic Sea (HELCOM) and the Mediterranean Sea Conventions list molybdenum as a noxious substance and call for strict control of emissions from land-based sources.

Content and release of "molybdenum" (which could originate from molybdenum trioxide) is subject to the EU flower eco-labelling criteria for sanitary tapware.

3. Manufacture and uses

3.1 Manufacturing

3.1.1 Manufacturing processes

Molybdenum is widely distributed in nature. It is found in the minerals molybdenite, wulfenite , ferrimolybdate, jordisite, and powellite (NTP, 1997).

The REACH Molybdenum Consortium outlines the manufacturing process for technical grade molybdenum trioxide ("Molybdenum sulphide (MoS_2), roasted") (Carey, 2014): "*The chemical form of molybdenum in these ores is molybdenum disulphide (MoS_2, also designated "molybdenite"). After mining, molybdenum disulphide is extracted from the ore by a physical separation, flotation: where a chemical reaction of the Mo component is not involved. The resulting product is the enriched ore, namely "molybdenite concentrate" (chemically: MoS_2). The "molybdenite concentrate" is then roasted in air at temperatures > 400°C, typically in multiple hearth furnaces. During this process, the majority of molybdenum is oxidised from MoS_2 to Mo oxides and sulphur is turned into sulphur dioxide. Due to the nature of the process and material, the reaction to MoO_3 is not complete. The resulting product, now called roasted molybdenite concentrate (RMC), is composed primarily of a mixture of molybdenum oxides, including molybdenum trioxide*."

Carey (2014) also outlines the manufacturing process for pure grade molybdenum trioxide: "*The typical production process uses ammonium dimolybdate ($(NH_4)2Mo_2O_7$) as the educt. Ammonium dimolybdate is calcined at approx. 500°C. During this process, ammonia is liberated and pure molybdenum trioxide is obtained*."

As already noted in Chapter 1, under REACH, technical grade molybdenum trioxide is considered a UVCB substance (Unknown or Variable Composition, Complex Reaction Products or Biological Materials), named after the starting material and the manufacturing process; i.e. " Molybdenum sulphide (MoS2), roasted".

The EU molybdenum trioxide industry purchases molybdenum ores from outside the EU, including USA, Chile, Peru and Russia (Carey, 2014).

3.1.2 Manufacturing sites

Globally

For the interested, the U.S. Geological Survey (USGS) provides a good overview of molybdenum mining sites and their magnitudes worldwide (USGS, 2012).

No information providing a global overview of molybdenum trioxide manufacturing sites has been identified.

EU

The REACH Molybdenum Consortium advises that two EU companies – one in Belgium and one in The Netherlands - roast molybdenum concentrates to technical grade molybdenum trioxide (Carey, 2014).

The REACH Molybdenum Consortium advises that there is one company in The Netherlands and potentially one in Germany (if production from the latter has not been relocated to the USA), which manufacture pure grade molybdenum trioxide (Carey, 2014).

Molybdenum trioxide may also be manufactured directly into catalysts from other molybdenum starting materials as is outlined in the next paragraph. To what extent this takes place in EU countries other than Denmark has not been quantified in this project.

Denmark
A Danish catalyst manufacturer advises that molybdenum trioxide forms the basis of certain catalysts. A part of this molybdenum trioxide is purchased as pure grade molybdenum trioxide. The other part is obtained via a calcination process from other molybdenum starting materials (it is not specified which). The molybdenum trioxide resulting from this calcination process is formed as part of the catalyst manufacturing process; thus, the molybdenum trioxide is manufactured directly into the catalyst mixture. Consequently, no free molybdenum trioxide results from this calcination process.

3.2 Volumes - Manufacturing, import, export and overall consumption

Molybdenum trioxide is also used to produce pure molybdenum metal as such, or as an alloying element for steel and other alloys. Import/export of molybdenum metal/alloys is considered outside the scope of this project.

It should be noted that tonnage figures given for "molybdenum in molybdenum trioxide" should be corrected with the molar weight. One kg "molybdenum in molybdenum trioxide" would correspond to approx. 1.5 kg molybdenum trioxide.

3.2.1 Globally

From USGS statistics, it appears that the worldwide molybdenum mine production was approx. 264,000 tonnes molybdenum/year in 2011, of which 63,700 tonne/year were produced in the USA (USGS, 2012).

The REACH Molybdenum Consortium estimates the total mine production to correspond to about 225,000 tonnes molybdenum/year, which is in the same range as the USGS figures.

As is outlined below, approximately half of this volume is converted into and used as molybdenum trioxide.

3.2.2 EU level

REACH
Pure grade molybdenum trioxide has been registered under REACH in an overall amount of 10,000 – 100,000 tons/year and the technical grade in amounts of 100,000 – 1,000,000 tons/year. These numbers include production of molybdenum trioxide within the EU as well as import of molybdenum trioxide as such, or as part of mixtures; see Table 1.

EUROSTAT

Statistics on EU external trade and EU production can be retrieved from EUROSTAT. In the recent nomenclature (Commission Regulation (EU) No 1001/2013 – Annex 1), there is no specific CN customs code available for molybdenum trioxide, but pure grade molybdenum trioxide is covered by the code 2825 70 00 “Molybdenum oxides and hydroxides”. According to the REACH Molybdenum Consortium, the technical grade is covered by the code 26 13 100000 "Molybdenum ores and concentrates – Roasted" (Carey, 2014).

Figures for "Molybdenum oxides and hydroxides" would be higher than for molybdenum trioxide alone. On the other hand, it might be reasonable to assume that the volumes for "Molybdenum oxides and hydroxides" provide a rough estimate of molybdenum trioxide volumes. For example, NTP (1997) notes that the production of molybdenum trioxide is the largest of all the molybdenum compounds examined in their evaluation.

Table 9 provides the EU external trade volumes for "Molybdenum oxides and hydroxides" and "molybdenum ores and concentrates – Roasted" as monitored by EUROSTAT.

The most recent import and export figures for "Molybdenum oxides and hydroxides" from 2013 are slightly lower than the average of the four preceding years, but still within the range of fluctuation in the same period. Numbers for "Molybdenum ores and concentrates – Roasted" are rather stable. It can be seen that EU is a net importer of these molybdenum compounds.

TABLE 9
EU28 EXTERNAL IMPORT AND EXPORT OF MOLYBDENUM OXIDES AND HYDROXIDES (EUROSTAT, 2014)

CN8 code*	Substance	Import, t/y		Export, t/y	
		Average 2009-2012	2013	Average 2009-2012	2013
2825 70 00	Molybdenum oxides and hydroxides	2,954	2,617	736	613
2613 10 00	Molybdenum ores and concentrates - Roasted	46,293	46,825	14,160	14,344

* Code numbers are assigned according to the “Combined Nomenclature” (Commission Regulation (EU) No 1001/2013 – Annex 1) and used for identifying goods.

Table 10 provides the EU production volumes for "Molybdenum oxides and hydroxides" as monitored by EUROSTAT. No PRODCOM code is available for “Molybdenum ores and concentrates - Roasted”. Production volumes for "Molybdenum oxides and hydroxides" (including pure grade molybdenum trioxide) within the EU appears to have been increasing in recent years. This increase is higher than the possibly slight decrease in net import; therefore, a higher amount of these molybdenum compounds must have been processed within the EU as compared with previous years.

TABLE 10
EU28 PRODUCTION OF MOLYBDENUM OXIDES AND HYDROXIDES (EUROSTAT, 2014)

PRODCOM code	Substance	Production, t/y	
		Average 2008-2011	2012
2012 1973	Molybdenum oxides and hydroxides	2,290	3,150

Comparing REACH and EUROSTAT figures
It should be noted that the EUROSTAT figures only account for pure substances and therefore do not capture molybdenum trioxide as part of mixtures.

For "Molybdenum oxides and hydroxides", EU production plus import figures amount to about 5000 tonnes/year for "Molybdenum oxides and hydroxides", which is significantly lower than the lower tonnage band of the EU registration figure for the pure grade (10,000 tonnes/year), which further only addresses molybdenum trioxide. This could in theory be explained if there was a large import of pure grade molybdenum trioxide as part of mixtures (captured by REACH and not the EUROSTAT statistics), but considering the uses of molybdenum trioxide, this likely does not account for the difference. The REACH Molybdenum Consortium speculates that the difference might be due to some kind of double-registration under REACH (downstream users registering although they do not need to), but it should be stressed that this is just speculation (Carey, 2014).

The net import figures for import of "Molybdenum ores and concentrates - Roasted ", representing technical grade molybdenum trioxide, is about 32,000 tonnes/years. In order to compare with REACH (100,000 to 1,000,000 tonnes/year registered), the EU manufacturing volumes should be added. However, such data are not available as there is no corresponding PRODCOM code.

Other sources
Annex V to the Report of the Ad-hoc Working Group on defining critical raw materials (European Commission, 2010) notes that "...*the EU molybdenum industry, which consists of only a few companies, features not only ferro-molybdenum production, but also molybdenum oxides (technical molybdenum oxide and pure molybdenum oxide) and metal powders and products. Their combined annual output is hovering between 65.000 t to 75.000 t Molybdenum.*"

The REACH Molybdenum Consortium has been asked to reflect on these data, but notes that it is unclear on which data the figures reported by the European Commission are based (Carey, 2014).

From the website of the International Molybdenum Association (IMOA), it can be seen that the "European use" of molybdenum was about 140 million lbs. molybdenum (corresponding to approx. 63,500 tonnes molybdenum/ year) (IMOA, 2014a). This figure is in line with the European Commission (2010) figures.

It can also be seen from the IMOA website that "some 40 to 50%" of mined molybdenum is used for technical grade molybdenum trioxide (IMOA, 2014b). As the technical grade is manufactured in significantly higher volumes as compared to the pure grade, it seems fair to estimate that approximately 50% of mined molybdenum is used for the two grades of molybdenum trioxide combined. This assumption is in line with data in Table 3 of USGS (2012), which indicate that 45-55% of the US consumption of molybdenum is accounted for by molybdenum trioxide.

Thus, taking roughly 50% of the IMOA European consumption figures, it may be estimated that about 32,000 tonnes molybdenum per year are used to produce molybdenum trioxide. Converted by molar mass, this would give about 48,000 tonnes molybdenum trioxide (both grades)/year. This figure is close to the Eurostat figures and therefore supports the above speculation regarding a possible over-reporting of volumes in the REACH registrations.

Overall, the figure of 48,000 tonnes molybdenum trioxide (both grades)/year will be used in the following discussions, although it should be stressed that this number is uncertain and seems to conflict with the REACH registration tonnages.

3.2.3 Danish level

Statistics Denmark

As noted above, trade/customs statistics do not address pure grade molybdenum trioxide as such, but there is an entry for "Molybdenum oxides and hydroxides" for which data on Danish import and export are shown in Table 11 together with data for "Molybdenum ores and concentrates – Roasted" based on data from Statistics Denmark (2014).

TABLE 11
DANISH PRODUCTION, IMPORT AND EXPORT OF MOLYBDENUM OXIDES AND HYDROXIDES (STATISTICS DENMARK 2014, EUROSTAT, 2014 - PRODCOM DATABASE)

CN8 code*	Substance	Import, t/y		Export, t/y		Production**	
		Average 2009-2012	2013	Average 2009-2012	2013	Average 2008-2011	2012
2825 70 00	Molybdenum oxides and hydroxides	348	570	-	-	-	-
2613 10 00	Molybdenum ores and concentrates - Roasted	0	0	0	0	-	-

* Code number is assigned according to the "Combined Nomenclature" (Commission Regulation (EU) No 1001/2013 – Annex 1) and used for identifying goods.

** Figures for 2013 have not yet been available from the PRODCOM database

The data indicate that there is no import/export or production of "Molybdenum ores and concentrates – Roasted" representing technical grade molybdenum trioxide.

Regarding "Molybdenum oxides and hydroxides", including pure grade molybdenum trioxide, there is, as expected, no production/manufacturing of "primary" molybdenum oxides and hydroxides in Denmark. As noted in Section 3.1.2, there is production of molybdenum trioxide from other molybdenum compounds directly into mixtures; a volume which, however, would fall under customs codes other than "Molybdenum oxides and hydroxides". It can also be seen that there is no export of such primary pure grade molybdenum compounds, i.e. the imported volumes of primary molybdenum trioxide is either consumed in Denmark or exported as part of mixtures, which are also not captured by these statistics.

Danish Product Registry

The Danish Product Registry includes substances and mixtures used occupationally and which contain at least one substance classified as dangerous in a concentration of at least 0.1% to 1% (depending on the classification of the substance). Molybdenum trioxide is classified as dangerous. As stated above, the amounts registered are for occupational use only, but for substances used for the manufacture of mixtures in Denmark, the data may still indicate the quantities of the substances in the finished products placed on the market for consumer applications. However, given the uses of molybdenum trioxide addressed in Section 3.3 and information from the REACH Molybdenum Consortium, the substance is assessed not to be used in consumer products to any significant degree.

Average data for 2012/2013 were retrieved directly in April 2014, while data from the previous years were retrieved from the SPIN database[2], which holds non-confidential information from the Product Registries of the Nordic countries.

[2] http://195.215.202.233/DotNetNuke/default.aspx

The searches revealed that there are no registrations for the CAS number for technical grade molybdenum trioxide (CAS number: 86089-09-0). The below figures therefore represent registrations for CAS number 1313-27-5, which in REACH terms would be the pure grade. It cannot be excluded that registrants to the Danish Product Registry have used this CAS number when registering products with the technical grade; however, the applications/uses of the technical grade (for manufacturing/production of steel, alloys, ferromolybdenum and other molybdenum chemicals; see Section 3.2.2) are not likely to take place in Denmark. The following figures therefore most likely represent pure grade molybdenum trioxide. The applications are further discussed in the next sections.

According to data from the SPIN Database (based on data from the Danish Product Registry), the total annual registered use of molybdenum trioxide in Denmark has been rather stable from 2005 to 2011:

- 2005: 426 tonnes/year
- 2006: 406 tonnes/year
- 2007: 406 tonnes/year
- 2008: 466 tonnes/year
- 2009: 396 tonnes/year
- 2010: 398 tonnes/year
- 2011: 400 tonnes/year.

Data from recent years (2012/2013) indicate an annual use of 448 tons/year. This is in line or possibly slightly higher than previous years.

Comparing data from Statistics Denmark and the Product Registry

Data from Statistics Denmark and the Danish Product Registry confirm that there is no import/export or production of technical grade molybdenum trioxide in Denmark.

The Statistics Denmark 2013 figures for import of "Molybdenum oxides and hydroxides" (570 tonnes/year) is of the same order of magnitude as those obtained for pure grade molybdenum trioxide from the Danish Product Registry. The figures are, however, not directly comparable as the Statistics Denmark data only account for import of pure substances, whereas the Danish Product Registry data also accounts for import as part of mixtures. The data might indicate that most of the molybdenum trioxide import occurs in the pure substance form, assuming that the Danish Statistics data for "Molybdenum oxides and hydroxides" are mainly attributable to molybdenum trioxide.

In terms of trends, data from Statistics Denmark seem to indicate an increase in import, whereas data from the Danish Product Registry and the SPIN database (Section 3.3.3) appear to indicate stable demand in Denmark. This would be logical if the export of mixtures with molybdenum trioxide is increasing. Data to confirm this has, however, not been available to the project.

