Survey of copper(I)oxide, copper(II)sulphate and copper(I)chloride

Part of the LOUS Review

Environmental Project No. 1538, 2014
Title:
Survey of copper(I)oxide, copper(II)sulphate and copper(I)chloride

Authors:
Erik Hansen¹, Gitte Sørensen², Sonja Mikkelsen¹, Jesper Kjølholt¹, Frans Møller Christensen¹, Carsten Lassen¹, Ulf Kjellerup¹

¹ COWI A/S, Denmark
² Danish Technological Institute

Publisher:
Danish Environmental Protection Agency
Strandgade 29
DK-1401 Copenhagen K
Denmark
www.mst.dk

Year: 2014

ISBN no.: 978-87-93026-92-6

Disclaimer:
The Danish Environmental Protection Agency will, when opportunity offers, publish reports and contributions relating to environmental research and development projects financed via the Danish EPA. Please note that publication does not signify that the contents of the reports necessarily reflect the views of the Danish EPA. The reports are, however, published because the Danish EPA finds that the studies represent a valuable contribution to the debate on environmental policy in Denmark.

While the information provided in this report is believed to be accurate, the Danish Environmental Protection Agency disclaims any responsibility for possible inaccuracies or omissions and consequences that may flow from them. Neither the Danish Environmental Protection Agency nor COWI or any individual involved in the preparation of this publication shall be liable for any injury, loss, damage or prejudice of any kind that may be caused by persons who have acted according to their understanding of the information contained in this publication.

May be quoted provided the source is acknowledged.
Content

Preface .................................................................................................................. 5

Summary and conclusion ...................................................................................... 7

Sammenfatning og konklusion ........................................................................... 13

1. Introduction to the substances ...................................................................... 19
   1.1 Definition of the substances ................................................................... 19
   1.2 Physical and chemical properties ............................................................ 20

2. Regulatory framework ..................................................................................... 23
   2.1 EU and Danish legislation ..................................................................... 23
      2.1.1 Biocidal products ........................................................................... 23
      2.1.2 Other existing legislation ............................................................... 25
   2.2 Classification and labelling .................................................................... 33
   2.3 REACH ............................................................................................... 34
   2.4 International agreements ...................................................................... 35
   2.5 Other relevant national regulation on copper(I)oxide, copper(II)sulphates and
      copper(I)chloride .................................................................................. 36
   2.6 Eco-labels ............................................................................................ 37
   2.7 Summary ............................................................................................... 37

3. Manufacture and uses ..................................................................................... 39
   3.1 Manufacturing ....................................................................................... 39
      3.1.1 Manufacturing processes .................................................................. 39
      3.1.2 Manufacturing sites ........................................................................ 39
      3.1.3 Manufacturing and consumption volumes - internationally .............. 40
   3.2 Import and export .................................................................................. 42
      3.2.1 Import and export of the copper compounds in question in Denmark .. 42
      3.2.2 Import and export of the copper compounds in question in EU .......... 42
   3.3 Use ....................................................................................................... 43
      3.3.1 Registered uses by ECHA ............................................................... 43
      3.3.2 Registrations by the Danish Product Register ................................. 44
      3.3.3 Substance flow analysis .................................................................. 45
      3.3.4 Updated assessment of consumption .............................................. 46
   3.4 Historical trends in use .......................................................................... 47
   3.5 Summary and conclusions ..................................................................... 48

4. Waste management ......................................................................................... 49
   4.1 Waste from manufacture and use of copper(I)oxide, copper(II)sulphates and
       copper(I)chloride etc. ............................................................................ 49
   4.2 Waste products from the use of copper(I)oxide, copper(II)sulphate and
       copper(I)chloride in mixtures and articles ............................................ 49
   4.3 Releases of copper(I)oxide, copper(II)sulphate and copper(I)chloride from waste
       disposal .................................................................................................. 50
   4.4 Summary and conclusions .................................................................... 51

5. Environmental effects and exposure ............................................................... 53
   5.1 Environmental Hazard .......................................................................... 53
Preface

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 and agricultural context in large quantities in Denmark, i.e. over 100 tons per year, are included in the list.

Over the period 2012-2015 all 40 substances and substance groups on LOUS will be surveyed. The surveys include collection of available information on the use and occurrence of the substances, internationally and in Denmark, and information on environmental and health effects, alternatives to the substances, existing regulation, monitoring and exposure, and information regarding ongoing 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 copper(I)oxide, copper(II)sulphate and copper(I)chloride. These substances were included in the 1998 list in LOUS and have remained on the list since that time. Attention should be paid to the fact that copper(II)sulphate actually covers several compounds with separate CAS numbers inclusive of the anhydrate (CAS no. 7758-98-7), the monohydrate (CAS No. 10257-69-1), and the pentahydrate (CAS No. 7758-99-8). The survey was originally designed to cover only CAS No. 7758-98-7. As copper(II)sulphate pentahydrate is the commercially dominant form of copper(II)sulphate, while the anhydrate has little commercial use, it has been specifically decided to include copper(II)sulphate pentahydrate in the survey. As a practical solution, the choice was made to include all relevant copper(II)sulphate compounds in the study. In the report the term copper(II)sulphates is used to cover all relevant copper(II)sulphate compounds.

As copper oxides and copper sulphates historically have been used for wood preservation and the actual compounds used for this purpose are not well defined (it is often uncertain whether copper(I)oxide or copper(II)oxide is being used), it has furthermore been decided to briefly include wood preservation and the major copper compounds used for this application in the review, in the sections on uses and waste management.

The entry in LOUS for copper(I)oxide, copper(II)sulphate and copper(I)chloride is "certain copper compounds". The reason for including this group of substances is that it covers those originally classified as R50/53 (very toxic to aquatic organisms; may cause long-term adverse effects in the aquatic environment). According to the CLP-regulation, the substances are classified as Aquatic Acute 1 and Aquatic Chronic 1, corresponding to very toxic to aquatic life with long lasting effects (H400/H410). The substances therefore have properties of concern with regard to the ‘List of hazardous substances’.
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 Danish Technological Institute from March to October 2013. The work has been followed by an advisory group consisting of:

- Annette L. Gondolf, Danish Environmental Protection Agency (chairperson)
- Christina Ihlemann, Danish Environmental Protection Agency
- Thilde Fruegaard Astrup, Danish Environmental Protection Agency
- Søren Wium-Andersen, Danish Society for Nature Conservation
- Anette Harbo Dahl, Confederation of Danish Industries
- Morten Brozek, Danish Nature Agency
- Birgitte Broesbol-Jensen, Danish Veterinary and Food Administration
- Niels J. Kjeldsen, Danish Agriculture and Food Council
- Erik Hansen, COWI.

Please note that the report does not necessarily reflect the views of the members of the advisory group.

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 data search included (but was not limited to) the following:

- 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 EU harmonised classification (CLP) from the C&L inventory database on ECHAs website;
- Data on ecolabels from the Danish Ecolabel Secretariat (Nordic Swan and EU Flower);
- Pre-registered and registered substances from ECHA’s website;
- Production and external trade statistics from Eurostat’s databases (Prodcom and Comext);
- 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 CIRCABC on active substances covered by the EU review process under the Biocidal Products Directive (98/8/EC). This Directive is by 1 September 2013 replaced by the EU Biocidal Products Regulation (EU) No 528/2012;
- Monitoring data from the National Centre for Environment and Energy (DCE), the Danish Veterinary and Food Administration and the European Food Safety Authority (EFSA);
- Reports, memorandums, etc. from the Danish EPA and other authorities in Denmark, and
- 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 Naturvårdsverket).

As well, direct enquiries were made to Danish and European trade organisations.
Summary and conclusion

Copper(I)oxide, copper(II)sulphate and copper(I)chloride are all subject to EU harmonised classification. They are classified as Aquatic Acute 1/H400 (very toxic to aquatic life) and Aquatic Chronic 1/H410 (very toxic to aquatic life with long lasting effects). They are also classified for Acute Tox 4/H302 (harmful if swallowed). Copper(II)sulphate is furthermore classified for Skin irrit. 2/H315 (Causes skin irritation) and Eye irrit. 2/H319 (causes serious eye irritation). Neither of these compounds, however, are considered as PBT or vPvB substances.

Uses and consumption
The total Danish consumption of copper(I)oxide, copper(II)sulphates and copper(I)chloride is estimated at 490-531 tons copper per year in 2012. This figure includes use of copper(II)sulphate pentahydrate as feed additive (365 tons), followed by the use of copper(I)oxide for antifouling (46-85 tons) and the use of copper(II)sulphates in fertilizers (32 tons). Consumption of cupricarbonate for pressure preservation of wood (47 tons) is also included in the figure, but anticipated minor applications has not been quantified apart from the use of copper(II)sulphates for plating (<2 tons).

The general trend in recent years for the use of copper(I)oxide is a clear decline in consumption. The consumption of copper(I)oxide for antifouling has, however, increased from less than 27-40 tons/year in 1992 to 46-85 tons/year in 2012. No significant development regarding the consumption of copper(II)sulphate as feed additive from 1992 to 2012 is observed. The consumption has been rather steady in the range of 300-400 tons/year. It may be noted that the import of copper(II)sulphates, raised by 26% from 2312 tons/year (average for 2007-2011) to 2912 tons/year in 2012.

