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Survey of manganese(II) sulphate

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Survey of manganese(II) sulphate

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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 manganese(II) sulphate.

The main reason for the inclusion of manganese(II) sulphate in LOUS is that the substance is classified as causing danger of serious damage to health by prolonged exposure; "Xn, R48" according to the dangerous substances directive (67/548). The full classification according to dangerous substances directive (67/548) is Xn; R48/20/22 N; R51-53 and according to the CLP regulation (1272/2008): STOT RE 2; H373 Aquatic Chronic 2; H411.

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 DTU Food from April 2014 to October 2014. The work has been followed by an advisory group consisting of:

- Frank Jensen, Danish EPA, Chemicals
- Jesper Gruvmark, Danish EPA, Chemicals
- Lise Kjærgaard Steffensen, Danish AgriFish Agency
- Troels Knudsen, Danish AgriFish Agency
- Marianne Lyngsaae, Brenntag Nordic
- Elsa Nilsen, DTU Food
- 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 ECHA's 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 Register (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 Naturvårverket), 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

Manganese(II) sulphate - MnSO_4 - is an inorganic compound appearing as white crystals in its anhydrous form. The substance is often supplied as the monohydrate - $\text{MnSO}_4(\text{H}_2\text{O})$. Other less frequent hydrates are tetra- and pentahydrate. Hydrates appear as pale pink solids.

The REACH Manganese Consortium states that all hydrated forms of manganese(II) sulphate are considered covered by the manganese(II) sulphate anhydrous registration, as hydrates of a substance - formed by association with water - are exempt from the obligation to register in accordance with Article 2(7)(b) and Annex V, provided that they have been registered using this exemption. Accordingly, when 'manganese(II) sulphate' without further specification is used in this report, it implicitly refers to all forms (anhydrous and hydrated).

Manganese is an essential element for nutrition. Manganese(II) sulphate is one of the manganese substances allowed for delivering manganese as mineral/micronutrient to animals, plants and humans and, correspondingly, the main applications of manganese(II) sulphate are as fertilisers and in food/feed.

Regulatory framework

Manganese(II) sulphate is regulated as a micronutrient in relation to fertilisers, feed (including as an animal nutrient in organic production) and within the food area. The latter includes use of manganese(II) sulphate as a general mineral, in foods for specific medical purposes, in infant formulae and other specific infant foods. Manganese(II) sulphate has also originally been notified as an active substance for use in biocidal products. However, it is no longer supported as an active substance.

A range of emission/concentration control legislation for manganese is in place including provisions for air and water. These are relevant in this context as manganese(II) sulphate may cause the emissions of manganese. Similarly, manganese and manganese compounds are addressed by a number of occupational health provisions, including a Danish Occupational Exposure Limit, a Danish Code number and the recognition of "Manganism" (manganese induced Parkinson-like disease) as an occupational disease.

Manganese(II) sulphate is subject to harmonised EU classification for possible damage to organs through prolonged or repeated exposure and as toxic to aquatic life with long lasting effects. The REACH Manganese Consortium/the manganese industry further supports classification of all forms of manganese(II) sulphate for eye damage. This additional classification has not (yet) been adopted by the majority of importers/distributors of manganese(II) sulphate on its own or as part of mixtures. Furthermore, the fact that the manganese industry considers all forms of manganese(II) sulphate as having similar hazards/classification and has self-classified all these forms for eye damage is not easy to interpret from the information and searches available on the ECHA website. Manganese(II) sulphate is currently not subject to other REACH procedures.

Manganese(II) sulphate is not subject to international conventions or specifically restricted in eco-label criteria. However, manganese/manganese ores are subject to some provisions of the United Nations Convention on the Law of the Sea (UNCLOS). Manganese compounds are discussed as a possible less-toxic alternative to cobalt as driers in printing colours in the Nordic Swan background document for "Printing companies, printed matter, envelopes and other converted paper products".

Manufacture and use

Manganese occurs naturally in ores.

Manganese(II) sulphate is manufactured from manganese ores. In the EU, it is manufactured in two facilities (Bulgaria and Belgium). Further, manganese(II) sulphate appears as a non-isolated intermediate in the manufacturing process of Electrolytic Manganese Dioxide (EMD) in at least two EU sites, but not in Denmark. This intermediate use is not addressed in detail in this survey.

Overall amounts of manganese(II) sulphate on the market are difficult to quantify, but the following has been estimated based on the information identified in this project:

- Globally: 250,000 tonnes/year
- EU: 10,000-100,000 tonnes/year
- Denmark: 1,800 – 2,700 tonnes/year.

Based on dialogue with industry, the following main EU uses/applications have been identified:

- 75% used in fertilisers
- 15% used in feed (not regulated by REACH)
- 5% used in formulating fungicides for pesticide use
- 5% used for other applications of which the main amounts are assumed to be used as:
 - Drying agents/siccative in inks and paints for print, surface coating and colouring of leather
 - For water purification (e.g. in the leather industry)
 - Laboratory agents.

Volume-wise the use/application as siccative/drying agent in inks, paint, and leather colouring products is assessed to be the main application by far among the 5% other uses.

In addition, manganese(II) sulphate is (allowed to be) used as a mineral and nutrient in a number of food applications. No data on the volume of use in minerals/nutrients has been identified, but this use probably accounts for a few percent of the total volume.

For the Danish situation, it appears that most of the imported manganese(II) sulphate is used as fertilisers and feed, i.e. more than 90% as estimated for the EU situation.

The most significant exposures (via inhalation) are likely to happen in occupational settings, where farmers handle manganese(II) sulphate powders/granulates in relation to fertiliser handling and in relation to feed mixing applications (this mixing is, however, not always done by the farmer himself). The manganese(II) sulphate level is rather low (<150 ppm) in the final feed. Such handling might also lead to eye exposure.

Based on the available information, the main consumer exposures appear to be:

- Oral exposure: via intake as food nutrient/supplements, an intake regulated by EFSA (European Food Safety Authority) assessments and positive lists
- Dermal exposure: Mainly to dissolved Mn⁺⁺ in e.g. paints and fertilisers
- Inhalation/eye: Possibly in some handling of fertiliser granulates, although it should be noted that this use is not supported by the REACH Manganese Consortium.

Based on available data, it has not been possible to identify trends in use, although the main applications areas (as fertilisers and in feed) might be considered relatively stable.

Waste management

When considering manganese(II) sulphate waste and possibly related emissions to the environment, it should be acknowledged that the majority of the applied manganese(II) sulphate is spread directly into the environment as fertiliser.

As manganese(II) sulphate is not manufactured in Denmark, losses with waste are deemed mainly to originate from waste packaging in the handling of the substance from fertiliser and feed applications. Based on limited data from other powdered/granulated materials (brominated flame retardants in factory settings), such losses are deemed minimal, likely below 1-2 tonnes/year in Denmark.

Additional losses with fertiliser remnants not spent cannot be ruled out. It is anticipated that this manganese(II) sulphate would be lost to waste incineration with general waste disposal. There are many other sources of manganese (apart from sulphate) to waste incineration.

Manganese(II) sulphate is manufactured in two EU facilities and appears as an intermediate in a few other facilities. Waste generated by these facilities has not been investigated in this project.

Similar considerations as for the Danish situation apply regarding waste generated from products in which manganese(II) sulphate is used in the EU.

Environment

Environmental fate and effects

Manganese is a naturally occurring element, which makes up around 0.1% of the earth's crust. Manganese(II) sulphate is very water soluble and in natural waters at pH 4-7 is present as the Mn^{2+} ion, while at higher pH (>8), it may be oxidised further to oxidation state +4.

A complex series of reactions take place in aerobic environments that eventually render manganese biologically unavailable as insoluble manganese dioxide.

In water, manganese may be significantly bioconcentrated at lower trophic levels. BCFs of manganese from 2,500-6,300 have been reported for phytoplankton, 300-5,500 for marine algae, 800-830 for intertidal mussels and 35-930 for coastal fish. Aquatic effect levels of the manganese (II) ion (the most relevant level in natural waters at pH 4-7) do not differ widely between taxonomic groups (e.g. fish, invertebrates and algae). Acute levels (LC₅₀/EC₅₀) are typically in the mg/l range while chronic no-effect levels are typically around 1 mg/l or in the sub-mg/l range. The Danish EQS for manganese in surface waters is 0.15 mg Mn/l (dissolved fraction; added to the natural background level), which is considerably higher than the PNEC values proposed by the registrant.

Terrestrial data are few but generally indicate low toxicity in soils typical of Denmark.

Releases to the environment

Soils, sediments and rocks are important natural sources of environmental exposure to manganese. Globally, about two thirds of the emissions of manganese (mostly other forms than sulfate) to air are estimated to be from natural sources.

The anthropogenic sources of manganese include municipal wastewater discharges, sewage sludge, mining and mineral processing (particularly nickel), emissions from steel and iron production, combustion of fossil fuels and, to a minor extent, emissions from vehicles (from the fuel additive MMT).

The anthropogenic releases of manganese(II) sulphate to the environment in Denmark are mainly due to its use as a fertiliser in field crops, which constitutes the main fraction of the total amount while most of the remainder is used as a nutrient in animal feed.

The release to the environment from use as fertiliser must in reality be 100% while the release from the use in feed would be somewhat less although still high.

Monitoring data – levels in the environment

Manganese (and manganese(II) sulphate) is not included in the Danish environmental monitoring programme, NOVANA. The Danish groundwater monitoring programme, GRUMO, reports for manganese that over the period 1989-2006, 78.2% of the measurements exceeded the threshold value for drinking water of 0.02 mg Mn/l. However, elements like manganese and iron etc. are normally removed at the waterworks before the water is distributed to the consumers, and is therefore not considered to constitute a drinking water problem.

Worldwide, the atmospheric concentrations of manganese are in the ng/m³ range. In natural waters not affected significantly by anthropogenic sources, the concentrations of dissolved manganese vary between 0.010 and 10 mg/l although the concentrations are usually less than 0.2 mg/l.

Environmental impact

No reports or scientific papers on environmental impact or risk assessments of manganese (or manganese(II) sulphate) have been identified. However, it should be noted that manganese is an essential element to animals as well as plants.

Human health

Human health hazard

Manganese is absorbed from the lungs after inhalation; absorption can be significant for workers who are exposed to excess levels of airborne manganese. Manganese has been reported to accumulate in certain regions of the brain, and it is indicated that manganese may be distributed directly to the brain from the nasal cavity via the olfactory pathway, thereby by-passing the blood-brain barrier.

Manganese is an essential element in the nutrition of humans and animals and is needed for the functioning of key enzymes. The concentration of manganese in the body is usually well regulated via normal physiological processes, i.e. the homeostatic system. However, the homeostatic system can become overloaded, resulting in adverse systemic effects.

Manganese(II) sulphate is of low acute toxicity in experimental animals following inhalation and of moderate acute toxicity following oral administration. Based solely on data in the REACH Registration Dossier and not from the original studies, classification of manganese(II) sulphate for eye irritation appears to be warranted, whereas classification for skin irritation does not seem to be warranted.

The central nervous system is the primary target of manganese toxicity following repeated exposure; neurotoxicity is the critical effect of excess manganese exposure. Manganese(II) sulphate is subject to harmonised classification for specific organ toxicity following repeated exposure (STOT RE 2), since several types of serious toxic effects after inhalation have been observed.

No overall conclusion can be made about the possible genotoxic hazard to humans from exposure to manganese(II) sulphate. However, based solely on data in the REACH Registration Dossier and not from the original studies, classification of manganese(II) chloride for mutagenicity or genotoxicity does not seem to be warranted. Read-across of these results to manganese(II) sulphate seems justifi-

fied as the manganese ion is the toxic moiety of manganese(II) sulphate in relation to systemic toxicity.

Based upon the available data, it cannot be evaluated whether manganese(II) sulphate is carcinogenic. Currently available studies in experimental animals indicate that manganese has the potential to cause reproductive and developmental effects when administered orally.

Based on the limited information available on endocrine effects of manganese, the potential of manganese to affect the endocrine system cannot be evaluated. However, given that manganese is an essential element for humans; endocrine effects are not likely at low/moderate exposure levels.

Human exposure and human health impacts

No thorough authoritative risk assessment of industrial applications of manganese(II) sulphate has been identified in this survey.

Given the identified evidence, there might be a significant occupational inhalation and eye exposure risk associated with handling manganese(II) sulphate powder/granulates as fertiliser or for feed applications. This risk seems to be particularly relevant to farmers who are not using personal protective equipment consistently.

Consumer exposure and exposure of the general population via the environment seems to be low. One exception might be consumer exposure to fertilisers granulates, which however seems to be rare or possibly non-existing.

This might also be the case for consumers handling fertiliser powder/granulates. Whether this use actually takes place is, however, uncertain.

Risks associated with exposure via other routes and from other products appear to be low.

Alternatives

For nutrient and fertiliser uses, the actual need is the manganese element itself, and therefore naturally manganese(II) sulphate could be substituted for by other manganese salts. However, as manganese is the toxic moiety, it makes little sense to substitute one manganese compound for the other.

It is therefore more relevant to consider alternative application methods aiming at reducing the exposure/risk, such as: i) using personal protection equipment (filter masks and eye protection), ii) supplying manganese(II) sulphate to the farmer as pellets rather than as powders/granulates, or iii) possibly by optimising how the manganese(II) sulphate fertiliser solution is supplied to the agricultural fields.

Alternatives to manganese siccatives ("driers") in paints, inks and coatings exist, but in many cases they include toxic metals.

Other minor uses of manganese(II) sulphate, which appear to be absent or rarely used in Denmark, have not been investigated further.

Main data gaps and discrepancies

Within the scope of this project, the following issues are considered the main data/information gaps for manganese(II) sulphate:

- Some confusion appears when searching the ECHA website:
 - It is not clear that all hydrated forms are within the scope of the lead registration of manganese (II) sulphate (registered under the CAS No of the anhydrous form), and
 - The different hydrated forms (having different CAS No.'s) appear separately and with different information when conducting various searches on the ECHA website.
- Overall volumes manufactured, imported and consumed in the EU and in Denmark are uncertain.
- Uncertainty pertains to the types and volumes of "minor applications". A long list of uses is registered in REACH, some of which, however, appear to be non-existent or rare in reality. Still, some of these uses might lead to consumer exposure to the manganese ion (Mn^{++}) or perhaps even manganese(II) sulphate (if e.g. fertiliser granulate is handled by consumers). Whether such uses would lead to any significant exposure is, however, questionable; any risk should be seen in light of manganese being an essential element in human nutrition.
- There appears to be a discrepancy between the harmonised EU classification for manganese(II)sulphate and the knowledge related to eye irritation/eye damage. Revisiting this issue may be warranted.
- Data on occupational exposure to manganese(II) sulphate are lacking, in particular for farmers handling manganese(II) sulphate powder.
- Linked to this lack of occupational exposure data, data on the particle size of manganese(II) sulphate used in the formulation of fertilisers and as a constituent in feed, and on the droplet size of manganese containing fertilisers on spray/aerosol form, are lacking.

Sammenfatning og konklusioner

Stoffet

Mangan(II)sulfat - $MnSO_4$ - er en uorganisk forbindelse, der forekommer som hvide krystaller i sin vandfri form. Stoffet leveres oftest som monohydratet - $MnSO_4(H_2O)$. Andre, mindre hyppigt forekommende hydrater er tetra- og pentahydrat. Hydrater forekommer som blegrøde faste stoffer.

REACH Mangan Konsortiet anfører, at alle hydratformer af mangan(II)sulfat betragtes som omfattet af registreringen for vandfrit mangan(II)sulfat, da hydrater af et stof - som dannes ved binding med vand - er fritaget for forpligtelsen til at registrere i henhold til REACH artikel 2(7)(b), og bilag V, forudsat at de er blevet registreret ved hjælp af denne undtagelse. Når 'mangan(II)sulfat' uden yderligere specifikation anvendes i denne rapport, refererer det implicit til alle former (både vandfri og hydreret).

Mangan er et essentielt næringsstof. Mangan(II)sulfat er et af de mangan-salte, som det er tilladt at tilsætte som mineral/mikronæringsstof til dyr, planter og mennesker. I tråd hermed er de vigtigste anvendelser af mangan(II)sulfat som gødning og i fødevarer/foder.

Lovgivning

Mangan(II)sulfat er reguleret som et mikronæringsstof i forhold til gødning, foder (herunder som et næringsstof i økologisk dyreopdræt) og inden for fødevarerområdet. Sidstnævnte inkluderer anvendelse af mangan(II)sulfat som mineral i fødevarer til særlige medicinske formål, i modermælkserstatninger og til anden mad til spædbørn. Mangan(II)sulfat er også oprindeligt anmeldt som et aktivt stof i biocidprodukter. Det er imidlertid ikke længere understøttet af industrien som et aktivt stof.

En række regler regulerer emission og koncentration af mangan i miljøet. Disse regler er relevante i forhold til mangan(II)sulfat, da stoffet kan medføre emissioner af mangan. Tilsvarende er mangan og manganforbindelser omfattet af en række bestemmelser vedr. arbejdsmiljø, herunder en dansk grænseværdi og et dansk kodenummer. "Manganisme" (mangan-induceret Parkinson-lignende sygdom) er desuden en anerkendt erhvervs sygdom.

Mangan(II)sulfat er underlagt harmoniseret EU-klassificering for at kunne give skade på organer ved længevarende eller gentagen eksponering og som giftig for vandlevende organismer, med langvarige virkninger. REACH Mangan Konsortiet/mangan industrien foreslår yderligere klassificering som øjenskadende for alle former for mangan(II)sulfat. Denne yderligere klassificering anvendes (endnu) ikke af flertallet af importører/distributører af mangan(II)sulfat som stof eller som en del af blandinger. Det forhold, at manganindustrien mener, at alle former for mangan(II)sulfat har samme fareprofil og klassificering, samt at manganindustrien har selvklassificeret alle former for øjensskade, er ikke let at fortolke ud fra søgeresultater fra Kemikalieagenturets (ECHAs) hjemmeside. Mangan(II)sulfat er ikke i øjeblikket underlagt andre REACH procedurer.

Mangan(II)sulfat er ikke omfattet af internationale konventioner eller specifikke miljømærkekriterier. Mangan/manganmalm er dog underlagt visse bestemmelser i De Forenede Nationers havrets-

konvention (UNCLOS). Manganforbindelser diskuteres desuden som et muligt, mindre giftigt alternativ til kobolt som tørremiddel/sikkativ i trykfarver i baggrundsdokumentet til "Trykkerier, tryksager, kuverter og andre forædlede papirprodukter" under det nordiske svanemærke.

Fremstilling og forbrug

Mangan forekommer naturligt i malme.

Mangan(II)sulfat fremstilles ud fra manganmalm. Det fremstilles i to anlæg i EU (Bulgarien og Belgien). Endvidere forekommer mangan(II)sulfat som et ikke-isoleret mellemprodukt i fremstillingen af elektrolytisk mangandioxid (EMD) på minimum to EU anlæg, men ikke i Danmark. Denne anvendelse som mellemprodukt er ikke behandlet i detaljer i denne undersøgelse.

Den totale mængde mangan(II)sulfat på markedet er vanskelig at kvantificere, men følgende er blevet estimeret på grundlag af oplysninger indsamlet i dette projekt:

- Globalt: 250.000 tons/år
- EU: 10.000-100.000 tons/år
- Danmark: 1.800 - 2.700 tons/år.

Baseret på dialog med industrien, er følgende vigtigste EU-anvendelser blevet identificeret:

- 75% anvendes i gødning
- 15% anvendes i foder (ikke reguleret af REACH)
- % anvendes ved formulering af fungicider til anvendelse som pesticid
- 5% anvendes til andre formål, hvoraf de vigtigste antages at være:
 - Tørremiddel/sikkativ i trykfarver og maling, overfladebehandling og farvning af læder
 - Til vandrensning (f.eks. i læderindustrien)
 - Laboratoriekemikalie.

Mængdemæssigt vurderes anvendelsen som sikkativ/tørremiddel i trykfarver, maling og læderfarve at være langt den vigtigste blandt de 5% "anvendelser til andre formål".