The data appear to indicate the following overall situation for Denmark:

- About 400-500 tonnes pure grade molybdenum trioxide is imported per year
- This import probably largely takes place as pure molybdenum trioxide and only to a minor extent as part of mixtures.

3.3 Uses and applications of molybdenum trioxide

As already noted in Chapter 1, a primary function of pure grade molybdenum trioxide is associated with its property as an oxidation catalyst precursor. Both grades of molybdenum trioxide are used as raw materials for production of the metal molybdenum, or as components of steel and other alloys. The alloys contain metallic (elemental) molybdenum and not molybdenum trioxide.

3.3.1 Globally

USGS (2012) notes the following: "*Molybdenum is a refractory metallic element used principally as an alloying agent in cast iron, steel, and super alloys to enhance hardenability, strength, toughness, and wear- and corrosion-resistance. To achieve desired metallurgical properties, molybdenum, primarily in the form of molybdic oxide (MoO3, called MoX) or ferromolybdenum (FeMo), is frequently used in combination with or added to chromium, manganese, nickel, niobium (columbium), tungsten, or other alloy metals. The versatility of molybdenum in enhancing a variety of alloy properties has ensured it a significant role in contemporary industrial technology, which increasingly requires materials that can sustain high stress, expanded temperature ranges, and highly corrosive environments. There is significant use of molybdenum as a refractory metal and in numerous chemical applications, including catalysts, lubricants, and pigments*" and states that 'MoX' (= molybdenum trioxide) was the leading form of molybdenum used by industry, particularly in making stainless steel.

USGS (2012) indicates that for the US market in 2011, about 88% percent (7,460 of 8,440 tonnes) of all molybdenum oxides were used in various steel production facilities, 0.02% (1.3 tonnes) for "Other alloys", 11% for catalysts (941 tonnes) and only 0.5% for “Other applications”. Data for "Super alloys" are not included in this statistic for 2011 for confidentiality reasons, but in 2010 it accounted for about 6%.

No better estimate for the global division on uses/applications has been identified. In addition, the REACH Molybdenum Consortium generally agrees with these numbers including those for the European situation (Carey, 2014).

In summary, it appears that the following approximate division of uses/applications of molybdenum trioxide would apply globally and at the EU level:

- Approx. 80-90% for various steel applications
- Approx. 10% for catalysts
- Approx. 5% for super alloys
- Approx. 0.5% for other applications.

3.3.2 EU level

The following list of registered uses under REACH can be taken from the ECHA dissemination tool website (ECHA, 2014a, b):

Pure grade molybdenum trioxide (CAS number 1313-27-5) for the formulation/production of:

- PC 0: Other: UCN P15500 Catalysts
- PC 2: Adsorbents
- PC 7: Base metals and alloys
- PC 9a: Coatings and paints, thinners, paint removes
- PC 9b: Fillers, putties, plasters, modelling clay
- PC 14: Metal surface treatment products, including galvanic and electroplating products
- PC 15: Non-metal-surface treatment products
- PC 19: Intermediate
- PC 20: Products such as ph-regulators, flocculants, precipitants, neutralisation agents
- PC 21: Laboratory chemicals
- PC 37: Water treatment chemicals.

Technical grade molybdenum trioxide (CAS number 86089-09-0):

- PC 7: Base metals and alloys
- PC 19: Intermediate.

The REACH Molybdenum Consortium (Carey, 2014) notes that the above lists of registered uses are currently under revision (Carey, 2014; Molybdenum Consortium, 2014).

The Consortium also advises that the main applications for technical grade molybdenum trioxide are as an alloying input to steel and alloys; for conversion into ferromolybdenum; and as feedstock for production of molybdenum chemicals such as ammonium dimolybdate and sodium molybdate (Carey, 2014). The Molybdenum Consortium further refers to the report "Assessment of 'Consumer Exposure' under REACH for MoCon Substances" (EBRC, 2010) prepared by EBRC for the REACH Molybdenum Consortium. This report confirms the above uses and concludes in relation to exposure to the technical grade (also termed "RMC"): "*In all uses identified for RMC, this substance is only used in industrial processes. In the steel- and alloy industries, RMC is used as a source for elemental molybdenum, which is then included in the steel/alloy matrix. During the production of molybdenum chemicals, RMC is chemically converted to another substance. In consequence, there is no known or foreseeable exposure of consumers to RMC.*" (EBRC, 2010).

Regarding the pure grade, the REACH Molybdenum Consortium notes the following main applications: "*Pure grade principal uses are for reduction to molybdenum metal (PC19: Intermediate), and as a component of catalyst production (mainly petro-chemical). It is also feedstock for production of the molybdenum chemical 'ammonium heptamolybdate'. It can also be used as an alloying input to steel and other alloys, but it is a more expensive product than technical grade moly trioxide so use volumes are lower, as often the desired effect i.e. molybdenum addition, is more cheaply and adequately achieved by using the technical grade moly trioxide*" (Carey, 2014). EBRC (2010) additionally notes the following uses where there potentially could be consumer exposure: water treatment chemicals; ceramic additives/enamel frits; flame retardants/smoke suppressants; pigments; metal surface treatment, and sintered metal additives. These uses are addressed in more detail and it is concluded that these uses do not lead to consumer exposure (EBRC, 2010) because molybdenum trioxide is either converted to other molybdenum compounds or molybdates before ending up in the consumer product or, in the case of flame retardants, the use was not reported as an EU use at the time of the REACH registration. Section 6.2.1 further elaborates on this.

As noted above, the REACH Molybdenum Consortium is currently aiming at updating the uses registered under REACH (Molybdenum Consortium, 2014). The uses which could potentially lead to consumer exposure are in line with those addressed in the EBRC (2010) report and the REACH Molybdenum Consortium confirms that since the 2010 registration, there have been no requests from downstream users to include use of molybdenum trioxide flame retardant as an identified use (Carey, 2014).

Further, articles with molybdenum trioxide as flame retardant could be imported to the EU. However, no data to confirm this has been identified and consumer exposure would likely be low.

No exact data for the volume of molybdenum trioxide for these above mentioned applications have been derived. However, as already noted in Section 3.3.1, it can roughly be assumed that about 0.5% of the molybdenum trioxide volume is used for "other applications" (i.e. other than for catalysts, molybdenum metal and alloys). The EU volume of molybdenum trioxide was estimated at approx. 48,000 molybdenum trioxide/year in Section 3.2.2. Thus, it can roughly be estimated that about 240 tonnes molybdenum trioxide is used per year for other applications, including the above discussed applications for water treatment chemicals; ceramic additives/enamel frits; pigments; metal surface treatment and sintered metal additives. *However, it should be stressed that this number of 240 tonnes molybdenum trioxide/year for "other applications", including production of such mixtures and articles as mentioned above, is associated with considerable uncertainties.*

Some sources (e.g. European Commission, 2010) mention that molybdenum compounds are used as lubricants. The REACH Molybdenum Consortium has advised that molybdenum sulphide (and not molybdenum trioxide) is used for this application (Carey, 2014).

3.3.3 Denmark

Danish Product Registry
Data on registered uses/applications of molybdenum trioxide can unfortunately not be disclosed for confidentiality reasons, as the number of registrants for *each use* registered is fewer than 3. It should be noted that the Danish EPA has insight into these registrations on a confidential basis, and thus might use this knowledge in their further considerations regarding molybdenum trioxide.

In general, as appears from Section 3.2.1 and 3.2.2, most of the industrial applications of molybdenum trioxide would be types of industrial uses, the facilities for which are not located in Denmark. Furthermore, in most of these instances, molybdenum trioxide would be transformed into molybdenum metal or other molybdenum compounds before possibly being imported to Denmark.

Data from Danish Companies
One Danish company producing catalysts has agreed to be cited in this report.

As described in Section 3.1.2, pure grade molybdenum trioxide is purchased and used for this production, whereas another part of the molybdenum trioxide in the final catalysts is manufactured directly into the catalysts from other molybdenum starting materials.

The applied volumes are confidential, but the company confirms that molybdenum trioxide is largely applied for production of catalysts for refineries. A minor amount is used for producing formaldehyde catalysts. More than 95% of the manufactured catalysts are exported from Denmark.

The catalysts as produced are not active. The catalysts are generally activated by an *in situ* sulphidation of the molybdenum trioxide.

Other Danish information sources
A Danish EPA project from 2003 notes that molybdenum trioxide is known to be used as a flame retardant, e.g. in polyester products (Kjølholt et al., 2003). As noted in section 3.2.2, this use is currently not supported in relation to the REACH registration process. However, import of such articles might take place.

3.4 Historical trends in use

As set out in Section 3.2.2 and 0 there seems to be the following trends:

EU

- There might be a slight decrease in import as well as export of pure grade molybdenum trioxide. Net import might decrease very slightly. The figures for technical grade molybdenum trioxide are rather stable.
- For pure grade molybdenum trioxide, there appears to be a significant increase in manufacturing volume from an average of about 2300 tonnes/year (2008-2012) to about 3150 tonnes/year in 2013.
- Taking import/export and production figures together, this could indicate an increasing consumption of pure grade molybdenum trioxide within the EU market and/or an increase in export of mixtures or articles containing molybdenum trioxide.

The above considerations are based on EUROSTAT statistics. As indicated in the text, there seems to be some discrepancies between EUROSTAT and REACH registration volumes; thus, some uncertainty exists.

Denmark
There seems to be a rather stable consumption of pure grade molybdenum trioxide in Denmark of approx. 400-450 tonnes/year over the past decade.

Globally
An interview with a representative from the catalyst industry has provided the following view on global trends: The use of molybdenum trioxide has been increasing for several decades and is expected to continue to increase in future. This assumption is to a large extent driven by an expected increase in the use of catalysts in the petroleum refining industry due to i) higher demands regarding desulfurization of oil (the US Environmental Protection Agency have recently reduced the threshold for sulphur in gasoline from 30 to 10 ppm); ii) the remaining oil in the reserves is more rich in sulphur and will thus require additional desulfurization; and iii) the demand for diesel and gasoline is still increasing globally. In addition, catalysts are likewise being applied in the hydrogenation of biodiesel (5-10%), where the catalysts removes oxygenates, nitrogen and sulphur.

USGS (2012) notes the following under "OUTLOOK": "*The principal uses for molybdenum were expected to continue to be in chemicals and catalysts and as an additive in steel manufacturing, most importantly alloy and stainless steel. Molybdenum plays a vital role in the energy industry, and it may become an increasingly essential factor in green technology, where it is used in high-strength steels for automobiles to reduce weight and improve fuel economy and safety. Molybdenum may play a critical role in reducing sulphur in liquid fuels by acting as a cracking agent. Production of diesel fuels having ultra-low-sulphur levels was expected to more than double the amount of molybdenum used in oil refineries. Analysts expected global demand for these types of catalysts to increase by more than 5% annually until 2013. The need for companies to reduce carbon dioxide emissions from coal-fired power stations will require plants to run at higher temperatures, resulting in greater demand for higher grade molybdenum-bearing steels.*" Although this is a statement for molybdenum and not molybdenum trioxide specifically, molybdenum trioxide is a precursor for the catalyst and metal applications discussed.

3.5 Summary and conclusions

Molybdenum trioxide is marketed in two grades:

- Pure grade molybdenum trioxide
- Technical grade molybdenum trioxide.

Molybdenum trioxide supplied to the market as pure grade molybdenum trioxide is manufactured at two EU sites and the technical grade in one or two EU sites. These sites are located outside Denmark. In addition, pure grade molybdenum trioxide can be manufactured directly into catalyst mixtures from other molybdenum starting materials. This process does not result in manufacture of molybdenum trioxide as a free substance. One such company is located in Denmark.

The following volumes (including import and manufacturing of pure molybdenum trioxide and import as part of mixtures) have been registered under REACH:

- Pure grade molybdenum trioxide: 10,000 – 100,000 tonnes/year
- Technical grade molybdenum trioxide: 100,000 – 1,000,000 tonnes/year.

However, based on data from the International Molybdenum Association (IMOA), supported by data from EUROSTAT and a 2010 report from the European Commission, total European use of about 48,000 tonnes molybdenum trioxide (both grades)/year can be estimated.

The reason for these discrepancies has not been identified, but might be due to REACH double-registrations.

Based on the available information, the following estimated shares between applications for the global and the EU levels have been estimated for molybdenum trioxide (Pure and Technical grades):

- Approx. 80-90% for various steel applications
- Approx. 10% for catalysts (mainly for refineries)
- Approx. 5% for super alloys
- Approx. 0.5% for other applications.

"Other applications" include use of molybdenum trioxide for formulating/producing the following mixtures/articles: Water treatment chemicals; ceramic additives/enamel frits; pigments; metal surface treatment, and sintered metal additives. These are uses for which molybdenum trioxide is converted to other molybdenum compounds/molybdates before possibly coming into contact with consumers. A rough estimate of "Other applications" amounts to approx. 240 tonnes molybdenum trioxide/year in the EU.

The pure grade molybdenum trioxide is used for catalysts (mainly for refineries) and the above "Other applications", whereas both grades can be used for steel and other alloy production. However, mainly the cheaper technical grade is used for the steel and alloy applications.

There might be some import to the EU of articles containing molybdenum trioxide as flame retardant (e.g. polyester based). Available data, however, do not allow confirmation or quantification of this.

To the knowledge of the authors, no steel or alloy production applying molybdenum trioxide takes place in Denmark, as confirmed by statistics showing a lack of registered import of technical grade molybdenum trioxide.

It is known that catalyst production takes place in Denmark, including using imported pure grade molybdenum trioxide, as well as other molybdenum compounds, for manufacturing molybdenum trioxide directly into the catalysts during the catalyst production process. More than 95% of these catalysts are exported. Data are too scarce or confidential to map other applications of molybdenum trioxide in Denmark. Overall, the Danish Product Registry indicates that about 400 – 450 tonnes pure grade molybdenum trioxide/year is imported to Denmark.

Generally, the use of molybdenum trioxide is expected to increase, due to increased demand for sulphur-reducing catalysts in the refinery industry (need for cleaner fuels based on fuel reserves containing more sulphur than in the past) and the need for high-strength steels, e.g. for lighter vehicles (requiring less fuel) and for coal-fired power stations which will need to run at higher temperatures in the future.

Data gaps
Some uncertainty exists in relation to the total amounts of molybdenum trioxide used on the EU market.

It is certain that the main applications of molybdenum trioxide are for production of refinery catalysts, steel and other alloys, but some uncertainties are associated with estimating the volume of the relatively minor amounts used for other applications.

4. Waste management

In order to generate data for this chapter, literature searches have been supplemented with information from a catalyst manufacturer and a major Danish waste disposal company, NORD, that has extensive experience with hazardous waste handling, including molybdenum as part of metal scrap and production waste.

4.1 Waste from manufacture and industrial use of molybdenum trioxide

As outlined in Chapter 3, the majority of molybdenum trioxide is used in metal/metallurgical applications (>85%) and for refinery catalysts (approx. 10%), while a smaller fraction (estimated to be below 1%) is used for other applications, including a number of mixtures and articles. Hence, waste from manufacture and industrial use of molybdenum trioxide primarily originates from metal/metallurgical applications, in particular steel, advanced alloys and catalysts. Molybdenum in waste from the manufacture of catalysts is either recycled within the companies or sent for recycling by specialized recycling companies, according to the available information. None of the specialized recycling companies are located in Denmark.