It is relevant to note that copper(II)sulphates cover several compounds, of which copper(II)sulphate pentahydrate is the dominant compound being manufactured and used. Copper(II)sulphate monohydrate has limited use compared with pentahydrate, while copper(II)sulphate anhydride has little commercial use.

Human health
The copper compounds in question do not generally represent a major human health concern and the use of copper products is generally safe for the health of European citizens. Risk of occupational exposure is possible at some industrial sites. No specific exposure data related to occupational conditions in Denmark or human biomonitoring data have been identified in order to allow an evaluation of the actual occupational exposure or the indirect copper exposure (via food, air etc.) of the general population in Denmark. Based on the main identified uses of copper(II)sulphates as feed additive, the use of copper(I)oxide for antifouling and the use of copper(II)sulphates in fertilizers are the main uses in Denmark. None of these uses are expected to result in risks that are significantly different from the EU scenarios.

General systemic toxicity (liver effects) following repeated oral exposure, gastrointestinal symptoms following acute oral exposure and respiratory effects from acute inhalation exposure represent the most significant endpoints in relation to human health for copper(I)oxide, copper(II)sulphate, copper(II)sulphate pentahydrate, and copper(I)chloride. The oral and the inhalation route repre-
sent the most significant routes of exposure. Adverse effects are seen both in relation to copper deficiencies and excess copper; copper status in the cells is regulated by mechanisms assisting to protect the cells against accumulation of copper.

According to WHO, the copper intakes from food in the Scandinavian countries are in the range of 1.0–2.0 mg/day for adults, 2 mg/day for lactovegetarians and 3.5 mg/day for vegans based on references from the 1990’s. The Scientific Committee on Food (SCF) has in 2003 defined a tolerable upper intake level (UL) of 5 mg/day for adults and 1 mg/day for toddlers (1-3 years).

Environmental impacts – feed additives
The use of copper(II)sulphate pentahydrate as feed additive, in particular for piglets, together with other sources results in increasing content of copper in Danish agricultural soils. An accumulation of copper in the top soil layer (ploughing layer) has been going on at least since the 1980’s. The current average rate of accumulation has been roughly estimated at about 0.5% yearly. The supply of copper to Danish agricultural soils is, however, not evenly distributed and areas exposed to supply of manure from pigs (piglets in particular) will be exposed to a supply of copper significantly exceeding the average. It is estimated that the soil concentration of copper for areas supplied with manure from piglets may reach the Danish eco-toxicological soil quality criterion for copper of 30 mg/kg in less than 100 years.

Existing studies have not confirmed the hypothesis that the "Funen roe deer disease" was caused by copper supplied to agricultural soils by application of manure. It was, however, concluded from the studies that further and more extensive investigations are needed, as the quantities of copper supplied to agricultural soils combined with the sensitivity of certain wildlife species are causes for concern.

EU model calculations have shown potential risks to soil organisms as a result of application of piglet manure. Potential environmental concern is also related to the contamination of sediment owing to drainage and the run-off of copper to surface water. Calculations have shown that the systems most vulnerable in this context were acid sandy soils, e.g. present in Denmark. According to the European Food Safety Authority (EFSA), final conclusions must await further model validation and additional data.

A special concern in relation to copper is the possible release of copper-resistant bacteria in the environment, primarily related to the spreading of copper-containing (pig) manure on agricultural soils. It is reported that data confirms a correlation between the development of resistance to copper and resistance to various antibiotics. At present EFSA finds that the available data does not allow an estimate of the practical relevance of these findings.

Environmental impacts – antifouling
No recent studies on generation or disposal of residues from antifouling activities in Denmark are available. However, emission factors quoted from the EU Emission Scenario Document clearly show that internationally application of antifouling paint and removal of old paint are considered activities responsible for significant losses of copper compounds to the environment.

Measurements available of the content of copper in the marine environments in Denmark are also old, but show that concentrations of copper measured in, and in the vicinity of, harbours are at the same level or higher than concentrations in which effects of copper have been measured. In other cases the concentrations at which effects of copper are measured are generally higher than the background concentrations observed for copper in the marine environment in Denmark.

An emission of copper to the water environment based on the use of antifouling paint also takes place, but cannot be quantified. As part of the ongoing EU assessment of copper(I)oxide as active
substance within product type 21 (Antifouling) under the Biocidal Products Regulation a comprehensive Risk Assessment incorporating the newest knowledge available will be prepared. The assessment is anticipated to be available relatively soon.

**Waste management**

In Denmark, waste is generated from use of mixtures and articles containing copper compounds and from used products being discarded as waste. Waste from manufacture of copper compounds and mixtures and articles based on copper(I)oxide, copper(II)sulphates and copper(I)chloride is not generated in Denmark.

The concentration of copper compounds in some products as e.g. antifouling paint is so high that residues qualify for characterisation as hazardous waste. Waste products classified as hazardous waste must be collected and treated as such. Emission factors quoted from the EU Emission Scenario Document for Antifouling Products clearly show that internationally application of antifouling paint and removal of old paint are considered activities responsible for significant losses of copper compounds to the environment if risk mitigation measures are not used.

Waste products from wood pressure preservation are limited to contaminated sludge. Shaping of pressure preserved wood dust etc. containing copper will end up in soil and solid waste. In Denmark, old pressure preserved wood being disposed of may be directed to landfill or exported for treatment abroad, as no facilities approved for treatment of pressure preserved wood exist in this country.

**Alternatives**

The assessment of alternatives is focused on antifouling and feed additives for piglets.

The information presented on alternatives is focused on antifouling and feed additives for piglets. Regarding alternatives to copper(I)oxide used in antifouling paint, a number of substances are currently being reviewed under the EU Biocidal Products Regulation together with copper(I)oxide for use in antifouling products. The outcome of this review process determines which biocidal substances are allowed for use in the EU in antifouling products, and thereby which substances may be approved for products in Denmark. Of the substances being reviewed only copper thiocyanate, copper, zineb, DCOIT, tralopyril and medetomidine has the same target organisms (hard fouling – barnacles, mussels) as copper(I)oxide and may be considered as biocidal alternatives to copper(I)oxide.

Significant efforts have been invested in investigating and developing alternatives to copper based antifouling paint in Denmark. The alternatives investigated include less toxic antifouling paint as well as other bottom coatings and several mechanical solutions inclusive of washing systems, algae cloths and boat lifts.

The best non-biocidal alternative is a siliconized epoxy coating that gives a very smooth and slippery surface that can prevent foulants from settling permanently on the surface. The solution is commercially available and applicable on ships or boats that sail with a high speed (>15 knots). For slower boats (<15 knots) this solution is not feasible, as the lower sailing speed allows the foulants to settle.

Promising results has been obtained for anti-fouling paint using silicate based encapsulation technologies with a minimised amount of the active compound/biocide and without substances as zinc oxide and copper(I)oxide. Mechanical solutions as washing systems etc. are not suitable for the majority of pleasure boats in Denmark.
American research shows that products based on silicon and fluoropolymers are also available for pleasure boats operated at low speed besides having costs comparable to copper based products. It is, however, not known with certainty whether these results are applicable to boats operated in Danish waters.

Regarding alternatives to the use of copper(II)sulphate pentahydrate as feed additives for piglets, the basic alternative is to postpone weaning to a time where no use of copper as feed additive would be needed in order to prevent diarrhoea and other relevant effects. The drawback of this alternative will be higher production costs. Other alternatives available (partly substitution of copper with zinc or organic acids) will reduce the consumption of copper, but no data on the size of the reduction to be obtained is available.

**Regulation**

Regulation specifically addressing copper(I)oxide, copper(II)sulphates and copper(I)chloride is limited to regulation of biocidal products, and regulation of feed and food as copper(II)sulphate pentahydrate is allowed as an additive to feed and food. Other relevant regulation is focused on copper as an element and not on specific copper compounds.

Currently the only applications of copper(I)oxide, copper(II)sulphates and copper(I)chloride allowed in Denmark as biocides are the uses of copper(II)sulphate pentahydrate within the product type "Private area and public health area disinfectants and other biocidal products" and copper(I)oxide within the product type "Antifouling products". For both applications the use of copper compounds is still subject to an EU review process.

In Denmark, special restrictions on the use of copper for antifouling paint exist. These restrictions address pleasure boats only. No specific Danish restrictions exist with respect to commercial ships and boats. Based on the EU rules, Risk Assessment of antifouling paint for pleasure boats and commercial ships will take place in the years to come, when the ongoing review process for product type 21 under the Biocidal Products Regulation has been finished.

Regarding supply of copper to agricultural soils, restrictions exist for the content in waste products (incl. sewage sludge), but not for content in manure and other residues from domestic animals, despite the fact that residues from domestic animals are a far more important source for supply of copper to agricultural soils than sewage sludge and similar waste products.