Endvidere er mangan(II)sulfat godkendt som et mineral og næringsstof i en række fødevarer. Det har ikke været muligt at indsamle information om mængden anvendt til sådanne formål, men det er estimeret, at denne anvendelse sandsynligvis tegner sig for nogle få procent af den samlede anvendte mængde.

For Danmark vurderes det, at størstedelen af den importerede mangan(II)sulfat anvendes som gødning og foder, og at denne anvendelse udgør mere end de 90%, som er anslået for situationen i EU.

Den væsentligste eksponering (indånding) forventes at forekomme i arbejdsmiljøet, hvor landmænd håndterer mangan(II)sulfat pulver/granulat i forbindelse med håndtering af gødning og i forbindelse med blanding af foder (foderblanding foregår dog ikke altid hos landmanden). Mangan(II)sulfatindholdet i færdigt foder er temmeligt lavt (<150 ppm). Disse anvendelser kan også medføre øjenkontakt.

På basis af de foreliggende oplysninger vurderes de vigtigste forbrugereksponeeringer at være:

- Oral eksponering: via indtag som næringsstof/kosttilskud; et indtag som reguleres af positivlister på basis af vurderinger fra Den Europæiske Fødevarsikkerhedsautoritet (EFSA)
- Dermal eksponering: Hovedsageligt opløst som Mn⁺⁺ i f.eks. maling og gødning
- Indånding/øje: Mulig håndtering af gødningsgranulat. Det skal bemærkes, at denne anvendelse ikke anbefales af REACH Mangan Konsortiet.

Baseret på tilgængelige data, har det ikke været muligt at identificere tidsmæssige tendenser i anvendelserne. Dog anses de vigtigste anvendelsesområder (som gødning og i foder) for relativt stabile.

Affaldshåndtering

Når man adresserer mangan(II)sulfat som affald og heraf eventuelt relaterede emissioner til miljøet, bør det erindres, at de væsentligste mangan(II)sulfat anvendelser indebærer, at stoffet spredes direkte i miljøet, herunder som gødning.

Da mangan(II)sulfat ikke fremstilles i Danmark, anses tab med affald primært at udgøres af emballageaffald fra anvendelser i gødning og foder. Baseret på begrænsede data fra andre pulveriserede/granulerede materialer (bromerede flammehæmmere i fabriksanvendelse), er sådanne tab skønnet minimale, sandsynligvis under 1-2 tons/år i Danmark.

Yderligere tab med ikke-anvendte gødningsrester kan ikke udelukkes. Det forventes, at dette mangan(II)sulfat ender i affaldsforbrændingsanlæg via bortskaffelse af almindeligt affald. Der er mange andre kilder til mangan (bortset fra sulfat) til affaldsforbrænding.

Mangan(II)sulfat fremstilles i to EU anlæg og optræder som et mellemprodukt i et par andre anlæg. Affaldet fra disse anlæg er ikke blevet undersøgt i dette projekt.

Tilsvarende betragtninger som for den danske situation, gælder med hensyn til affald fra produkter, hvori mangan(II)sulfat anvendes i EU.

Miljø

Miljømæssig skæbne og effekter

Mangan er et naturligt forekommende grundstof, der udgør omkring 0,1 % af jordskorpen. Mangan(II)sulfat er meget vandopløseligt og forekommer som Mn^{2+} ionen i naturligt vand ved pH 4-7. Ved højere pH (>8) kan det blive oxideret yderligere til oxidationstrin +4.

I aerobe miljøer bliver mangan omdannet til ikke biotilgængeligt mangan dioxid via en række komplekse kemiske reaktioner.

I vand kan mangan biokoncentreres i betydelig grad på lavere trofiske niveauer. Biokoncentreringsfaktorer på 2.500-6.300 er rapporteret for fytoplankton, 300-5.500 for marine alger, 800-830 for muslinger i tidevandszonen og 35-930 for kystnære fisk. Akvatiske effektive niveauer for mangan(II) ionen (den mest relevante i naturlige vandområder ved pH 4-7) afviger ikke meget mellem taksonomiske grupper (f.eks. fisk, hvirvelløse dyr og alger). Akutte effektive niveauer (LC50/EC50) er typisk i mg/l niveauer, mens kroniske nuleffektive niveauer typisk ligger omkring 1 mg/l eller i sub-mg/l området. Det danske miljøkvalitetskrav for mangan i overfladevand er 0.15 mg Mn/l (opløst fraktion; lagt til det naturlige baggrundsniveau), hvilket er væsentligt højere end de PNEC-niveauer, som foreslås af REACH registranten.

Terrestriske data er få, men indikerer generelt lav toksicitet i jordtyper typiske for Danmark.

Udslip til miljøet

Jord, sedimenter og sten/klipper er vigtige naturlige kilder til miljømæssig eksponering for mangan. På verdensplan er det estimeret, at ca. to tredjedele af manganemissionen til luften (hovedsageligt som andre former end mangan(II)sulfat) stammer fra naturlige kilder.

De menneskeskabte kilder til mangan omfatter kommunale spildevandsudledninger, slam fra rensningsanlæg, minedrift og forarbejdning af malm (især nikkel), emissioner fra stål- og jernprodukti-

on, forbrænding af fossile brændsler, og i mindre omfang emissioner fra køretøjer (fra tilsætningsstoffet MMT).

De menneskeskabte udslip af mangan(II)sulfat til omgivelserne i Danmark er primært fra anvendelse som gødning på marker, som udgør den væsentligste andel, mens størstedelen af den øvrige mængde anvendes som næringsstof i dyrefoder.

Frigivelsen til miljøet fra anvendelse som gødning anses for at være 100%, mens frigivelse fra anvendelse i foder anses at være noget mindre, men dog stadig høj.

Moniteringsdata for koncentrationer i miljøet

Mangan (og mangan(II)sulfat) er ikke medtaget i det danske miljøovervågningsprogram, NOVANA. Det danske grundvandsovervågning program, GRUMO, rapporterer, at 78,2% af mangan-målingerne i perioden 1989-2006 overskred tærskelværdien for drikkevand på 0,02 mg Mn/l. Dog fjernes grundstoffer som mangan og jern normalt på vandværkerne inden vandet fordeles til forbrugerne, og de anses derfor ikke for at udgøre et drikkevandsproblem.

På verdensplan er koncentration af mangan i atmosfæren i størrelsesordenen ng/m³. I naturlige vandområder, som ikke påvirkes væsentligt af menneskeskabte kilder, varierer koncentrationen af opløst mangan mellem 0,010 og 10 mg/l. Koncentrationerne er dog normalt mindre end 0,2 mg/l.

Miljøpåvirkning

Der er ikke identificeret rapporter eller videnskabelige artikler med miljømæssige risikovurderinger af mangan (eller mangan(II)sulfat). Det skal dog bemærkes, at mangan som nævnt er et livsvigtigt næringsstof for såvel dyr som planter.

Sundhed

Sundhedsfare for mennesker

Mangan optages fra lungerne efter inhalation; optagelsen kan være betydelig for arbejdstagere, der er udsat for høje niveauer af luftbåren mangan. Mangan er blevet rapporteret til at kunne ophobe sig i visse områder af hjernen, og der er indikationer på, at mangan kan fordeles direkte til hjernen fra næsehulen via lugteorganerne og derved omgå blod-hjerne-barrieren.

Mangan er et livsvigtigt næringsstof for mennesker og dyr og er nødvendigt for funktionen af vigtige enzymer. Koncentrationen af mangan i kroppen er normalt reguleret via normale fysiologiske processer, nemlig det homeostatiske system. Dog kan det homeostatiske system blive overbelastet, hvilket medfører systemiske effekter.

Mangan(II)sulfat har lav akut toksicitet i forsøgsdyr efter indånding og har moderat akut toksicitet efter oral administration. Baseret udelukkende på data i REACH registreringer og ikke på de oprindelige undersøgelser, synes klassificering af mangan(II)sulfat for øjenirritation at være berettiget, mens klassificering for hudirritation ikke synes at være berettiget.

Centralnervesystemet er det primære målorgan for mangantoksicitet efter gentagen eksponering; neurotoksicitet er den kritiske effekt ved høj mangan eksponering. Mangan(II)sulfat er genstand for harmoniseret klassificering for specifik målorgantoksicitet efter gentagen eksponering (STOT RE 2), idet flere typer af alvorlige toksiske effekter er observeret efter indånding.

Der kan ikke laves nogen overordnet konklusion om den mulige genotoksicitet for mennesker som følge af eksponering for mangan(II)sulfat. Baseret udelukkende på data i REACH registreringer og ikke på de oprindelige undersøgelser, anses klassificering af mangan(II) chlorid for mutagenicitet eller genotoksicitet dog ikke at være berettiget. Analogislutning (read-across) af disse resultater til

mangan(II)sulfat forekommer berettiget, da mangan-ionen er den toksiske bestanddel af mangan(II)sulfat i forhold til systemisk toksicitet.

Baseret på de tilgængelige data kan det ikke vurderes, om mangan(II)sulfat er kræftfremkaldende. Aktuelt tilgængelige undersøgelser i forsøgsdyr indikerer, at mangan har potentiale til at forårsage reproduktions- og udviklingsmæssige effekter, når det administreres oralt.

Mangans mulige hormonforstyrrende effekter kan ikke vurderes pga. begrænset tilgængelig viden. Da mangan er et livsnødvendigt mineral, er det dog usandsynligt at mangan forårsager hormonforstyrrende effekter ved lave/moderate eksponerings-niveauer.

Eksponering og sundhedspåvirkning

Der er ikke identificeret autoritative risikovurderinger af mangan(II)sulfat i denne undersøgelse.

Den indsamlede information indikerer, at der kunne være risiko for en betydelig arbejdsmiljømæssig indåndings- og øjeneksponering forbundet med håndtering af mangan(II)sulfat pulver/granulater som gødning eller til anvendelser i foder. Denne risiko synes at være særlig relevant for landmænd, i det omfang de ikke anvender de foreskrevne personlige værnemidler.

Forbrugereksponeering og eksponering af befolkningen via miljøet synes lav. En undtagelse kunne være forbrugereksponeering ved håndtering af granulátgødning. Forekomsten af denne anvendelse synes dog begrænset eller ikke-eksisterende.

Dette kunne også være tilfældet for forbrugerne, som håndterer gødning som pulver/granulater. Det er dog uvist, hvorvidt en sådan anvendelse faktisk finder.

Risici forbundet med andre eksponeringsveje og andre anvendelser/produkter synes at være lav.

Alternativer

For anvendelser som næringsstof, herunder som gødning, er det grundstoffet mangan, som er det væsentlige element, og derfor kan mangan(II)sulfat substitueres af andre mangansalte. Men da mangan samtidig er den toksiske bestanddel, giver det ikke meget mening at erstatte én manganforbindelse med den anden.

Det er derfor mere relevant at overveje alternative anvendelsesmetoder, som sigter mod at reducere eksponering/risici, såsom: i) anvendelse af personlige værnemidler (masker og øjenbeskyttelse), ii) levering af mangan(II)sulfat til landmanden som piller/kugler snarere end som pulver/granulat, og/eller iii) eventuelt ved at optimere, hvordan mangan(II)sulfat-gødningsopløsningen udbringes på markerne.

Alternativer til mangan som tørremiddel/sikkativ i maling, trykfarver og overfladebelægninger findes men er i mange tilfælde baseret på toksiske metaller.

Andre mindre udbredte anvendelser af mangan(II)sulfat, som synes at være ubetydelige i Danmark, er ikke blevet undersøgt yderligere i dette studie.

Vigtigste datamangler og uoverensstemmelser

Inden for rammerne af dette projekt er følgende forhold vurderet at være de væsentligste informations- og datamangler for mangan(II)sulfat:

- Søgning på Kemikalieagenturets (ECHAs) hjemmeside giver anledning til nogen forvirring:
 - Det er ikke klart, at alle hydrerede former er omfattet af 'lead registrant' registreringer for mangan(II)sulfat (registreret under CAS-nummeret for den vandfri form), og
 - De forskellige hydrerede former (der har forskellige CAS-numre) optræder særskilt og med forskellige oplysninger, når der foretages forskellige søgninger på ECHAs hjemmeside.
- De samlede mængder, som fremstilles, importeres og forbruges i EU og i Danmark er usikkert bestemt.
- Der er usikkerhed forbundet med typen og omfanget af "mindre anvendelser". En lang række anvendelser er registreret under REACH, hvoraf nogle synes at være ikke eksisterende eller sjældne. Dog kan nogle af disse anvendelser føre til forbrugereksposering for mangan-ionen (Mn^{++}) eller måske endda for mangan(II)sulfat (hvis f.eks. gødningsgranulat håndteres af forbrugerne). Hvorvidt sådanne anvendelser vil føre til nogen væsentlig eksponering er dog tvivlsomt, da mulige risici skal ses i lyset af, at mangan er et livsvigtigt næringsstof for mennesker.
- Der synes at være et misforhold mellem den harmoniserede EU-klassificering for mangan(II)sulfat og viden om stoffets øjenirriterende/-skadende virkning. Det kunne derfor være berettiget at genvurdere denne.
- Data om eksponering for mangan(II)sulfat i arbejdsmiljøet mangler, specielt for landmænd som håndterer mangan(II)sulfat i pulverform.
- Knyttet til denne mangel på viden om eksponering i arbejdsmiljøet mangler der data om partikelstørrelsen af mangan(II)sulfat anvendt til formulering af gødning og som bestanddel i foder, og om dråbestørrelsen, når manganholdig gødning sprøjtes ud på markerne.

1. Introduction to the substance group

1.1 Definition of the substance group

Manganese(II) sulphate - MnSO_4 - is an inorganic compound appearing as white crystals in its anhydrous form. The substance is often supplied as the monohydrate - $\text{MnSO}_4(\text{H}_2\text{O})$. Other less frequent hydrates are tetra- and pentahydrate. Hydrates appear as pale pink solids. Table 1 provides an overview of these forms and their REACH registration status as presented on the website of the European Chemicals Agency.

TABLE 1
MANGANESE(II) SULPHATE AND ITS HYDRATES AND THEIR REACH REGISTRATION STATUS

CAS No	EC Number	Hydrate form	Registered, tonnage band, t/y	Pre-registered?	C&L
7785-87-7	232-089-9	Anhydrous	10,000 – 100,000	YES	Harmonised
10034-96-5	600-072-9	Monohydrate	Covering both substances	YES	781 notifications in C&L inventory
10101-68-5	600-150-2	Tetrahydrate	-*	YES	81 notifications in C&L inventory
13465-27-5	-	Pentahydrate	-*	-	-

* The REACH Manganese Consortium states that all hydrates are covered by the manganese(II) sulphate registration.

The table shows that three of four forms have been pre-registered under REACH. From the ECHA dissemination tool website (ECHA, 2014), it appears that the anhydrous and the monohydrate forms have been registered together (under CAS No 7785-87-7).

Of the other hydrated forms, the tetrahydrate appears to be used commercially, as evidenced by 81 self-classifications, but not yet registered.

However, dialogue with the REACH Manganese Consortium reveals that all hydrated forms of manganese(II) sulphate are considered covered by the manganese(II) sulphate anhydrous registration (REACH registration number: 01-2119456624-35-000; CAS number: 7785-87-7; EINECS number: 232-089-9) as hydrates of a substance formed by association with water. These forms are considered exempt from the obligation to register in accordance with Article 2(7)(b) and Annex V, provided that the substance has been registered using this exemption (Harlow, 2014).

This information is not entirely clear from the information and search options available on the ECHA website, probably due to different actors having applied different approaches in the pre-registration phase.

In this project, it will be assumed as a starting point that all forms of manganese(II) sulphate have similar hazard profiles. Further, unless otherwise stated in reviewed information sources, the forms

will be considered similar in terms of applications and properties, and simply referred to as manganese(II) sulphate.

As manganese(II) sulphate is a soluble salt which easily dissociates in water, the health and environmental considerations in this report logically address the manganese ion (Mn^{++}) where relevant. Therefore, the review of legislation in chapter 2 will also aim at capturing how "manganese" is addressed in legislation addressing waste/waste streams and occurrence in environmental media.

1.2 Physical and chemical properties of manganese(II) sulphate

Physical and chemical properties of manganese(II) sulphate are shown in Table 2.

TABLE 2
PHYSICAL AND CHEMICAL PROPERTIES OF MANGANESE(II)SULPHATE

Property	Value	Reference
EC number	232-089-9	ECHA (2014)
CAS number	7785-87-7	ECHA (2014)
IUPAC name	Manganese (II) sulphate	-
Synonyms	Manganese sulphate Manganous sulphate Manganese(II) sulphate Manganese(2+) sulphate Sulfuric acid, manganese salt Manganese monosulphate Manganese sulphate (1:1) Manganese(II) sulphate (1:1) Manganese(2+) sulphate (1:1) Sulfuric acid, manganese(2+) salt (1:1) MnSO ₄ Winkler's solution #1 Manganese sulphate anhydrous manganese(2+) ion sulphate Sulfuric acid, manganese (II) salt (1:1) Sulfuric acid, manganese(2++) salt (1:1) sulfuric acid manganese salt (1:1) monohydrate	Chemind. website ¹
Molecular formula	MnSO ₄ /MnSO ₄ (n*H ₂ O), n: 1, 4 or 5	Various
Appearance/Physical state	Extremely pale pink powder (monohydrate)	ECHA (2014)
Melting point (K/°C)	> 723 Kelvin (> 450°C)	ECHA (2014)
Boiling point (°C)	Decomposes at 850 °C	Chemind. website ¹
Flash point (closed cup) (°C)	NA	-
Relative density	2.93 (22 °C)	ECHA (2014)

¹ <https://www.chemindustry.com/chemicals/0525516.html>

Vapour pressure (at 40°C)	NA	-
Surface tension	NA	-
Water solubility (mg/l)	very soluble (> 10,000 mg/l)	ECHA (2014)
Log P (octanol/water)	NA	-
Molecular weight	Anhydrous: 151; Monohydrate: 169	Chemind. website ¹

1.3 Function of the substances for main application areas

Manganese is an essential element and as will be further illustrated in Chapter 2, the water-soluble form of manganese(II) sulphate is one of the manganese substances allowed for delivering manganese as mineral/micronutrient to animals, plants and humans. Indeed, the main applications of manganese(II) sulphate as such are as fertilisers and in food/feed. This function will be further elaborated in Chapter 3, along with a description of minor technical applications.

A significant amount of manganese(II) sulphate also appears as an intermediate in the manufacturing of manganese dioxide used in batteries, where manganese(II) sulphate is formed, but consumed again within the process. In REACH terms, according to Harlow (2014), this function is a non-isolated intermediate outside the scope of the REACH registration requirements. According to the REACH definitions (REACH, article 3(15)(a)), non-isolated intermediates are not removed from the reactions equipment. Therefore, this use will be briefly addressed in Chapter 3, but otherwise considered of lower priority in this project given its status as a non-isolated intermediate.

2. Regulatory framework

2.1 Legislation

This section first lists existing legislation addressing manganese(II) sulphate and subsequently provides an overview of on-going regulatory activities, focusing on substances in the pipeline in relation to various REACH provisions. Finally, it will be indicated 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 3 provides an overview of existing legislation addressing manganese(II) sulphate. For each area of legislation, the table first lists the EU legislation (if applicable) and then (as concerns directives) existing transposition of this legislation into Danish law and/or other national rules. The latter will only be elaborated upon where Danish rules differ from EU rules.

Table 3 shows that manganese(II) sulphate is regulated as a micronutrient in relation to fertilisers, feed (including as an animal nutrient in organic production) and within the food area. The latter includes use of manganese(II) sulphate as a general mineral, in foods for specific medical purposes, in infant formulae and other specific infant foods. Manganese(II) sulphate has also originally been notified as an active substance for use in biocidal products. However, it is no longer supported as an active substance.

Whereas manganese is an essential element for living organisms, it may cause toxicity at high concentrations and exposures, as is further addressed in Chapter 6. Therefore, a range of emission/concentration control legislation for manganese is in place including provisions for air and water. These are relevant in this context as manganese(II) sulphate may cause emissions of the manganese. Similarly manganese and manganese compounds are addressed by a number of occupational health provisions, including a Danish Occupational Exposure Limit (OEL), a Danish Code number and the recognition of "Manganism" (manganese-induced Parkinson-like disease) as an occupational disease.