As discussed in Section 3.1.2, there are only a few sites manufacturing primary pure and technical grade molybdenum trioxide in the EU. These are not located in Denmark and it is outside the scope of this project to attempt to describe how waste from these facilities is disposed of, although it is assumed that attempts are made to recycle molybdenum internally or externally due to the its economic value (see below).

No data have been identified on waste from industrial uses of molybdenum trioxide, e.g. for producing the mixtures and articles listed in the next section.

4.2 Waste products from the use of molybdenum trioxide in mixtures and articles

A major source of waste comes from the disposal of catalysts used in the petroleum (oil) refining industry; however, the bulk of this waste is recycled and is not in the form of molybdenum trioxide (as molybdenum trioxide is sulfurized/reduced in spent catalysts).

According to a recent report from 2010 on consumer exposure (EBRC, 2010) and, as introduced in chapter 3, molybdenum trioxide is used for production of a number of mixtures and articles intended for consumers, including water treatment chemicals; ceramic additives/enamel frits; pigments; metal surface treatment, and sintered metal additives. As noted and as will be further elaborated in Section 6.2.1, molybdenum trioxide is converted to other molybdenum compounds or to molybdate in the final consumer products, which will enter various waste streams depending on product type. As the amount of other such applications has been estimated to be very low compared to other molybdenum trioxide applications (accounting for about 0.5% of the molybdenum trioxide volume), we will not further elaborate on these minor waste streams.

EBRC (2010) notes that use of molybdenum trioxide as a flame retardant was not reported as a use in the EU by the time of the REACH joint registration. However, it cannot be excluded that molybdenum trioxide would be incorporated as a flame retardant in imported products. However, no quantitative data on this usage have been identified.

A complementary internet search using a combination of key words ('waste disposal', 'molybdenum', 'articles' and 'mixtures') did not reveal any relevant information regarding waste disposal of articles and mixtures containing molybdenum. This finding corresponds with the report prepared for the REACH Molybdenum Consortium (EBRC, 2010), which states that only limited information regarding the historic use of molybdenum trioxide in mixtures and articles is available.

4.3 Recycling and material recovery

Recycling of molybdenum and other metal scrap occurs throughout the European region including countries such as United Kingdom, Germany, Spain, Belgium, France, Turkey, Lithuania, Montenegro, Belarus, Denmark, Hungary, The Netherlands, Poland, Portugal and Serbia (full list of companies is available at http://www.environmental-expert.com/companies/keyword-scrap-metal-1853/location-europe#). According to Blossom (2002), alloy and stainless steel constitute a considerable source of molybdenum scrap in the US. Although molybdenum is not recovered separately from scrap steel and super alloys that contain it, recycling of these alloys is significant in ensuring reuse of the molybdenum they contain.

Material recovery of molybdenum occurs primarily from metal scrap (e.g. alloys) and spent catalysts. In the case of metal scrap, simple alloys, Mo-containing stainless steels and scrap blends are re-moltened during the scrap melting process and then added back into the steel-making process. Spent catalysts can be roasted in an oxidizing atmosphere followed by leaching to dissolve molybdenum and other metals. The metals in the leachate solution are then separated by e.g. filtration, precipitation and/or solvent extraction (e.g. Ference & Sebenik, 1982).

Due to the value of molybdenum, the recycling loop for molybdenum trioxide is as closed as technologically possible. According to a Danish manufacturer, catalysts generally have a 'life-span' of 1-3 years depending on the particular application, and they are normally regenerated to be used as 'new' catalysts again, up to three times before they are spent. Production waste is recycled internally to the extent possible. The remaining molybdenum-containing waste is sent for recycling outside Denmark to specialized European metal reclaiming companies. Molybdenum is recovered and re-used for different applications. The same applies for catalyst customers (mainly refineries), which send spent catalysts containing molybdenum to the specialised metal reclaiming facilities.

Notifications to the Waste Data System (Affaldsdatasystemet) under the Danish EPA (2014) show how molybdenum scrap from used catalysts was disposed of during 2011-2013 in Denmark (Table 12 and Table 13). It should be noted that these data are for molybdenum and molybdenum compounds and therefore do not only represent molybdenum trioxide. The vast majority of the molybdenum scrap is exported (80.6-98.5 %) to European metal scrap companies in Germany, Sweden and United Kingdom (Table 12). The tonnage for 2011 is particularly high, approximately 18-32 times higher than tonnages for 2012 and 2013, respectively. The main reason is that one Danish company exported 405 tonnes of molybdenum containing scrap to the United Kingdom, which is likely due to restoration of large industrial processing equipment and thus constitutes an event that would occur relatively infrequently (perhaps once in 10 years).

TABLE 12
DANISH WASTE DISPOSAL OF MOLYBDENUM SCRAP (DATA FROM THE WASTE DATA SYSTEM)

	2011, t/y	2012, t/y	2013, t/y
Danish collector/recipient	6.2	2.5	1.7
Export	8.4 (Sweden) 405 (UK)	10.4 (Germany)	21.1 (Germany)
Import	-	-	0.2
Total tonnage	419.6	12.9	22.9

The recycling rate of molybdenum scrap is very high ranging from 81.4 % in 2012 to >98 % in 2011 and 2013 with the average recycling of molybdenum scrap for the entire period (2011-2013) being >98 % (Table 13).

TABLE 13
DISPOSAL ROUTE OF MOLYBDENUM SCRAP FROM DANISH COMPANIES (DATA FROM THE WASTE DATA SYSTEM)

	2011, t/y	2012, t/y	2013, t/y
Recycling (incl. pre-treatment)	414.1	10.5	22.5
Incineration (incl. pre-treatment)	5.5	1.8	0.4
Export*		0.7	
Total tonnage	419.6	12.9	22.9

*Unknown fate of disposed molybdenum scrap.

4.4 Release of molybdenum trioxide and degradation products from waste disposal

4.4.1 Solid waste incineration

The Danish waste disposal company, NORD, advises that they occasionally may receive, and incinerate, production waste from molybdenum containing applications, e.g. steel, alloy and catalysts (Andreasen, 2014).

The fraction of metal scrap that is being incinerated is very low (<2 %, see Table 13); and the intensive recycling and material recovery (see above) makes incineration an infrequent (unlikely) route for molybdenum. Still, like other metal-containing waste undergoing incineration, it may end up in the slag and ash, and to a very small extent become airborne, entering the atmospheric environment with the flue gas, subsequently precipitating on land (Andreasen, 2014).

A small fraction of consumer products containing molybdenum may end up in household waste to become incinerated (e.g. in Denmark). However, the bulk of these consumer products end up at municipal recycling stations, where they are separated as e.g. hazardous waste (paint, electronics), metal scrap or building materials (e.g. tiles).

4.4.2 Releases from landfills

Depending on different European national waste management practises, release of molybdenum (as molybdate) from landfills may occur from deposited slag and ash from incinerators (see above) or from household waste deposited at landfills. Currently, there is no deposition of ash and slag at landfills in Denmark; according to NORD, ash and slag is transported to e.g. Norway where is it deposited at impermeable (bedrock) landfills (Andreasen, 2014).

4.4.3 Molybdenum trioxide waste water and sewage sludge

The likelihood of molybdate from molybdenum trioxide entering waste water and sewage sludge is assumed to be low considering that the vast majority is recycled and that the remaining part is possibly being incinerated. A recent report from the Australian science agency CSIRO finds that molybdenum concentrations in waste water are in the low µg/l level. The report likewise states that there is limited data on the sources that contribute to this load (Tjandraatmadja et al., 2010).

4.5 Summary and conclusions

The vast majority of molybdenum waste originating from molybdenum trioxide applications comes from using molybdenum trioxide for catalysts and alloys manufacturing. Most of the waste generated is recycled due to the economic incentive in reusing molybdenum. Molybdenum trioxide is likewise, although to a much lesser extent, an input material into different mixtures and articles (e.g. ceramics, pigments and water treatment chemicals). In most of these products, molybdenum trioxide is chemically transformed into other molybdenum compounds (e.g. in aqueous media it will be transformed into molybdate ions), entering the environment or various waste streams as these molybdenum compounds. There are no data available that estimate the level of molybdenum trioxide present in the different waste streams described in this chapter; however, it is reasonable to conclude that it is minimal because of the chemical transformation that molybdenum trioxide undergoes in various applications.

The release of molybdenum trioxide or molybdenum compounds originating from molybdenum trioxide to the environment from e.g. landfills and waste water is considered limited, particularly due to the largely closed recycling loop for its main applications.

5. Environmental hazards and exposure

5.1 Environmental fate and behaviour

Molybdenum is a naturally occurring element belonging to the group of transition metals and it is widespread in nature where it, among others, is a constituent of a number of minerals. It is present at an average concentration of 12 to 16 ppm in seawater and 1 ppm in the earth's crust (NTP, 1997).

In molybdenum trioxide, molybdenum is in oxidation state +6, which is considered to be the most prominent in oxidised aquatic and terrestrial environments (Kjølholt et al., 2003; Mitchell, 2010). Molybdenum is oxidised at high temperatures, and therefore the element is emitted as molybdenum trioxide from sources such as coal and/or oil fuelled power plants, waste incineration plants, metallurgical plants and natural sources such as volcanic activity and forest fires.

Molybdenum trioxide is rather soluble in water (between 560-1000 mg Mo/l; see Table 3) and occurs typically in oxidised aquatic and terrestrial environments as the molybdate ion, MoO_4^{2-}; however, at acidic pH polymerisation can occur and lead to paramolybdate ($Mo_7O_{24}^{6-}$) as the dominant form (van Vlaardingen et al., 2005). Other forms, such as e.g. sulphides, can/will be present under anoxic and anaerobic conditions but no specific information on these conditions has been obtained.

In the soil environment, molybdenum (as molybdate) is considered to be relatively immobile with a sorption constant of 150-2000 mg/kg depending on the soil's content of clay and organic material (Kjølholt et al., 2003). The OECD Screening Information Dataset (SIDS) Initial Assessment Profile for molybdenum salts (OECD, 2013) reports a typical Kd for molybdenum in soil of 871 L/kg.

Molybdenum in the atmospheric compartment is likely present in the oxidised form, i.e. as molybdenum trioxide, but no specific information on this was identified in the data collection.

5.2 Environmental hazard

5.2.1 Classification

Pure grade molybdenum trioxide is subject to harmonised EU classification; however, it does not have any classification for environmental effects; see Table 5. Likewise, technical grade molybdenum trioxide has not been self-classified by industry for environmental effects.

5.2.2 Ecotoxicity

Aquatic ecotoxicity

Recently, a SIDS Initial Assessment Profile was published by the OECD (OECD, 2013) for "highly soluble molybdenum salts" as a group based on data provided by industry. The data and the report was agreed at the OECD CoCAM[3] meeting held in the US, 15-17 October 2013, and is therefore considered to have been reviewed by authorities and, as such, applicable to this survey. The SIDS pro-

[3] CoCAM = Cooperative Chemicals Assessment Meeting.

file documents contain a summary of aquatic ecotoxicological data generated from tests using sodium molybdate as test substance, among others.

With reference to the aquatic environmental chemistry of molybdenum (see Section 5.1), the use of molybdate to test the aquatic effects of molybdenum trioxide is considered relevant and justified. Therefore a summary of the data of tests using soluble molybdenum salts (molybdates) are used here to give an overview of and represent the aquatic ecotoxicity of molybdenum (trioxide); see Table 14 (short term aquatic toxicity), Table 15 (chronic toxicity to freshwater organisms) and Table 16 (chronic toxicity to marine organisms).

TABLE 14
OVERVIEW OF SHORT TERM TOXICITY ENDPOINTS FOR SOLUBLE MOLYBDENUM SALTS (MOLYBDATES) TO AQUATIC ORGANISMS (DATA FROM OECD, 2013). ONLY THE LOWEST ENDPOINTS FOR THE MOST SENSITIVE SPECIES WITHIN EACH TAXONOMIC GROUP ARE PRESENTED.

Group	Species	Study type	Endpoint	Value (mg Mo/l)
Fish	*Pimephales promelas*	96 h, semi-static	LC50	609.1
Invertebrates	*Daphnia magna*	48 h, static	LC50	130.9
Algae	*Pesudokirchneriella subcapitata*	72 h, static	E_rC50	289.2

TABLE 15
OVERVIEW OF CHRONIC TOXICITY ENDPOINTS FOR SOLUBLE MOLYBDENUM SALTS (MOLYBDATES) TO FRESHWATER ORGANISMS (DATA FROM OECD, 2013). ONLY THE LOWEST ENDPOINTS FOR THE MOST SENSITIVE SPECIES WITHIN EACH TAXONOMIC GROUP ARE PRESENTED.

Group	Species	Study type	Endpoint	Value (mg Mo/l)
Fish	*Onchorhynchus mykiss*	12 months, flow-through	$NOEC_{mort., growth}$	>17
Invertebrates	*Cerodaphnia dubia*	7 d, semi-static	$EC10_{, reproduction}$	50.8
Gastropods	*Lymnaea stagnalis*	28 d, semi-static	$EC10_{, growth rate}$	221.8
Amphibians	*Xenopus laevis*	4 d, semi-static	$EC10_{, development}$	115.9
Algae	*Pesudokirchneriella subcapitata*	72 h, static	$E_rC10_{, growth rate}$	61.2
Higher plants	*Lemna minor*	7 d, static	$E_rC10_{, growth rate}$	241.5

TABLE 16
OVERVIEW OF CHRONIC TOXICITY ENDPOINTS FOR SOLUBLE MOLYBDENUM SALTS (MOLYBDATES) TO MARINE ORGANISMS (DATA FROM OECD, 2013). ONLY THE LOWEST ENDPOINTS FOR THE MOST SENSITIVE SPECIES WITHIN EACH TAXONOMIC GROUP ARE PRESENTED.

Group	Species	Study type	Endpoint	Value (mg Mo/l)
Fish	*Cyprinodon variegatus*	28 d, flow-through	$EC10_{, biomass}$	84.1
Invertebrates	*Acartia tonsa*	20 d, semi-static	$EC10_{, development}$	7.96
Molluscs	*Mytilus edulis*	48 h, static	$EC10_{, development}$	4.4
Echinoderms	*Dendraster excentricus*	48 h, static	$EC10_{, development}$	233.6
Algae	*Phaeodactylum tricornutum*	72 h, static	$E_rC10_{, growth rate}$	169.9

In total, chronic toxicity data are presented by OECD (2013) for the following number of species within each taxonomic group (for freshwater and saltwater, respectively):

- Freshwater, chronic (no. of species): 3 fish, 4 invertebrates, 1 gastropod, 1amphibian, 1 alga, 1 higher plant.
- Saltwater, chronic (no. of species): 1 fish, 2 invertebrates, 2 molluscs, 2 echinoderms, 3 algae/higher plants.

The number of species and taxonomic groups tested for chronic toxicity justifies that the REACH Molybdenum Consortium for registration of molybdenum and molybdenum compounds has determined aquatic PNEC values for molybdenum/molybdate based on statistical extrapolation (species sensitivity distribution) (ECHA, 2014a).

The following aquatic PNECs are presented at the ECHA dissemination tool website under the CAS number for molybdenum trioxide (values proposed by the REACH Molybdenum Consortium)[4]:

$PNEC_{freshwater}$ = 19.05 mg MoO_3/l (statistical extrapolation; AF = 3)

$PNEC_{saltwater}$ = 2.85 mg MoO_3/l (statistical extrapolation; AF = 3)

$PNEC_{sediment,\ freshwater}$ = 33,900 mg MoO_3/kg dw (partition coefficient; AF = 1)

$PNEC_{sediment,\ saltwater}$ = 2,970 mg MoO_3/kg dw (partition coefficient; AF = 1).