**Data gaps**

Important data gaps include:

- Detailed up to date information on copper(I)oxide, copper(II)sulphates and copper(I)chloride and consumption figures by application areas in Denmark for major applications.

- Up to date figures on waste generation and disposal for major applications.

- Up to date figures on emission of copper compounds to the environment for major applications.

- Up to date figures on distribution of copper to agricultural soils with manure and the content and accumulation of copper in Danish agricultural soils, focused on investigating the average as well as the variation in supply, content and accumulation. The figures should preferably include all relevant sources of supply and removal of copper from agricultural soils, including atmospheric deposition, sewage sludge, loss of crops, infiltration etc.

- Potential impacts of present and continued supply of copper with manure and other sources to Danish agricultural soils and relevant remedial actions.
• Up to date figures on the content of copper in Danish harbours and other marine areas (sediments, water phase etc.).

• Actual occupational exposure levels from the uses applied in Denmark as well as bio-monitoring data, providing an evaluation of indirect copper exposure of the general population.

No research is suggested related to release of copper-resistant bacteria in the environment, as this issue is assumed to be addressed in a Danish research project at Copenhagen University.
Sammenfatning og konklusion

Kobber(I)oxid, kobber(II)sulfat og kobber(I)klorid har alle en EU-harmoniseret klassificering. De er klassificeret som Aquatic Acute 1/H400 (meget giftig for vandlevende organiser) og Aquatic Chronic 1/H410 (meget giftig for vandlevende organiser og med langvarige virkninger). De er tillige klassificeret for Acute Tox 4/H302 (farlig ved indtagelse). Herudover er kobber(II)sulfat klassificeret for Skin irrit.2/H315 (forårsager hudirritation) og Eye irrit. 2/H319 (forårsager alvorlig øjenirritation). Ingen af stofferne betragtes som PBT- eller vPvB-forbindelser.

Anvendelser og forbrug

Det totale danske forbrug af kobber(I)oxid, kobber(II)sulfater og kobber(I)klorid er estimeret til 490-531 tons kobber årligt for 2012. Dette tal inkluderer brugen af kobber(II)sulfat pentahydrat som fodertilskæTNingsstof (365 tons) fulgt af brugen af kobber(I)oxid til antifouling (46-85 tons) og brugen af kobber(II)sulfater i kunstgødning (32 tons). Forbruget af cupricarbonat til trykimprægnering af træ (47 tons) er også inkluderet, mens forventede mindre anvendelser ikke er kvantificeret med undtagelse af kobber(II)sulfater til overfladebehandling (<2 tons).


Det er relevant at bemærke, at kobber(II)sulfater omfatter flere forbindelser. Kobber(II)sulfat pentahydrat er den dominerende forbindelse, som fremstilles og anvendes. Kobber(II)sulfat monohydrat anvendes i begrænset omfang sammenlignet med kobber(II)sulfat pentahydrat, mens kobber(II)sulfat anhydrid (indeholder ikke vand) kun har beskeden kommersiel anvendelse.

Sundhed

De pågældende kobberforbindelser giver som helhed ikke anledning til væsentlig bekymring for menneskers sundhed og brugen af kobber anses generelt for at være sikker for borgere i Europa. Risiko for arbejdsmiljømæssig eksponering kan dog forekomme på nogle industrianslæg. Der er ikke fundet specifikke data til belysning af den arbejdsmiljømæssige eksponering og heller ikke humane biomonitoringsdata, der kan muliggøre evaluering af den indirekte kobbereksponering (via føden, luft etc.) af den danske befolkning.

Generel systemisk toksicitet (levereffekter) efter gentagen oral eksponering, symptomer på effekter i mave-tarmkanalen efter akut oral eksponering og effekter på luftvejene som følge af akut eksponering ved indånding repræsenterer de væsentligste effekter på menneskers sundhed ved udsættelse for kobber(I)oxid, kobber(II)sulfat, kobber(II)sulfat pentahydrat og kobber(I)klorid. Eksponering via indåndelse og indånding udgør de væsentligste eksponeringsveje. Bivirkninger er set både i forhold til kobbermangel og overskydende kobber i cellerne, hvor kobberniveauet er regulær af mekanismer, der hjælper til at beskytte cellerne mod ophobning af kobber.

I folge WHO er indtaget af kobber med føden i de Skandinaviske lande i størrelsen 1.0–2.0 mg/dag for voksne, 2 mg/dag for lactovegetarer og 3.5 mg/dag for veganere. Dette overslag er baseret på
data fra 1990'erne. EU's Videnskabelige komite for fødevarer (SCF) har i 2003 defineret et tolerable nivå for indtag (UL) på 5 mg/dag for voksne og 1 mg/dag for småbørn (1-3 år).

**Miljøpåvirkninger – fodertilsætnings**

Brugen af kobber(I)sulfater i foder og særligt i foder til smågrise betyder sammen med andre kilder til tilførsel af kobber til landbrugsjorden, at indholdet af kobber i dansk landbrugsjord øges. Akkumulering af kobber i pløjelaget har fundet sted som minimum siden 1980'erne. Den nuværende gennemsnitlige akkumuleringrate er groft skønnet til ca. 0,5% årligt. Tilførslen af kobber er dog ikke jævn fordelt. Arealer hvor der tilføres gylle fra grise og særligt fra smågrise vil være udsat for en tilførsel, som ligger væsentligt over den gennemsnitlige tilførsel. Det er estimeret at koncentrationen af kobber i jord, hvor der tilføres gylle fra smågrise kan nå op på 30 mg/kg (det danske økotoksikologiske jordkvalitetskriterie) på mindre end 100 år.

Eksisterende undersøgelser har ikke bekræftet den hypotese, at kobber tilført landbrugsjorden med gylle er årsag til den "Fynske rådyrsyge". Ud fra disse undersøgelser er dog konkluderet, at der er behov for yderligere og mere omfattede undersøgelser af spørgsmålet, da de mængder af kobber, der tilføres landbrugsjorden kombineret med følsomheden hos visse typer vildt giver anledning til bekymring.


En særlig bekymring knyttet til kobber er den mulige spredning af kobberresistente bakterier i miljøet primært i forbindelse med spredningen af kobberholdig grise-gylle på landbrugsjorden. Det er rapporteret, at data bekræfter et sammenhæng mellem udviklingen af bakterieresistens overfor kobber. Bag grundssituationen er det bemærkelsesværdigt, at miljøet i Danmark er generelt lavere end de koncentrationer, hvor der kan observeres effekter af kobber. Baggrundskoncentrationer for kobber observeret i det marine miljø i Danmark er generelt lavere end de koncentrationer, hvor der kan observeres effekter af kobber.

Emission af kobber til vandmiljøet ved brug af antifouling maler også sted, men kan ikke kvantificeres. Som beskrevet i EU-vurderingen af kobber(I)oxid som aktivstof indenfor produktgruppe 21 (antifouling) under EU’s Biocid Regulering vil der blive udarbejdet en omfattende risikovurdering, der medtager den nyeste viden på området. Denne vurdering forventes at ligge klar indenfor en kortere tidshorisont.

**Miljøpåvirkninger – antifouling**

Ingen nylige undersøgelser om generering og bortskaffelse af affald fra brug af antifouling maler (også kaldet bundmaling) i Danmark er tilgængelige. I EU’s “Emission Scenario Document” for antifouling er imidlertid præsenteret emissionsfaktorer, der tydeligt viser, at internationalt betragtes påføring af antifouling maler og fjernelse af gammel maler som aktiviteter, der er ansvarlige for et væsentligt tab af kobber til miljøet.

De tilgængelige målinger af kobber i det marine miljø i Danmark er også gamle, men viser, at koncentrationen af kobber i øget indehold af havne er på samme niveau eller højere end de koncentrationer hvor der er observeret effekter af kobber. Baggrundskoncentrationer for kobber observeret i det marine miljø i Danmark er generelt lavere end de koncentrationer, hvor der kan observeres effekter af kobber.

Affaldsbehandling
I Danmark genereres affald fra brug af produkter som indeholder kobber og fra kasserede produkter, der bortskaffes som affald. Produktion af kobberforbindelser og produkter baseret på kobber(I)oxid, kobber(II)sulfater og kobber(I)klorid finder ikke sted i Danmark og der opstår derfor ikke affald fra disse former for produktion.


Affaldsprodukter fra fremstilling af trykimprægneret træ er begravet til forurenent slam. Ved tildannelse af trykimprægneret træ opstår træstøv etc. som ender på jorden eller i affald. Kasseret trykimprægneret træ bortskaffes som affald i Danmark vil blive tilført lossepladser eller eksporter til udland, da der ikke findes anlæg, der er godkendt til behandling af trykimprægneret træ i Danmark.

Alternativer
Vurderingen af alternativer er fokuseret på antifouling og fodertilsætning til smågrise.