TABLE 3
EU AND DANISH LEGISLATION ADDRESSING MANGANESE(II) SULPHATE (AS OF APRIL 2014)

Legal instrument *1	EU/ National	Substances (as indicated in the instrument)	Requirements as concerns manganese(II)sulphate
Legislation addressing products			
Fertilisers			
REGULATION (EC) No 2003/2003 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 13 October 2003 relating to fertilisers	EU	Manganese, including manganese (II) salts; i.e. implicitly including manganese(II) sulphate	Defines "manganese" as a micronutrient and sets out conditions for their marketing and use including product formulations and concentration, as well as labelling

Legal instrument *1	EU/ National	Substances (as indicated in the instrument)	Requirements as concerns manga- nese(II)sulphate
<p>COMMISSION REGULATION (EU) No 223/2012 of 14 March 2012 amending Regulation (EC) No 2003/2003 of the European Parliament and of the Council relating to fertilisers for the purposes of adapting Annexes I and IV thereto to technical progress</p> <p>as well as other amendments</p>	EU	As above	Extends the allowed types of product formulations with "suspensions" in order to reduce occupational exposure to previously allowed/applied powder forms
<p>Bekendtgørelse om gødning og jordforbedringsmidler m.v. BEK nr 862 af 27/08/2008 [Statutory Order on fertilisers, soil improvement agents, etc.] *</p>	DK	As above	Mirrors the above regulation in relation to manganese(II) sulphate
<p>Bekendtgørelse om handel med gødning og grundforbedringsmidler m.m. BEK nr 664 af 15/12/1977 [Statutory Order on fertilisers, soil improvement agents, etc.] *</p>	DK	Water soluble manganese (i.e. implicitly manganese(II) sulphate)	Specifies limits for when and when not to declare content of "water soluble manganese".
Legislation addressing food			
<p>COMMISSION DIRECTIVE 2008/100/EC of 28 October 2008 amending Council Directive 90/496/EEC on nutrition labelling for foodstuffs as regards recommended daily allowances, energy conversion factors and definitions</p>	EU	Manganese	Specifies a Recommended Daily Allowance (RDA) of 2 mg manganese.
<p>Bekendtgørelse om næringsdeklaration m.v. af færdigpakkeede fødevarer BEK nr 910 af 24/09/2009 [Statutory Order on nutritional declarations etc. of repackaged foodstuff] *</p>	DK	As above	As above
<p>COMMISSION REGULATION (EC) No 1170/2009 of 30 November 2009</p>	EU	Manganese sulphate (and a range of other manganese sources)	Included in Annex II.B as a mineral substance that may be used in the manufacture of food supplements.

Legal instrument *1	EU/ National	Substances (as indicated in the instrument)	Requirements as concerns manga- nese(II)sulphate
<p>amending Directive 2002/46/EC of the European Parliament and of Council and Regulation (EC) No 1925/2006 of the European Parliament and of the Council as regards the lists of vitamin and minerals and their forms that can be added to foods, including food supplements</p> <p>Bekendtgørelse om tilsætning af næringsstoffer til fødevarer BEK nr 1104 af 26/11/2012 [Statutory Order on addition of nutrient to food] *</p>	DK	Manganese sulphate (and a range of other manganese sources)	<p>Included in Annex III.B as a mineral substance which may be added to food.</p> <p>Implements above directive and specifies Danish approval system for adding manganese compounds to food. However, the following applications of manganese are exempt (as dedicated legislation applies):</p> <ul style="list-style-type: none"> - Food supplements - Infant formulae and follow-on formulae - Diet replacements - Processed cereal-based foods and baby foods for infants and young children - Food for special medical purposes - Products for weight control
<p>Bekendtgørelse om kosttilskud BEK nr 1440 af 15/12/2009 [Statutory Order on food supplements] *</p>	DK	Manganese(II) sulphate	<p>Implements above directive 2002/46/EC as amended by Commission regulation 1170/2009 in relation to manganese(II) sulphate as used in food supplements. Specifies recommended daily doses of 1-5 mg manganese.</p>
<p>COMMISSION DIRECTIVE 2006/141/EC of 22 December 2006 on infant formulae and follow-on formulae and amending Directive 1999/21/EC</p> <p>Bekendtgørelse om modermælkserstatninger og tilskudsblandinger til spædbørn og småbørn BEK nr 116 af 31/01/2014 [Statutory Order on infant formulae and follow-on formulae for infants and young children] *</p>	<p>EU</p> <p>DK</p>	<p>Manganese sulphate (as one of several mineral substances that can be used to provide manganese)</p> <p>As above</p>	<p>Manganese sulphate is included in Annex III, Part 2 as one (of several) mineral substances that can provide manganese to infant formulae and follow-on formulae.</p> <p>Essential compositions of infant formulae (Annex I) and follow-on formulae (Annex II) should contain between 0.25 and 25 µg Mn per 100 kJ.</p> <p>As above</p>
<p>COMMISSION REGULATION (EC) No 953/2009 of</p>	EU	Manganese sulphate (as well as other man-	Listed under "Category 2. Minerals" in the Annex specifying substances that may be added for specific nutri-

Legal instrument *1	EU/ National	Substances (as indicated in the instrument)	Requirements as concerns manga- nese(II)sulphate
13 October 2009 on substances that may be added for specific nutritional purposes in foods for particular nutritional uses		manganese compounds)	tional purposes in foods for particular nutritional uses. Conditions of use: Dietetic foods.
REGULATION (EU) No 609/2013 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 12 June 2013 on food intended for infants and young children, food for special medical purposes, and total diet replacement for weight control	EU	Manganese sulphate (and a number of other manganese salts)	Included in the Union list set out in the Annex of this regulation. According to the Annex, it may be added to the following categories of food: (a) infant formula and follow-on formula; (b) processed cereal-based food and baby food; (c) food for special medical purposes; (d) total diet replacement for weight control.
COMMISSION DIRECTIVE 2006/125/EC of 5 December 2006 on processed cereal-based foods and baby foods for infants and young children	EU	Manganese sulphate	Manganese salt that may be added as nutritional substance to cereal-based foods for infants and young children (Annex I) and baby foods for infants and young children (Annex II). In both cases the maximum allowed manganese level is 0.6 mg per 100 kcal.
Bekendtgørelse om forarbejdet børnemad til spædbørn og småbørn BEK nr 1100 af 26/11/2012 [Statutory Order on processed children food for infants and young children] *	DK	Manganese sulphate	Implements the above.
COMMISSION REGULATION (EU) No 432/2012 of 16 May 2012 establishing a list of permitted health claims made on foods, other than those referring to the reduction of disease risk and to children's development and health	EU	Manganese	"Manganese" is listed with four entries in the Annex "List of permitted health claims". The following four claims are permitted given the below conditions: - Manganese contributes to normal energy-yielding metabolism - Manganese contributes to the maintenance of normal bones - Manganese contributes to the normal formation of connective tissue - Manganese contributes to the protection of cells from oxidative stress Condition: "The claim may be used only for food which is at least a source of manganese as referred to in the claim SOURCE OF [NAME OF VITAMIN/S] AND/OR [NAME OF MINERAL/S] as listed in the Annex to Regulation (EC) No 1924/2006."
Feed and Veterinary applications			

Legal instrument *1	EU/ National	Substances (as indicated in the instrument)	Requirements as concerns manga- nese(II)sulphate
COMMISSION REGULATION (EU) No 37/2010 of 22 December 2009 on pharmacologically active substances and their classification regarding maximum residue limits in foodstuffs of animal origin	EU	Manganese sulphate (and other manganese compounds)	Included in Table 1 of the ANNEX as allowed pharmacologically active substance for oral use.
COMMISSION REGULATION (EC) No 1334/2003 of 25 July 2003 amending the conditions for authorisation of a number of additives in feedstuffs belonging to the group of trace elements	EU	Various sources of manganese, including manganous sulphate, tetrahydrate and manganous sulphate, monohydrate As above	Authorised as additive in feed in the following concentrations: - Fish: 100 mg Mn/kg - Other species: 150 mg Mn/kg
COMMISSION REGULATION (EC) No 889/2008 of 5 September 2008 laying down detailed rules for the implementation of Council Regulation (EC) No 834/2007 on organic production and labelling of organic products with regard to organic production, labelling and control COMMISSION IMPLEMENTING REGULATION (EU) No 505/2012 of 14 June 2012 amending and correcting Regulation (EC) No 889/2008 laying down detailed rules for the implementation of Council Regulation (EC) No	EU	Manganous (II) sulphate, mono- and/or tetrahydrate (as one of several Mn sources) Manganous sulphate, monohydrate	Included in Annex VI listing feed additives and certain substances that can be used in animal nutrition in organic production. However, regarding the tetrahydrate, see below. Implementing rules for the above and the tetrahydrate is no longer listed in Annex VI.

Legal instrument *1	EU/ National	Substances (as indicated in the instrument)	Requirements as concerns manganese(II)sulphate
<p>834/2007 on organic production and labelling of organic products with regard to organic production, labelling and control</p> <p>NB! Latest amendment of Regulation 889/2008 (COMMISSION IMPLEMENTING REGULATION (EU) No 836/2014 of 31 July 2014) does not affect manganese compounds.</p>			
Active substances (biocidal products)			
<p>COMMISSION REGULATION (EC) No 1451/2007 of 4 December 2007 on the second phase of the 10-year work programme referred to in Article 16(2) of Directive 98/8/EC of the European Parliament and of the Council concerning the placing of biocidal products on the market</p>	EU	Manganese sulphate and manganese sulphate tetrahydrate	<p>Identified as existing active substance for use in biocidal products (included in Annex I of this regulation).</p> <p>(However, as also confirmed by the REACH Manganese Consortium (Harlow, 2014), manganese(II) sulphate is currently not supported as an active substance.)</p>
Legislation addressing emissions			
<p>DIRECTIVE 2010/75/EU OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 24 November 2010 on industrial emissions (integrated pollution prevention and control)</p>	EU	Manganese and its compounds, expressed as manganese (Mn)	Annex VI addressing provisions relating to waste incineration plants and waste co-incineration plants specifies a "total" average emission limit at 0.5 mg/Nm ³ over a sampling period of 30 minutes and a maximum of 8 hours. "Total" refers to the accumulated amount for Mn as well as 11 other heavy metals.
<p>Bekendtgørelse om anlæg, der forbrænder affald BEK nr 1451 af 20/12/2012 [Statutory Order on waste incineration facilities] *</p>	DK	As above	As above
<p>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</p>	DK	Manganese (where manganese(II) sulphate, e.g. from fertilisers, is assumed to be a main source)	<p>Defines national Danish environmental quality criteria for water:</p> <ul style="list-style-type: none"> - freshwater general: 150 µg Mn/l - marine water general: 150 µg Mn/l - fresh water short term: 420 µg Mn/l - marine water short term: 420 µg Mn/l

Legal instrument *1	EU/ National	Substances (as indicated in the instrument)	Requirements as concerns manganese(II)sulphate
bodies and provisions for emission of polluting substances to stream, lakes and the sea] *			
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	Manganese (where manganese(II) sulphate, e.g. from fertilisers, is assumed to be a main source)	Defines the following quality criteria for drinking water: - upon leaving the water work: 0.02 mg Mn/l - upon entry to a property: 0.05 mg Mn/l - at the consumer tap: 0.05 mg Mn/l
Bekendtgørelse om deponeringsanlæg BEK nr 650 af 29/06/2001 [Statutory order on facilities for landfilling] *	DK	Manganese which can be washed out	Specifies a maximum level of 0.15 mg manganese/L (which can be washed out in a batch washout test) for wastes which can be included in a positive list for landfilling inert waste.
Bekendtgørelse om kvalitetskrav til miljømålinger BEK nr 231 af 05/03/2014 [Statutory order on demands to quality of environmental measurements] *	DK	Manganese (where manganese(II) sulphate, e.g. from fertilisers, is assumed to be a main source)	Specifies quality demands for measurements of manganese in a range of environmental media.
Supplement til B-værdivejledningen 2008 VEJ nr 10702 af 19/11/2008 [Supplement to the B-value guideline of 2008] *	DK	Manganese compounds in inorganic dust	Establishes a "B-value" for manganese compounds in inorganic dust: (measured as Mn) of 0.001 mg/m ³
Forskrift om fælles arbejdsmetoder for jordbundsanalyser FSK nr 13377 af 25/08/1988 [Directions for common working procedures for soil analyses] *	DK	Manganese (where manganese(II) sulphate, e.g. from fertilisers, is assumed to be a main source)	Specifies common working procedures for soil analyses, including determination of manganese in soils.
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 manganese(II) sulphate	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	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

Legal instrument *1	EU/ National	Substances (as indicated in the instrument)	Requirements as concerns manga- nese(II)sulphate
with Substances and Materials (chemical agents)]*			processes with less hazardous substances, materials and work processes, and - develop workplace guidelines for the use of hazardous substances and materials.
COMMISSION RECOM- MENDATION of 19 Septem- ber 2003 concerning the European schedule of occu- pational diseases	EU	Manganese or com- pounds thereof	Included in Annex I for which it is recommended that Member States introduce provisions concerning scientifi- cally recognised occupational diseases as soon as possi- ble, including the right of worker compensation, measures to reduce occupational illness and statistics.
Bekendtgørelse om forteg- nelse over erhvervsbyg- domme anmeldt fra 1. janu- ar 2005 BEK nr 1226 af 24/10/2013 [Statutory Order with a cata- logue of occupational diseases reported from 1. January 2005] *	DK	Manganese and cer- tain manganese com- pounds	"Manganism" (manganese-induced Parkinson-like dis- ease) is included in "Group I: Illness after chemical substances" as an occupational disease.
Bekendtgørelse om grænse- værdier for stoffer og mate- rialer BEK nr 507 af 17/05/2011 [Statutory Order on occupation- al exposure limits] *	DK	Manganese	Establishes the following OELs: - Manganese, powder, dust and inorganic compounds: 0.2 mg/m ³ (measured as Mn) - Respirable manganese: 0.1 mg/m ³ (measured as Mn)
Bekendtgørelse om fastsæt- telse af kodenumre BEK nr 301 af 13/05/1993 [Statutory Order on establishing code numbers] *	DK	Manganese com- pounds	Defines the following in relation to code numbers for manganese compounds: - MAL factor: 0 - Number after the dash ("-"): -2 (when mixture contains >= 1% by weight) These rules apply for products mentioned in Annex 1 of Statutory Order No. 302.

* 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 manganese(II) sulphate (cf. Annex 5 to BEK No 486 of 25/05/2012).

Classification and labelling

Manganese(II) sulphate is subject to harmonised classification as depicted in Table 4. However, as is also further elaborated in the next section and in Chapter 6, the REACH Manganese Consortium supports an additional classification for Eye damage 1, H318.

TABLE 4
HARMONISED CLASSIFICATION OF MANGANESE(II) SULPHATE 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) *
025-003-00-4	manganese sulphate	7785-87-7	STOT RE 2 Aquatic Chronic 2	H373 H411

* Hazard statement codes: H373: May cause damage to organs through prolonged or repeated exposure; H411: Toxic to aquatic life with long lasting effects

Self-classification

The Classification & Labelling (C&L) Inventory database on the website of the European Chemicals Agency (ECHA) contains classification and labelling information on notified and registered substances received from manufacturers and importers. The database also includes the harmonised classification. Companies have provided this information in their CLP notifications or registration dossiers. ECHA maintains the Inventory, but does not verify the accuracy of the information.

Please note that in some instances, the substances are not classified because data are lacking. The absence of a classification for a specific endpoint does not necessarily mean that the substances are not hazardous towards this endpoint. Reference is made to the C&L inventory for more information on the self-classification of substances.

The C&L database has been searched for the various hydrated forms of manganese(II) sulphate as listed in Table 1. Self-classifications for the hydrated forms are listed in Table 5. The table shows that self-classifications are available for the mono- and tetrahydrated forms and that the self-classifications by and large follow the harmonised classification for the anhydrous form.

However, it is worth noting that the REACH Manganese Consortium representing the manganese industry supports the classification for Eye damage 1, H 318 (ECHA, 2014; Harlow, 2014), although this classification is only supported by 21 out of 931 notifiers! Furthermore, as indicated in Chapter 1, the Consortium considers all forms of manganese(II) sulphate to be covered by the same registration and, thus, that the same classification applies to the anhydrous as well as all hydrated forms of manganese(II) sulphate.

The significant number of notifications which do not self-classify for eye damage (910 of 931) originate from notifications by importers/distributors of manganese(II) sulphate on its own or as part of mixtures.

Overall, the following can be concluded:

- The REACH Manganese Consortium/the manganese industry supports classification of all forms (anhydrous and all hydrated forms) of manganese(II) sulphate for eye damage Cat.1, H318, in addition to the harmonised classification (Harlow, 2014). This is not entirely clear when searching the ECHA web-site.
- This additional classification is not reflected by the self-classifications by most importers/distributors of manganese(II) sulphate as such, or as part of mixtures.

TABLE 5

CLASSIFICATION INFORMATION ON HYDRATED FORMS OF MANGANESE(II) SULPHATE NOTIFIED AND REGISTERED BY MANUFACTURERS AND IMPORTERS (C&L LIST AS OF APRIL 2014)

CAS No	Substance name	Hazard Class and Category Code(s)	Hazard Statement Codes	Number of notifiers
10034-96-5	Manganese (II) sulphate monohydrate	Total		931
		STOT RE 2	H373	903
		Aquatic Chronic 2	H411	903
		Acute tox. 4	H302	5
		Acute tox. 4	H332	5
		Eye damage 1	H318	21
		Aquatic chronic 4	H413	1
		"Not classified"	-	27
10101-68-5	Manganese (II) sulphate tetrahydrate	Total		83
		STOT RE 2	H373	83
		Aquatic Chronic 2	H411	83

* Hazard statement codes: H373: May cause damage to organs through prolonged or repeated exposure; H411: Toxic to aquatic life with long lasting effects; H302: Harmful if swallowed; H332: Harmful if inhaled; H318: Causes serious eye damage; H413: May cause long lasting harmful effects to aquatic life.

2.1.2 REACH

Community rolling action plan (CORAP)

Manganese(II) sulphate is not listed in CORAP.

Registry of Intentions

There are no notifications of intentions for manganese(II) sulphate in the Registry of Intentions.

Candidate list

Manganese(II) sulphate is not listed on the Candidate List.

Annex XIV recommendations

Manganese(II) sulphate is not listed in Annex XIV (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

Manganese(II) sulphate does not appear to be addressed by international agreements. It can be mentioned that the Danish transposition of The United Nations Convention on the Law of the Sea; UNCLOS (Bekendtgørelse af De Forenede Nationers Havretskonvention af 10. december 1982 til-lige med den dertil knyttede aftale af 28. juli 1994 om anvendelse af konventionens kapitel XI) lists a number of specific provisions related to mining and transport and production of manga-nese/manganese ores.

2.3 Eco-labels

No eco-label criteria addressing manganese(II) sulphate have been identified.

The Nordic Swan background document for "Printing companies, printed matter, envelopes and other converted paper products" refers to the Chabanne et al. (2004) discussion on manganese compounds possibly being less toxic alternatives to cobalt as driers in printing colours. Manganese(II) sulphate is not mentioned among various manganese compounds addressed in this report; however, as will be shown in Chapter 3, the REACH Manganese Consortium notes that this manganese(II) sulphate application is relevant.

2.4 Summary and conclusions

Manganese(II) sulphate is regulated as a micronutrient in relation to fertilisers, feed (including as an animal nutrient in organic production) and within the food area. The latter includes use of manganese(II) sulphate as a general mineral, in foods for specific medical purposes, in infant formulae and other specific infant foods. Manganese(II) sulphate has also originally been notified as an active substance for use in biocidal products. However, it is no longer supported as an active substance.

A range of emission/concentration control legislation for manganese is in place including provisions for air and water. These are relevant in this context as manganese(II) sulphate may cause the emissions of manganese. Similarly, manganese and manganese compounds are addressed by a number of occupational health provisions, including a Danish Occupational Exposure Limit, a Danish Code number and the recognition of "Manganism" (manganese induced Parkinson-like disease) as an occupational disease.