An earlier review of aquatic ecotoxicity data on molybdenum exists (van Vlaardingen et al., 2005) in which the data also predominantly originate from studies using (sodium) molybdate as the test compound (a few tests were conducted with another molybdenum species in oxidation state +6, namely $(NH_4)_6Mo_7O_{24}$ (in reality also a molybdate)). Less data are included in this review (totals of 6 fish, 4 crustacean, 1 algae, 2 mollusc and 1 annelidae species). Therefore van Vlaardingen et al. (2005) derived Environmental Risk Limits, ERLs ("PNEC"s) for molybdenum based on the lowest acute endpoint of 29 mg/l (for annelidae) and applying an assessment factor (AF) of 1,000 (for freshwater). The ERL value produced is for the dissolved phase and should be added to the natural background level of molybdenum and therefore named MPA (Maximum Permissible Addition).

An ERL/MPA for molybdenum in freshwater = 29 µg/l was proposed initially but this value was later revised by the Dutch authorities to the current annual average JG-MKN (Jaargemiddelde Milieukwaliteitsnorm) for molybdenum in surface waters of 136 µg/l published in 2010 (Staatscourant, 2010). This value is equal to an Annual Average Environmental Quality Standard (AA-EQS). The corresponding MAC-MKN (max. short term EQS; MAC-EQS) for molybdenum is 340 µg/l.

In the Danish statutory Order No. 1022 of 25 August 2010, an AA-EQS for molybdenum in surface water is established at 67 µg/l for freshwater and 6.7 µg/l for marine water.

It is noted that there is a significant discrepancy between the Dutch and Danish EQS values for molybdenum in surface water and the PNEC value proposed in the REACH registration data submitted by industry. This is likely due to different data being available for the assessment (date and amount) and therefore different calculation approaches applied (probably assessment factor (AF) method by the Danish and Dutch authorities against statistical extrapolation by the REACH registrant). As well, data may have been interpreted differently by the authorities and industry leading to

[4] The PNEC values are presented in "mg/l" without specification of whether they represent mg MoO3/l or mg Mo/l. The REACH Molybdenum Consortium advises that the values are for molybdenum trioxide (Carey, 2014).

different opinions on the assessment factors to be applied. Investigating this is further detail would entail access to the full version of the confidential REACH registration dossier, specifying assumptions and justifications.

Terrestrial ecotoxicity

The SIDS Initial Assessment Profile for "highly soluble molybdenum salts" (OECD, 2013) also comprises some terrestrial ecotoxicity data (ten soil types), which are presented in Table 17.

TABLE 17
OVERVIEW OF CHRONIC TOXICITY ENDPOINTS FOR SOLUBLE MOLYBDENUM SALTS (MOLYBDATES) IN THE SOIL ENVIRONMENT (DATA FROM OECD, 2013). ONLY THE LOWEST ENDPOINTS FOR THE MOST SENSITIVE SPECIES WITHIN EACH TAXONOMIC GROUP ARE PRESENTED.

Group	Species	Study type	Endpoint	Value (mg Mo/kg dw)
Invertebrates	*Eisenia Andrei*	56 d	EC10	8.88
Plants	*Brassica napus; trifolium pratense*	21 d	EC10	5
Soil microbial processes	*Substrate-induced respiration*	24 h	EC10	10

The REACH Molybdenum Consortium proposes a $PNEC_{soil}$ = 14.25 mg MoO_3/kg dw (statistical extrapolation; AF = 1) based on the data submitted for the registration (ECHA, 2014a)[5].

No data on terrestrial organisms are presented in the review by van Vlaardingen et al. (2005). However, based on the aquatic results they derive MPA values for the soil environment. The value derived for molybdenum in soil is: MPA_{soil} = 760 µg/kg soil.

Kjølholt et al. (2003) refers to an ecotoxicological criterion of 2 mg/kg for molybdenum in soil published by the Danish EPA in 1997.

Other environmental effects

No other relevant environmental effects of molybdenum/molybdenum trioxide have been identified.

5.2.3 Effects of combined exposure

No information identified.

5.3 PBT and vPvB assessment

According to REACH Annex XIII and the associated guidance, the PBT and vPvB criteria of Annex XIII do not apply to inorganic substances.

None of the environmental information identified gives any indication that molybdenum should be considered bioaccumulative (molybdenum is an essential micro-nutrient).

[5] It is not specified whether the mg/kg refer to mg Mo/kg or mg MoO3/kg. The REACH Molybdenum Consortium informs that the values are for molybdenum trioxide (Carey, 2014).

5.4 Environmental exposure

5.4.1 Sources of release

Releases in Denmark

Considering the applications of molybdenum trioxide in Denmark, it appears likely that the main fraction of molybdenum trioxide releases originates from emissions from coal power plants and waste incineration plants where molybdenum, present as an element (or in other chemical forms) is oxidised to molybdenum trioxide during the combustion process. No data on the amounts released have been identified.

Releases at EU level

At the EU level, the same sources of release as mentioned for Denmark are also relevant. However, some of the other EU countries have significant metallurgical industries e.g. producing steel with molybdenum as a component, which contribute further to environmental releases of this element. No data on such emission have been identified in this review.

5.4.2 Monitoring data

The Danish NOVANA environmental monitoring programme

Molybdenum is not included in the standard programme of national Danish environmental monitoring activities, the NOVANA programme, with the exception of effluents from sewage treatment plants and groundwater wells for drinking water production.

The Danish Nature Agency (Naturstyrelsen, 2012) reported a median level of molybdenum in effluents from Danish public sewage treatment plants (STPs) in 2011 of 1.4 µg/l and a 95^{th}-percentile of 3.83 µg/l. A national mean concentration of molybdenum in STP effluents based on national monitoring data from about 40 STPs in the period 1998-2009 was calculated by Kjølholt et al. (2011) to be 5,0 µg/l.

GEUS (2007) reported monitoring data for groundwater (intake at waterworks) covering the period 1989-2006. The average concentration of molybdenum (only 10 analyses in total) was 1.20 µg/l while the maximum value was 2.9 µg/l (the Danish drinking water quality criterion is 20 µg/l).

Environmental monitoring data included in the registration data for molybdenum trioxide at ECHA's website also include a mean background value for Danish surface water of 0.26 µg/l (based on a data set of less than 10) and for sediment of 0.61 mg/kg dw. The background value for soil is reported to be 0.30 mg/kg dw. For grazing land and for agricultural land "reasonable worst case" (RWC) PEC values have been calculated at 0.45 and 0.37 mg/kg dw, respectively.

Data from other countries/regions

The median background values of molybdenum concentrations in surface water, sediment and topsoils in Europe is reported in the ECHA REACH registration data to be 0.28 µg/l and 0.58 and 0.59 mg/kg dw, respectively. The median European RWC PEC values for grazing land and agricultural land are 1.04 mg/kg dw and 0.86 mg/kg dw, respectively.

A recent report from the Australian science agency CSIRO finds that molybdenum concentrations in waste water are in the low µg/l level (Tjandraatmadja et al., 2010).

5.4.3 Other exposure data

None identified.

5.5 Environmental impact

No publicly available environmental risk assessments of molybdenum (trioxide) have been identified.

It should be noted that the identified background concentrations of molybdenum in aquatic and terrestrial environments are well below the relevant environmental threshold values or quality criteria.

5.6 Summary and conclusions

Environmental fate and effects

Molybdenum is a naturally occurring element, present at an average concentration of 12 to 16 ppm in seawater and 1 ppm in the earth's crust. Oxidation state +6 is considered to be the most prominent in oxidised aquatic and terrestrial environments i.e. typically as the molybdate ion, MoO_4^{2-}. In the soil, environmental molybdenum is considered to be relatively immobile with a sorption constant of 150-2000 mg/kg depending on the soil's content of clay and organic material. In the atmospheric compartment molybdenum is likely present only in the oxidised form.

Effect data are available for a significant number of organisms in the aquatic environment (based on tests with the molybdate ion). Molybdenum (tested as molybdate) is not particularly toxic in the aquatic environment; the reported acute EC50/LC50 values are all above 100 mg Mo/l while the lowest chronic effect value is >17 mg Mo/l in freshwater and 4.4 mg Mo/l in saltwater.

Releases to the environment

In Denmark, the main emissions of molybdenum trioxide are considered to be emissions from coal power plants and waste incineration plants. At the EU level, the same sources of release are also relevant and, additionally, some of the other EU countries have significant metallurgical industries, which contribute further to releases of this element to the environment. No data on the amounts released have been identified.

Monitoring data – levels in the environment

The environmental monitoring data on molybdenum are rather few but do indicate that, generally speaking, the molybdenum concentrations in surface water, groundwater and soil are low and not exceeding the relevant threshold values or quality criteria.

Environmental impact

No assessments of environmental impact/risk of molybdenum have been identified but the identified environmental background concentrations are below the relevant threshold values/quality criteria.

Data gaps

Danish monitoring data for molybdenum in the environment are limited. Such levels are, however, assumed to be associated with natural sources and emissions from coal-burning power plants rather than from emissions of molybdenum trioxide.

6. Human health effects and exposure

As set out in Chapter 1, this survey will focus on molybdenum trioxide as such, and not consider the constituents/impurities present in technical grade molybdenum trioxide. This choice is further substantiated by the fact that although the volume of the technical grade is larger than that of pure grade in the EU, the technical grade is applied in limited types of upstream industrial processes (for steel and other alloy production and for manufacturing of other molybdenum chemicals). Furthermore, no Danish applications of the technical grade have been identified; see Chapter 3.

6.1 Human health hazard

6.1.1 Classification

Molybdenum trioxide is subject to harmonised EU classification as a suspected carcinogen, with a potential for respiratory irritation and serious eye irritation properties; see Table 18. This classification applies to pure grade molybdenum trioxide. As set out in Chapter 1 of this report, technical grade molybdenum trioxide contains about 80% molybdenum trioxide and the REACH Molybdenum Consortium considers molybdenum trioxide as being the leading substance for classification of the technical grade (Molybdenum Consortium, 2010). However, the REACH Molybdenum Consortium does not agree with all of the components of the harmonised EU classification for the pure grade and has therefore not classified the technical grade for respiratory and eye irritation, but "only" as a suspected carcinogen. The reasoning is summarised in a note from the Consortium (Molybdenum Consortium, 2010), the essence of which is summarised in the following.

In relation to eye irritation, the note reproduces data from two OECD 405 guideline-conforming studies for pure and technical grade molybdenum trioxide, respectively, showing that the calculated mean scores for eye irritation are below the cut-off values for the eye irritation classification. These studies are also included in the REACH registrations and summaries are therefore available on the ECHA dissemination site (ECHA 2014 a, b), where it is concluded for the pure grade that installation into the rabbit eye "elicited transient mild conjunctival inflammation only" and for the technical grade "transient slight to well-defined conjunctival inflammation only". These studies were conducted in 1990 and the results were possibly available when agreeing on the harmonised EU classification for molybdenum trioxide as stipulated in the 2009 1st ATP (Adaptation to Technical Progress) to the EU CLP regulation. However, as the reasoning and documentation behind the EU harmonised classification is not available, it is difficult to judge whether other information was taken into account when agreeing on the EU harmonised classification.

In relation to respiratory irritation, the REACH Molybdenum Consortium (2010) refers to an OECD 403 guideline-conforming study on acute inhalation toxicity with extended histopathology, the result of which, according to the Consortium, shows that molybdenum trioxide does not require classification for either acute inhalation toxicity or for respiratory irritation. This study is included in the REACH registrations and a summary is therefore available on the ECHA dissemination site (ECHA 2014 a, b). This summary notes that there was no loss of body weight, no pathological changes and no test material-related histopathological changes in the nose (5 levels of the nasal turbinates), larynx, trachea and lungs (5 levels). In relation to clinical signs it is concluded that: "*A 4-hour inhalation exposure to molybdenum trioxide at a concentration of 5.05 mg/L air revealed slight dyspnoea (reduced frequency of respiration with increased volume) on test day 1 immediately after end of exposure until 3 hours post exposure in all 3 male and 3 female animals. However, this effect is considered to be an overall clinical sign of general toxicity common to dust exposure, but not necessarily substance-related. Since the detailed histopathology of the respiratory tract revealed no pathological findings, molybdenum trioxide is not considered to be irritating to the respiratory system.*" This study was conducted in 2010, after the stipulation of the EU harmonised classification in 2009. However, as for eye irritation, the reasoning and documentation behind the EU harmonised classification is not available and it is therefore difficult to discuss in relation to recent findings as it cannot be ruled out that when establishing the harmonised EU classification, available human data or data from longer term animal testing for a range of molybdenum compounds were considered in an overall weight of evidence approach.

Overall, it appears that it might be relevant to revisit the EU harmonised classifications for eye and respiratory irritation. To this end, it could be noted that endpoints for irritation are generally not prioritised in relation to authority activities on harmonised classification as outlined on page 7 of "Guidance on the preparation of dossiers for harmonised classification and labelling" (ECHA, 2010).

TABLE 18
CLASSIFICATION ACCORDING TO REGULATION (EC) NO 1272/2008 (CLP REGULATION)

Index No	International Chemical Identification	CAS No	Classification	
			Hazard Class and Category Code(s)	Hazard statement Code(s) *
042-001-00-9	Molybdenum trioxide (Pure grade molybdenum trioxide) **Harmonised classification**	1313-27-5	Carc. 2 STOT SE 3 Eye Irrit. 2	H351 H335 H319
-	Molybdenum sulphide (MoS2), roasted (Technical grade molybdenum trioxide) **Industry self-classification**	86089-09-0	Carc. 2	H351

* Hazard statement codes: H351: Suspected of causing cancer; H 335: May cause respiratory irritation; H319: Causes serious eye irritation.

6.1.2 Toxicity

Molybdenum – deficiency and mode of action
Molybdenum is an essential element via its involvement in various enzyme systems including xanthine oxidase, aldehyde oxidase and sulphite oxidase (WHO, 1996; EVM, 2002; Arbete och Hälsa, 2010).

Deficiency symptoms (tachycardia, severe bifrontal headache, night blindness, nausea, vomiting and periods of lethargy, disorientation and coma) in humans have been seen following diet intake of total parenteral nutrition (TPN). Deficiency symptoms have also been seen in young adults with Crohn's disease (WHO, 1996) and children with inborn metabolic disorders showing, between others, neurological disorder, dislocated ocular lenses and failure to thrive (EVM, 2002). According to a UK Expert Group on Vitamins and Minerals (EVM), "naturally occurring" molybdenum deficiency has never been identified in "free living" humans or animal species (EVM, 2002). A goat study with molybdenum deficient diet (24 µg molybdenum/kg dietary dry matter) caused a decline in conception rate, an increase in abortion rate and a significant rise in the mortality of molybdenum-deficient dams and their offspring (WHO, 1996).

The toxic mode of action of molybdenum is often associated with the fact that molybdenum, copper and sulphate have a complex interrelationship in the body. The balance between molybdenum and copper in the body may be disrupted following exposure to molybdenum. This may lead to copper deficiency (especially when sulphate intake is insufficient). Prominent symptoms of severe copper-deficiency are anemia, neutropenia and osteoporosis. Low blood count is the first indication of copper deficiency (WHO, 1996; Arbete och Hälsa, 2010).