Med hensyn til alternativer til kobber(I)oxid som antifouling maling er en række aktiverstoffer for tiden ved at blive vurderet under EU’s Biocidforordning sammen med kobber(I)oxid til anvendelse i antifouling produkter. Resultatet af denne EU-vurderingsproces vil bestemme hvilke biocid aktiverstoffer, der er tilladt at bruge til antifouling på EU-plan og dermed hvilke biocider, der kan blive godkendt i produkter i Danmark. Blandt de aktiverstoffer, som vurderes, er det kun biociderne kobberthiocyanat, metallisk kobber zineb, DCOIT, tralopyril og medetomidine, som er effektive overfor de samme organismer (hårde organismer - muslinger, rurer og langhalse) som kobber(I)oxid og kan overvejes som alternativer til kobber(I)oxid.

I Danmark er investeret en betydelig indsats i at undersøge og udvikle alternative til kobberbaserede antifouling maling. De undersøgte alternative omfatter mindre giftig maling samt anden form for bundbehandling og flere mekaniske løsninger herunder vaskesystemer, algeduge og hådlifte.

Det bedste ikke-biocid alternativ er en silikone-epoxy beklædning, som giver en meget glat overflade, der kan forhindre begroning i at fastgøre sig permanent til overfladen. Denne løsning er kommercielt tilgængelig og kan anvendes på skibe og bade, der sejler med høj hastighed (>15 knob). For langsomme både (<15 knob) er løsningen ikke velegnet, da den lave sejhlastighed gør det muligt for begroning at sætte sig fast.

Loven resultater er opnået for maling, hvor der bruges silikatbaserede indkapslingsteknologier med mindre stoffer som aktive biocider uden brug af stoffer som zink oxid and kobber(I)oxid. Mekaniske løsninger som vaskesystemer etc. er ikke egnet for hovedparten af lystbåde i Danmark.

Amerikanske undersøgelser viser, at produkter baseret på silikone og fluoropolymerer er til rådighed også for lystbåde, der sejler ved lave hastigheder foruden at omkostningerne svarer til kobberholdige produkter. Det vides dog ikke med sikkerhed, om disse resultater er brugbare også for både i danske farvande.

Med hensyn til brugen af kobber(II)sulfat pentahydrat som fodertilsætningsstof for smågrise er et nærliggende alternativ at udskyde fravænning af smågrise fra modermælk til et tidspunkt, hvor der ikke er behov for kobber som fodertilskud for at forebygge diarre og andre effekter. Ulempen ved...
dette alternativ er højere produktionsomkostninger. Andre tilgængelige alternativer (delvis substitution af kobber med zink eller organiske syrer) vil reducere forbruget af kobber, men der er ingen oplysninger om størrelsen af den reduktion af kobberforbruget, der kan opnås.

Regulering
Regulering som specifikt er rettet mod kobber(I)oxid, kobber(II)sulfater og kobber(I)klorid er begrænset til regulering af biocider samt til regulering af foder og fødevarer, idet kobber(II)sulfat pentahydrat er tilladt som tilægning til foder og fødevarer. Den øvrige relevante regulering er fokuseret på kobber som grundstof og ikke på særlige kobber-forbindelser.

I dag er kobber(I)oxid, kobber(II)sulfater og kobber(I)klorid kun tilladt som biocid i Danmark i form af kobber(II)sulfat pentahydrat i produkttype 2: ”Desinfektionsmidler til privat brug og brug i det offentlige sundhedsvæsen og andre biocidholdige produkter ” samt i form af kobber(I)oxid i produkttype 21: ”Antifoulingsmidler”. For begge anvendelser er brugen af kobber stadig genstand for en vurdering på EU-plan under biocid-reguleringen.

I Danmark er der indført særlige restriktioner for frigivelsen af kobber fra antifouling maling (også kaldet bundmaling) til vandmiljøet. Disse restriktioner er rettet mod lystfartøjer, der betegnes som fritidsbåde i den gældende bundmalingsbekendtgørelse. Der er ingen særlige danske restriktioner med hensyn til de kommercielle skibe. På baggrund af EU-reglerne vil der indenfor de kommende år ske en risikovurdering af brugen af bundmalingsprodukter på både lystfartøjer og kommercielle skibe.

Hvad angår tilførsel af kobber til landbrugsjorden er der restriktioner for tilførslen med affaldsprodukter (inkl. spildevandsslam), men ikke for forsyning med gylle og affald fra husdyr på trods af, at affaldsprodukter fra husdyr er en langt vigtigere kilder til tilførsel af kobber til landbrugsjorden end spildevandsslam og tilsavarende affaldsprodukter.

Manglende data
I forbindelse med denne undersøgelse er registreret følgende mangler på data:

- Detaljeret ajourført viden om anvendelsen af kobber(I)oxid, kobber(II)sulfater og kobber(I)klorid og omfanget af forbruget fordelt efter anvendelser i Danmark for hovedanvendelser.
- Ajourført viden om affaldsgenerering og bortskaffelse for hovedanvendelser.
- Ajourført viden om emissionen af kobber(I)oxid, kobber(II)sulfater og kobber(I)klorid til omgivelserne for hovedanvendelser.
- Ajourført viden om tilførslen af kobber til landbrugsjorden med gylle og andre kilder, samt viden om indholdet og akkumuleringen af kobber i dansk landbrugsjord rettet mod at bestemme gennemsnit såvel som variation hvad angår tilførsler, indhold og akkumulering. Den udviklede viden bør om muligt dække alle relevante kilder til tilførsel og fjernelse af kobber fra landbrugsjorden inklusive atmosfærisk deposition, spildevandsslam, tab af afgrøder, nedsivning etc.
- De mulige miljøpåvirkninger fra den nuværende og fortsatte tilførsel af kobber med gylle og andre kilder til dansk landbrugsjord og relevante afhjælpningsforanstaltninger.
- Ajourført viden om indholdet af kobber i danske havne og andre marine områder (sedimenter, vandfase etc.).
• Data for aktuel eksponering i arbejdsmiljøet i Danmark samt bio-monitoring data, der angiver den indirekte kobberbelastning af befolkningen i Danmark.

Der er ikke foreslået indsats rettet mod frigivelsen af kobber resitente bakterier i omgivelserne, da dette emne forventes at være genstand for forskning under et dansk forskningsprojekt ved Københavns Universitet.
1. Introduction to the substances

1.1 Definition of the substances

The substances copper(I)oxide, copper(II)sulphates inclusive of copper(II)sulphate pentahydrate and copper(I)chloride are chemical compounds. Copper(II)sulphates inclusive of copper(II)sulphate pentahydrate and copper(I)chloride are more precisely characterised as metal salts. Basic characteristics are presented in Table 1 below.

<table>
<thead>
<tr>
<th>TABLE 1</th>
<th>NAME AND OTHER IDENTIFIERS OF THE SUBSTANCES IN QUESTION</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Copper(I)oxide</td>
</tr>
<tr>
<td>EC number</td>
<td>215-270-7</td>
</tr>
<tr>
<td>CAS number</td>
<td>1317-39-1</td>
</tr>
<tr>
<td>Synonyms</td>
<td>Dicopper oxide, Copper bis oxide Cuprous oxide, Brown copper oxide</td>
</tr>
<tr>
<td>Molecular formula</td>
<td>Cu$_2$O</td>
</tr>
<tr>
<td>Molecular weight range</td>
<td>143.1</td>
</tr>
</tbody>
</table>

*1. Besides data on copper(II)sulphate (CuSO$_4$, CAS No. 7758-98-7), data on copper(II)sulphate, monohydrate (CuSO$_4$·H$_2$O, 10257-69-1) and copper(II)sulphate pentahydrate (CuSO$_4$·5(H$_2$O), CAS No. 7758-99-8) is also presented.
### 1.2 Physical and chemical properties

Basic physical and chemical properties are presented in Table 2 below.

<table>
<thead>
<tr>
<th>Property</th>
<th>Copper(I)oxide</th>
<th>Copper (II) sulphates *2</th>
<th>Copper(I) chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Physical state</strong></td>
<td>Opaque solid in the form of a fine, easily compactable powder, orange in colour and odourless</td>
<td>Copper sulphate is a white-green, odourless, amorphous powder or crystalline solid. Copper sulphate pentahydrate is a blue, odourless, triclinic crystalline solid</td>
<td>White crystalline odourless powder or as cubic crystals</td>
</tr>
<tr>
<td><strong>Melting/freezing point</strong></td>
<td>&gt;400°C at 101.72 kPa</td>
<td>CuSO₄: 560°C (decomposition) CuSO₄, pentahydrate: 110°C (decomposition)</td>
<td>423°C</td>
</tr>
<tr>
<td><strong>Freezing point</strong></td>
<td>&gt;400°C at 101.72 kPa</td>
<td>CuSO₄: 560°C (decomposition) CuSO₄, pentahydrate: 110°C (decomposition)</td>
<td>423°C</td>
</tr>
<tr>
<td><strong>Boiling point</strong></td>
<td>n.d. *3</td>
<td>CuSO₄: 560°C (decomposition) CuSO₄, pentahydrate: 110°C (decomposition)</td>
<td>1490°C</td>
</tr>
<tr>
<td><strong>Relative density</strong></td>
<td>5.87 g/cm³</td>
<td>CuSO₄: 3.6 g/cm³ CuSO₄, pentahydrate: 2.286 g/cm³</td>
<td>4.14 g/cm³</td>
</tr>
<tr>
<td><strong>Vapour pressure</strong></td>
<td>n.d. *3</td>
<td>Negligible volatility at environmentally relevant temperatures.</td>
<td>Negligible volatility at environmentally relevant temperatures.</td>
</tr>
<tr>
<td><strong>Surface tension</strong></td>
<td>n.d.</td>
<td>Surface tension is not applicable to inorganic salts</td>
<td>Surface tension is not applicable to inorganic salts</td>
</tr>
<tr>
<td><strong>Water solubility (mg/L)</strong></td>
<td>0.639 mg/l at pHs 6.5 – 6.6; 20°C.</td>
<td>CuSO₄, pentahydrate: 220 g/lit. at 25°C.</td>
<td>47 mg/l at 20°C</td>
</tr>
</tbody>
</table>

n.d.: No data.