Manganese(II) sulphate is subject to harmonised EU classification for possible damage to organs through prolonged or repeated exposure and as toxic to aquatic life with long lasting effects. The REACH Manganese Consortium/the manganese industry further supports classification of all forms of manganese(II) sulphate for eye damage. This additional classification has not (yet) been adopted by the majority of importers/distributors of manganese(II) sulphate on its own or as part of mixtures. Furthermore, the fact that the manganese industry considers all forms of manganese(II) sulphate as having similar hazards/classification and has self-classified all these forms for eye damage is not easy to interpret from the information and searches available on the ECHA website.

Manganese(II) sulphate is currently not subject to other REACH procedures.

Manganese(II) sulphate is not subject to international conventions or specifically restricted in eco-label criteria. However, manganese/manganese ores are subject to some provisions of the United Nations Convention on the Law of the Sea (UNCLOS). Manganese compounds are discussed as a possible less-toxic alternative to cobalt as driers in printing colours in the Nordic Swan background document for "Printing companies, printed matter, envelopes and other converted paper products".

3. Manufacture and uses

This chapter will identify volumes and uses/applications of manganese(II) sulphate as manufactured, imported or exported with a focus on the situation in the EU and in Denmark.

3.1 Manufacturing

This section will outline manufacturing processes and manufacturing sites in the EU.

3.1.1 Manufacturing processes

The REACH Manganese Consortium states that the two main manufacturing processes of manganese(II) sulphate are (Harlow, 2014):

- Mn carbonate ores (Rhodocrosite) + sulphuric acid → impure MnSO₄ + CO₂ + residual gangue (Mn ore tailings)
- Mn oxides ores (Hausmanite or Pyrolusite) → thermal reduction to Mn(II) monoxide → + sulphuric acid → impure MnSO₄ + residual gangue (Mn ore tailings).

The above is followed by a purification step to further reduce the levels of various undesirable metals (Fe, Al, Ni, Co etc.) to obtain the manganese(II) sulphate end product. This is achieved by pH adjustment (Harlow, 2014).

As already noted in Chapter 1, manganese(II) sulphate also appears as a non-isolated intermediate within the process of manufacturing Electrolytic Manganese Dioxide (EMD) for the production of alkaline batteries. The steps in the processing may involve variations on the following (Harlow, 2014):

- Natural ore → reduction to MnO → + sulphuric acid / heat → MnSO₄ (intermediate) → purification to remove heavy metals → electrolysis → pure MnO₂

3.1.2 Manufacturing sites

According to the REACH Manganese Consortium there are two manufacturing sites of manganese(II) sulphate in the EU, one in Bulgaria and one in Belgium (Harlow, 2014).

The Consortium further estimates that there are at least two EU manufacturing sites of manganese dioxide in which manganese(II)sulphate appears as a non-isolated intermediate (Harlow, 2014).

3.2 Volumes - Manufacturing, import, export and overall consumption

This section addresses manufacturing and import/export volumes globally, in the EU and in Denmark.

3.2.1 Globally and non-EU

The REACH Manganese Consortium estimates that around 250,000 tonnes manganese(II) sulphate is manufactured globally per year for the main feed / fertiliser / fungicides applications (Harlow, 2014). The applications are addressed below.

This estimate excludes the tonnage in which manganese(II) sulphate appears as a non-isolated intermediate in the manufacturing of EMD (Electrolytic Manganese Dioxide) used for the production of alkaline batteries (estimated at > 400,000 tonnes/y) (Harlow, 2014).

3.2.2 EU level

EUROSTAT

No data on production volumes of manganese(II) sulphate could be retrieved from the Eurostat PRODCOM database (Eurostat, 2014) because no specific code has been assigned for manganese(II) sulphate. Manganese(II) sulphate is included in the group “Sulphates (excluding those of aluminium and barium)”, 20134157, which nonetheless covers a large range of other substances and therefore would not provide any precise estimate.

Similarly, there is no customs code assigned specifically to manganese(II) sulphate (Commission Regulation (EU) No 1001/2013), but only for the group of “other sulphate salts”. It has therefore not been possible to identify import and export data for manganese(II) sulphate either for Denmark or for the EU from this database.

REACH

As can be seen from Table 1, manganese(II) sulphate has been registered under REACH in a volume of 10,000 – 100,000 tonnes/year. This amount covers manufacturing volumes in the EU, as well as manganese(II) sulphate import as such, and as part of mixtures. It should be noted that this volume does not address manganese(II) sulphate for use in food and feed, which are exempt from REACH registration as such uses are addressed by other EU legislation.

As is shown later in this chapter, the REACH registration volume is estimated to cover about 85% of the manganese(II) sulphate volume used in the EU.

As also noted in Chapter 1, manganese(II) sulphate appearing as non-isolated intermediate in EMD manufacturing is not included within these figures, as non-isolated intermediates are outside the scope of REACH registration. In line with the justification provided in Chapter 1, this intermediate use is not considered any further in this project.

3.2.3 Denmark

Statistics Denmark

As there is no customs code specific for manganese(II) sulphate (see Section 3.2.2), no relevant data can be extracted from Statistics Denmark.

To the knowledge of the authors of this report, no industrial scale manufacturing of manganese(II) sulphate takes place in Denmark.

Danish Product Registry

The Danish Product Register includes substances and mixtures used occupationally and which contain at least one substance classified as dangerous in a concentration of at least 0.1% (or 1%, depending on the classification of the substance). Manganese(II) sulphate 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 also for consumer applications. Given the uses of manganese(II) sulphate, however, it is assessed that most are occupational uses.

Data on manganese(II) sulphate registered in the Danish Product Register were retrieved in April 2014, providing average data for 2012/2013, while data from the previous years were retrieved from

the SPIN database², which holds non-confidential information from the product registers of the Nordic countries.

THE TOTAL USE VOLUMES OF MANGANESE(II) SULPHATE FOR THE PERIOD 2007-2011 AS EXTRACTED FROM THE SPIN DATABASE ARE PROVIDED IN

Table 6.

TABLE 6
TOTAL USE OF MANGANESE(II)SULPHATE IN DENMARK ACCORDING TO THE NORDIC SPIN DATABASE

Year	# of preparations	Total Danish use (tonnes/year)
2011	14	787.4
2010	15	866.6
2009	15	866.6
2008	12	1039.2
2007	12	932.2

The most recent (year 2012/2013) data from the Danish Product register provides the following information for manganese(II) sulphate:

- Total amount: 791 tonnes per year - as there is no manufacturing of manganese(II) sulphate in Denmark, this must account for the imported amount;
- Exported amount: 0 tonnes/year.

Therefore, the total imported manganese(II) sulphate amount is consumed in Denmark.

The SPIN database has no entries for the tetrahydrated and pentahydrated manganese(II) sulphate forms. There is an entry for the monohydrated form but no data are reported for the Danish market. However, the 2012/2013 extracts from the Danish Product Registry shows an amount of monohydrated manganese(II) sulphate below 1 tonne/year. Overall, it must be assumed that the volume of hydrated manganese(II) sulphate forms are included in the data registered under the CAS number of the anhydrous manganese(II) sulphate form.

As will be shown below, the main use of manganese(II) sulphate is as fertiliser. This use has to be registered with a (confidential) Danish fertiliser register administered by the Danish AgriFish Agency. During the project, consultation with stakeholders has revealed that Danish volumes are considerably higher than what can be retrieved from the Danish Product Registry data. Based on confidential contact with the main Danish importers of manganese(II) sulphate, it appears that the correct volume would be 2-3 times higher, i.e. probably in the range of 1500 – 2200 tonne/year. These importers have been invited to register their imported amounts to the Danish product register as well, which in turn should provide more accurate figures in the years to come.

Feed is exempt from registration with the Danish Product Registry. As shown below, it can roughly be assumed that of the overall EU volume of manganese(II) sulphate, approx. 75% is used as fertiliser and about 15% in feed applications. Dialogue with Danish distributors of manganese(II) sulphate indicates that about the same split for these two applications apply to Danish conditions. Thus, an estimated volume of about 300-450 tonnes manganese(II) sulphate appears to be imported to Denmark for feed applications per year. However, this is a figure associated with substantial uncertainty.

² <http://195.215.202.233/DotNetNuke/default.aspx>

Further, manganese(II) sulphate amounts used as food nutrients/supplements are not covered by the Danish Product Registry. Dialogue with the Danish Veterinary and Food Administration reveals that the main amount of manganese used as food nutrients/supplements is as an ingredient in vitamin tablets for humans. This may be delivered as manganese(II) sulphate or a range of other manganese salts as appears from Chapter 2. The Danish Veterinary and Food Administration agrees that the following assumptions can be used to derive a worst case estimate (Langkilde, 2014):

- 2.5 million Danes eat one vitamin tablet per day, 365 days per year
- The tablets on average contain 2 mg Mn (Recommended Daily Dose).

This gives about 2 tonnes manganese per year (if all manganese was supplied as the sulphate, this would correspond to about 6 tonnes manganese(II) sulphate). This volume is much lower than manganese(II) sulphate in fertilisers and feed.

Overall, the following can be concluded:

- There seems to be a current total Danish use of manganese(II) sulphate of about 1800-2600/2700 tonnes manganese(II) sulphate per year. This estimate is, however, associated with uncertainty given the cited incomplete Product Registry data.
- This volume is imported as there is no Danish export of manganese(II) sulphate, either as such or as part of mixtures/preparations.

3.3 Uses and applications of manganese(II) sulphate

As already noted in Chapter 1, the main application of manganese(II) sulphate is as fertiliser. It is also used and approved for use (see regulatory overview in Chapter 2) as a mineral/micronutrient in food and feed. This section attempts to further specify and quantify these applications as well as more technical applications.

3.3.1 EU level

The ECHA dissemination tool provides a long list of registered uses, which is not straightforward to interpret. Among the identified uses are listed (ECHA, 2014):

- Leather tanning
- Printing
- Surface treatment
- Fertilisers / Fertilizer (liquid) /Fertilizer (granulate)
- Manufacture of Leather
- Construction Products
- Base Metals and Alloys
- Water Treatment (including as a water softener)
- Washing and Cleaning Products (but not for consumer use)
- Chemical Processing Aids
- Cosmetics Personal Care (but not as an ingredient in cosmetics)
- Chemical Processing Aids
- Use as laboratory reagent
- Manufacture of fungicides

And specifically for consumer use:

- Use of granulate fertilizers and professional and private use of fertilizer granulates containing MnSO₄
- Coatings and paints, thinners, paint removers
- Non-metal-surface treatment products.

As already noted, this list does not include food and feed applications which are exempt from REACH registration.

The above registered uses result from a range of registrations of manganese(II)sulphate and not only the lead registrant (Harlow, 2014).

In order to learn a bit more about which of the above long list of uses are significant and/or relevant, the REACH Manganese Consortium was approached. The Consortium has provided an extract of the Chemical Safety Report (CSR) for the joint registration. This CSR extract indicates that the following uses are supported in their registration:

- Leather tanning
- Printing (ink, toners, textile dyes and impregnation)
- Surface treatment (coatings and paints and non-metal-surface treatments)
- Laboratory reagent
- Fertilizer

Exact figures on volumes are confidential among REACH registrants. Still the REACH Manganese Consortium estimates the following approximate division among main uses as a rule of thumb based on generally accepted knowledge within the industry (Harlow, 2014):

- 75% used in fertilisers
- 15% used in feed (not regulated by REACH)
- 5% used in formulating fungicides for pesticide use
- 5% used for other applications of which the main amounts are assumed to be used as:
 - Drying agents/siccative in inks and paints for print, surface coating and colouring of leather;
 - For water purification (e.g. in the leather industry), and
 - Laboratory agents.

Of the other uses/applications, the use as a drying agent/siccative is thought to be the major application.

Furthermore, it is known that manganese(II) sulphate, among other manganese salts, is used as food nutrient/supplement. No data on amounts used as food additive/supplement for the EU situation have been identified, but as shown for the Danish situation in Section 3.2.3, this amount must be assumed to be low (a maximum of a few percent) compared to other applications.

Manganese(II) sulphate is referred to in a number of the test guidelines addressed in Council Regulation (EC) No 440/2008 of 30 May 2008, laying down test methods pursuant to Regulation (EC) No 1907/2006 of the European Parliament and of the Council on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH). This supports its use a laboratory agent, but amounts used for such applications are assumed to be small.

According to the REACH Manganese Consortium, manganese(II) sulphate is only used by professionals, never by consumers. Manganese(II) sulphate will not be present in the final products as such, only as manganese ion (Mn^{++}) (Harlow, 2014).

Based on the above, it appears that consumers might mainly come into contact with the manganese ion (Mn^{++} originating from manganese(II) sulphate) via paints and inks, painted/coloured articles such as leather and textile products, and fertilisers. To the knowledge of the REACH Manganese Consortium, consumer use of fertilizers to which manganese(II) sulphate is added would be liquid suspensions with manganese in the ppm range, e.g. in fertiliser products for minor applications such as for flower soils (Harlow, 2014). This usage, however, seem to conflict with some registrants having registered consumer use of granulate fertilisers.

Based on the available information, the main consumer exposures seem to be:

- Oral exposure: via intake as food nutrient/supplements, an intake regulated by EFSA (European Food Safety Authority) assessments and positive lists;
- Dermal exposure: Mainly to dissolved Mn⁺⁺ in e.g. paints and fertilisers, and
- Inhalation: Possibly in some handling of fertiliser granulates, although it should be noted that this use is not supported as a consumer use by the REACH Manganese Consortium (Harlow, 2014).

As will be further elaborated in Chapter 6, the manganese exposure of main concern is likely by inhalation, related to use of fertilisers and feed in powder form, an application mainly carried out by professionals (farmers).

3.3.2 Denmark

Danish Product Registry

FOR CONFIDENTIALITY REASONS, SUBDIVISION OF THE REGISTERED USES OF DATA FROM THE DANISH PRODUCT REGISTRY CAN ONLY BE REVEALED IF THERE ARE MORE THAN THREE REGISTRANTS FOR THE SAME REGISTERED USE.

Table 6 indicated that the number of registered preparations (mixtures) fluctuates around 12 and 15. For reasons of confidentiality, only the detailed registered amounts of manganese(II) sulphate used for fertilisers can be revealed; see Table 7.

TABLE 7
AMOUNT OF MANGANESE(II) SULPHATE REGISTERED IN THE DANISH PRODUCT REGISTRY FOR USE AS FERTILISER AS COMPARED TO TOTAL AMOUNTS

Year	Amount used for fertilisers	Total Danish amount (tonnes/year)
2012/2013*	9.8	791.2
2011**	6.2	787.4
2010**	3	866.6
2009**	3.8	866.6
2008**	701.4	1039.2
2007**	722.1	932.2

* Data taken by direct extract from the Danish Product Registry delivered to the project

** Data taken from the SPIN database

The data indicate a dramatic decrease in amount registered for fertiliser use from 70-80% in 2007 and 2008 to about 1% in recent years. However, dialogue with key importers reveals that this change represents a change in reporting practice rather than a shift in application.

Furthermore, as noted in Section 3.2.3, the Danish Product Registry data are not complete and should probably be multiplied by a factor 2 to 3.

Confidential dialogue with a number of importers/distributors indicates that the division of volumes between fertilisers and feed additives is somewhat similar to that of the EU (see Section 3.2.3 and 3.3.1). However, according to these importers, other uses (estimated at around 10% in the EU) are much lower or non-existent in Denmark. This seems to be confirmed by a broad Internet search on Danish Safety Data Sheets performed for this study, which largely refer to fertiliser and other micronutrient applications. Some water purification (odour reducing) mixtures containing manganese(II) sulphate have been identified with a manganese(II) sulphate contents of <0.25%.

It should be noted that the Danish Product Registry data would not include manganese(II)sulphate imported as part of food products or for feed. It is assumed that the food amount would be negligible as compared to feed and fertiliser applications.

In general, the same exposure considerations as given for the EU level (see Section 3.3.1) would be relevant for Danish consumers.

Fertiliser use

In relation to use of manganese(II) sulphate as fertiliser, it should be noted that soil already contains a high amount of manganese, which is, however, not bioavailable. According to a number of importers/distributors, several attempts have been made to change the redox properties of the soil to effect release of the oxidised manganese. However, this has not been successful. The manganese⁺⁺ ion (as manganese(II) sulphate) is therefore applied in smaller amounts 3-5 times a year to secure availability of manganese. Before applications, the manganese(II) sulphate is dissolved in water and spread as aerosols, sometimes in a solution also containing plant protection products.

The following observations have largely been elaborated via interview with The Danish Knowledge Centre for Agriculture (Knudsen, 2014):

- Manganese in the earth crust is abundant; however, a large fraction is bound as manganese oxide that is not bioavailable. This is particularly the case for sandy soils.
- Thus, the manganese ion (Mn⁺⁺) - mainly as dissolved manganese(II) sulphate - is supplied to such sandy soils and to other soils, in particular soils on which winter crops (wheat and barley) are grown.
- Other manganese compounds such as manganese nitrate, - carbonate and - chelates are also used as manganese⁺⁺ sources, but in much lower quantities.
- Manganese(II) sulphate is typically applied 2-3 times/year, but sometimes up to 5-6 times/year.
- An average of 2 kg is applied per hectare – typically by dissolving this amount of manganese(II) sulphate powder in 200-300 litres of water.
- The solution is sprayed onto the soils - typically from a tank on the back of a tractor.
- Manganese(II) sulphate is typically applied together with plant protection products to reduce the need for driving and fuel. However, sometimes the substance is applied alone. Manganese(II) sulphate is typically not applied along with other fertilisers.
- The farmer handles and dissolves the powder manganese(II) sulphate prior to application.
- To the knowledge of The Danish Knowledge Centre for Agriculture, personal protective equipment to reduce inhalation is typically not used during dissolution or the subsequent spray/aerosol application.
- The Danish Knowledge Centre for Agriculture cannot provide information about assessments addressing exposure levels during these operations and assumes they would have known if such data exist for Danish conditions.

A Danish manganese(II) sulphate supplier is of the impression that personal protective equipment is increasingly in use when preparing the fertiliser solution.

Feed applications

As outlined in Section 3.2.3, an estimated volume of 300-450 tonnes manganese(II) sulphate per year is applied in Denmark.

One consulted supplier notes that normally manganese oxide is used to supply manganese in feed. However, as manganese oxide also contains iron as a constituent/impurity, it cannot be used for animals which cannot tolerate that iron. In these cases, manganese(II) sulphate can be used instead. One supplier indicates that manganese(II) sulphate is mainly used for fish-farming. However,

er, as shown below, it appears that applications for fish feed amount to less than 2 tonnes manganese(II) sulphate/year.

The following information regarding use of manganese(II) sulphate in feed has been identified based on dialogue with feed experts of The Danish Knowledge Centre for Agriculture and Danish Aquaculture branch organisation:

- For cattle, 95% of the supplied manganese is as manganese oxide. It is recommended that a cow receives supplements of 200-250 g manganese per year. This is supplied as part of mineral preparations with about 4 gram manganese/kg (Aaes, 2014).
- For pigs about 99% of the supplied manganese is provided as manganese oxide or chelated manganese compounds. The norm is to use 40 mg per food unit (1 to 1.12 food units per kg). Typically 2-3 grams manganese oxide is applied per kg mineral preparation. The mineral preparation is typically mixed with the ordinary animal feed. Mixing often takes place in automatic mixing units, but some farmers do the mixing themselves, whereby they handle and open sacks manually. No knowledge about possible use of personal protective equipment during this handling of powdery products is available (Tybirk, 2014).
- The branch organisation for Danish fish farms (Danish Aquaculture Organisation) confirms that the manganese source in fish farming feed origins from manganese(II) sulphate. The feed contains between 8 – 12 mg manganese per kg. In 2012 the total amount of feed for fish farming was 42,348 tonnes (Henriksen, 2014). This amounts to about 0.35 – 0.5 tonne manganese per year (approx. 1-1.5 tonnes manganese(II) sulphate per year. Henriksen (2014) informed the authors that fish feed is bought as a final formulation from fish feed producing companies. This fish feed (containing 8-12 mg manganese/kg) is in powder form. The fish farmer does normally not use personal protective equipment when handling fish feed.