Authoritative reviews such as WHO (1996), EVM (2002) and Arbete och Hälsa (2010) generally address the toxicity of molybdenum in all its forms and compounds, as deficiency and toxicity is largely considered in relation to the molybdenum moiety. Linked to this, animal data indicate that soluble molybdenum compounds seem to induce more toxicity than insoluble. Molybdenum trioxide is less soluble than molybdate salts, but more soluble than molybdenum sulphides. OECD (2013) notes that the strong acidification during the dissolution/dissociation reaction with water is considered to impart the unique irritation potential of molybdenum trioxide, which is not observed with highly soluble molybdate salts.

The summary below of metabolism and toxicity will attempt to address molybdenum as such or molybdenum trioxide specifically where deemed most relevant and is, *unless otherwise identified* based on Arbete och Hälsa (2010).

Toxicokinetics and metabolism

Animal data shows 40-85% oral absorption of soluble hexavalent molybdenum compounds[6]. Molybdenum trioxide also appears to be readily absorbed via inhalation based on experiments with guinea pigs, mice and rats. An inhalation study with exposures to 6.7, 20 and 67 mg molybdenum/m^3 as molybdenum trioxide showed that average blood concentrations of molybdenum were respectively about 800, 1,800 and 6,000 µg/l for male rats, 350, 650 and 2,400 µg/l for female rats, 100, 210 and 770 µg/l for male mice, and 70, 200 and 520 µg/l for female mice. Low/no oral and inhalation uptake is seen for insoluble molybdenum sulphide.

In the blood, molybdenum is bound as molybdate to red blood cells and plasma proteins, and it distributes rapidly to most tissues such as liver, kidneys and bones. Fat tissue levels are, however, low.

Molybdenum metabolism is less well studied, although it is known that molybdenum passes through the cell membrane as molybdate. Within the cell it forms a cofactor - in a copper-dependant process – being incorporated into various enzyme systems linked to the essentiality of molybdenum.

The biological half-life of molybdenum (molybdates) in humans is reported to be "rapid" by OECD (2013) and "on the order of weeks" by Arbete och Hälsa (2010). The substance is excreted as molybdates, mostly in urine. It can also be excreted via breast milk.

[6] Molybdenum trioxide is a hexavalent molybdenum compound and partly soluble

Acute toxicity
The REACH registrations for pure or technical grade molybdenum trioxide refer to oral and dermal toxicity studies in rats (OECD test guideline 401 and 402) for pure and technical grade molybdenum trioxide, respectively, indicating in all cases LD50 values above 2000 mg/kg body weight (ECHA 2014 a, b).

Regarding inhalation, the REACH registration refers to acute inhalation studies in rats performed in 1990 according to OECD guideline 403, indicating LC50 values > 5.84 mg/l air and > 3.92 mg/l air for pure and technical grade molybdenum trioxide, respectively.

A more recent OECD 404 guideline-conforming study (2010) with extended histopathology is also included in the REACH registration, which, as discussed in Section 6.1.1, is assessed not to indicate acute inhalation toxicity (ECHA 2014a,b; Molybdenum Consortium, 2010).

Irritation and sensitization
As noted above, molybdenum trioxide is considered more irritating than e.g. molybdates (OECD, 2013) and it is subject to harmonised classification for eye and respiratory irritation. However, as discussed in Section 6.1.1, the REACH Molybdenum Consortium disagrees with these classifications as they find molybdenum trioxide only slightly irritating to the eye (below the classification threshold) and not a respiratory irritant. The latter is mainly based on a recent acute inhalation study, which was not available when the EU classification was established.

The REACH registrations for pure and technical grade molybdenum trioxide, respectively, refer to skin irritation/corrosion tests in rabbits (OECD test guideline 404), indicating no evidence of skin irritation (ECHA 2014 a, b).

The REACH registrations for pure or technical grade molybdenum trioxide refer to guinea pig maximisation tests (OECD test guideline 406) for pure or technical grade molybdenum trioxide, respectively, indicating no evidence of skin sensitisation (ECHA 2014 a, b).

Sub-chronic and chronic toxicity

Human data
Molybdenum compounds are used in some therapeutic applications (although not molybdenum trioxide) and side effects such as bone marrow suppression, anaemia and leukopenia have been seen. A case report (poisoning where victim add "half a spoonful" of ammonium heptamolydate to a cup of coffee), caused severe gastritis (bloody vomiting and severe diarrhoea) and after some days moderate anaemia and kidney effects were seen.

In a part of Armenia where the earth and vegetation contain high levels of molybdenum, calculated daily molybdenum intake for the population reached 10 – 15 mg, compared to 1 – 2 mg molybdenum/day in a control area, an elevated prevalence of a gout-like condition has been reported. Daily intake of copper was also somewhat lower in those with higher molybdenum exposure (5 – 10 mg vs. 10 – 15 mg). Elevated uric acid levels in serum correlated with elevated levels of molybdenum and with elevated activity of xanthine oxidase. Uric acid levels in serum were higher for sick subjects as compared to healthy subjects and control subjects living in another area. The latter had the lowest levels. The average level of copper in blood was somewhat (significantly) lower in subjects with symptoms. Enlarged livers, digestive disturbances and renal disease were also reported in the sick subjects. NB: the study was reported in 1961.

A number of human studies investigate workers exposed via inhalation to molybdenum and/or molybdenum compounds. One electrician exposed to molybdenum (while grinding, cutting and heating metallic molybdenum) experienced metatarsal joint and moderately elevated serum urate and ultimately received a definite diagnosis of gout. However, the authors of this study cannot establish a clear connection between this diagnosis and the occupational molybdenum exposure.

One study investigated workers in a factory producing molybdenum oxides from molybdenum disulphide (i.e. the roasting process; see Chapter 3). Average exposure levels of 9.5 mg molybdenum/m^3 as 8-hour TWA[7] (in total dust) (range 3-33 mg/m^3) and 1-4.5 mg molybdenum/m^3 (in respirable dust) were measured. Some health problems were reported – joint pain, backache, unspecific changes in skin or hair and diarrhoea. However, no clear correlation can be established between these symptoms and molybdenum exposure as blood profiles (complete blood count) and serum uric acid levels were not significantly different from controls.

In a study where workers were exposed to 1 to 25 mg molybdenum/m^3 as metallic molybdenum and molybdenum trioxide for 4 to 7 years, 3 of 19 workers experienced breathing difficulties and coughing. In a subsequent study (no exposure data given), 33/43 workers experienced respiratory symptoms. X-ray indicated discrete abnormalities in 29/33 individual symptoms (no clear indications of interstitial lung disease were seen) and cytologic examinations of bronchoalveolar lavage fluid (BAL) indicated possible sub-clinical alveolitis. Lung function tests were better for exposed workers than for controls.

Animal studies
Following repeated oral exposure to rats (length not indicated), a "repeated exposure LD50" of 125 mg molybdenum/kg bw/day for molybdenum trioxide was found. A four week rat diet exposure study (77 mg molybdenum/100 g feed – not recalculated to daily doses) showed reduced weight gain and increased activity of alkali phosphate for molybdenum trioxide and other soluble molybdenum compounds. A range of other oral studies with other molybdenum compounds (some of which used as food supplements) are available, typically with the rat as test species. No consistent findings are provided. One study reports anaemia, diarrhoea, skeletal damage growth retardation and fur dislocations at a dose level of 0.6 mg molybdenum/kg bw/day. Another study (dose levels 0.4, 1.5 and 4.5 mg molybdenum/kg bw/day) for one month (female) and two months (male) did not observe any clinical observations of toxicity, although significantly lower body weight, feed consumption and mild anaemia was seen at 4.5 mg molybdenum/kg bw/day. Mild kidney effects were seen in a study with very high doses (40 and 80 mg molybdenum/kg bw/day).

In a 5 week (1 hour/day; 5 days/week) inhalation study, guinea pigs were exposed to 205 mg molybdenum/m^3 in the form of molybdenum trioxide dust. This very high concentration level was extremely irritating (eye and nostrils) and diarrhoea, weight loss, ataxia, hair loss, and changes in liver spleen and lungs were reported. Half of the animals died. When exposed to 53 and 191 mg molybdenum/m^3 in the forms of molybdenum trioxide smoke, only 1/25 animals died at the high dose and no signs of toxicity were observed.

In a 14 days (6 hours/day, 5 days/week) dose range finding inhalation study, rats and mice were exposed to molybdenum trioxide in air concentrations of 3 to 300 mg/m^3. Significantly lower body weights were noted at 100 mg/m3 (male rats only) and 300 mg/m3 (both species, both sexes), but there were no clinical indications of toxicity. Mice and rats were then exposed for 13 weeks to molybdenum trioxide dust in air concentrations of 1 to 100 mg/m^3. There were no significant effects on body weights or organ weights and no clinical indications of toxicity, and no significant exposure-related differences were seen in histopathologic, hematologic and clinical-chemical examinations. There were, however, significantly elevated copper levels in livers of the mice (females at 30 mg/m^3, both sexes at 100 mg/m^3). Based on this, rats and mice were exposed to 10, 30 or 100 mg molybdenum trioxide/m^3 (about 6.7, 20 or 67 mg Mo/m^3) for 2 years. No symptoms typical of molybdenum poisoning (diarrhoea, anaemia) or toxicologically significant differences in bone density or

[7] Time weighted average

"bending" of the femur were found, but histopathologic examination revealed exposure-related changes in respiratory passages, including elevated incidences of chronic alveolar inflammation at the two higher exposure levels (very mild to moderate; both severity and incidence increased with dose). Higher incidences of hyaline degeneration of respiratory and olfactory epithelium and squamous cell metaplasias in epiglottal epithelium were also seen at all exposure levels, but these changes were regarded as nonspecific defence mechanisms/adaptations. The mice showed similar slight changes in nose and larynx (non-specific or indications of defence/adaptation), but had no chronic inflammation in alveoli.

Effect on reproduction and offspring

A human study examined 219 men having sought treatment at two infertility clinics. Among the men there were both normal and deviant semen findings as fertility problems can also be due to the partner. Various semen parameters were measured and blood samples were analysed for molybdenum and 10 other metals. The study reports significant or suggestive associations and dose-dependent trends for elevated molybdenum levels in blood and elevated risk of sub-normal sperm concentration and sperm morphology. Less consistent relationships were seen for the other metals investigated. The statistical analyses addressed smoking habits, age and presence of other metals in the blood. The authors of the study call for more/larger and mechanistic studies and note as weaknesses that only one blood and one semen sample was taken from each participant and that only 30% of the participants had blood levels above the detection limit of 1.0 µg/l.

In a 2 year inhalation study by the National Toxicology Programme (NTP, 1997), rats and mice were exposed to molybdenum trioxide concentrations of 0, 10, 30, or 100 mg/m³ (corresponding to 0, 6.7, 20 or 67 mg molybdenum/m³), 6 hours/day, 5 days/week. No significant effects on sperm count or sperm motility were reported in either species, nor were any definite exposure-related changes visible in histopathologic examination of reproductive organs (e.g. testes, epididymis, prostate, seminal vesicles, uterus, ovaries). The blood levels of molybdenum (mean values) in the 2-year study with molybdenum trioxide were reported to be about 220, 800, 1800 and 6000 µg/l in male rats and 60, 350, 650 and 2,400 µg/l in female rats, at 0, 6.7, 20 and 67 mg Mo/m³ respectively. Molybdenum levels in the blood of the mice at these exposures were much lower.

Nanoparticles (30 nm) of molybdenum trioxide have been tested for cytotoxicity on mouse spermatogonia *in vitro* (5 – 100 µg/ml; 48 hours). No distinct effects on cell morphology were observed under a phase-contrast microscope, but apoptosis tests indicated increased apoptosis at concentrations >25 µg/ml. Reduced mitochondrial function was noted at concentrations ≥50 µg/ml, and increased leakage of lactate dehydrogenase was observed at levels as low as 5 µg/ml.

Arbete and Hälsa (2010) also reviewed a range of studies for other molybdenum compounds and concluded that effects on reproduction have been seen in some studies in which mice and rats were given soluble molybdate in drinking water at daily doses corresponding to about 1.5 mg molybdenum/kg body weight.

This corresponds to about 100 mg/day for an adult and appears to be a very high dose, three orders of magnitude above the estimated daily requirement for molybdenum between 100 and300 µg/day for adults as set out in the WHO drinking water guideline (WHO, 1993).

Mutagenicity/Genotoxicity

Molybdenum trioxide was not mutagenic in *Salmonella typhimurium* strains TA97, TA98, TA100, TA1535 or TA1537 (with or without metabolic activation) nor in rec assays with *B. subtilis*. No increase in incidence of sister chromatid exchange (SCE) or chromosome aberrations in Chinese hamster ovary (CHO) cells *in vitro* were seen (with or without metabolic activation).

In a micronuclei test (250 – 750 µg/ml) and in a cell transformation test (50 – 200 µg/ml) on Syrian hamster embryo (SHE) cells *in vitro*, molybdenum trioxide yielded positive results at the higher dose levels. Molybdenum trioxide is inactive in a cell transformation test on BALB/c-3T3 cells (2.3 – 11 mM).

No *in vivo* mutagenicity/genotoxicity studies with molybdenum trioxide have been identified, but weak positive results in *in vivo* micronuclei and dominant-lethal tests with mice for sodium molybdate monohydrate are reported.

Carcinogenicity
Molybdenum trioxide is subject to harmonised classification as a suspected carcinogen. In relation to carcinogenicity of molybdenum trioxide, all reviewed sources refer to a 1997 study conducted by the National Toxicology Programme (NTP, 1997) exposing F344/N rats and B6C3F1 mice to molybdenum trioxide concentrations of 0, 10, 30, or 100 mg/m^3 (corresponding to 0, 6.7, 20 or 67 mg molybdenum/m^3), 6 hours/day, 5 days/week for 2 years. The incidences of alveolar/bronchiolar adenoma or carcinoma increased in the male rats with a marginally significant positive trend, but were of the same order of magnitude as in historic controls. For male mice, there were significantly elevated incidences of alveolar/bronchiolar carcinoma at all dose levels. The combined incidences of alveolar/bronchiolar adenoma and carcinoma were significantly elevated at the two lower dose levels. Female mice had significantly higher incidences of alveolar/bronchiolar adenoma at 30 and 100 mg/m^3 and adenoma/carcinoma combined at 100 mg/m^3. According to NTP (1997), the study provides “some evidence” that molybdenum trioxide is carcinogenic to male and female mice, “equivocal evidence” of carcinogenic activity in male rats, and “no evidence” of carcinogenic activity in female rats.

No evaluation of molybdenum trioxide by the International Agency for Research on Cancer (IARC) has been identified.

Endocrine disruption
No data addressing endocrine disruption properties of molybdenum trioxide have been identified.

6.1.3 Combination and additive effects
As stipulated above, molybdenum is involved in a complex interrelationship with copper and sulphate. High exposure to molybdenum concurrent with low sulphate intake may trigger toxicity.

Given that molybdenum/molybdate is the toxic moiety of molybdenum compounds in general, concurrent exposure to various molybdenum compounds/sources may result in integrated exposure, and thus toxicity, from these sources.

In line with this, exposure (next section) and toxicity data are often given as molybdenum content per weight unit.