*1 Based on ECHA registrations [ECHA, 2013].

*2 Copper(II)sulphates includes copper(II)sulphate, monohydrate as well as copper(II)sulphate pentahydrate.

*3 It is not possible to determine a vapour pressure due to the high melting point (and hence high boiling point) of cuprous oxide [ECHA, 2013]. ECI [2008] informs that the vapour pressure is negligible.
*4 It is generally considered that the determination of octanol/water partition coefficients for copper from sparingly soluble compounds is impractical for technical reasons [ECHA, 2013]. ECI [2008] informs that the partition coefficient (Log Kow) is not available.

*5 In the ECHA database on registered substances is for copper sulphate noted [ECHA, 2013]: “The octanol:water partition coefficient, Pow, is defined as the ratio of the equilibrium concentrations of a dissolved substance in each of the phases in a two phase system consisting of octanol and water. It is usually expressed on a log scale. It is a key parameter in studies of the environmental fate of organic pesticides, indicating the potential for bioaccumulation and soil absorption. However, the mechanisms of absorption of Cu²⁺ into organic matter and living cells are understood to be different from those traditionally attributed to carbon-based pesticides and the parameter therefore has little relevance to ionic copper. The parameter is therefore not considered to be relevant to copper(II) sulphate pentahydrate”.

*6 No explanation has been stated by ECHA [2013]. According to OECD [2005], the partition coefficient is not applicable as copper(I)chloride is an inorganic salt.
Survey of copper(I) oxide, copper(II) sulphates and copper(I) chloride
2. Regulatory framework

This chapter gives an overview of how copper(I)oxide, copper(II)sulphate inclusive of copper(II)sulphate pentahydrate and copper(I)chloride are addressed in existing and forthcoming EU and Danish legislation, international agreements and eco-label criteria. The overview reflects the findings from the data search (reference is made to the data collection strategy in Preface).

For readers not used to dealing with legislative issues, Appendix 1 provides a brief overview of and connections between legislative instruments in EU and Denmark. The Appendix also gives a brief introduction to chemicals legislation, an explanation for lists referred to in Section 2.3, and a brief introduction to international agreements and the aforementioned eco-label schemes.

2.1 EU and Danish legislation

This section first lists existing legislation addressing copper(I)oxide, copper(II)sulphates and copper(I)chloride and then gives an overview of ongoing activities, focusing on substances in the pipeline in relation to various REACH provisions.

2.1.1 Biocidal products

Within the countries of the EU and the EEA, all import and placing on the market of biocidal products have been regulated by the Biocidal Products Directive (BPD, 98/8/EC) up to 1 September 2013. From this date, the BPD is repealed and replaced by the Biocidal Products Regulation (BPR, EC No. 528/2012). As the Biocidal Products Regulation is continuing the activities implemented by BPD, the following presentation is focused on the BPD.

The BPD includes a review programme to investigate biocidal active substances and biocidal products within the EU. The review programme establishes criteria for the EU harmonised use of biocidal active substances in biocidal products in order to assure that the related products on the market are effective and safe for humans and the environment. The review programme of the BPD investigates the active substances as such and the biocidal products containing the active substance. The active substances are reviewed by EU expert groups. The biocidal active substances are evaluated according to their use and categorized into different product types.

In the BPD, biocides are subdivided into 23 product types as listed below (in the Biocidal Products Regulation the list is reduced to 22 product types, as product type 20 (preservatives for food or feedstocks) has been eliminated as a separate product type:

Product type 1: Human hygiene biocidal products
Product type 2: Private area and public health area disinfectants and other biocidal products
Product type 3: Veterinary hygiene biocidal products
Product type 4: Food and feed area disinfectants
Product type 5: Drinking water disinfectants
Product type 6: In-can preservatives
Product type 7: Film preservatives
Product type 8: Wood preservatives
Product type 9: Fibre, leather, rubber and polymerised materials preservatives
Product type 10: Masonry preservatives
Product type 11: Preservatives for liquid-cooling and processing systems
Product type 12: Slimicides
Product type 13: Metalworking-fluid preservatives
Product type 14: Rodenticides
Product type 15: Avicides
Product type 16: Molluscicides
Product type 17: Piscicides
Product type 18: Insecticides, acaricides and products to control other arthropods
Product type 19: Repellents and attractants
Product type 20: Preservatives for food or feedstocks
Product type 21: Antifouling products
Product type 22: Embalming and taxidermist fluids
Product type 23: Control of other vertebrates.

Based on the evaluation of the active substances for specific product types, the substances are approved or rejected for use within the product types in question. The substances approved for use within specific product types are listed by product type in Annex 1 to the BPD (a positive list). Under the BPR, the list will be continued as an Union list of approved active substances and be electronically available to the public.

If the active substances are approved in the EU review process, biocidal products containing the substances may later be authorised at national level following application according to BPD/BPR procedures. Under the BPR a procedure has been established that will allow biocidal products to be authorised at the Union level without the need to obtain separate national authorisations or going through the mutual recognition procedure. The Union authorisation will confer the same rights and obligations in each Member State as an authorisation issued by the competent authority of that Member State. Union authorisation is, however, not possible for biocidal products covered by product types 14, 15, 17, 20 and 21.

Existing active substances (meaning all active substances in biocidal products already on the market on 14 May 2000) for which a decision on non-inclusion in the positive list has been adopted are listed (the “list of not-included substances”) on the EU homepage. In accordance with Regulation (EC) No 2032/2003, biocidal products containing active substances for which a non-inclusion decision was taken shall be removed from the market within 12 months of the entering into force of such a decision, unless otherwise stipulated in that non-inclusion decision. The list of not-included substances will also include substances for which application for renewed approval has not been submitted.

The status for copper(I)oxide, copper(II)sulphates and copper(I)chloride with respect to BPD may be summarized as follows:

Currently none of the substances are listed on the positive list.

Copper(II)sulphate pentahydrate is presently being reviewed for use within product type 2 "Private area and public health area disinfectants and other biocidal products". Decision on copper(II)sulphate pentahydrate is anticipated to be made by September 2013 under the BPR. The Assessment Report for copper(II)sulphate pentahydrate by the Rapporteur Member State, France, was published on the CIRCA website in May 2013 [France, 2013].

---

1 (http://ec.europa.eu/environment/biocides/non_inclusions.htm)
Copper(I)oxide is similarly being reviewed for use within product type 21 “Antifouling products”. France is also the Rapporteur Member State for this evaluation [EC, 2007]. No Assessment Report for the use of copper(I)oxide within product type 21 has so far been published.

Copper(I)chloride is not being reviewed for any product type.

Copper(II)sulphate is not included for use for the following product types:
- Product type 1 "Human hygiene biocidal products" - phase-out by 1 February 2013;
- Product type 4 "Food and feed area disinfectants" - phase-out by 1 February 2013;
- Product type 8 "Wood preservatives" - phase-out by 1 September 2006.

Copper(I)oxide is not included for use for the following product type:
- Product type 8 "Wood preservatives" - phase-out by 1 September 2006.

In Denmark, only biocidal products containing active substances included on the positive list or in the EU review process are allowed for use. Therefore, the only applications of copper(I)oxide, copper(II)sulphate and copper(I)chloride currently allowed in Denmark are the uses of copper(II)sulphate pentahydrate within product type 2 "Private area and public health area disinfectants and other biocidal products" and the use of copper(I)oxide within product type 21 “Antifouling products”.

2.1.2 Other existing legislation

Table 3 gives an overview of the main pieces of existing legislation addressing copper(I)oxide, copper(II)sulphate and copper(I)chloride, inclusive of Directive 98/8/EC and Regulation (EC) No. 528/2012. For each area of legislation, the table first lists applicable EU legislation and its possible transposition into Danish law and/or other national rules. Copper(I)oxide, copper(II)sulphate and copper(I)chloride may, however, be mentioned in other legal instruments (e.g. defining commodity groups for statistics) not in focus for this survey.