To the knowledge of the REACH Manganese Consortium, manganese(II) sulphate is not normally used in chicken feed; rather, oxides are applied (Harlow, 2014).

Overall, given the data identified in this project, it has not been possible to assess in detail for which feed application the estimated 300-450 tonne manganese(II) sulphate used in Denmark is applied.

In relation to feed, it should be noted that in final feed, only up to 150 ppm manganese is allowed (see Chapter 2). Thus, the main human exposure is related to mixing the feed, not applying it. Often this feed mixing takes place by feed formulators and not by the farmers.

3.4 Historical trends in use

Given the inaccuracy and uncertainties in volumes on the Danish and EU markets, it is difficult to indicate any trends in overall and specific uses, although these appear to be relatively constant.

Specifically for food supplements/additives, the Danish Veterinary and Food Administration notes that work is ongoing to reduce the recommended daily manganese intake from 2 to 0.5 mg per day (Langkilde, 2014). This step will likely reduce the consumer/general population exposure. However, as this use is estimated to account for only a few percent of the total manganese(II) sulphate volume, such a reduction will not significantly affect the overall volumes related to the occupationally applied volumes for fertilisers and feed, and thereby also not affect the emissions to the environment significantly.

3.5 Summary and conclusions

Manganese occurs naturally in ores.

Manganese(II) sulphate is manufactured from manganese ores. In the EU, it is manufactured in two facilities (Bulgaria and Belgium). Further, manganese(II) sulphate appears as a non-isolated inter-

mediate in the manufacturing process of Electrolytic Manganese Dioxide (EMD) in at least two EU sites, but not in Denmark. This intermediate use is not addressed in detail in this survey.

Overall amounts of manganese(II) sulphate on the market are difficult to quantify, but the following has been estimated based on the information identified in this project:

- Globally: 250,000 tonnes/year
- EU: 10,000-100,000 tonnes/year
- Denmark: 1,800 – 2,700 tonnes/year.

Based on dialogue with industry, the following main EU uses/applications have been identified:

- 75% used in fertilisers
- 15% used in feed (not regulated by REACH)
- 5% used in formulating fungicides for pesticide use
- 5% used for other applications of which the main amounts are assumed to be used as:
 - Drying agents/siccative in inks and paints for print, surface coating and colouring of leather
 - For water purification (e.g. in the leather industry)
 - Laboratory agents.

Volume-wise the use/application as siccative/drying agent in inks, paint, and leather colouring products is assessed to be the main application by far among the 5% other uses.

In addition, manganese(II) sulphate is (allowed to be) used as a mineral and nutrient in a number of food applications. No data on the volume of use in minerals/nutrients has been identified, but this use probably accounts for a few percent of the total volume.

For the Danish situation, it appears that most of the imported manganese(II) sulphate is used as fertilisers and feed, i.e. more than 90% as estimated for the EU situation.

The most significant exposures (via inhalation) are likely to happen in occupational settings, where farmers handle manganese(II) sulphate powders/granulates in relation to fertiliser handling and in relation to feed mixing applications (this mixing is, however, not always done by the farmer himself). The manganese(II) sulphate level is rather low (<150 ppm) in the final feed. Such handling might also lead to eye exposure.

Based on the available information, the main consumer exposures appear to be:

- Oral exposure: via intake as food nutrient/supplements, an intake regulated by EFSA (European Food Safety Authority) assessments and positive lists
- Dermal exposure: Mainly to dissolved Mn⁺⁺ in e.g. paints and fertilisers
- Inhalation/eye: Possibly in some handling of fertiliser granulates, although it should be noted that this use is not supported by the REACH Manganese Consortium.

Based on available data, it has not been possible to identify trends in use, although the main applications areas (as fertilisers and in feed) might be considered relatively stable.

Data gaps

Overall volumes manufactured, imported and consumed in the EU and in Denmark are uncertain.

A long list of uses is registered in REACH, some of which, however, appear to be non-existent or rare in reality. Still, some of these uses may lead to consumer exposure to the manganese ion (Mn⁺⁺) or perhaps even manganese(II) sulphate (if e.g. fertiliser granulate is handled by consumers). Whether such uses would lead to any significant exposure is, however, questionable and should be seen in the light of manganese being an essential element.

4. Waste management

This chapter will address amounts and handling of manganese(II) sulphate containing waste.

Denmark

As mentioned in Chapter 3, manganese(II) sulphate is not manufactured in Denmark and the majority of the manganese(II) sulphate consumption is for use in fertilisers and feed. Little or no manganese(II) sulphate is present (as such) in consumer products.

The key waste issue with relevance for the actual compound is therefore the disposal of bags and containers in which the substance was delivered or stored. No data were found in an Internet search on manganese(II) sulphate losses by this route. As an example of other powder/granulate handling, VECAP (2010) reports results of a campaign for reducing releases of certain brominated flame retardants from used packaging. Before campaigning, the substance losses with emptied packaging were in the range of 0.01-0.04 percent of the consumption (~100-400 g/tonne).

The actual physical form of the substance in the packaging likely influences the amounts of the substance left in the packaging when empty. It may likely affect the losses quite substantially. Therefore, these figures can only be used as a rough indication of how much manganese(II) sulphate may be lost with packaging disposal from agricultural fertilisers and feeds. However, for lack of better data, using these figures indicates losses of manganese(II) sulphate with waste packaging of less than 1 tonne/year in Denmark, considering an estimated consumption of about 2,000 tonnes/year, as described in section 3.2.3. Even if the relative loss of manganese(II) sulphate is 10 times higher, this would still be a modest amount.

Additional losses with fertiliser remnants not spent (for example in opened but not emptied bags) cannot be ruled out, but farmers are cost-conscious and major losses by this route seem unlikely.

It is anticipated that the majority of this manganese(II) sulphate in packaging will be lost to waste incineration with general waste disposal. Given the generally abundant presence of manganese/manganese compounds in nature and materials, there are many other sources of manganese to waste incineration.

Losses of manganese, but likely not as its sulphate, may take place from solid residues from waste incineration. Flue gas cleaning residues are generally disposed safely in special deposits (e.g. in Norway), whereas the slag is mainly used for construction work.

In general, when considering manganese(II) sulphate waste, it should be considered that e.g. manganese(II) sulphate fertilisers are spread directly into the environment.

EU

For the EU situation, the main applications of manganese(II) sulphate are also for fertilisers and feed applications (about 90%). The other applications cover formulating fungicides for pesticide use (estimated 5%) and other minor applications, in particular as siccativ/drier in paints and inks. These other applications would probably have similar waste handling considerations as the main applications. Given the uncertain EU volumes, it does not appear appropriate to provide estimates,

but seems fair to conclude that waste generated is probably minor compared to other sources (including natural sources) of manganese/the manganese ion.

As outlined in Chapter 3, manufacturing of manganese(II) sulphate takes place in two sites (Bulgaria and Belgium) and it appears as an intermediate in a few other EU sites outside Denmark. This manufacturing might generate some waste, but it is considered outside the scope of this project to further map this type of waste handling.

4.1 Summary and conclusions

When considering manganese(II) sulphate waste and possibly related emissions to the environment, it should be acknowledged that the majority of the applied manganese(II) sulphate is spread directly into the environment as fertiliser.

Denmark

As manganese(II) sulphate is not manufactured in Denmark, losses with waste are deemed mainly to originate from waste packaging in the handling of the substance from fertiliser and feed applications. Based on limited data from other powdered/granulated materials (brominated flame retardants in factory settings), such losses are deemed minimal, likely below 1-2 tonnes/year.

Additional losses with fertiliser remnants not spent cannot be ruled out. It is anticipated that this manganese(II) sulphate would be lost to waste incineration with general waste disposal. There are many other sources of manganese (apart from sulphate) to waste incineration.

EU

Manganese(II) sulphate is manufactured in two EU facilities and appears as an intermediate in a few other facilities. Waste generated by these facilities has not been investigated in this project.

Similar considerations as for the Danish situation apply regarding waste generated from products in which manganese(II) sulphate is used.

Data gaps

Accurate data on manganese(II) sulphate losses with waste are missing, but such data is likely to be of minor relevance.

5. Environmental hazards and exposure

5.1 Environmental fate and behaviour

Manganese is a naturally occurring element that is an essential micro-nutrient to animals and plants and is found in rock, soil, water and biological material (plants as well as animals). It is a component of more than 100 minerals and comprises about 0.1% of the Earth's crust. It can exist in 11 oxidation states ranging from -3 to +7, but the most common ones are +2, +4 and +7 (WHO, 2004).

Manganese(II) sulphate is very water soluble, 520 g Mn/l (WHO, 2004), and in natural waters at pH 4-7 is present as the Mn^{2+} ion, while at a higher pH (>8) it may be oxidised further to oxidation state +4. The environmental chemistry of the element is largely governed by the pH and redox potential in its surroundings. However, the kinetics of Mn(II) oxidation are slow in waters with pH <8.5 (WHO, 2004). Manganese is only weakly bound to dissolved organic carbon and, hence, organic complexation of this element in natural waters does not play an important role in its aquatic speciation. Average natural levels of manganese in soil range from 40-900 mg/kg (ATSDR, 2012).

A complex series of oxidation/precipitation and adsorption reactions occurs when Mn(II) is present in aerobic environments, which eventually renders the manganese biologically unavailable as insoluble manganese dioxide. Thus, natural manganese in soils is largely adsorbed to soil particles and present as manganese dioxide and therefore largely not bioavailable to plants, although it is an essential element (WHO, 2004). The degree of sorption to soil is highly variable; the sorption constant can vary from 0.2 to 10,000 mL/g (increasing with OC content and cation exchange capacity) (ATSDR, 2012).

In air, manganese (compounds) occur mainly in the particulate form (originating from both natural and anthropogenic sources). The half-life of airborne particles is usually on the order of days, depending on particle size and atmospheric conditions (ATSDR, 2012). Eighty percent of the manganese in airborne particulate matter is associated with particles of <5 μm and about 50% with particles of <2 μm . Some removal by wash-out can occur but dry deposition is the most important removal mechanism in air (ATSDR, 2012).

In water, manganese may be significantly bio-concentrated at lower trophic levels. BCFs (Bioconcentration Factors) of manganese from 2,500-6,300 have been reported for phytoplankton, 300-5,500 for marine algae, 800-830 for intertidal mussels and 35-930 for coastal fish. Others have reported BCFs from 10,000-40,000 for invertebrates and 100-600 for fish (ATSDR, 2012). Mn(II) is bioavailable and can readily be taken up by benthic fauna (WHO, 2004). Bioconcentration of Mn(II) in terrestrial plants is highly variable, while a BCF of 2 has been calculated for earthworms (WHO, 2004).

5.2 Environmental hazard

5.2.1 Classification

The harmonised CLP classification of various forms of manganese(II) sulphate is presented in Table 8 and Table 9 below.

TABLE 8

HARMONISED ENVIRONMENTAL CLASSIFICATION OF MANGANESE(II) SULPHATE 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) *
025-003-00-4	manganese sulphate	7785-87-7	Aquatic Chronic 2	H411

* Hazard statement codes: H411: Toxic to aquatic life with long lasting effects.

TABLE 9

ENVIRONMENTAL CLASSIFICATION INFORMATION ON HYDRATED FORMS OF MANGANESE(II) SULPHATE NOTIFIED AND REGISTERED BY MANUFACTURERS AND IMPORTERS (C&L LIST).

CAS No	Substance name	Hazard Class and Category Code(s)	Hazard Statement Codes	Number of notifiers
10034-96-5	Manganese (II) sulphate monohydrate	Total Aquatic Chronic 2 Aquatic chronic 4 "Not classified"	H411 H413 -	931 903 1 27
10101-68-5	Manganese (II) sulphate tetrahydrate	Total Aquatic Chronic 2	H411	83 83

* Hazard statement codes: H411: Toxic to aquatic life with long lasting effects; H413: May cause long lasting harmful effects to aquatic life.

5.2.2 Aquatic ecotoxicity

Most aquatic toxicity tests have been carried out using ionic manganese in oxidation state +2, mainly $MnCl_2$ or $MnSO_4$ (the two most soluble forms). Little is known about the aquatic ecotoxicity of colloidal, particulate or complexed manganese but the toxicity of these forms is assumed to be less than the toxicity of the ionic form (as for many other metals) (WHO, 2004).

WHO presents an overview of results of mainly short term toxicity values for manganese, all originating from studies with either the chloride or the sulphate in its environmental review of manganese (WHO, 2004). Selected results from this review, i.e. most critical (lowest) endpoints, are shown in Table 10 for the main groups of organisms tested.

TABLE 10

OVERVIEW OF SHORT TERM TOXICITY ENDPOINTS FOR MANGANESE (II) TO AQUATIC ORGANISMS (DATA FROM WHO, 2004). ONLY THE LOWEST ENDPOINTS FOR THE MOST SENSITIVE SPECIES WITHIN EACH TAXONOMIC GROUP ARE PRESENTED.

Group	Species	Study type	Endpoint	Value (mg Mn/l)
Fish, freshwater	<i>Onchorhynchus mykiss</i> (rainbow trout)	96 h	LC ₅₀	4.8
	<i>Onchorhynchus kisutch</i> (brown trout)	96 h	LC ₅₀	2.4-17.4*
Invertebrates, freshwater	<i>Daphnia magna</i> (water flea)	48 h	LC ₅₀	0.8-76.3*
	<i>Hyalella azteca</i> (amphipod)	96 h	LC ₅₀	3.0-13.7**
Invertebrates, saltwater	<i>Heliocidaris tuberculata</i> (sea urchin)	72 h	EC ₅₀	5.2
Algae, freshwater	<i>Pseudokirchneriella subcapitata</i>	72 h	E _r C ₅₀	8.3***
Algae, marine	<i>Asterionella japonica</i> (diatom)	72 h	E _r C ₅₀	4.9

* Depending on water hardness (25-250 mg calcium carbonate/l), lowest in soft water.

** Depending on water hardness (26-184 mg calcium carbonate/l), lowest in soft water.

*** A lower value of 1.9 mg/l is reported; however, this number originates from a study with non-standard endpoint and duration.

It is noted that there is no indication in the acute toxicity data in Table 10 that marine organisms are either more or less sensitive to the manganese ion than freshwater organisms.

While the WHO review covers the important acute aquatic endpoints presented by the REACH Manganese Consortium on the ECHA website (public REACH dissemination tool, accessed in August 2014), it does not provide much information on the results regarding chronic studies. The results for chronic toxicity in Table 11 are, therefore, a summary of the data available from the ECHA dissemination tool website (ECHA, 2014).

TABLE 11

OVERVIEW OF CHRONIC TOXICITY ENDPOINTS FOR MANGANESE (II) TO AQUATIC ORGANISMS (DATA FROM ECHA, 2014). ONLY THE LOWEST ENDPOINTS FOR THE MOST SENSITIVE SPECIES WITHIN EACH TAXONOMIC GROUP ARE PRESENTED.

Group	Species	Study type	Endpoint	Value (mg Mn/l)
Fish	<i>Onchorhynchus mykiss</i> (rainbow trout)	4 months, flow-through	NOEC _{growth}	0.6
	<i>Salvelinus fontinalis</i> (brook trout)	65 d, early life stage test	NOEC _{growth}	0.55
Invertebrates	<i>Crassostrea gigas</i> (oyster, marine)	20 d, static	NOEC	0.02
	<i>Daphnia magna</i> (water flea)	3 wk, read across	EC ₁₆ _{reprod.}	4.1
Algae	<i>Pseudokirchneriella subcapitata</i> (green alga)	72 h, static	NOEC _{growth}	1.11
	<i>Desmodesmus suspicatus</i> (green alga)	72 h, static	NOEC _{growth}	1.0

Based on the above acute and chronic aquatic toxicity data (and some further supporting data not mentioned here), the REACH registrant has proposed the following Predicted No-Effect Concentration (PNEC) values for the aquatic environment:

$PNEC_{AQUA (fresh)} = 0.0128 \text{ mg Mn/l}$ (assessment factor (AF) method; AF = 5)

$PNEC_{AQUA (marine)} = 0.0004 \text{ mg Mn/l}$ (assessment factor (AF) method; AF = 50)

$PNEC_{SEDIMENT (fresh)} = 0.0114 \text{ mg Mn/kg dw}$ (assessment factor (AF) method; AF = 50)

$PNEC_{SEDIMENT (marine)} = 0.00114 \text{ mg Mn/kg dw}$ (assessment factor (AF) method; AF = 500)

$PNEC_{STP} = 56 \text{ mg Mn/l}$ (assessment factor (AF) method; AF = 10)

At present, no EU Environmental Quality Standard (EQS) has been established for manganese. However, in the Danish Statutory Order No. 1022 of 25 August 2010, an annual average EQS for manganese has been set at 0.15 mg Mn/l (maximum concentration above the natural background level, for the dissolved fraction) for both freshwater and marine water. It is noted that this value is approx. 10 times higher than the freshwater PNEC proposed by the REACH registrant.

5.2.3 Terrestrial ecotoxicity

The terrestrial toxicity of manganese is not well documented, with the exception of studies on terrestrial plants, in particular crop plants. However, it is found that toxic manganese concentrations in crop plant tissues vary considerably with critical values ranging from 100 to 5000 mg Mn/kg (WHO, 2004). Although manganese toxicity to plants has been observed on acidic, poorly drained mineral soils (e.g. in Hawaii) (WHO, 2004), manganese deficiency is much more common in agricultural land, including in Denmark, where manganese(II) sulphate is widely used for fertilizing of agricultural crops (see section 3.3.2).

In an 8-week toxicity tests using activated sludge, no significant effects on the growth of the earthworm *Eisenia fetida* was observed at the highest test concentration (22,000 mg Mn/kg soil, as Mn(II) sulphate) (WHO, 2004).

In an acute toxicity test with the soil nematode *Caenorhabditis elegans* an $LC_{50} = 76\text{-}108 \text{ mg Mn/kg soil}$ was found for the manganese ion (98-132 mg/kg for total manganese) (WHO, 2004).

5.2.4 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.

5.4 Environmental exposure

5.4.1 Sources of release

Manganese is ubiquitous in the environment and constitutes about 0.1% of the Earth's crust; it is a constituent of more than 100 minerals. Therefore, soils, sediments and rocks are important natural sources of environmental exposure. It has been estimated that two thirds of manganese air emissions are from natural sources, which, in addition to the above, include e.g. ocean spray, forest fires, vegetation and volcanic activity (WHO, 2004). However, we assess that only a minor part of this natural exposure is due to manganese as manganese(II) sulphate.

The anthropogenic sources of manganese include municipal wastewater discharges, sewage sludge, mining and mineral processing (particularly nickel), emissions from steel and iron production, combustion of fossil fuels and, to a minor extent, emissions from vehicles (from the fuel additive MMT³) (WHO, 2004).

In the following paragraphs, only specific sources of manganese(II) sulphate to the environment will be addressed.

Releases in Denmark

The consumption of manganese(II) sulphate in recent years in Denmark amounts to around 1800-2600/2700 tonnes/year (see section 3.3.2). The main part of this amount is for use as a fertiliser in field crops, while the majority of the remainder is used as a nutrient in animal feed. Other uses of manganese(II)sulphate in Denmark are considered to be of little significance (see section 3.3.2).

The release to the environment from use as fertiliser must in reality be 100% while the release from the use in feed would be somewhat less, although a large proportion would be excreted with faeces and urine, of which the majority will be applied to soil as an organic fertiliser.

Releases at EU level

For the EU the distribution of manganese(II) sulphate uses by category is approx. 75% to fertilisers, 15% to animal feed, 5% for formulating fungicides for pesticide use and the remaining 5 % largely as a drying agent in inks/paints (section 3.3.1). In the EU, similarly to Denmark, the vast majority of the consumed amount will be released to the environment (directly or indirectly).

5.4.2 Monitoring data

The Danish NOVANA assessment programme

Manganese (and manganese(II) sulphate for that matter) is not included in the Danish environmental monitoring programme, NOVANA, for point sources or any of the environmental compartments except groundwater.