6.2 Human exposure

6.2.1 Direct exposure

Occupational exposure
In a factory producing molybdenum oxides from molybdenum disulphide (i.e. the roasting process; see Chapter 3), average exposure levels of 9.5 mg molybdenum/m^3 as 8-hour TWA (in total dust) (range 3-33 mg/m^3) and 1-4.5 mg molybdenum/m^3 (in respirable dust) were measured (referred to in Arbete och Hälsa, 2010).

In a another study (facility not indicated), workers were exposed to 1 to 25 mg/m³ metallic molybdenum and molybdenum trioxide for 4 to 7 years (referred to in Arbete och Hälsa, 2010).

Molybdenum trioxide is largely used for producing molybdenum as such, or as part of steel and other alloys. Molybdenum levels (total dust) of ≤ 2.3 µg/m³ (personal monitors) and ≤ 4 µg/m³ (stationary monitors) were measured around arc furnaces during production of stainless steel, whereas 100 – 300 µg/m³ (total dust, personal monitor, 30 minutes) were observed during welding in stainless steel. Lower levels (0.2 – 18 µg/m³) were observed in a study where the welders used coated electrodes for gas arc welding in mild and stainless steel. A study reports significantly higher exposure levels during grinding, cutting and heating metallic molybdenum: 1.5 – 7.9 mg molybdenum/m³ (referred in Arbete och Hälsa, 2010).

No data addressing occupational exposure in Denmark has been identified. Via the Danish Product Registry, the Danish EPA has confidential knowledge about the few Danish facilities using molybdenum trioxide in case this issue needs to be investigated further.

Consumer exposure
Given the known uses/applications of technical grade molybdenum trioxide, it appears as discussed in Chapter 3, reasonable to assume that technical grade molybdenum trioxide would be converted to metallic molybdenum before reaching the consumer as part of e.g. steel and other alloys.

As set out in Chapter 3, pure grade molybdenum trioxide is used in production/formulation of some products that may potentially reach consumers in relation to uses such as water treatment chemicals; ceramic additives/enamel frits; flame retardants/smoke suppressants; pigments; metal surface treatment, and sintered metal additives. EBRC (2010) on behalf of the REACH Molybdenum Consortium addresses these uses in relation to consumer exposure based on dialogue with relevant downstream users and literature searches with the main focus of assessing whether consumers are exposed to molybdenum trioxide.

In relation to water treatment chemicals, it is noted that molybdenum trioxide might be used in watery solutions in heating systems with molybdenum trioxide concentrations of 0.02-0.6% and that the molybdenum trioxide, given the water solubility, dissociates into molybdate ions (MoO_4^{2-}) (EBRC, 2010). It can be argued that the potential for molybdenum consumer exposure still exists, but given the applications and concentration, any potential consumer exposure must be considered very low.

In relation to ceramics, EBRC (2010) notes that it can safely be assumed that the high ceramic production temperatures during sintering and baking will ensure that molybdenum trioxide is no longer present in the finished product. It is furthermore noted that the molybdenum content will be tightly bound in a matrix (EBRC, 2010). All in all, possible molybdenum exposure from this application must indeed be considered very low.

Regarding application of molybdenum trioxide in flame retardants and as a smoke suppressant, it is noted that this was not reported to the REACH Molybdenum Consortium as an identified use at the time of registration and it was therefore not included in the REACH registration (EBRC, 2010). The REACH Molybdenum Consortium confirms that as of today there has been no renewed wish from downstream users to include use as flame retardants as an identified use. It cannot be excluded that molybdenum trioxide is incorporated as a flame retardant in imported products/articles which are not addressed by REACH registrations, unless there is an intentional release from such articles. It may be assumed that there is no significant release from molybdenum trioxide incorporated in articles such as cables, and that consumer exposure to molybdenum trioxide during such applications would normally be low or non-existent. Information on possible release in case of fire has not been identified.

In relation to pigments, paints and anticorrosion applications, molybdenum trioxide is not in itself contained in a pigment or corrosion inhibitor, but rather used as feedstock for the preparation of molybdate solutions (EBRC, 2010). This application could thus lead to consumer molybdate exposure (but not molybdenum trioxide). In this context, it can be noted that the literature reviewed in this project does not indicate any significant dermal toxicity of molybdenum compounds.

Use for metal surface treatment is mainly an industrial application, thus inherently excluding consumer exposure. Furthermore, for this application a molybdate solution is generated and no molybdenum trioxide is present in the finished product (EBRC, 2010).

When used as a sintered metal additive, molybdenum trioxide is converted to molybdenum, thus no molybdenum trioxide consumer exposure occurs (EBRC, 2010).

All in all, given known applications/uses of molybdenum trioxide, consumers do not seem to be exposed to molybdenum trioxide, but could be exposed to resulting molybdates in particular in relation to pigments in paints and corrosion inhibitors. There might also be an exposure during fire if molybdenum trioxide is used as a flame retardant/smoke depressor. It is, however, questionable how widespread this use is and no data on possible exposure levels during fire have been identified.

6.2.2 Indirect exposure via the environment

Air, drinking water and food
As evidenced in other parts of this report, molybdenum is an essential element occurring naturally in environmental media and foodstuff. Molybdenum compounds (but not molybdenum trioxide) is added as a food supplement and molybdenum used in industrial processes, although as set out in Chapter 4, attempts are made to recycle molybdenum due to its commercial value, might end up in environmental media. Manufacturing and further processing/conversion of molybdenum trioxide is one source of emissions of molybdenum to the environment, but other sources, e.g. coal power plants, might be the main contributors (see Chapter 5). Chapter 5 reports maximum measured concentrations of 2.9 µg/l in Danish drinking water, well below the drinking water quality criterion of 20 µg/l (see Chapter 2). Other concentrations found in the environment (e.g. soils), also seem to be low and unlikely to cause significant human intake via the environment. Chapters 2 and 5 addresses "molybdenum" limit values in various environmental media.

Indoor climate
No data have been identified.

6.3 Biomonitoring data

As discussed under sub-chronic and chronic toxicity in Section 6.1.2, serum uric acid levels are often measured as markers in relation to molybdenum exposure studies. Levels of around 40-50 mg/l appear to be normal, whereas the sick individuals in one study had an average level of 81 mg/l. In the study addressing workers in a molybdenum oxide manufacturing factory, average levels of 59 mg molybdenum/l were found.

Blood levels were used in the human study discussed under reproductive toxicity (also in Section 6.1.2); the highest blood level of molybdenum measured was 5.4 µg molybdenum/l, whereas 70% of the subjects in that study had concentrations below the detection limit of 1 µg molybdenum/l. This study also reports significant or suggestive associations and dose-dependent trends for elevated molybdenum levels in blood and elevated risk of sub-normal sperm concentration and sperm morphology.

Literature addressing biomonitoring data related to molybdenum compounds used in relation to medical and food applications has not been reviewed as molybdenum compounds other than molybdenum trioxide are used for these applications.

6.4 Human health impact

No authoritative risk assessments for molybdenum trioxide have been identified.

In relation to molybdenum trioxide, the main exposure and possible risks appear to involve inhalation exposure in occupational settings.

Over the past 10 years there have been no entries related to molybdenum in the Danish Register of occupational diseases (Høyer, 2014).

In relation to molybdenum compounds in general, some human studies indicate effects following high doses used therapeutically. However, molybdenum trioxide is not used for such treatments.

In relation to molybdenum in the environment, human effects have been seen or obtained in areas with high natural occurrence in plants (in an old study from Armenia).

Molybdenum trioxide might contribute to molybdenum concentrations in the environment, but given the applications and recycling in place for the main uses, these environmental levels are probably merely related to natural sources and e.g. molybdenum emitted from coal power plants.

A human study indicates some correlation between blood molybdenum levels and sub-normal sperm concentration and sperm morphology in individuals seeking treatment in fertility clinics. It is not clear whether these increased blood molybdenum levels originate from occupational or environmental sources.

6.5 Summary and conclusions

Human health hazard

Molybdenum is an essential element via its involvement in various enzymes systems. Deficiency symptoms (tachycardia, severe bifrontal headache, night blindness, nausea, vomiting and periods of lethargy, disorientation and coma) in humans have been seen following diet intake of total parenteral nutrition (TPN) and in children/young adults with Crohn’s disease and inborn metabolic disorders, but no "naturally occurring" molybdenum deficiency has been identified in "free living" humans or animal species.

The systemic toxicity of molybdenum compounds seems to be associated with the molybdate ion and thus with the solubility of the molybdenum compounds. Molybdenum trioxide is partially soluble, although to a lesser degree than molybdate salts. The toxic mode of action is often associated with the fact that molybdenum, copper and sulphate have a complex interrelationship in the body. The balance between molybdenum and copper in the body may be disrupted following exposure to molybdenum. This may lead to copper deficiency (especially when sulphate intake is insufficient) with symptoms of severe copper-deficiency: anaemia, neutropenia and osteoporosis.

These systemic toxicity symptoms were, however, not observed in a two-year carcinogenicity study on molybdenum trioxide in mice and rats. Symptoms have been seen in human studies related to high exposures to molybdenum compounds, but it is generally not possible to draw firm conclusions based on those studies.

Molybdenum trioxide is thought to have some irritating potential due to the strong acidification during the dissolution/dissociation reaction with water. Indeed the above mentioned carcinogenicity study showed effects in the respiratory airways including alveolar/bronchiolar carcinoma, especially in mice, concluded to indicate some evidence of carcinogenicity. Thus molybdenum trioxide is subject to harmonised classification as a suspected carcinogen.

Molybdenum trioxide is also classified for eye and respiratory irritation. The data/reasoning behind these classifications is not available, but the REACH Molybdenum Consortium disagrees with these classifications based on available evidence from irritation studies and a recent acute inhalation study.

Some effects on reproduction have been seen at relatively high molybdate dose levels and indications of effects are seen in a non–conclusive human study. Available data have not led to classification for this endpoint.

Human exposure and biomonitoring

Consumer exposure and humans exposed via the environment to molybdenum trioxide or molybdenum compounds originating from molybdenum trioxide is generally assessed to be low. Environmental exposure data are scarce, but those available indicate low molybdenum levels; levels which integrate all molybdenum sources, including e.g. molybdenum/molybdenum trioxide emitted from coal power plants.

Relatively high inhalation exposures are seen in some occupational settings, as e.g. evidenced by measurement data from a molybdenum sulphide roasting process, possibly manufacturing technical grade molybdenum trioxide. Blood biomonitoring data from such studies are, however, not always consistent with exposure levels and clinical symptoms.

Available data are not robust enough to indicate any trends in exposure levels.

Human health impact

No authoritative risk assessments for molybdenum trioxide have been identified.

In relation to molybdenum trioxide, the main exposure and possible risks seem to be inhalation exposure in occupational settings.

Molybdenum trioxide is not expected to contribute significantly to human exposure to molybdenum via the environment, given the applications and recycling in place for the main uses and considering molybdenum occurring from natural sources and emitted from coal power plants.

A human study suggests some correlation between blood molybdenum levels and sub-normal sperm concentration and sperm morphology in individuals seeking treatment in fertility clinics. It is not clear whether these increased blood molybdenum levels originate from occupational or environmental sources.

Data gaps

Main data gaps seem to be associated with occupational inhalation exposure levels in manufacturing sites and sites using molybdenum trioxide industrially, in particular in steels and alloy productions. Such manufacturing/productions take place outside Denmark.

Indications of a correlation between molybdenum blood levels and sub-normal sperm concentration and sperm morphology in a human study could lead to consideration for further human and mechanistic studies for this endpoint.

There are different views on the need to classify molybdenum trioxide for respiratory and eye irritation. The reasoning behind the harmonised classification for these endpoints might be revisited, including consideration of recent data.

7. Information on alternatives

7.1 Alternatives to molybdenum trioxide in steel and other alloys

Molybdenum is used in carbon steels and alloy steels to obtain high level properties in terms of strength, toughness, fire resistance, crash resistance and creep resistance (see e.g. Naka et al., 1979). According to the REACH Molybdenum Consortium, the combination of such properties cannot be achieved by alternative substituting alloying elements. Substituting typically refers to the hardenability of steel only. To achieve a comparable effect to that of molybdenum, twice the amount of chromium or three times the amount of manganese has to be alloyed. However, these substituting elements do not comprise the other beneficial alloying effects of molybdenum. Consequently, production of current high performance steel grades according to existing specifications would become very difficult if not impossible. This would have an immediate negative impact on safety in e.g. cars, gas pipelines and buildings as well as lower efficiency in power generation (Carey, 2014).

In stainless steel, the most important function of molybdenum is to increase corrosion resistance in chloride containing solutions. In these solutions the influence of alloying elements on pitting corrosion resistance of a stainless steel can be estimated through the Pitting Resistance Equivalent formula (PRE) = % chromium + 3.3x% molybdenum + 16x% nitrogen. Hence, molybdenum is 3.3 times more efficient at increasing corrosion resistance than chromium. The base corrosion resistance of stainless steel is achieved with about 17-18 % chromium (10.5 % as the absolute minimum); and molybdenum is only added (most often at 2 %) if there is a need for higher corrosion resistance due to e.g. a more severe environment. Both chromium and nitrogen are to some extent substitutes for molybdenum, but there is a limit to how much can be substituted before problems are generated with the production of stainless steel and/or precipitation of undesirable phases. Thus, molybdenum has a very specific role to increase corrosion resistance beyond a basic corrosion resistance of stainless steel, which is imparted by chromium. It is not always needed (only about 8-10 % of all stainless steels contain molybdenum), but when there is a need for improved corrosion resistance then it is very difficult to substitute molybdenum (Carey, 2014).

7.2 Alternatives to molybdenum trioxide in catalysts

As for alloys, the use of molybdenum trioxide in catalysts is due to the superior properties that this metal provides in terms of e.g. strength, toughness and catalytic functionality; the combination of such properties is difficult to achieve through alternative substitutes.

In the petroleum industry, the main application of molybdenum trioxide containing catalysts is desulphurization of oil (see also Chapter 3). Platinum metals perform as well as molybdenum trioxide in catalysts, but the cost of using this alternative is very high as compared to molybdenum trioxide. However, more importantly, the consumption of molybdenum trioxide for this application is approx. 100 times higher than the global annual supply of platinum (Hansen et al., 2014).

Wolfram can also be used as an alternative to molybdenum trioxide, but only in specific catalyst application under high pressure (>100 bar); it does not perform as well as molybdenum trioxide under normal conditions for catalysts (Absi-Halabi et al., 1998). Furthermore, when wolfram is in a chemical form suitable for catalyst production, it is approx. two to three times more expensive as compared to molybdenum trioxide (Danish Manufacturer).

Over the last decades, the conventional hydro-desulfurization approach using molybdenum-based catalysts has been challenged by several research initiatives into alternatives to desulfurizing oil. Approximately 10-15 years ago, a promising research area was emerging with a focus on oxidative desulfurization (see review by e.g. Campos-Martin et al., 2010). However, eventually, this alternative was not able to outperform the traditional approach; hydro-desulfurization using molybdenum-based catalysts is still the preferred choice in desulfurization of oil.

7.3 Alternatives to molybdenum trioxide in mixtures and articles

Molybdenum trioxide is used for production of a number of mixtures and articles (see Chapter 3) such as water treatment chemicals, ceramics, pigments, metal surface treatment and sintered metal additives (EBRC, 2010). However, from a volume perspective, these applications are much smaller than use of molybdenum trioxide for catalysts and alloys and will therefore not be subject to further investigations. Furthermore, it should be noted that molybdenum trioxide does generally not form part of the final mixtures/articles, as it has been converted to other molybdenum compounds or molybdate (see Section 6.2.1).