The following table lists the main instruments regulating the use and disposal of copper(I)oxide, copper(II)sulphates and copper(I)chloride. Regulations specifically addressing the substances as well as issues related to these substances are listed. As the general rule are regulations addressing copper in general not listed, but regulation relevant to the issues identified in this survey is included (e.g. as land application of pigs manure is a key issue, legislation on land application of waste is included). As can be seen, copper(I)oxide, copper(II)sulphates and copper(I)chloride are regulated through chemicals legislation, as well as sector-specific (e.g. food, feed) and media-specific (e.g. air, water) legislation.

<table>
<thead>
<tr>
<th>Legal instrument</th>
<th>Requirements as concern copper(I)oxide, copper(II)sulphates and copper(I)chloride and issues related to these substances (includes amendments to the parent instruments)</th>
</tr>
</thead>
</table>
| Regulation (EC) No. 528/2012 of 22 May 2012 concerning the making available on the market and use of biocidal products | This Regulation lays down rules for:  
- the establishment at Union level of a list of active substances which may be used in biocidal products;  
- the authorisation of biocidal products, inclusive the option of Union authorisation;  
- the mutual recognition of authorisations within the Union;  
- the making available on the market and the use of biocidal products within one or more Member States or the Union;  
- the placing on the market of treated articles. |
<table>
<thead>
<tr>
<th>Legal instrument</th>
<th>Requirements as concern copper(I)oxide, copper(II)sulphates and copper(I)chloride and issues related to these substances (includes amendments to the parent instruments)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Regulation (EC) No 2032/2003 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, and amending Regulation (EC) No 1896/2000</strong></td>
<td>The Regulation is by 1. September 2013 replacing Directive 98/8/EC (see below). The scope of the Regulation has been extended compared to the former Directive to cover articles and materials treated with biocidal products, including furniture and textiles. The Regulation also applies to active substances generated <em>in situ</em>, and to biocidal products used in materials that come into contact with food. Other products that are sufficiently covered by existing legislation (including food and feed, food and feed additives and processing aids) are excluded from the scope of the new Regulation.</td>
</tr>
<tr>
<td><strong>Directive No 98/8/EC of the European Parliament and of the Council of 16 February 1998 concerning the placing of biocidal products on the market.</strong></td>
<td>This Regulation lays down detailed rules for the implementation of the second phase of the programme of work for the systematic examination of all active substances already on the market on 14 May 2000 as active substances of biocidal products, hereinafter &quot;the review programme&quot;, referred to in Article 16(2) of Directive 98/8/EC.</td>
</tr>
<tr>
<td><strong>Danish Statutory Order: Bekendtgørelse om bekæmpelsesmidler BEK nr 1088 af 6/09/2013 (Statutory Order No. 1088 of 6 September 2013 on pesticides and biocides)</strong></td>
<td>The Directive concerns authorization and the placing on the market for use of biocidal products within the Member States; recognition of authorizations within the Community; and the establishment of a positive list of active substances which may be used in biocidal products. For further details reference is made to Section 2.1.1. The Directive is by 1. September 2103 replaced by Regulation (EC) 528/2012 (see above). This Statutory Order lays down rules on pesticides to the extent they must be approved according to the rules in §§ 33-38 c in the Danish Chemicals Act or by the rules in the EU Regulation on plant protection products. The Statutory Order furthermore implements Directive No. 98/8/EC in Danish legislation.</td>
</tr>
<tr>
<td><strong>Bekendtgørelse om begrænsning af import, salg og anvendelse af biocidholdig bundmaling BEK nr 1257 af 15/12/2011 (Statutory Order No. 1257 of 15 December 2011 on restrictions on the import, sale and use of biocidal antifouling products)</strong></td>
<td>The import, sale and use of antifouling paint containing biocides on pleasure boats that mainly sail in fresh waters is prohibited. The import, sale and use of antifouling paint containing biocides, where the release of copper exceeds 200 µg Cu/cm² after the first 14 days and 350 µg Cu/cm² after the first 30 days, calculated from the time of application, on pleasure boats of 200 kg or more that mainly sail in salt water, is prohibited. The import, sale and use of antifouling paint containing biocides on pleasure boats of less than 200 kg that mainly sail in salt water is prohibited. This does, however, not apply to wooden boats and pleasure boats that have permanent mooring space in harbours designated as A and B harbours by the insurance-sector harbour survey. The import, sale and use of antifouling paint containing biocides which releases substances</td>
</tr>
<tr>
<td>Legal instrument</td>
<td>Requirements as concern copper(I)oxide, copper(II)sulphates and copper(I)chloride and issues related to these substances (includes amendments to the parent instruments)</td>
</tr>
<tr>
<td>------------------</td>
<td>--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Regulation (EC) No 1223/2009 of on cosmetic products</td>
<td>Neither copper(I)oxide, copper(II)sulphates and copper(I)chloride are listed as substances allowed or prohibited in cosmetic products. Copper and certain other copper compounds are allowed as colorants in cosmetic products.</td>
</tr>
<tr>
<td>Danish Statutory Order: Bekendtgørelse om sikkerhedskrav til legetøjsprodukter BEK nr. 13 af 10/01/2011 (Statutory Order No. 13 of 13 January 2011 on the safety of toys) *1</td>
<td></td>
</tr>
</tbody>
</table>

### REGULATION ADDRESSING WASTE

| Regulation (EC) No 1013/2006 on shipments of waste | This Regulation establishes procedures and control regimes for the shipment of waste, depending on the origin, destination and route of the shipment, the type of waste shipped and the type of treatment to be applied to the waste at its destination. The Regulation requires that export of certain waste types (also waste intended for recovery) shall be prohibited depending on the type of waste and the country of destination. Waste subject to export prohibition (included in Annex V) that may contain copper(I)oxide, copper(II)sulphates or copper(I)chloride includes:  
- Spent etching solutions containing dissolved copper  
- Spent electrolytic solutions from copper electrorefining and electrowinning operations  
- Waste cupric chloride and copper cyanide catalysts  
- Waste sludges, excluding anode slimes, from electrolyte purification systems in copper electrorefining and electrowinning operations  
- Copper oxide mill-scale  
Other waste types containing copper may also contain copper(I)oxide, copper(II)sulphate or copper(I)chloride. (Implementation of the Basel Convention in EU). |
| Regulation (EC) No 1418/2007 concerning the export for recovery of certain waste to certain non-OECD countries | Sets conditions for export of copper in waste to certain non-OECD countries. Neither copper(I)oxide, copper(II)sulphate or copper(I)chloride are specifically addressed by the regulation and it is not known whether these substances could be included in the waste types listed. |
### Legal instrument

<table>
<thead>
<tr>
<th>Legal instrument</th>
<th>Requirements as concern copper(I)oxide, copper(II)sulphates and copper(I)chloride and issues related to these substances (includes amendments to the parent instruments)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>in particular of the soil, when sewage sludge is used in agriculture</strong></td>
<td>Danish Statutory order: Limit value for copper in waste products (incl. sludge) for use in agriculture: 1000 mg/kg dw; Limit value for copper in soil to be used for application of waste products: 40 mg/kg dw.</td>
</tr>
</tbody>
</table>

**Danish Statutory Orders**

**Bekendtgørelse om anvendelse af affald til jordbrugsformål (Slambekendtgørelsen)**

BEK nr 1650 af 13/12/2006 (Statutory Order No. 1650 of 13 December 2006 on land application of waste (the Sludge Order))

<table>
<thead>
<tr>
<th><strong>Danish Statutory Order:</strong> Bekendtgørelse om anlæg, der forbrænder affald</th>
<th>Waste water from cleaning of flue (exhaust) gas: 0.5 mg/L. Flue gas emission limit for copper: The sum of emissions of Cu, As, Cr, Mn, Ni, Pb, Sb and V must not exceed 0.5 mg/Nm³.</th>
</tr>
</thead>
<tbody>
<tr>
<td>BEK nr 1451 af 20/12/2012 (Statutory Order No. 1451 of 20 December 2012 on waste incineration plants)</td>
<td>Transposes part of the provisions of Directive 2010/75/EU on industrial emissions</td>
</tr>
</tbody>
</table>

**REGULATION ADDRESSING EMISSIONS TO THE ENVIRONMENT**


<table>
<thead>
<tr>
<th>Regulations concerning industrial emissions (integrated pollution prevention and control)</th>
<th>Releases of copper and copper compounds shall be reported by operators with activities above a certain activity threshold if the releases are above a certain threshold releases:</th>
</tr>
</thead>
<tbody>
<tr>
<td>To air: 100 kg/year To water: 50 kg/year To land: 50 kg/year.</td>
<td>Emission values for copper and its compounds (expressed as Cu): The total emission to air of copper, antimony, arsenic, lead, chromium, nickel, manganese, vanadium and their compounds for waste incineration plants: ≤0.5 mg/Nm³. Emission limit values for discharges of copper and its compounds with waste water from the cleaning of waste gases from co-incineration of waste: 0.5 mg Cu/L.</td>
</tr>
</tbody>
</table>