Manganese is included in the groundwater monitoring programme, GRUMO, as one of 26 so-called "major constituents" of groundwater. It is monitored regularly at the waterworks (intake); however, the results are only occasionally reported in the summary reports of the programme.

The most recent identified GRUMO report containing data on manganese (GEUS, 2007) provides neither average or median values nor ranges of the element. The report only states that over the period 1989-2006, 78.2% of the measurements (1953 measurements) exceeded the threshold value for drinking water of 0.02 mg Mn/l, and the maximum value measured was 86 mg Mn/l. However, the report notes that elements like manganese and iron etc. are normally removed at the waterworks before the water is distributed to the consumers, and is therefore not considered to constitute a drinking water problem.

Data from other countries/regions

WHO (2004) summarises information on environmental levels of manganese (no specific data on manganese(II) sulphate are available or considered relevant as the compound will typically quickly be dissolved and transformed upon release).

Worldwide, the atmospheric concentrations of manganese are in the ng/m³ range. The average continental concentration at remote locations (background) is 3.4 ng Mn/m³, while in rural areas, the average is 40 ng Mn/m³ and in urban areas in Europe, 166 ng Mn/m³ (WHO, 2004).

³ MMT = methylcyclopentadienyl manganese tricarbonyl

In natural waters not affected significantly by anthropogenic sources, the concentrations of dissolved manganese vary between 0.010 - >10 mg Mn/l, although the concentrations rarely exceed 1 mg Mn/l and are usually less than 0.2 mg Mn/l (WHO, 2004). For the US, the median concentration in surface waters in urban areas has been reported as 0.036 mg Mn/l, while in other categories such as agricultural, range land and forests, the median concentrations are in the range 0.011-0.019 mg Mn/l (ATSDR, 2012).

ATSDR (2012) reports average natural ("background") levels of manganese in soils to range from 40 to 900 mg Mn/kg with an estimated mean of 330 mg Mn/kg. WHO (2004) reports the mean background level in soils to be in the range 300-600 mg Mn/kg soil dw.

5.4.3 Other exposure data

According to WHO (2004), concentrations of manganese in marine and freshwater fish tissues tend to be in the range <0.2 to 19 mg Mn/kg dw, while mean levels in mussels from the north-west Pacific Ocean were in the range 2.8-9.3 mg Mn/kg dw. In the North Sea and in the Baltic Sea, levels of manganese in mussels (*Mytilus edulis*) were 29 and 46 mg Mn/kg dw, respectively. Mean concentrations of 128-392 mg Mn/kg dw in seaweed has been reported from south-west England (WHO, 2004).

Manganese levels in terrestrial plants typically appear to range from 20 to 500 mg Mn/kg but significantly higher concentrations have also been reported (WHO, 2004).

Mean manganese concentrations in birds' eggs from a variety of geographical locations range from 1 to 5 mg Mn/kg dw. In the liver of the European otter (*Lutra lutra*), the manganese concentrations were in the range 3.5-7.4 mg Mn/kg dw (WHO, 2004).

5.5 Environmental impact

No reports or scientific papers on environmental impact or risk assessments of manganese (or manganese(II) sulphate) have been identified.

Manganese is an essential element for living organisms, which however might cause some toxicity as high concentration and exposure levels.

The environmental levels of manganese as well as the tolerance of organisms to this element vary significantly and therefore a general assessment of the risk is difficult. There are reports of toxic effects of manganese, but in most places, the current environmental levels appear to be lower than the effect levels.

5.6 Summary and conclusions

Environmental fate and effects

Manganese is a naturally occurring element, which makes up around 0.1% of the earth's crust. Manganese(II) sulphate is very water soluble and in natural waters at pH 4-7 is present as the Mn²⁺ ion, while at higher pH (>8), it may be oxidised further to oxidation state +4.

A complex series of reactions take place in aerobic environments that eventually render manganese biologically unavailable as insoluble manganese dioxide.

In water, manganese may be significantly bioconcentrated at lower trophic levels. BCFs of manganese from 2,500-6,300 have been reported for phytoplankton, 300-5,500 for marine algae, 800-830 for intertidal mussels and 35-930 for coastal fish. Aquatic effect levels of the manganese (II)

ion (the most relevant level in natural waters at pH 4-7) do not differ widely between taxonomic groups (e.g. fish, invertebrates and algae). Acute levels (LC₅₀/EC₅₀) are typically in the mg/l range while chronic no-effect levels are typically around 1 mg/l or in the sub-mg/l range. The Danish EQS for manganese in surface waters is 0.15 mg Mn/l (dissolved fraction; added to the natural background level), which is considerably higher than the PNEC values proposed by the registrant.

Terrestrial data are few but generally indicate low toxicity in soils typical of Denmark.

Releases to the environment

Soils, sediments and rocks are important natural sources of environmental exposure to manganese. Globally, about two thirds of the emissions of manganese (mostly other forms than sulfate) to air are estimated to be from natural sources.

The anthropogenic sources of manganese include municipal wastewater discharges, sewage sludge, mining and mineral processing (particularly nickel), emissions from steel and iron production, combustion of fossil fuels and, to a minor extent, emissions from vehicles (from the fuel additive MMT).

The anthropogenic releases of manganese(II) sulphate to the environment in Denmark are mainly due to its use as a fertiliser in field crops, which constitutes the main fraction of the total amount while most of the remainder is used as a nutrient in animal feed.

The release to the environment from use as fertiliser must in reality be 100% while the release from the use in feed would be somewhat less although still high.

Monitoring data – levels in the environment

Manganese (and manganese(II) sulphate) is not included in the Danish environmental monitoring programme, NOVANA. The Danish groundwater monitoring programme, GRUMO, reports for manganese that over the period 1989-2006, 78.2% of the measurements exceeded the threshold value for drinking water of 0.02 mg Mn/l. However, elements like manganese and iron etc. are normally removed at the waterworks before the water is distributed to the consumers, and is therefore not considered to constitute a drinking water problem.

Worldwide, the atmospheric concentrations of manganese are in the ng/m³ range. In natural waters not affected significantly by anthropogenic sources, the concentrations of dissolved manganese vary between 0.010 and 10 mg/l although the concentrations are usually less than 0.2 mg/l.

Environmental impact

No reports or scientific papers on environmental impact or risk assessments of manganese (or manganese(II) sulphate) have been identified. However, it should be noted that manganese is an essential element to animals as well as plants.

Data gaps

Danish environmental monitoring data are virtually absent, but are considered to be of minor importance.

6. Human health effects and exposure

As manganese(II) sulphate (as well as its hydrates) is very soluble in water and in biological fluids, it will not exist as the salt itself in these media, but will easily dissociate to the manganese ion (Mn^{2+}) and sulphate. Furthermore, the manganese ion is the toxic moiety of manganese(II) sulphate in relation to systemic toxicity (ATSDR, 2012). Therefore, the human health effects of manganese(II) sulphate in this report will also focus on information on the manganese ion. The term 'manganese' in the following is used in a generic way for the manganese ion released from inorganic manganese compounds.

The toxicity of manganese has been thoroughly investigated in both humans and experimental animals and has been described in a detailed manner in the 'Toxicological Profile for Manganese' by the U.S. Agency for Toxic Substances and Disease Registry (ATSDR, 2012). Manganese has also been evaluated by the U.S. EPA as part of the 'Integrated Risk Information System' (IRIS) (US-EPA, 1996) and as part of the 'Toxicity and Exposure Assessment for Children's Health' (TEACH) (US-EPA, 2007). It has also been addressed comprehensively by the WHO in relation to the establishment of drinking water guidelines (WHO, 2011), in relation to air quality guidelines (WHO, 2001), and in form of an 'Environmental Health Criteria' (EHC) report (WHO, 1981) as well as a 'Concise International Chemical Assessment Document' (CICAD) report (WHO, 1999). The Scientific Committee for Food (SCF) also describes manganese in relation to the derivation of a tolerable upper intake level (SCF, 2000, also included in EFSA, 2006).

In a project with the purpose of compiling and evaluating the available toxicological information on selected coformulants in pesticide formulations performed by the Institute of Food Safety and Toxicology, Danish Veterinary and Food Administration (now DTU Food) as a contract work under the pesticides research programme administrated by the Danish EPA, manganese(II) sulphate and manganese(II) sulphide were evaluated (Tobiassen et al., 2003a,b). The evaluation was based on the previously mentioned ATSDR 'Toxicological Profile for Manganese' (ATSDR, 2000), the U.S. EPA IRIS evaluation (US-EPA, 1996), the previous WHO drinking water guideline evaluation (WHO, 1996), the WHO air quality guidelines (WHO, 2001), the WHO EHC report (WHO, 1981), and the SCF opinion on a tolerable upper intake level (SCF, 2000).

The data on toxicokinetics and human health effects have been summarised in the following based primarily on the DTU Food evaluation (Tobiassen et al., 2003a,b). This evaluation has been updated and supplemented to accommodate new relevant information in the more recent ATSDR 'Toxicological Profile for Manganese' (ATSDR, 2012) and the more recent WHO drinking water guideline evaluation (WHO, 2011).

For some endpoints, unpublished studies not included in the above-mentioned publicly available sources, but available in the REACH registration dossier, have also been included in the present report. It should be noted that generally only limited information is available from the publicly available summaries of the confidential substance registrations reports. Furthermore, the information as provided by the registrant has not been subject to scrutiny by ECHA or any EU expert group, or by the authors of this report.

6.1 Human health hazard

6.1.1 Classification

Manganese(II) sulphate is subject to harmonised classification for specific target organ toxicity after repeated exposure (cat. 2) (Table 12).

TABLE 12
HARMONISED HUMAN HEALTH CLASSIFICATION OF MANGANESE(II) SULPHATE 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) *
025-003-00-4	manganese sulphate	7785-87-7	STOT RE 2	H373

* Hazard statement codes: H373: May cause damage to organs through prolonged or repeated exposure

Manganese(II) sulphate monohydrate and tetrahydrate are not subject to harmonised classification, but several notified self-classifications are available in the Classification & Labelling (C&L) Inventory (Table 13).

TABLE 13
HUMAN HEALTH CLASSIFICATION INFORMATION ON HYDRATED FORMS OF MANGANESE(II) SULPHATE NOTIFIED AND REGISTERED BY MANUFACTURERS AND IMPORTERS (C&L INVENTORY)

CAS No	Substance name	Hazard Class and Category Code(s)	Hazard Statement Codes	Number of notifiers
10034-96-5	Manganese (II) sulphate monohydrate	Total		931
		STOT RE 2	H373	903
		Acute tox. 4	H302	5
		Acute tox. 4	H332	5
		Eye damage 1	H318	21
	"Not classified"	-	27	
10101-68-5	Manganese (II) sulphate tetrahydrate	Total STOT RE 2	H373	83 83

* Hazard statement codes: H373: May cause damage to organs through prolonged or repeated exposure; H302: Harmful if swallowed; H332: Harmful if inhaled; H318: Causes serious eye damage.

At a first glance, the table shows that these self-classifications largely follow the harmonised classification for the anhydrous form.

However, these self-classifications have been notified by the manufacturers as well as a range of importers/distributors (also importers/distributors below the 1 tonne/year REACH registration threshold). As set out in Chapter 2, the manganese industry as represented by the REACH Manganese Consortium, including the lead and member registrants, are captured by the 21 notifiers supporting the classification for eye damage. As also set out in Chapters 1 and 2, the REACH Manganese Consortium considers all hydrated forms as equal in terms of toxicity and thus supports this classification for all hydrated forms.

In conclusion, the manganese industry supports that "Eye damage 1, H 318" is added to the harmonised classification for all forms of manganese(II) sulphate.

6.1.2 Toxicokinetics

The toxicokinetics of manganese have been studied in both humans and animals. The data are summarised in the following, primarily based on the DTU Food evaluation (Tobiassen et al., 2003a,b) and updated and supplemented to accommodate new relevant information in the ATSDR 'Toxicological Profile for Manganese' (ATSDR, 2012) and the WHO drinking water guideline evaluation (WHO, 2011).

Manganese is absorbed from the gastrointestinal tract only to a limited extent with about 3-5% being absorbed in humans. Factors that affect manganese bioavailability include age and intake levels of manganese and other trace elements such as iron, calcium and phosphorus, as well as intake of dietary fibre, oxalic acids and phytic acids.

Manganese is absorbed from the alveolar lining of the lungs after inhalation of manganese-containing dust or fumes. No specific data regarding the absorbed fraction of inhaled manganese by humans have been located; however, absorption via the lungs can be significant for workers or for individuals in the general population who are exposed to excess levels of airborne manganese. It has been shown that the pharmacokinetics of inhaled manganese are influenced by particle solubility and that manganese delivery to the brain is favoured when soluble manganese particles such as manganese(II) sulphate are inhaled (Dorman et al., 2006a).

No data regarding absorption of manganese in humans following dermal exposure have been located, but manganese uptake across intact skin would be expected to be extremely limited. The REACH Manganese Consortium advises that a skin absorption study of manganese chloride on reconstituted human skin exists as part of the REACH registration, but that this study is not available on the ECHA dissemination tool website. The results of this study, which according to the Consortium (Harlow, 2014) supports extremely limited skin absorption of the manganese ion (Mn^{++}), is therefore available to relevant authorities via the confidential registration dossier.

Manganese is present in all tissues and fluids with the highest levels found in the liver, kidney, pancreas and adrenals and the lowest levels in bone and fat. Manganese has been reported to accumulate in certain regions of the brain (basal ganglia, especially the globus pallidus and the substantia nigra) following oral exposure in humans with liver diseases. Accumulation in certain brain regions has also been reported for infants and young animals. In rats, most manganese was distributed to the olfactory bulb and the brain following inhalation, but also to other organs such as the lungs, the liver, the kidneys, and the pancreas. Studies in experimental animals indicate that manganese may be distributed directly to the brain from the nasal cavity via the olfactory pathway, thereby bypassing the blood-brain barrier (Dorman et al., 2006a,b). Manganese can cross the placenta and enter the foetus. Manganese is secreted into human breast milk.

In humans, absorbed manganese is eliminated from the blood by the liver, where it is conjugated with bile and then excreted in the faeces, the major route of manganese excretion. Small amounts of manganese are also excreted in urine (0.1-2 %), sweat, and milk. In humans, elimination is biphasic with reported whole-body retention half-lives of 13 and 37 days.

6.1.3 Toxicity

The toxicity of manganese has been thoroughly investigated in both humans and experimental animals. The data are summarised in the following based on the DTU Food evaluation (Tobiassen et al., 2003) and updated and supplemented to accommodate new relevant information in the ATSDR 'Toxicological Profile for Manganese' (ATSDR, 2012) and the WHO drinking water guideline evaluation (WHO, 2011).

Unpublished studies not included in the above-mentioned publicly available sources, but available in the REACH registration dossier, have also been included in the present report.

Manganese is an essential element in the nutrition of humans and animals and is needed for the functioning of key enzymes that play a role in cellular protection from damaging free radical species, maintenance of healthy skin and synthesis of cholesterol. Manganese probably also plays a role in bone mineralisation, metabolism of proteins, lipids and carbohydrates, energy production, metabolic regulation, and nervous system functioning.

The concentration of manganese in the body is usually well regulated via normal physiological processes, i.e. the homeostatic system by which the rate and amount of manganese absorbed from the gastrointestinal tract, and its distribution and rate of excretion, are controlled. However, the homeostatic system can become overloaded, resulting in adverse systemic effects.

Acute toxicity

Most studies in experimental animals indicate that manganese is of low acute oral toxicity when administered in the feed. However, following gavage, manganese(II) sulphate is of moderate acute toxicity in experimental animals with an oral LD₅₀-value of 780 mg/kg bw reported for the rat.

A key acute inhalation toxicity study located in the ECHA dissemination tool website and performed according to OECD TG 403, reported that the LC₅₀ value in rats was greater than 4.98 mg/l for manganese(II) sulphate monohydrate; the equivalent LC₅₀ value for the anhydrous form was considered to be >4.45 mg/l (ECHA, 2014). It should be noted that generally only limited information is available from the publicly available summaries of the confidential substance registrations reports. Furthermore, the information as provided by the registrant has not been subject to scrutiny by ECHA or any EU expert group, or by the authors of this report.

Acute inhalation exposure to high concentrations of manganese dusts can cause an inflammatory response in the lung. This phenomenon is characteristic of nearly all inhalable particulate matter and therefore, it may not be manganese alone that causes the inflammatory response, but the particulate matter itself.

No data regarding acute toxicity in experimental animals following dermal contact to manganese(II) sulphate or other inorganic manganese compounds have been located.

No human data have been located.

Based on the available data, classification of manganese(II) sulphate for acute oral toxicity might be warranted.

Based on the data in the REACH Registration Dossier, classification of manganese(II) sulphate for acute inhalation toxicity does not seem to be warranted; however, it should be noted that the author of this chapter did not have access to the original study reports for scrutiny of the data and conclusions, precluding a final conclusion.

Irritation and sensitization

No data regarding skin, eye and respiratory tract irritation in humans or experimental animals following exposure to manganese(II) sulphate or other inorganic manganese compounds have been located in the open literature.

A key skin irritation study located in the ECHA dissemination tool website and performed according to OECD TG 404 concluded that manganese(II) sulphate is not irritating to rabbit skin (ECHA, 2014).

A key eye irritation study located in the ECHA dissemination tool website and performed according to OECD TG 405 concluded that manganese(II) sulphate should be classified for eye irritation because of irreversible ocular damage in one rabbit (ECHA, 2014).

It should be noted that generally only limited information is available from the publicly available summaries of the confidential substance registrations reports. Furthermore, the information as provided by the registrant has not been subject to scrutiny by ECHA or any EU expert group, or by the authors of this report.

Based on the data in the REACH Registration Dossier, classification of manganese(II) sulphate for eye irritation seems to be warranted, whereas classification for skin irritation does not seem to be warranted. However, it should be noted that the authors of this report did not have access to the original study reports for scrutiny of the data and conclusions, precluding a final conclusion.

No data regarding skin and respiratory tract sensitisation in humans or experimental animals following exposure to manganese(II) sulphate have been located in the open literature.

Among 48 workers from the ceramics industry positively sensitised to at least one substance, positive sensitisation test results with manganese dioxide (which has a different valency from MnSO_4) were found in 2 of the workers.

Inorganic manganese compounds have been reported to be negative for skin sensitisation in the local lymph node assay (LLNA) in mice.

Based on the available data, classification of manganese(II) sulphate for skin sensitisation does not seem to be warranted.

Sub-chronic and chronic toxicity

The central nervous system (CNS) is the primary target of manganese toxicity following repeated exposure, and neurotoxicity is the critical effect of excess manganese exposure. The neurotoxicity of the manganese ion (Mn^{2+}) has been linked to its ability to substitute for the calcium ion (Ca^{2+}) under physiological conditions (ATSDR, 2012).

Neurological effects are well recognised based on case reports and epidemiological studies of workers, as well as on results from animal inhalation studies.

In humans, manganese toxicity can result in a progressive, disabling and permanent neurological syndrome 'manganism' that typically begins with relatively mild symptoms and evolves to include altered gait, fine tremor and facial muscle spasms. These symptoms are also frequently accompanied by apathy and dullness along with effects like impotence and loss of libido. The symptoms of manganese toxicity may appear slowly over months and years. Some studies suggest that manganese also can result in adverse cognitive effects, including difficulty with concentration and memory problems. Some of the symptoms of manganism resemble those of Parkinsonism and therefore, terms such as 'Parkinsonism-like disease' and 'manganese-induced Parkinsonism' have been used to describe symptoms observed with manganese toxicity. Although symptoms of manganism resemble those of Parkinsonism, there are significant differences in terms of clinical presentation.

Although a dose-response curve for manganese-induced neurotoxicity has not been well-defined, several epidemiological studies of workers have provided consistent evidence of neurotoxicity associated with low-level manganese exposure over time. Older studies have described overt manganism following long-term inhalation exposures to 2-22 mg/m^3 as total manganese dust. More recent occupational studies indicate that early or preclinical signs of neurological effects can occur in gen-

erally asymptomatic workers following exposure to levels of manganese of about 0.14-1 mg/m³ (total manganese dust) for several years (span from 1 to 35 years).