It can be mentioned that molybdenum is used as a colorant (at a concentration of 1 % according to Radian Corporation (1987)); but likely substitutes more toxic alternatives such as chromium.

7.4 Historical and future trends

No information on trends in the use or future R&D of alternatives has been identified.

7.5 Health and environmental aspects related to alternatives

As described in previous sections, there are alternatives to molybdenum trioxide; however, they either have an inferior performance level (cobalt, chromium and nickel) or are substantially more expensive or low in supply (platinum and wolfram). Furthermore, as shown in Table 15, many of the alternatives are classified for several of the same hazardous properties as molybdenum trioxide (e.g. see Table 14, section 6.1.1), including carcinogens (or suspected carcinogens). Hence, from a human health and environmental perspective, these substances, in particular cobalt, chromium and nickel, cannot be considered as preferred alternatives.

TABLE 15
HARMONISED CLASSIFICATION OF ALTERNATIVES TO MOLYBDENUM TRIOXIDE (ACCORDING TO ANNEX VI OF REGULATION (EC) NO 1272/2008 (CLP REGULATION))

Alternative substance	CAS No	Classification	
		Hazard Class and Category Code(s)	Hazard statement Code(s) *
Cobalt (sulphate)	10124-43-3	Acute Tox 4* Skin Sens. 1 Resp. Sens. 1 Muta 2 Carc 1B Repr 1B Aquatic Acute 1 Aquatic Chronic 1	H302 H317 H334 H341 H350i H360F*** H400 H410
Chromium	7440-47-3	No harmonised CLP classification (suspected carcinogen)	-

Alternative substance	CAS No	Classification	
		Hazard Class and Category Code(s)	Hazard statement Code(s) *
Nickel	7440-02-0	Skin Sens. 1 Carc 2 STOT RE 1 Aquatic Chronic 3	H317 H351 H372** H412
Platinum (dichloride)	10025-65-7	No harmonised CLP classification	-
Wolfram (Tungsten trioxide)	1314-35-8	No harmonised CLP classification (suspected carcinogen)	-

* Hazard statement codes. Health hazards: H302 Harmful if swallowed, H317 May cause an allergic skin reaction, H334 May cause allergy or asthma symptoms or breathing difficulties if inhaled, H341 Suspected of causing genetic defects, H350i May cause cancer by inhalation, H351 Suspected of causing cancer, H360f May damage fertility, H372 Causes damage to organs through prolonged or repeated exposure; Environmental hazards: H400 Very toxic to aquatic life, H410 Very toxic to aquatic life with long lasting effects, H412 Harmful to aquatic life with long lasting effects. * The classification as obtained under Annex VII shall then substitute the minimum classification indicated in this Annex if it differs from it; ** The classification under 67/548/EEC indicating the route of exposure has been translated into the corresponding class and category according to this Regulation, but with a general hazard statement not specifying the route of exposure as the necessary information is not available; *** In order not to lose information from harmonised classifications for fertility and developmental effects under Directive 67/548/EEC, the classifications have been translated only for those effects classified under that Directive.

7.6 Summary and conclusions

There are alternatives to molybdenum trioxide; however, they are either significantly more expensive, not able to meet demands (e.g. platinum) or their performance is inferior as compared to molybdenum trioxide for the specific application. This is in regard to alternatives to molybdenum trioxide in the production of catalysts, steel and other alloys in particular.

The study does not elaborate on alternatives for a range of minor applications for producing mixtures and articles, as these applications are estimated to only account for approx. 0.5% of the volume and as molybdenum trioxide has been converted to other molybdenum compounds or molybdate before reaching the consumer.

In conclusion, molybdenum trioxide is currently the best candidate from an economic, performance and health and environmental perspective; in particular as regards applications that require materials with strong endurance such as catalysts, steel and other alloys.

8. References

Absi-Halabi M, Stanislaus A, Al-Dolama K (1998). Performance comparison of alumina-supported Ni-MO, Ni-W and Ni-Mo-W catalysts in hydrotreating vacuum residue. Fuel 77: 787-790.

Andreasen PA (2014). Personal communication with Per A Andreasen representing the Danish waste disposal company NORD (http://www.nordgroup.eu/).

Arbete och Hälsa (2010). Scientific basis for Swedish occupational standards XXX. Arbete och Hälsa, University of Gothenburg and Arbetsmiljöverket. ISBN 978-91-85971-22-0.

Blossom (2002). Molybdenum recycling in the United States in 1998. U.S. Department of the Interior. U.S. Geological Survey. Open File Report 02-165. Available at: http://infohouse.p2ric.org/ref/45/44149.pdf

Campos-Martin JM, Capel-Sanchez MC, Perez-Presas P, Fierro JLG (2010). Oxidative processes of desulfurization of liquid fuels. Journal of Chemical Technology and Biotechnology 85: 879–890

Carey S (2014). Personal communication with Sandra Carey representing the REACH Molybdenum Consortium.

Danish EPA (2011). List of undesirable substances. 2009. Environmental Review 3/2011. Danish Environmental Protection Agency, Copenhagen.

Danish EPA (2014). Waste Data System (Affaldsdatasystemet) under the Danish EPA. Available at: http://mst.dk/virksomhed-myndighed/affald/affaldsdatasystemet/

DCE (2010). Tilførsel af syntetiske stoffer samt ikke-syntetiske stoffer og forbindelser til de danske farvande. NOTAT 2.7. DCE - Danish Centre for Environment and Energy [In Danish]

EBRC (2010). Assessment of 'Consumer Exposure' under REACH for MoCon Substances. Prepared by EBRC Consulting for the REACH Molybdenum Consortium.

ECHA (2010). Guidance on the preparation of dossiers for harmonised classification and labelling. European Chemicals Agency. Available at: http://echa.europa.eu/documents/10162/13626/clh_en.pdf

ECHA (2012). Community Rolling Action Plan (CoRAP), 29 February 2012.

ECHA (2013). Community Rolling Action Plan (CoRAP) update covering years 2013, 2014 and 2015. European Chemicals Agency. 20 March 2013.

ECHA (2014a). ECHA Dissemination Site Database: Registration Dossier for Pure Grade Molybdenum trioxide. Cited with permission from REACH Molybdenum Consortium. http://apps.echa.europa.eu/registered/data/dossiers/DISS-9eb02551-2a99-62df-e044-00144f67d031/DISS-9eb02551-2a99-62df-e044-00144f67d031_DISS-9eb02551-2a99-62df-e044-00144f67d031.html

ECHA (2014b). ECHA Dissemination Site Database: Registration Dossier for Technical Grade Molybdenum trioxide. http://apps.echa.europa.eu/registered/data/dossiers/DISS-9ec12d24-887f-

5cb5-e044-00144f67d031/DISS-9ec12d24-887f-5cb5-e044-00144f67d031_DISS-9ec12d24-887f-5cb5-e044-00144f67d031.html

European Commission (2010). Annex V to the Report of the Ad-hoc Working Group on defining critical raw materials. Version 30 July 2010. European Commission Enterprise and Industry.

European Commission (2011). Database of priority list of chemicals developed within the EU-Strategy for Endocrine Disruptors. European Commission. Available at: http://ec.europa.eu/environment/chemicals/endocrine/strategy/substances_en.htm

Eurostat (2014). Eurostat 2013. Accessed April 2014 at: http://epp.eurostat.ec.europa.eu/portal/page/portal/statistics/search_database

EVM (2002). Expert Group on Vitamins and Minerals. Review of Molybdenum. Expert Group in Vitamins and Minerals Secretariat, Food Standards Agency, London.

Ference RA, Sebenik RF (1982) Molybdenum recovery from two types of direct catalytic coal liquefaction processes. Report by Climax Molybdenum Company of Michigan. Available at: https://web.anl.gov/PCS/acsfuel/preprint%20archive/Files/27_3-4_KANSAS%20CITY_09-82_0071.pdf

GEUS (2007). Grundvand. Status og udvikling 1989-2006. Rapport, GEUS, 2007. Availalble via: http://www.grundvandsovervaagning.dk. (Geological Survey of Denmark and Greenland: Groundwater. Status and trends 1989-2006) (in Danish)

Hansen LP, Johnson E, Brorson M, Helveg S (2014). Growth mechanism for single- and multi-layer MoS2 nanocrystals. The Journal of Physical Chemistry. In press. dx.doi.org/10.1021/jp5069279.

HELCOM (2009). Hazardous substances of specific concern to the Baltic Sea - Final report of the HAZARDOUS project. Baltic Sea Environment Proceedings No. 119. Accessed October 2013 at: helcom.fi/lists/Publications/BSEP119.pdf#search=85535-84-8.

Høyer S (2014). Personal communication with Susanne Høyer representing the Danish Working Environment Authority.

IMOA (2014a). International Molybdenum Association web-site. http://www.imoa.info/molybdenum/molybdenum-global-production-use.php

IMOA (2014b). International Molybdenum Association web-site. http://www.imoa.info/molybdenum-media-centre/facts-and-figures.php

Intrastat (1994). Combined nomenclature. Accessed October 2013 at http://ec.europa.eu/eurostat/ramon/other_documents/index.cfm?TargetUrl=DSP_CN_88_94.

Kjølholt J, Stuer-Lauridsen F, Mogensen AS, Havelund S (2003). The Elements in the Second Rank. Environmental Project no. 770, Danish EPA, Copenhagen.

Kjølholt J, Arnbjerg-Nielsen K, Olsen D, Jørgensen K-R (2011). Nøgletal for miljøfarlige stoffer i spildevand fra renseanlæg. Rapport, Naturstyrelsen, 2011. www.naturstyrelsen.dk (National mean concentrations of environmentally hazardous substances in effluents from sewage treatment plants (in Danish with an English summary))

Mitchell PCH (2010). Speciation of molybdenum compounds in water – Ultraviolet spectra and REACH read across. Report for the International Molybdenum Association. Department of Chemistry, University of Reading, UK. 24 pp.

Molybdenum Consortium (2010). Substance Identification and Hazard Classification of "Molybdenum Sulfide (MoS2), roasted". Final V8. 16 July 2010-updated Aug to include briqs. http://www.molybdenumconsortium.org/assets/files/CLP/MoCon%20RMC%20Substance%20Identification%20doc%20for%20SIEF-V8FF.pdf

Molybdenum Consortium (2014). See: http://www.molybdenumconsortium.org/list-of-uses.html (accessed July 2014).

Naka M, Hashimoto K, Inoue A, Masumoto T (1979). Corrosion-resistant amorphous Fe-C alloys containing chromium and/or molybdenum. Journal of Non-Crystalline Solids 31: 347-354.

Naturstyrelsen (2012). Punktkilder 2011. (Danish Nature Agency, 2012. Point sources 2011 (in Danish)). Available via: http://www.naturstyrelsebn.dk.

NOVANA (2011). Det Nationale Overvågningsprogram for Vand og Natur. 2011-2015. Programbeskrivelse [The national monitoring program for water and nature. 2011-2015]. Nature Agency, National Environmental Research Institute (NERI) and Geological Survey of Denmark and Greenland (GEUS), Denmark.

NTP (1997). NTP technical report on the toxicology and carcinogenesis studies of molybdenum trioxide (CAS NO. 1313-27-5) in F344/n rats and B6c3F mice (inhalation studies). NTP TR 462. NIH Publications No. 97-3378. National Toxicology Program. Us Department of Health and Human Services.

OECD (2013). SIDS initial Assessment profile. OECD Agreed Conclusions. CoCAM 5, 15-17 October 2013. OECD, Paris. Available from: http://webnet.oecd.org/HPV/UI/SIDS_Details.aspx?id=5c88d62f-4401-4cad-b521-521a4bd710f3

Radian Corporation (1987). Chemical additives for the plastics industry – Properties, applications, toxicologies. Noyes Data Corporation, New Jersey. ISBN 0-8155-1114-0.

Staatscourant (2010). Staatscourant 2010 nr. 5615, 14 April 2010, p. 7.

Statistics Denmark (2014). Udenrigshandel, produktion og forsyning [Foreign trade, production and supply]. Accessed April 2014 at: http://www.dst.dk/da/informationsservice/oss/UHprod.aspx

Tjandraatmadja G, Pollard C, Sheedy C, Gozukara Y (2010). Sources of contaminants in domestic wastewater: nutrients and additional elements from household products. CSIRO: Water for a Healthy Country National Research Flagship. Available at: http://www.clw.csiro.au/publications/waterforahealthycountry/2010/wfhc-contaminants-domestic-wastewater.pdf

USGS (2012). 2011 Minerals Yearbook. Molybdenum [advance release]. UU Geological Services. US Department of the Interior. December 2012.

Van Vlaardingen PLA, Posthumus R, Posthuma-Doodeman CJAM (2005). Environmental Risk Limits for Nine Trace Elements. RIVM Report 601501029/2005. 247 pp.

WHO (1993). Guidelines for drinking water quality, second edition. World Health Organization, Geneva.

WHO (1996). Trace elements in human nutrition and health. World Health Organization, Geneva. ISBN 92 4 156173 4.

Appendix 1: Abbreviation and acronyms

AA-EQS	Annual Average – Environmental Quality Standard
AF	Assessment Factor
ATP	Adaptation to Technical Progress
BAL	Bronchoalveolar Lavage Fluid
BCF	Bioconcentration factor
BMF	Biomagnification factor
CAS	Chemical Abstract Service
CEFIC	European Chemical Industry Council
C&L	Classification and Labelling
CHO	Chinese Hamster Ovary
CLP	Classification, Labelling and Packaging (Regulation)
CMR	Carcinogenic, mutagenic or toxic to reproduction
CoRAP	Community Rolling Action Plan
CSIRO	Commonwealth Scientific and Industrial Research Organisation
DCE	Danish Centre for Environment and Energy
DEFRA	Department for Environment, Food and Rural Affairs (UK)
EC	Effect Concentration (or European Commission)
EBRC	EBRC Consulting GmbH
ECB	European Chemicals Bureau
ECHA	European Chemicals Agency
EFSA	European Food Safety Authority
EPA	Environmental Protection Agency
EQS	Environmental Quality Standard
ERL	Environmental Risk Limit
ESIS	European Chemical Substances Information System
EU	European Union
EVM	Expert Group on Vitamins and Minerals
GEUS	Geological Survey for Denmark and Greenland
HELCOM	The Baltic Marine Environment Protection Commission (Helsinki Commission)
IARC	International Agency for Research on Cancer
IMOA	International Molybdenum Association
JG-MKN	Jaargemiddelde Milieukwaliteitsnorm (=AA-EQS)
LC	Lethal Concentration
LD	Lethal Dose
LOUS	List of Undesirable Substances (of the Danish EPA)
MAC-MKN	Maximaal Aanvaardbare Concentratie Milieukwaliteitsnorm (=MAC-EQS)
MPA	Maximum Permissible Addition
NA	Not Applicable
NOAEL	No observable adverse effect level
NOEC	No observable effect concentration
NOVANA	Danish national monitoring and assessment programme
NTP	National Toxicology Program
OECD	Organisation for Economic Co-operation and Development
OSPAR	Convention for the Protection of the Marine Environment of the North-East Atlantic
PBT	Persistent, bioaccumulative and persistent
PC	Product Category
PEC	Predicted environmental concentration
PIC	Prior Informed Consent
PNEC	Predicted no effect concentration

POPs	Persistent Organic Pollutants
PRTR	Pollutant Release and Transfer Register
RAR	Risk Assessment Report
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals (Regulation)
RMC	Roasted Molybdenite concentrates (synonym for technical grade molybdenum trioxide)
SCE	Sister Chromatid Exchange
SHE	Syrian Hamster Embryo
SIDS	Screening Information Dataset
SVHC	Substance of Very High Concern
TMF	Trophic Magnification Factor
TPN	Total Parenteral Nutrition
TWA	Time Weighted Average
UBA	Umweltbundesamt (Germany)
USGS	U.S. Geological Survey
UVCB	Unknown or Variable Composition, Complex Reaction Products or Biological Materials
USA	United States of America
vBvP	Very bioaccumulative and very persistent
WHO	World Health Organization

Appendix 2: Background information to chapter 2 on legal framework

The following annex provides some background information on subjects addressed in Chapter 2. The intention is that the reader less familiar with the legal context may read this concurrently with chapter 2.