<p>| Requires EU member states to reduce pollution of inland surface waters, territorial waters and internal coastal waters by copper and copper compounds. | Requires EU member states to reduce pollution of inland surface waters, territorial waters and internal coastal waters by copper and copper compounds. |</p>
<table>
<thead>
<tr>
<th>Legal instrument</th>
<th>Requirements as concern copper(I)oxide, copper(II)sulphates and copper(I)chloride and issues related to these substances (includes amendments to the parent instruments)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2006 on certain dangerous substances discharged into the aquatic environment of the Community</td>
<td>Establishes national environmental quality standards for copper (maximum concentrations) in Danish waters. The standards address the total amount of copper. For fresh and salt waters the general maximum concentration is 1 µg dissolved Cu/L, if necessary added the background concentration. An absolute maximum of 12 µg dissolved Cu/L applies. No standards are established for specific copper compounds. Higher concentrations may be allowed, if this is justified by natural environmental conditions.</td>
</tr>
<tr>
<td>Danish Statutory Orders: Bekendtgørelse om miljø-kvalitetskrav for vandområder og krav til udledning af forurenende stoffer til vandløb, søer eller havet BEK nr 1022 af 25/08/2010 (Statutory Order No. 1022 of 25 August 2010 on environmental quality requirements for water recipients and requirements for discharges of polluting substances to streams, lakes and the sea)*1</td>
<td>Require MS to consider establishing threshold values for groundwater.</td>
</tr>
<tr>
<td>Directive 2006/118/EC on the protection of groundwater against pollution and deterioration</td>
<td>This Statutory Order lay down rules for development and implementation of monitoring programs for surface waters and groundwater etc. The monitoring shall ensure a national overview of the status for water recipients and specially protected areas.</td>
</tr>
<tr>
<td>Danish Statutory Order: Bekendtgørelse nr 1434 af 06/12/2009 om overvågning af overfladevand, grundvand, beskyttede områder og om naturovervågning i internationale naturbeskyttelsesområder mv. (Statutory Order No. 1434 of 6 December 2009 on monitoring of surface waters, ground water, protected areas and on nature monitoring in nature conservation areas of international importance)*1</td>
<td>Sets quality values for shellfish waters for copper and other substances.</td>
</tr>
<tr>
<td>Directive 2006/113/EC on the quality required of shellfish waters (codified version)</td>
<td>The concentration of copper must not exceed the maximum concentration allowed by the current</td>
</tr>
</tbody>
</table>
Survey of copper(I)oxide, copper(II)sulphates and copper(I)chloride

### Legal Instruments

<table>
<thead>
<tr>
<th>Legal instrument</th>
<th>Requirements as concern copper(I)oxide, copper(II)sulphates and copper(I)chloride and issues related to these substances (includes amendments to the parent instruments)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bekendtgørelse om kvalitetstkrav for skaldyrvande</strong> BEK nr 38 af 19/01/2011 (Statutory Order No. 38 of 19 January 2011 on quality requirements for shellfish waters)*1</td>
<td>Statutory Order on environmental quality standards for copper in Danish waters (see Statutory Order 1022 of 25/08/2010 above).</td>
</tr>
<tr>
<td><strong>Bekendtgørelse af lov om beskyttelse af havmiljøet</strong> (Havmiljøloven) BEK nr 963 af 03/07/2013 (Statutory Order No. 963 of 3 July 2013 of the law on protection of the marine environment (the Law on the Marine Environment))*1 and</td>
<td>Copper should only be found in insignificant amounts and concentrations in dredging material. The phrase “insignificant amounts” is not defined in the Law. The guideline on disposal of dredged materials, however, defines a lower level (20 mg/kg) below which the materials can always be dumped at sea and a higher (90 mg/kg) above which the materials must as the default solution be placed on land. For materials having a content of copper in the range of 20 – 90 mg/kg, dumping at sea requires special consideration in order to reduce impact on the marine environment.</td>
</tr>
<tr>
<td><strong>Bekendtgørelse om dumpning af optaget havbundsmateriale (klapning)</strong> BEK nr. Nr. 32 af 07/01/2011 (Statutory Order No. 32 of 7 January 2011 on disposal of dredged materials)*1 and</td>
<td>Sets minimum and maximum daily levels for copper as mineral to food supplement and establishes a positive list of substances to be used for manufacturing of the food supplement. Among the copper compounds included on the positive list is copper(II)oxide and copper(II)sulphate, but not copper(I)oxide or copper(I)chloride. Only copper compounds that are listed in annex 2 and 3 in Commission regulation 1170/2009 of 30 November 2009 can be added to food or used in the manufacture of food [EC, 2009].</td>
</tr>
<tr>
<td><strong>Vejledning om dumpning af optaget havbundssediment</strong> VEJ nr. 9702 af 20/10/2008 (Guideline no. 9702 of 20 October 2008 on disposal of dredged materials)*1</td>
<td>Sets maximum limit for addition of copper to food for babies and small children. Establishes a positive list of substances to be used for manufacturing of such food. Among the copper compounds included on the positive list is cupric sulphate (copper(II)sulphate). Copper compounds allowed in food for babies and small children are listed in annex 4.</td>
</tr>
<tr>
<td>Legal instrument</td>
<td>Requirements as concern copper(I)oxide, copper(II)sulphates and copper(I)chloride and issues related to these substances (includes amendments to the parent instruments)</td>
</tr>
<tr>
<td>------------------</td>
<td>--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td><strong>(Statutory Order No. 1100 of 26 November 2012 on food for babies and small children)</strong></td>
<td>The Regulation lists substances that may be added for specific nutritional purposes in the manufacture of foodstuffs for particular nutritional uses. According to the Regulation, copper(II)sulphate can be added to &quot;Dietetic foods&quot;, meaning foods for particular nutritional uses including foods for special medical purposes but excluding infant formulae, follow-on formulae, processed cereal-based foods and baby foods intended for infants and young children. Copper(I)oxide and copper(I)chloride are not included on the list and thus not permitted for being added to foodstuffs for particular nutritional uses. According to Council Directive of 3 May 1989 on the approximation of the laws of the Member States relating to foodstuffs intended for particular nutritional uses, foodstuffs for &quot;particular nutritional uses&quot; are foodstuffs which, owing to their special composition or manufacturing process, are clearly distinguishable from foodstuffs for normal consumption, which are suitable for their claimed nutritional purposes and which are marketed in such a way as to indicate such suitability.</td>
</tr>
<tr>
<td><strong>Commission Regulation (EC) No 953/2009 of 13 October 2009 on substances that may be added for specific nutritional purposes in foods for particular nutritional uses</strong></td>
<td>Copper compounds allowed in infant formulas and follow-on formulas for infants and toddlers are specified in annex 3. The compounds permitted include copper(II)sulphate, but not copper(I)oxide nor copper(I)chloride.</td>
</tr>
<tr>
<td><strong>Bekendtgørelse om modermælkserstatninger og tilskudsblandinger til spædbørn og småbørn</strong></td>
<td>The general regulation on food contact materials has requirements in article 3 on safety. Copper used in food contact materials shall comply with the general requirements, e.g. for safety on potential migration.</td>
</tr>
<tr>
<td><strong>Regulation (EC) No 1935/2004 of the European Parliament and of the Council of 27 October 2004 on materials and articles intended to come into contact with food and repealing Directives 80/590/EEC and 89/109/EEC</strong></td>
<td>The regulation on plastic is a positive list on substances that are accepted to be used in plastics. Some of the substances can be used when complying with specific restrictions and for all substances a total migration limit is set. Substances on the positive list have been evaluated by the EU Food Safety Authority, EFSA. Copper salts are among the substances accepted for used in plastics. Therefore copper(II)sulphate and copper(I)chloride is permitted for use in plastics while copper(I)oxide is not permitted.</td>
</tr>
<tr>
<td><strong>Commission Regulation (EU) No 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food</strong></td>
<td>The Regulation approves a number of copper compounds as additives in feed. The compounds permitted include copper(II)sulphate pentahydrate, but not copper(I)oxide or copper(I)chloride. The following maximum content of copper in mg/kg of the complete feed is allowed: Pigs - piglets up to 12 weeks: 170</td>
</tr>
<tr>
<td><strong>Regulation (EC) No 1334/2003 of 25 July 2003 amending the conditions for authorisation of a number of additives in feeding stuffs</strong></td>
<td>The following maximum content of copper in mg/kg of the complete feed is allowed: Pigs - piglets up to 12 weeks: 170</td>
</tr>
<tr>
<td>Legal instrument</td>
<td>Requirements as concern copper(I)oxide, copper(II)sulphates and copper(I)chloride and issues related to these substances (includes amendments to the parent instruments)</td>
</tr>
<tr>
<td>------------------</td>
<td>-------------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
</tbody>
</table>
| belonging to the group of trace elements | - other pigs: 25  
Bovine  
- bovine before the start of rumination: milk replacers: 15; other complete feedingstuffs: 15.  
- other bovine: 35  
Ovine: 15  
Fish: 25  
Crustaceans: 50  
Other species: 25. |
| Regulation (EC) No 1831/2003 of the European Parliament and of the Council of 22 September 2003 on additives for use in animal nutrition | Sets conditions for placing on the market, approval, labelling and use of feed additives and premixtures. Feed additives are approved for different purposes and for different categories of animals, and must only be marketed and used as such. Only feed additives listed in the ‘Community register of Feed Additives’ must be marketed and used.  
Nine different copper compounds (copper(II)sulphate pentahydrate is included, but not copper(I)oxide and copper(I)chloride) are listed in the register, they are all only approved in the category 3. ‘nutritional additives’, (b) ‘compounds of trace elements’.  
A feed additive must only be used for the animal categories for which it is approved, and the concentration in the daily ration (moisture content 12%) must not exceed the maximum limits specified in the approval (regulation). |
| REGULATION (EC) No 396/2005 of the European Parliament and of the Council of 23 February 2005 on maximum residue levels of pesticides in or on food and feed of plant and animal origin and amending Council Directive 91/414/EEC | Sets maximum residual levels for pesticides in food and feed. ‘Maximum residue level’ (MRL) means the upper legal level of a concentration for a pesticide residue in or on food or feed set in accordance with this Regulation, based on good agricultural practice and the lowest consumer exposure necessary to protect vulnerable consumers. Maximum residual level has been established for copper, because it can be used as pesticide. Actual MRLs are stated in the EU Pesticides Database: http://www.eubusiness.com/topics/food/eu-mrl-database/view. |
| Bekendtgørelse om gødnings og jordforbedringsmidler m.v. BEK nr 862 af 27/08/2008 (Statutory Order No. 862 of 27 August 2008 on fertilizers and soil improvement medias)*1 | This Statutory Order lists requirements regarding quality, content of specific compounds and packaging and labelling to be complied with by sale of fertilizers and soil improvement medias. Requirements have been established for copper oxide and copper salts. These requirements are thus valid for copper(I)oxide as well as copper(II)sulphates and copper(I)chloride. |