One specific occupational epidemiological study (Roels et al., 1992) on male workers exposed to manganese dioxide dust in a Belgian alkaline battery plant has been used as the basis for setting various standards such as the US-EPA inhalation reference concentration (RfC), the WHO air quality guideline and the ATSDR minimal risk level (MRL) for chronic inhalation exposure (section 6.1.5.). The manganese-exposed workers performed significantly worse than the controls on several measures of neurobehavioral function, with particular differences in simple reaction time, eye-hand coordination, and hand steadiness. The manganese-exposed workers had been exposed for an average (geometric mean) of 5.3 years (range: 0.2–17.7 years). The geometric means of the workers' time weighted average (TWA) airborne concentrations, as determined by personal sampler monitoring at the breathing zone, were 0.215 mg manganese/m³ for respirable dust and 0.948 mg manganese/m³ for total dust. No data on particle size or purity was presented in the article, but the median cut point for the respirable dust fraction was reported to be 5 µm. Occupational lifetime integrated exposure to manganese was estimated for each worker. The geometric mean occupational lifetime integrated respirable dust (IRD) concentration was estimated to 0.793 mg manganese/m³ * years (range: 0.040-4.443 mg manganese/m³ * years). By dividing the IDR with the average duration of the workers' exposure to manganese (5.3 years) a LOAEL of 0.15 mg/m³ can be derived for neurotoxic effects of manganese (US-EPA, 1996). It can be noted, that the study was based on MnO₂ which has a different valency (+4) compared with MnSO₄ (+2).

Several studies provide evidence for associations between decreased neuronal cell counts in the globus pallidus and neurobehavioral changes (increased locomotor activity) in rats exposed by inhalation for 13 weeks to manganese(II) sulphate (at concentrations of 0.09 and 0.9 mg manganese/m³); increased manganese levels were observed in all regions of the brain.

Several studies have also examined the influence of inhalation exposure to manganese(II) sulphate on biochemical endpoints associated with oxidative stress or inflammation in the brain of rats and monkeys. ATSDR concluded that the results from these studies indicate that acute or intermediate duration inhalation exposure to concentrations ranging from about 0.1 to 1 mg manganese/m³ can affect brain biochemical markers of neurotoxicity, but understanding of the neurotoxic mechanism of manganese is inadequate to confidently define any one of the observed changes as biologically adverse (ATSDR, 2012).

There is only limited evidence that oral exposure to manganese leads to the severe neurological effects associated with high-level occupational exposure to manganese. However, the limited human data and extensive animal data clearly identify neurobehavioral changes as the most sensitive effect of oral exposure to excess inorganic manganese.

A number of reports indicate that oral exposure to manganese, especially from contaminated water sources, can produce significant health effects. These effects have been most prominently observed in children and are similar to those observed from inhalation exposure. An actual threshold level at which manganese exposure produces neurological effects in humans via this exposure route has not been established. ATSDR concluded that while many of the studies reporting oral effects of excess manganese have limitations that preclude firm conclusions about the potential for adverse effects, these studies collectively suggest that ingestion of water and/or foodstuffs containing increased concentrations of manganese may result in adverse neurological effects. Furthermore, inconsistencies in the dose-response relationship information across studies evaluating different neurological endpoints under different experimental conditions in different species, as well as a lack of information concerning total intakes of manganese (e.g., dietary intakes plus administered doses), make it difficult to derive MRLs using standard MRL derivation methodology from the human or animal studies (ATSDR 2012).

As described above, available data suggest that neurological effects can occur following inhalation exposures in humans and in experimental animals to different manganese compounds. Manganese-induced neurological effects have been reported at lower airborne manganese concentrations in humans than in animals. These data suggest that animal models, particularly rodent species, might be less useful for defining quantitative dose-response relationships, but helpful in elucidating the mechanism(s) for these effects. The basis for the difference in susceptibility across species is not yet understood and may be related to possible differences in the sensitivity of test methods used to detect neurobehavioural effects in animals compared with methods used to detect neurobehavioural effects in humans.

Manganese(II) sulphate is classified for specific organ toxicity following repeated exposure (STOT RE 2) with the hazard statement H373 (may cause damage to organs through prolonged or repeated exposure), since several types of serious toxic effects after inhalation have been observed.

Mutagenicity/Genotoxicity

The evidence for the mutagenicity and genotoxicity of manganese(II) sulphate, as well as for other inorganic manganese compounds, is equivocal with both negative and positive results observed in various test systems (ATSDR, 2012).

In vitro, manganese(II) sulphate was reported to be negative in an Ames test performed with *Salmonella typhimurium* strains TA 97, TA 98, TA 100, TA 1535 or TA 1537, with or without metabolic activation, whereas a positive result was observed in another Ames test with *Salmonella typhimurium* strain TA 97 without metabolic activation. Positive results have also been reported for manganese(II) sulphate *in vitro* in a fungal gene conversion/reverse mutation assay in *Saccharomyces cerevisiae* strain D7, in an assay for sister chromatid exchange in Chinese hamster ovary (CHO) cells with and without metabolic activation, and in an assay for chromosomal aberrations in CHO cells without metabolic activation.

In vivo assays in mice showed that oral doses of manganese(II) sulphate caused an increased incidence of micronuclei and chromosomal aberrations in the bone marrow. Manganese sulphate was negative for sex-linked recessive lethal mutations in male germ cells in fruit flies (*Drosophila melanogaster*).

No relevant human data have been located.

Based on these studies, ATSDR concluded that no overall conclusion can be made about the possible genotoxic hazard to humans from exposure to manganese(II) sulphate, as well as to other inorganic manganese compounds (ATSDR, 2012).

Studies with manganese(II) chloride performed in 2009 (unpublished reports) have been located in the ECHA dissemination tool website (ECHA, 2014). *In vitro*, manganese(II) chloride was reported to be non-mutagenic in an Ames test with *Salmonella typhimurium* strains TA 1535, TA 1537, TA 98 and TA 100 (performed according to OECD TG 471) and in a mammalian cell gene mutation assay with mouse lymphoma L5178Y cells (performed according to OECD TG 476), and was considered to be non-clastogenic in a mammalian chromosome aberration test with human lymphocytes (performed according to OECD TG 473). *In vivo*, manganese(II) chloride was reported to be non-genotoxic in a mouse micronucleus assay (performed according to OECD TG 474).

It should be noted that generally only limited information is available from the publicly available summaries of the confidential substance registrations reports. Furthermore, the information as provided by the registrant has not been subject to scrutiny by ECHA or any EU expert group, or by the author of this chapter.

Based on the data in the REACH Registration Dossier, classification of manganese(II) chloride for mutagenicity or genotoxicity does not seem to be warranted. However, it should be noted that the author of this chapter did not have access to the original study reports for scrutiny of the data and conclusions, precluding a final conclusion. Read-across of these results to manganese(II) sulphate seems justified as the manganese ion is the toxic moiety of manganese(II) sulphate in relation to systemic toxicity.

Carcinogenicity

Chronic (2-year) feeding studies performed by the U.S. National Toxicology Program (NTP) in 1993 in F344 rats and B6C3F₁ mice have yielded equivocal evidence for the carcinogenic potential of manganese. A significantly increased incidence of follicular cell hyperplasia and a marginally increased incidence of thyroid gland follicular cell adenomas were observed in mice fed 731 mg manganese/kg bw per day as manganese(II) sulphate monohydrate, whereas no increased tumour incidence was found in mice fed 228 mg manganese/kg bw per day. This was considered by NTP to be “*equivocal evidence of carcinogenic activity of Mn(II) sulphate monohydrate in male and female B6C3F1 mice*”. No increased tumour incidence was found in rats fed up to 228 mg manganese/kg bw per day.

WHO concluded that the significance of these results and their relevance to normal human exposure to manganese is questionable (WHO, 2011). ATSDR concluded that there are little data to suggest that inorganic manganese is carcinogenic, although no firm conclusions can be drawn from the mixed results in animal studies (ATSDR, 2012).

No human data regarding carcinogenic effects after oral exposure to manganese(II) sulphate or other inorganic manganese compounds have been located.

No data regarding carcinogenic effects in humans or experimental animals after inhalation or dermal exposure to manganese(II) sulphate or other inorganic manganese compounds have been located.

According to U.S. EPA, manganese is not classifiable with regard to human carcinogenicity (Group D) (US-EPA, 1996). IARC has not evaluated manganese(II) sulphate or other inorganic manganese compounds for a carcinogenic potential.

Effect on reproduction and offspring

Information from the available human inhalation studies has revealed conflicting evidence for whether occupational exposure to manganese causes adverse reproductive effects in men. Decreased libido, impotence, sexual dysfunction and reduced sperm quality have been reported in male workers with clinical signs of manganism following inhalation exposure to high levels of manganese dusts, but the information on the effect of manganese on male fertility (as measured by birth rate in wives of affected workers) is inconclusive. ATSDR concluded that the reported effects may occur as secondary to neurotoxicity and that the available data do not provide information on any direct effect of manganese on the reproductive organs in male workers exposed to manganese by inhalation (ATSDR, 2012). No studies evaluating reproductive effects in women exposed to manganese by inhalation or in humans following oral or dermal exposure to manganese(II) sulphate or other inorganic manganese compounds have been located.

Limited information is available on the developmental effects of inorganic manganese in humans. Increased incidences of neurological disorders, birth defects and stillbirths have been observed in a small population of people living on an island with rich manganese deposits; however, several limitations in the study preclude ascribing these effects to manganese. Potential developmental effects of manganese in the form of high infant mortality were reportedly linked to a local drinking water supply with high levels of manganese in a Bangladesh community. Similarly, an association be-

tween increased risk for infant mortality and increased groundwater manganese concentration has been suggested in a pilot ecological study in North Carolina. Two studies of school children have associated poorer performance in school and on neurobehavioral tests with increased oral exposure to manganese in drinking water and food. ATSDR concluded that although the observed effects in these studies cannot be causally linked to manganese exposure exclusively, taken together, they support the hypothesis that oral exposure to elevated manganese may exert developmental effects in humans.

Studies in experimental animals indicate that manganese has the potential to cause reproductive and developmental effects when administered orally. Available inhalation data concerning these effects are scarce and not definitive. However, the REACH Manganese Consortium notes that a two-generation inhalation study on manganese chloride, which might be used in a read-across approach, now exists (Harlow, 2014) and according to Harlow (2014) this study demonstrates no reprotoxic effects. The results of this study will be included in the REACH registration update and subsequently be available to the relevant authorities.

Studies in mice and rats indicate that ingestion of high oral doses of manganese (from about 1050 mg manganese/kg b.w. per day for 90 days) can lead to delayed maturation of the reproductive function in male animals, probably due to decreased testosterone secretion by Leydig cells, but apparently without affecting sperm count and fertility. When manganese(II) sulphate was given by gavage to mice at 23-198 mg/kg bw per day for 21 days, sperm head abnormalities and percentage of abnormal sperm was significantly increased in all exposed mice as compared to controls. No reproductive effects were observed in female rats fed manganese(II) sulphate in their diet at doses up to 187 mg manganese/kg bw per day (highest dose tested) for 8 weeks prior to mating and until gestational day 21, or in pregnant rats ingesting other inorganic manganese compounds at even higher doses. In contrast, decreased numbers of implantations and viable foetuses were observed in female mice exposed to manganese chloride in drinking water at a dose level of 277 mg manganese/kg bw per day for 12 weeks before mating with unexposed males. In standard developmental toxicity studies, no distinct effects of manganese intake on foetal survival, gross foetal malformations, or skeletal or visceral malformations or alterations have been reported. Similarly, no gross malformations and no skeletal abnormalities were observed in the foetuses of rats fed manganese(II) sulphate in their diet for 8 weeks prior to mating and until gestational day 21, but the highest dose tested (187 mg manganese/kg bw per day) caused a significant increase in foetal manganese and a decrease in foetal iron content.

Numerous studies have reported changes in brain neurochemistry and/or neurobehaviour following neonatal or juvenile exposure to manganese in drinking water or by gavage. ATSDR concluded that while the results from these studies varied and were inconsistent, taken together, the weight-of-evidence suggests that excess manganese exposure during development can lead to alterations in brain chemistry and behavioural development (ATSDR, 2012).

Endocrine effects

Studies of endocrine effects in humans following exposure to inorganic manganese are limited. One study reported elevated prolactin and cortisol levels in foundry workers exposed to manganese for approximately 10 years (0.04-1.1 mg manganese/m³ (particulate matter) and 0.05-0.9 mg/m³ as fumes), while no changes in the levels of follicle stimulating hormone (FSH) and luteinizing hormone (LH) were observed. In another study, serum prolactin levels were increased in a group of workers from a ferroalloy plant who were exposed occupationally to elevated levels of airborne manganese.

Two dietary studies in rats reported that manganese (350 mg manganese/kg bw per day starting on day 1 of gestation and continuing for 224 days; or 214 mg manganese/kg bw per day for up to 28 days) resulted in reduced testosterone levels in male rats. ATSDR concluded that the biological

significance of this effect is unknown because the decrease had no result on fertility in the latter study, and there were no observed effects on the hypothalamus or pituitary (ATSDR, 2012).

Increases in serum levels of LH, FSH, and oestradiol (E2) was observed in female pups exposed to manganese by daily gavage (2 mg manganese/kg bw per day) from postnatal day (PND) 12 to 29. In a follow-up study, manganese (4.4 mg manganese/kg bw per day) given by gavage from PND 12 to 29 to female pups resulted in elevated expression levels of genes involved in neuroendocrine axis control of puberty onset.

In male rats, increased LH, FSH, and testosterone levels were observed at 55 days of age following administration of manganese (11 mg manganese/kg bw per day) by daily oral gavage on PNDs 15-48 or 15-55.

6.1.4 Combination effects

No information on combination effects has been identified in this survey.

6.1.5 No-effect levels

Occupational exposure limit values

Occupational exposure limit values for manganese(II) sulphate for selected European countries are presented in Table 14.

TABLE 14
OCCUPATIONAL EXPOSURE LIMIT VALUES FOR MANGANESE IN SELECTED COUNTRIES

	Limit value 8-hours		Limit value short term	
	ppm	mg/m ³	ppm	mg/m ³
Denmark	█	0.2* 0.1 (respirable fraction)**	█	█
Germany	█	0.2 (inhalable fraction)** 0.02 (respirable fraction)**	█	█

* Manganese, powder, dust and inorganic compounds, expressed as Mn

** Expressed as Mn

Derived no-effect levels

The proposed derived no-effect levels (DNELs) for manganese(II) sulphate are provided in the ECHA dissemination website (ECHA, 2014) and presented in Table 15. It should be noted that only limited information on derivation and justification is available from the publicly available reporting from the confidential substance registrations report. Furthermore, the proposed DNELs as provided by the registrants have not been subject to scrutiny by ECHA or any EU expert group, or to the author of this chapter.

TABLE 15
PROPOSED DERIVED NO-EFFECT LEVELS (DNELs) FOR MANGANESE(II) SULPHATE (ECHA, 2014)

Population - route	Exposure	DNEL	Most sensitive end-point	Comment (DNEL derivation method)*
Workers - inhalation	Long term exposure - systemic effects	0.2 mg/m ³	Not specified	Neither dose descriptor starting point nor method are specified
	Acute/short term exposure - systemic effects			No threshold effect and/or no dose-response information available
Workers - dermal	Long term exposure - systemic - local	0.00414 mg/kg bw/day	Not specified	Systemic: Neither dose descriptor starting point nor method are specified Local: No threshold effect and/or no dose-response information available
	Acute/short term exposure - systemic effects - local effects			Systemic and local: No threshold effect and/or no dose-response information available
General population - inhalation	Long term exposure - systemic effects	0.043 mg/m ³	Not specified	Neither dose descriptor starting point nor method are specified
	Acute/short term exposure - systemic effects - local effects			Systemic: No threshold effect and/or no dose-response information available Local: Exposure based waiving
General Population - dermal	Long term exposure - systemic effects	0.0021 mg/kg bw/day	Not specified	Neither dose descriptor starting point nor method are specified
	Acute/short term exposure - systemic effects - local effects			Systemic and local: No threshold effect and/or no dose-response information available
General population - oral	Long term exposure - systemic effects			No threshold effect and/or no dose-response information available
	Acute/short term exposure - systemic effects			Exposure based waiving

Tolerable daily intake

The WHO air quality guideline for manganese of 0.00015 mg/m³ was based on an estimated NO-AEL (the lower 95% confidence limit of the BMDL₅) of 0.030 mg/m³ for neurotoxic effects reported in an occupational epidemiological study on male workers exposed to manganese dioxide dust in a Belgian alkaline battery plant (Roels et al., 1992). The guideline value of 0.00015 mg/m³ was de-

rived by dividing the estimated NOAEL by a factor of 4.2 to adjust for continuous exposure and an assessment factor of 50 (10 for inter-individual variation and 5 for developmental effects in younger children) (WHO, 2001).

The US-EPA has also set their inhalation reference concentration (RfC) of 0.00005 mg Mn/m³ based on a LOAEL of 0.15 mg/m³ for impairment of neurobehavioral function in the epidemiological study (Roels et al. 1992) and adjusted to a continuous exposure of 0.05 mg/m³. An assessment factor of 1000 was applied (10 for inter-individual variation, 10 for use of a LOAEL, and 10 for database limitations) (US-EPA 1996).

ATSDR has based their Minimal risk level (MRL) of 0.0003 mg Mn/m³ for chronic inhalation on the same epidemiological study (Roels et al., 1992) as WHO and US-EPA. ATSDR considered a BMCL₁₀ of 0.142 mg/m³ as the so-called point of departure (POD) for the MRL and the value of 0.0003 mg Mn/m³ was obtained by adjusting the POD to a continuous exposure basis (0.142 mg Mn/m³ x 5/7 x 8/24) and dividing by an assessment factor of 100 (10 for inter-individual variation and a factor of 10 for limitations/uncertainties in the database) (ATSDR, 2012).

The WHO drinking water guideline for manganese of 0.4 mg/l was based on a TDI of 0.06 mg/kg bw. The TDI was derived from a NOAEL of 11 mg/day by dividing by an assessment factor of 3 (to allow for the possible increased bioavailability of manganese from water) and an adult body weight of 60 kg. The NOAEL was the upper range of manganese intake from typical Western and vegetarian diets with intakes ranging from 0.7 to 10.9 mg/day (WHO, 2011).

The US-EPA has set an oral reference dose (RfD) of 0.14 mg/kg bw/day based on a NOAEL of 10 mg/day (0.14 mg/kg bw/day for 70 kg adult) for chronic human consumption of manganese in the diet from a composite of data from several studies (US-EPA, 1996).

Discussion of no-effect levels

Assumptions and justifications in relation to applied studies and assessment factors are not available in the ECHA dissemination tool. Therefore, it is difficult to discuss why DNELs as presented in REACH registration dossiers are generally higher than levels from authoritative and international organisations. The following provides some further details on how other reference values were derived.

The critical effect of excess manganese inhalation exposure is neurotoxicity. The critical study on which the US-EPA based their inhalation reference concentration (0.00005 mg Mn/m³), the WHO their air quality guideline (0.00015 mg Mn/m³) and the ATSDR their Minimal risk level for chronic inhalation (0.0003 mg Mn/m³), is the occupational epidemiological study performed by Roels et al. (1992).

The so-called 'Point of Departure' (POD) for the setting of the respective inhalation standards was 0.15 mg Mn/m³ (US-EPA: LOAEL), 0.030 mg Mn/m³ (WHO: BMDL₅), and 0.142 mg Mn/m³ (ATSDR: BMCL₁₀) and the inhalation standards were derived from the POD by adjustment to a continuous exposure and by applying an assessment factor (US-EPA: 1000; WHO: 50; and ATSDR: 100).

All three bodies applied the general assessment factor of 10 for inter-individual variation in the general population. US-EPA applied an additional assessment factor of 100 because of a LOAEL as the POD (factor of 10) and for database limitations (factor of 10), WHO applied an additional assessment factor of 5 for developmental effects in younger children, and ATSDR applied an additional assessment factor of 10 for limitations/uncertainties in the database.