EU and Danish legislation
Chemicals are regulated via EU and national legislations, the latter often being a national transposition of EU directives.

There are four main EU legal instruments:

- Regulations (DK: Forordninger) are binding in their entirety and directly applicable in all EU Member States.
- Directives (DK: Direktiver) are binding for the EU Member States as to the results to be achieved. Directives have to be transposed (DK: gennemført) into the national legal framework within a given timeframe. Directives leave a margin for manoeuvring as to the form and means of implementation. However, there are great differences in the space for manoeuvring between directives. For example, several directives regulating chemicals previously were rather specific and often transposed more or less word-by-word into national legislation. Consequently, and to further strengthen a level playing field within the internal market, the new chemicals policy (REACH) and the new legislation for classification and labelling (CLP) were implemented as Regulations. In Denmark, Directives are most frequently transposed as laws (DK: love) and statutory orders (DK: bekendtgørelser).

The European Commission has the right and the duty to suggest new legislation in the form of regulations and directives. New or recast directives and regulations often have transitional periods for the various provisions set out in the legal text. In the following, we will generally list the latest piece of EU legal text, even if the provisions identified are not yet fully implemented. On the other hand, we will include currently valid Danish legislation, e.g. the implementation of the cosmetics directive) even if this will be replaced with the new Cosmetic Regulation.

- Decisions are fully binding on those to whom they are addressed. Decisions are EU laws relating to specific cases. They can come from the EU Council (sometimes jointly with the European Parliament) or the European Commission. In relation to EU chemicals policy, decisions are e.g. used in relation to inclusion of substances in REACH Annex XVII (restrictions). This takes place via a "comitology procedure" involving Member State representatives. Decisions are also used under the EU ecolabelling Regulation in relation to establishing ecolabelling criteria for specific product groups.
- Recommendations and opinions are non-binding, declaratory instruments.

In conformity with the transposed EU directives, to some extent Danish legislation regulate chemicals via various general or sector specific legislation, most frequently via statutory orders (DK: bekendtgørelser).

Chemicals legislation
REACH and CLP
The REACH Regulation[8] and the CLP Regulation[9] are the overarching pieces of EU chemicals legislation regulating industrial chemicals. The below will briefly summarise the REACH and CLP provi-

[8] Regulation (EC) No 1907/2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)
[9] Regulation (EC) No 1272/2008 on classification, labelling and packaging of substances and mixtures

sions and give an overview of 'pipeline' procedures, i.e. procedures which may (or may not) result in an eventual inclusion under one of the REACH procedures.

(Pre-)Registration
All manufacturers and importers of chemical substances > 1 tonne/year have to register their chemicals with the European Chemicals Agency (ECHA). Pre-registered chemicals benefit from tonnage and property dependent staggered deadlines:

- 30 November 2010: Registration of substances manufactured or imported at 1000 tonnes or more per year, carcinogenic, mutagenic or toxic to reproduction substances above 1 tonne per year, and substances dangerous to aquatic organisms or the environment above 100 tonnes per year.
- 31 May 2013: Registration of substances manufactured or imported at 100-1000 tonnes per year.
- 31 May 2018: Registration of substances manufactured or imported at 1-100 tonnes per year.

Evaluation
A selected number of registrations will be evaluated by ECHA and the EU Member States. Evaluation covers assessment of the compliance of individual dossiers (dossier evaluation) and substance evaluations involving information from all registrations of a given substance to see if further EU action is needed on that substance, for example as a restriction (substance evaluation).

Authorisation
Authorisation aims at substituting or limiting the manufacturing, import and use of substances of very high concern (SVHC). For substances included in REACH annex XIV, industry has to cease use of those substance within a given deadline (sunset date) or apply for authorisation for certain specified uses within an application date.

Restriction
If the authorities assess that that there is a risk to be addressed at the EU level, limitations of the manufacturing and use of a chemical substance (or substance group) may be implemented. Restrictions are listed in REACH annex XVII, which has also taken over the restrictions from the previous legislation (Directive 76/769/EEC).

Classification and Labelling
The CLP Regulation implements the United Nations Global Harmonised System (GHS) for classification and labelling of substances and mixtures of substances into EU legislation. It further specifies rules for packaging of chemicals.

Two classification and labelling provisions are:

1. **Harmonised classification and labelling** for a number of chemical substances. These classifications are agreed at the EU level and can be found in CLP Annex VI. In addition to newly agreed harmonised classifications, the annex has taken over the harmonised classifications in Annex I of the previous Dangerous Substances Directive (67/548/EEC); classifications which have been 'translated' according to the new classification rules.

2. **Classification and labelling inventory**. All manufacturers and importers of chemicals substances are obliged to classify and label their substances. If no harmonised classification is available, a self-classification shall be done based on available information according to the classification criteria in the CLP regulation. As a new requirement, these self-classifications should be notified to ECHA, which in turn publishes the classification and labelling inventory based on all notifications

received. There is no tonnage trigger for this obligation. For the purpose of this report, self-classifications are summarised in Appendix 6 to the main report.

Ongoing activities - pipeline
In addition to listing substances already addressed by the provisions of REACH (pre-registrations, registrations, substances included in various annexes of REACH and CLP, etc.), the ECHA website also provides the opportunity for searching for substances in the pipeline in relation to certain REACH and CLP provisions. These will be briefly summarised below:

Community Rolling Action Plan (CoRAP)
The EU Member States have the right and duty to conduct REACH substance evaluations. In order to coordinate this work among Member States and inform the relevant stakeholders of upcoming substance evaluations, a Community Rolling Action Plan (CoRAP) is developed and published, indicating when and by whom a given substance is expected to be evaluated.

Authorisation process; candidate list, Authorisation list, Annex XIV
Before a substance is included in REACH Annex XIV and therefore subject to Authorisation, it has to go through the following steps:

1. It has to be identified as a SVHC leading to inclusion in the candidate list[10]
2. It has to be prioritised and recommended for inclusion in ANNEX XIV (These can be found as Annex XIV recommendation lists on the ECHA web-site)
3. It has to be included in REACH Annex XIV following a comitology procedure decision (substances on Annex XIV appear on the Authorisation list on the ECHA web-site).

The candidate list (substances agreed to possess SVHC properties) and the Authorisation list are published on the ECHA web-site.

Registry of intentions
When EU Member States and ECHA (when required by the European Commission) prepare a proposal for:

- a harmonised classification and labelling,
- an identification of a substance as SVHC, or
- a restriction.

This is done as a REACH Annex XV proposal.

The 'registry of intentions' gives an overview of intentions in relation to Annex XV dossiers divided into:
- current intentions for submitting an Annex XV dossier,
- dossiers submitted, and
- withdrawn intentions and withdrawn submissions

for the three types of Annex XV dossiers.

[10] It should be noted that the candidate list is also used in relation to articles imported to, produced in or distributed in the EU. Certain supply chain information is triggered if the articles contain more than 0.1% (w/w) (REACH Article 7.2 ff).

International agreements

OSPAR Convention

OSPAR is the mechanism by which fifteen Governments of the western coasts and catchments of Europe, together with the European Community, cooperate to protect the marine environment of the North-East Atlantic.

Work to implement the OSPAR Convention and its strategies is taken forward through the adoption of decisions, which are legally binding on the Contracting Parties, recommendations and other agreements. Decisions and recommendations set out actions to be taken by the Contracting Parties. These measures are complemented by other agreements setting out:

- issues of importance;
- agreed programmes of monitoring, information collection or other work which the Contracting Parties commit to carry out;
- guidelines or guidance setting out the way that any programme or measure should be implemented, and
- actions to be taken by the OSPAR Commission on behalf of the Contracting Parties.

HELCOM - Helsinki Convention

The Helsinki Commission, or HELCOM, works to protect the marine environment of the Baltic Sea from all sources of pollution through intergovernmental co-operation between Denmark, Estonia, the European Community, Finland, Germany, Latvia, Lithuania, Poland, Russia and Sweden. HELCOM is the governing body of the "Convention on the Protection of the Marine Environment of the Baltic Sea Area" - more usually known as the Helsinki Convention.

In pursuing this objective and vision the countries have jointly pooled their efforts in HELCOM, which is works as:

- an environmental policy maker for the Baltic Sea area by developing common environmental objectives and actions;
- an environmental focal point providing information about (i) the state of/trends in the marine environment; (ii) the efficiency of measures to protect it and (iii) common initiatives and positions which can form the basis for decision-making in other international fora;
- a body for developing, according to the specific needs of the Baltic Sea, Recommendations of its own and Recommendations supplementary to measures imposed by other international organisations;
- a supervisory body dedicated to ensuring that HELCOM environmental standards are fully implemented by all parties throughout the Baltic Sea and its catchment area; and
- a co-ordinating body, ascertaining multilateral response in case of major maritime incidents.

CLRTAP - Convention on Long-range Transboundary Air Pollution

Since 1979 the Convention on Long-range Transboundary Air Pollution (CLRTAP) has addressed some of the major environmental problems of the UNECE (United Nations Economic Commission for Europe) region through scientific collaboration and policy negotiation.

The aim of the Convention is that Parties shall endeavour to limit and, as far as possible, gradually reduce and prevent air pollution including long-range transboundary air pollution. Parties develop policies and strategies to combat the discharge of air pollutants through exchanges of information, consultation, research and monitoring.

The Convention has been extended by eight protocols that identify specific measures to be taken by Parties to cut their emissions of air pollutants. Three of the protocols specifically address the emission of hazardous substances of which some are included in LOUS:

The 1998 Protocol on Persistent Organic Pollutants (POPs); 33 Parties. Entered into force on 23 October 2003.
The 1998 Protocol on Heavy Metals; 33 Parties. Entered into force on 29 December 2003.
The 1991 Protocol concerning the Control of Emissions of Volatile Organic Compounds or their Transboundary Fluxes; 24 Parties. Entered into force 29 September 1997.

Stockholm Convention on Persistent Organic Pollutants (POPs)
The Stockholm Convention on Persistent Organic Pollutants is a global treaty to protect human health and the environment from chemicals that remain intact in the environment for long periods, become widely distributed geographically, accumulate in the fatty tissue of humans and wildlife, and have adverse effects to human health or to the environment. The Convention is administered by the United Nations Environment Programme and is based in Geneva, Switzerland.

Rotterdam Convention – PIC Convention
The objectives of the Rotterdam Convention are:
- to promote shared responsibility and cooperative efforts among Parties in the international trade of certain hazardous chemicals in order to protect human health and the environment from potential harm;
- to contribute to the environmentally sound use of those hazardous chemicals, by facilitating information exchange about their characteristics, by providing for a national decision-making process on their import and export and by disseminating these decisions to Parties.
- The Convention creates legally binding obligations for the implementation of the Prior Informed Consent (PIC) procedure. It built on the voluntary PIC procedure, initiated by UNEP and FAO in 1989 and ceased on 24 February 2006.

The Convention covers pesticides and industrial chemicals that have been banned or severely restricted for health or environmental reasons by Parties and which have been notified by Parties for inclusion in the PIC procedure. One notification from each of two specified regions triggers consideration of addition of a chemical to Annex III of the Convention. Severely hazardous pesticide formulations that present a risk under conditions of use in developing countries or countries with economies in transition may also be proposed for inclusion in Annex III.

Basel Convention
The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal was adopted on 22 March 1989 by the Conference of Plenipotentiaries in Basel, Switzerland, in response to a public outcry following the discovery, in the 1980s, in Africa and other parts of the developing world of deposits of toxic wastes imported from abroad.

The overarching objective of the Basel Convention is to protect human health and the environment against the adverse effects of hazardous wastes. Its scope of application covers a wide range of wastes defined as “hazardous wastes” based on their origin and/or composition and their characteristics, as well as two types of wastes defined as “other wastes” - household waste and incinerator ash.

The provisions of the Convention center around the following principal aims:

- the reduction of hazardous waste generation and the promotion of environmentally sound management of hazardous wastes, wherever the place of disposal;
- the restriction of transboundary movements of hazardous wastes except where it is perceived to be in accordance with the principles of environmentally sound management, and
- a regulatory system applying to cases where transboundary movements are permissible.

Eco-labels

Eco-label schemes are voluntary schemes where industry can apply for the right to use the eco-label on their products if these fulfil the ecolabelling criteria for that type of product. An EU scheme (the flower) and various national/regional schemes exist. In this project we have focused on the three most common schemes encountered on Danish products.

EU flower

The EU ecolabelling Regulation lays out the general rules and conditions for the EU ecolabel; the flower. Criteria for new product groups are gradually added to the scheme via 'decisions'; e.g. the Commission Decision of 21 June 2007 establishing the ecological criteria for the award of the Community eco-label to soaps, shampoos and hair conditioners.

Nordic Swan

The Nordic Swan is a cooperation between Denmark, Iceland, Norway, Sweden and Finland. The Nordic Ecolabelling Board consists of members from each national Ecolabelling Board and decides on Nordic criteria requirements for products and services. In Denmark, the practical implementation of the rules, applications and approval process related to the EU flower and Nordic Swan is hosted by Ecolabelling Denmark "Miljømærkning Danmark" (http://www.ecolabel.dk/). New criteria are applicable in Denmark when they are published on the Ecolabelling Denmark's website (according to Statutory Order no. 447 of 23/04/2010).

Survey of molybdenum trioxide

This survey is part of the Danish EPA's review of the substances on the List of Undesirable Substances (LOUS). The report presents information on the use and occurrence of molybdenum trioxide, internationally and in Denmark, information on environmental and health effects, releases and fate, exposure and presence in humans and the environment, on alternatives to the substances, on existing regulation, waste management and information regarding ongoing activities under REACH, among others.

Kortlægning af molybdæn trioxid

Denne kortlægning er et led i Miljøstyrelsens kortlægninger af stofferne på Listen Over Uønskede Stoffer (LOUS). Rapporten indeholder blandt andet en beskrivelse af brugen og forekomsten af molybdæn trioxid, internationalt og i Danmark, en beskrivelse af miljø- og sundhedseffekter af stofferne, udslip og skæbne, eksponering og forekomst i mennesker og miljø, viden om alternativer, eksisterende regulering, affaldsbehandling og igangværende aktiviteter under REACH.

Danish Ministry of the Environment
Environmental Protection Agency

Strandgade 29
1401 Copenhagen K, Denmark
Tel.: (+45) 72 54 40 00

www.mst.dk