6.2 Human exposure

The general population is exposed to manganese through natural and commercial sources via food and drinking water, inhalation of air, and dermal contact with air, water, soil, and potentially via consumer products that contain manganese. Workers can also be exposed to manganese(II) sulphate and manganese by inhalation and dermal contact during manufacturing and use of manganese(II) sulphate.

6.2.1 Direct exposure

Occupational exposure

Workers can be exposed to manganese(II) sulphate during manufacturing and use. As there is no manufacturing of manganese(II) sulphate in Denmark (cf. section 3.1.2 and 3.2.3), this section will only focus on occupational exposure during (downstream) use of manganese(II) sulphate.

The main uses of manganese(II) sulphate in Denmark are in fertilisers and in feed (see Chapter 3).

Inhalation of manganese(II) sulphate as dust particles is assessed to be the main occupational exposure route in relation to handling manganese(II) sulphate fertilisers in powder/granulate form and when mixing manganese(II) sulphate into feed formulations. In particular farmers handling these products are expected to be exposed via inhalation as it does not appear that personal protective equipment is used regularly (see Chapter 3). The farmer is exposed to a much lesser extent when buying final feed formulations in which manganese(II) sulphate is added in amounts < 150 ppm. Farmers can also be exposed to manganese by inhalation when fertiliser solutions are sprayed onto the fields.

No data on occupational inhalation exposure to manganese(II) sulphate or to manganese when handling manganese(II) sulphate containing products have been located.

Dermal exposure to manganese(II) sulphate can occur in the form of dust particles, to manganese when manganese(II) sulphate is used in fertilisers on spray/aerosol form, and to manganese ions (Mn^{++}) during dissolution of manganese(II) sulphate to be applied in the field. Systemic exposure following dermal contact is considered to be insignificant as manganese uptake across intact skin is expected to be extremely limited.

Considering the proposed classification for eye damage, it should be noted that eye exposure to dust cannot be excluded. No information regarding use of safety goggles has been identified.

No data on occupational dermal exposure to manganese(II) sulphate or to manganese ions (Mn^{++}) when handling manganese(II) sulphate containing products have been identified.

Consumer exposure

No data on consumer exposure to manganese(II) sulphate or manganese ions (Mn^{++}) resulting from use of manganese(II) sulphate have been identified.

As discussed in Chapter 3, the main consumer exposures resulting from manganese(II) sulphate applications are assessed to be:

- Oral exposure: via intake as food nutrient/supplements; a desired intake of manganese as an essential element regulated by positive lists based on EFSA (European Food Safety Authority) assessments
- Dermal exposure: Mainly to dissolved Mn^{++} in e.g. paints and fertilisers
- Inhalation/eye: Possibly in some handling of fertiliser granulates, although it should be noted that this use is not supported by the REACH Manganese Consortium.

As noted, the oral exposures are intentional. Further, dermal exposures are probably of less relevance given the observed low dermal absorption of manganese.

The extent to which consumer application of fertiliser granulates actually takes place is uncertain, (Chapter 3). However, if it does take place and if larger amounts are handled, a significant inhalation and eye exposure may take place. However, no specific data on this issue have been identified.

Finally, as discussed in Chapter 3, manganese(II) sulphate seems to be registered under REACH for a range of uses, which possibly could lead to consumer exposure. However, for such uses, the same considerations as those given above are assumed to be relevant.

6.2.2 Indirect exposure via the environment

Manganese(II) sulphate can be released to the environment following production and handling of products containing manganese(II) sulphate in Denmark, predominantly through fertilisers and feed (cf. section 3.3.2).

As manganese(II) sulphate (as well as its hydrates) is very soluble in water, in aqueous environments and in biological fluids of fish and farm animals, it would not exist as the salt itself, but easily dissociate to the manganese ion (Mn^{2+}) and sulphate. Consequently there is no indirect exposure of the general population to manganese(II) sulphate via the environment.

Exposure to the manganese ion (Mn^{2+}) results from natural sources as well as manganese chemicals. Manganese(II) sulphate, the main manganese fertiliser, must be considered to be a considerable contributor to bioavailable manganese in the environment. See also Chapter 5 in relation to existing knowledge on this issue.

In this context it should also be kept in mind that manganese is an essential element.

Indoor climate

Given the identified manganese(II) sulphate applications, this issue does not appear relevant.

6.3 Bio-monitoring data

Manganese can be measured in biological fluids and tissues and manganese levels in blood, urine, faeces and hair could be possible biomarkers of exposure to manganese (ATSDR 2012).

One study of workers indicated that manganese levels in blood and urine, on an individual basis, are positively correlated with exposure levels a few weeks following cessation of exposure. In chronically exposed workers, a positive correlation between manganese levels in total dust and in blood was found when evaluated while exposure was ongoing; this correlation was, however, not found for cumulative exposure index and blood levels of manganese.

Other studies have indicated that, on an individual basis, the correlation between the level of workplace exposure and manganese levels in blood or urine is not a reliable predictor of exposure.

In addition to individual variability, the relatively rapid rate of manganese clearance from the body limits the usefulness of measuring manganese in blood, urine, or faeces as a measure of excess manganese exposure. Furthermore, homeostatic mechanisms largely prevent fluctuations of manganese concentration in whole blood. Also manganese is mainly excreted by the biliary route.

No information on relationships between exposure to manganese(II) sulphate and biomarkers has been identified in this survey.

6.4 Human health impact

No thorough authoritative risk assessment of industrial applications of manganese(II) sulphate has been identified in this survey. However, it should be noted that work on PBPK⁴ modelling over the past decade has increased the understanding of exposure concentration versus responses for oral as well as inhalation exposure. Such models are suggested to be used in a risk assessment context (see e.g. Andersen et al., 2010; Boyes, 2010).

Further, as indicated in Section 6.2.1, no actual exposure data have been identified, a fact which limits the possibilities for discussing possible risk.

However, human case studies have shown that inhalation exposure to high manganese levels might trigger neurotoxic effects. Extracts from the Danish Register of occupational diseases show a few manganese-related cases (4 case in the period 2008-2010) (Høyer, 2014). None of these cases are related to handling of manganese(II) sulphate.

To this end, it should be noted that the potential of experiencing adverse health effects of manganese(II) sulphate as dust particles depends on the particle size, as only particles with a Mass Median Aerodynamic Diameter (MMAD) $\leq 5 \mu\text{m}$ are considered as being respirable and thus potentially bioavailable. No information on the particle size of manganese(II) sulphate used in the production of fertilisers and feed constituent, or on the droplet size of manganese-containing fertilisers on spray/aerosol form have been located.

As manganese(II) sulphate is proposed (by industry) to be classified for eye damage, it cannot be excluded that handling of manganese(II) sulphate powder/granulates might lead to risks associated with eye exposure.

Manganese(II) sulphate did not show skin irritation or skin sensitisation potential in the available studies. Consequently, it is assessed that there is no significant risk for workers of experiencing adverse local effects following dermal contact to manganese(II) sulphate as dust particles.

Systemic exposure to manganese following dermal contact to manganese(II) sulphate as dust particles is considered to be insignificant as manganese uptake across intact skin is expected to be extremely limited. Consequently, it is assessed that there is no significant risk for workers of experiencing adverse health effects of manganese following dermal contact to manganese(II) sulphate as dust particles, or to manganese when manganese(II) sulphate is used in fertilisers on spray/aerosol form.

As already discussed in Section 6.2.1, consumer exposure is generally considered to be of low risk, except for inhalation exposure, which might occur if manganese(II) sulphate is handled in powder/granulate form. Such consumer handling is indicated as a registered use under REACH, but actual occurrence is uncertain.

Given the environmental levels identified in Chapter 5 and considering that manganese is an essential element, it is qualitatively assessed that there is no/low risk associated with manganese exposure via the environment. Furthermore, as also discussed in Chapter 5, natural sources account for a significant amount of the manganese in the environment.

Finally, it should be noted that accumulated exposure, and thereby possible risks associated with the manganese ion (Mn^{++}) being the toxic moiety of systemic toxicity, might result from a range of manganese salts.

⁴ PBPK: Physiologically-based pharmacokinetic

6.5 Summary and conclusions

Human health hazard

Manganese is absorbed from the lungs after inhalation of manganese-containing dust or fumes and absorption can be significant for workers who are exposed to excess levels of airborne manganese. Manganese is absorbed from the gastrointestinal tract only to a limited extent with about 3-5% being absorbed in humans. Manganese uptake across intact skin would be expected to be extremely limited. Manganese has been reported to accumulate in certain regions of the brain. Studies in experimental animals indicate that manganese may be distributed directly to the brain from the nasal cavity via the olfactory pathway, thereby by-passing the blood-brain barrier. Manganese is excreted primarily in the faeces.

Manganese is an essential element in the nutrition of humans and animals and is needed for the functioning of key enzymes. The concentration of manganese in the body is usually well regulated via normal physiological processes, i.e. the homeostatic system. However, the homeostatic system can become overloaded resulting in adverse systemic effects.

Manganese(II) sulphate is of low acute toxicity in experimental animals following inhalation and of moderate acute toxicity following oral administration.

No data regarding skin, eye and respiratory tract irritation, or skin and respiratory tract sensitisation following exposure to manganese(II) sulphate have been located in the open literature. Based on data in the REACH Registration Dossier, classification of manganese(II) sulphate for eye irritation seems to be warranted, whereas classification for skin irritation does not seem to be warranted. However, it should be noted that the author of this chapter did not have access to the original study reports for scrutiny of the data and conclusions precluding a final conclusion. It can be noted that the manganese industry supports classification for this endpoint.

The central nervous system is the primary target of manganese toxicity following repeated exposure, and neurotoxicity is the critical effect of excess manganese exposure. Manganese(II) sulphate is subject to harmonised classification for specific organ toxicity following repeated exposure (STOT RE 2), since several types of serious toxic effects after inhalation have been observed.

The evidence for the mutagenicity and genotoxicity of manganese(II) sulphate is equivocal, with both negative and positive results observed in various test systems. No overall conclusion can be made about the possible genotoxic hazard to humans from exposure to manganese(II) sulphate. Based on data in the REACH Registration Dossier, classification of manganese(II) chloride for mutagenicity or genotoxicity does not seem to be warranted. Read-across of these results to manganese(II) sulphate seems justified as the manganese ion is the toxic moiety of manganese(II) sulphate in relation to systemic toxicity. However, it should be noted that the author of this chapter did not have access to the original study reports for scrutiny of the data and conclusions, precluding a final conclusion.

Based upon the available data, it cannot be evaluated whether manganese(II) sulphate is carcinogenic, but the evidence is not considered strong enough to fulfil the EU criteria for classification for carcinogenicity.

No human data regarding toxicity to reproduction following exposure to manganese(II) sulphate have been located. Studies in experimental animals indicate that manganese has the potential to cause reproductive and developmental effects when administered orally. Inhalation data concerning these effects are scarce and not definitive, although the manganese industry states that the REACH registration is being updated with a relevant study.

Based on the limited information available on endocrine effects of manganese, the potential of manganese to affect the endocrine system cannot be evaluated. However, given that manganese is an essential element in nutrition; endocrine effects are not likely at low/moderate exposure levels.

Human exposure and human health impacts

No thorough authoritative risk assessment of industrial applications of manganese(II) sulphate has been identified in this survey.

Given the identified evidence, there might be a significant occupational inhalation and eye exposure risk associated with handling manganese(II) sulphate powder/granulates as fertiliser or for feed applications. This risk seems to be particularly relevant to farmers who are not using personal protective equipment consistently.

Consumer exposure and exposure of the general population via the environment seems to be low. One exception might be consumer exposure to fertilisers granulates, which however seems to be rare or possibly non-existing.

This might also be the case for consumers handling fertiliser powder/granulates. Whether this use actually takes place is, however, uncertain.

Risks associated with exposure via other routes and from other products appear to be low.

Data gaps

There seems to be a discrepancy between the harmonised EU classification for manganese(II)sulphate and the knowledge related to eye irritation/eye damage. The manganese industry supports additional classification for eye damage.

Data on occupational exposure to manganese(II) sulphate are lacking.

Knowledge regarding consumer use of granulate fertilisers, which is qualitatively assessed to pose potential risk, is equivocal.

Data on the particle size of manganese(II) sulphate used in the formulation of fertilisers and as a constituent in feed, and on the droplet size of manganese containing fertilisers on spray/aerosol form, are lacking.

7. Information on alternatives

7.1 Alternatives to identified uses and applications

7.1.1 Alternatives to nutrients uses

As mentioned in Chapter 3, the majority of the manganese(II) sulphate consumption in the EU and in Denmark is for nutrients (including fertilisers). Here, the actual need is the manganese element itself, and therefore manganese(II) sulphate could be substituted for by other manganese salts. As outlined in Chapter 2, several sources of manganese can indeed be used for these applications.

From confidential dialogue with a Danish supplier, it appears that the main alternative for fertiliser applications is manganese nitrate, which according to self-classifications retrieved from the ECHA website should be classified in line with, or perhaps even more strictly, than manganese(II)sulphate.

In general, as "manganese" is simultaneously the desired nutrient and the toxic moiety, it makes little sense to substitute one manganese salt for the other.

For these nutrient uses, it therefore seems more relevant to consider alternative handling and application methods aiming at reducing the exposure/risk. The key route for human exposure seems to be via inhalation in occupational settings. Furthermore, it appears relevant to avoid eye contact given the suggested classification for eye damage.

Reducing inhalation and eye exposure in the working environment can be achieved by using personal protection devices (filter masks and eye protection) while handling the manganese(II)sulphate, such as when preparing the solution of manganese(II) sulphate to be applied to fields in agriculture or when mixing feeds. It might also be possible to supply the manganese(II) sulphate to the farmer as pellets rather than as powder/granulates, thereby reducing exposure.

If aerosol dispersion from the application of aqua solutions of manganese(II) sulphate on fields is a critical exposure route, this can possibly be reduced by applying the solution directly into the top soil (similarly to ammonium) instead of applying it as an aerosol as done currently. However, according to a Danish supplier, manganese(II) sulphate is often applied to the leaves of the crops. In this case, it might be possible to further target the aerosol application.

Another option, which according to a Danish supplier is often applied, is to use tractors with pressurized cabins.

7.1.2 Alternatives to siccatives/driers

Chabanne et al. (2004) identifies a number of manganese substances as drying agents/siccatives (used in paints/coatings and similar), which can substitute for cobalt siccatives:

- Manganese 2-ethylhexanoate (CAS-no. 13434-24-7) - Xi R38 [2]
- Manganese salt (type and CAS-no. confidential) – classification not known
- Manganese salt of C6-19 branched fatty acid and naphthenic acid (not further specified, CAS-no. confidential) – Xi R38
- Manganese dipropionate (CAS-no. 21129-18-0) – Xi R38

- Manganese (II) isooctanoate (CAS-no. 37449-19-7) – Xi R38
- Manganese isononate (CAS-no. 29826-51-5) – Xi R38.

Again, as they all contain manganese, the health benefits of using these as alternatives (rather than manganese(II) sulphate) may likely be minimal.

Depending on the specific polymers used in the paints, coatings or inks, it may be possible to use other, non-manganese, siccatives. The primary siccatives mainly consist of organo-metallic compounds of toxic or rare metals such as lead, cobalt, zinc and copper, which are generally considered to be more toxic than manganese-based siccatives. It should be noted that the choice of siccative is highly dependent on the polymers/oils used and the application of the paint/coating/ink.

7.1.3 Alternatives to other uses

As other uses constitute considerably lower volumes than applications for fertiliser and feed applications in the EU and seem to have no/minimal application in Denmark, alternatives to those uses have not been addressed in any further detail.

7.2 Summary and conclusions

For nutrient and fertiliser uses, the actual need is the manganese element itself, and therefore naturally manganese(II) sulphate could be substituted for by other manganese salts. However, as manganese is the toxic moiety, it makes little sense to substitute one manganese compound for the other.

It is therefore more relevant to consider alternative application methods aiming at reducing the exposure/risk, such as: i) using personal protection equipment (filter masks and eye protection), ii) supplying manganese(II) sulphate to the farmer as pellets rather than as powders/granulates, or iii) possibly by optimising how the manganese(II) sulphate fertiliser solution is supplied to the agricultural fields.

Alternatives to manganese siccatives ("driers") in paints, inks and coatings exist, but in many cases they include toxic metals.

Other minor uses of manganese(II) sulphate, which appear to be absent or rarely used in Denmark, have not been investigated further.

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Appendix 1: Abbreviation and acronyms

AF	Assessment Factor
ATSDR	Agency for Toxic Substances and Disease Registry (US)
BCF	Bioconcentration factor
BMDL	BenchMark Dose Level
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
CNS	Central Nervous System
CoRAP	Community Rolling Action Plan
CSIRO	Commonwealth Scientific and Industrial Research Organisation
CSR	Chemical Safety Report
DCE	Danish Centre for Environment and Energy
DEFRA	Department for Environment, Food and Rural Affairs (UK)
DNEL	Derived No-Effect Level
DTU	Danmarks Tekniske Universitet (Technical University of Denmark)
EASE	Estimation and Assessment of Substance Exposure
EC	Effect Concentration (or European Commission)
ECB	European Chemicals Bureau
ECHA	European Chemicals Agency
EFSA	European Food Safety Authority
EHC	Environmental Health Criteria
EINECS	European Inventory of Existing Commercial Substances
EMD	Electrolytic Manganese Dioxide
EPA	Environmental Protection Agency
EQS	Environmental Quality Standard
ESIS	European Chemical Substances Information System
EU	European Union
FSH	Follicle Stimulating Hormone
GEUS	Geological Survey for Denmark and Greenland
GRUMO	Groundwater Monitoring programme
HELCOM	The Baltic Marine Environment Protection Commission (Helsinki Commission)
IARC	International Agency for Research on Cancer
IPCS	International Programme on Chemical Safety
IRD	Integrated Respirable Dust
IRIS	Integrated Risk Information System
LC	Lethal Concentration
LD	Lethal Dose
LH	Luteinizing Hormone
LLNA	Local Lymph Node Assay
LOAEL	Lowest Observable Adverse Effect Level
LOUS	List of Undesirable Substances (of the Danish EPA)
MAL	Måleteknisk Arbejdshygiejnisk Luftbehov
MMAD	Mass Median Aerodynamic Diameter
MMT	Methylcyclopentadienyl Manganese Tricarbonyl
MRL	Minimal Risk Level

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
OEL	Occupational Exposure Limit
OSPAR	Convention for the Protection of the Marine Environment of the North-East Atlantic
PBPK	Physiologically-Based Pharmacokinetic (modelling)
PBT	Persistent, bioaccumulative and persistent
PEC	Predicted environmental concentration
PND	Postnatal Day
PNEC	Predicted no effect concentration
POD	Point of Departure
POPs	Persistent Organic Pollutants
PRTR	Pollutant Release and Transfer Register
RDA	Recommended Daily Allowance
RfC	Reference Concentration
RAR	Risk Assessment Report
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals (Regulation)
SVHC	Substance of Very High Concern
SPIN	Substances in Preparations In the Nordic countries (database)
STOT	Specific Target Organ Toxicity
STP	Sewage Treatment Plant
TDI	Tolerable Daily Intake
TEACH	Toxicity and Exposure Assessment for Children's Health
TG	Test Guideline
TWA	Time Weighted Average
UBA	Umweltbundesamt (Germany)
UNCLOS	United Nations Convention on the Law of the Sea
USA	United States of America
vBvP	Very bioaccumulative and very persistent
VECAP	The Voluntary Emissions Control Action Programme
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 Regulation⁵ and the CLP Regulation⁶ are the overarching pieces of EU chemicals legislation regulating industrial chemicals. The below will briefly summarise the REACH and CLP provi-

⁵ Regulation (EC) No 1907/2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)

⁶ 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 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 list⁷
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.

⁷ 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 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.

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 manganese(II) sulphate

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 Manganese(II)Sulphate, 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 mangan(II) sulfat

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 mangan(II)sulfat, internationalt og i Danmark, en beskrivelse af miljø- og sundhedseffekter af stofferne, udslip af skæbne, eksponering og forekomst i mennesker og miljø, viden om alternativer, eksisterende regulering, affaldsbehandling og igangværende aktiviteter under REACH.



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