*2 ‘Premixtures’ means mixtures of feed additives or mixtures of one or more feed additives with feed materials (e.g. barley and soybean extractions) or water used as carriers, not intended for direct feeding to animals.”

Link to Community register of Feed Additives which is updated continuously http://ec.europa.eu/food/food/animalnutrition/feedadditives/comm_register_feed_additives_1831-03.pdf
Survey of copper(I)oxide, copper(II)sulphates and copper(I)chloride

**2.2 Classification and labelling**

Substances and mixtures placed on the market in the EU are to be classified, labelled and packaged according to the CLP regulation (1272/2008/EC).

Table 4 lists the EU harmonised classification and labelling for copper(I)oxide, copper(II)sulphate and copper(I)chloride according to Annex VI of the CLP Regulation. The table shows that the substances are classified for acute toxicity ("harmful if swallowed") and aquatic toxicity ("very toxic to aquatic life" and "with long lasting effects"). Copper(II)sulphate is furthermore classified for skin and eye irritation.
## Table 4
EU Harmonised Classification According to Annex VI of Regulation (EC) No 1272/2008 (CLP Regulation)

<table>
<thead>
<tr>
<th>Index No</th>
<th>International chemical identification</th>
<th>CAS No</th>
<th>Classification</th>
<th>Hazard Class and Category Code(s) *1</th>
<th>Hazard statement Code(s)</th>
</tr>
</thead>
</table>
| 029-002-00-x | Copper (I)oxide | 1317-39-1 | Acute Tox.4*  
Aquatic Acute 1  
Aquatic Chronic 1 | H302  
H400  
H410 |
| 029-004-00-0 | Copper (II)sulphate, *2 | 7758-98-7 | Acute Tox.4*  
Eye Irrit. 2  
Skin Irrit. 2  
Aquatic Acute 1  
Aquatic Chronic 1 | H302  
H319  
H315  
H400  
H410 |
| 029-001-00-4 | Copper(I)chloride | 7758-89-6 | Acute Tox.4*  
Aquatic Acute 1  
Aquatic Chronic 1 | H302  
H400  
H410 |

*1 Use of “*” in connection with a hazard category (e.g. Acute Tox. 4 *) implies that the category stated shall be considered as a minimum classification.

*2 No separate classification has been stated for the monohydrate (CAS No. 10257-69-1) and the pentahydrate (CAS No. 7758-99-8). It is therefore assumed that the classification stated for copper (II)sulphate covers all relevant compounds inclusive of the monohydrate and the pentahydrate.

### 2.3 REACH

#### Authorisation List / REACH Annex XIV
The Authorisation List contains all SVHC substances included in ANNEX XIV under REACH (Appendix 1) requiring uses to be authorised for use. No copper compounds are included in the Authorisation List as of March 2013.

#### Ongoing activities - pipeline

**Community Rolling Action Plan (CoRAP)**
The Community Rolling Action Plan (CoRAP) is a tool for coordination of substance evaluation between EU Member States, indicating when a given substance is expected to be evaluated and by whom (Appendix 1).

No copper compounds are included in the Community Rolling Action Plan (CoRAP) (ECHA, 2013) as of 15 March 2013.

**Registry of Intentions (EU)**
The 'registry of intentions' gives an overview of intentions by EU Member States in relation to ANNEX XV dossiers. Such intentions made include EU harmonised classification and labelling, identification of a substance as being in the group of Substances of Very High Concern (SVHC) or a restriction related to the substance (Appendix 1).

Currently, copper(I)oxide and copper(II)sulphate pentahydrate is on the list of submitted EU harmonised classification and labelling intention. No intentions are registered for copper(I)chloride.
2.4 International agreements

Table 5 gives an overview of how copper and copper compounds are addressed by various international agreements. Relevant international agreements include Sea Conventions (OSPAR and HELCOM) together with the UN Basel Convention. Copper or copper compounds are not listed in the Rotterdam and Stockholm Conventions.

<table>
<thead>
<tr>
<th>Agreement</th>
<th>Substances</th>
<th>Requirements</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>OSPAR Convention</strong></td>
<td>Copper</td>
<td>The Convention aims at preventing pollution of the North East Atlantic Sea by continuously reducing discharges, emissions and losses of hazardous substances, with the ultimate aim to achieve concentrations in the OSPAR maritime area near background values for naturally occurring substances and close to zero for synthetic substances. Relevant recommendations include: PARCOM Recommendation 94/6 on Best Environmental Practice for the Reduction of Inputs of Potentially Toxic Chemicals from Aquaculture Use.</td>
</tr>
<tr>
<td><strong>HELCOM (Helsinki Convention)</strong></td>
<td>Heavy metals and their compounds</td>
<td>Heavy metals and their compounds are regarded as priority substances, which shall be given priority by the Contracting Parties in their preventive measures. Relevant recommendations include: Reduction of discharges and emissions from production of and formulation of pesticides: Waste waters should be treated to meet the following requirements for discharge into waters: Cu ≤0.5 mg/l. Reduction of discharges and emissions from the metal surface treatment: Before discharging into sewers or surface waters the treatment should be provided so the concentrations of copper do not exceed the following level: Cu ≤0.5 mg/l.</td>
</tr>
<tr>
<td><strong>Basel Convention</strong></td>
<td>Copper</td>
<td>Set out control measures of the movements of hazardous waste incl. of waste containing copper between nations, and restricts transfer of hazardous waste from developed to less developed countries (non-adopted). The Convention also intends to minimize the amount and toxicity of wastes generated, to ensure their environmentally sound management as closely as possible to the source of generation, and to assist least developed countries (LDC) in environmentally sound management of the hazardous and other wastes they generate.</td>
</tr>
</tbody>
</table>

Table 5 shows that copper(I)oxide, copper(II)sulphates and copper(I)chloride are not addressed specifically by any international agreement. Copper is, however, on the OSPAR priority list with intentions of reducing discharges in order to reach near-background concentrations in the OSPAR maritime area (the North-East Atlantic). Copper as well as copper compounds are regarded as priority substances by the HELCOM (Baltic Sea) Convention, to be prioritised by preventive measures and for which restrictions for discharges to water from specific industrial activities are recommended.

Finally, copper-containing waste is addressed by the Basel Convention on the control of transboundary movements of hazardous wastes and their disposal, implemented by the EU in Regulation 1013/2006 on the shipment of waste (See Table 3). Copper and copper compounds are not covered
by the Rotterdam Convention on prior informed consent (the PIC-procedure), nor the Stockholm Convention on POP-substances (implemented in the EU as Regulation 850/2004/EC).

An International Convention on the Control of Harmful Antifouling Systems on Ships has been established under IMO (International Maritime Organisation). This Convention entered into force on 17 September 2008. The Convention prohibits the use of organotin compounds for antifouling on ships and other marine constructions. No restriction on the use of copper compounds has so far been established.

#### 2.5 Other relevant national regulation on copper(I)oxide, copper(II)sulphates and copper(I)chloride

Only regulation addressing the use of copper for antifouling has been identified:

In Sweden, antifouling paint is approved by the Swedish Chemicals Agency. As the Baltic is considered particularly sensitive the Swedish Chemicals Agency are generally more restrictive in approvals of antifouling paint for the Swedish East Coast than the West Coast. Copper (I)oxide are approved for use on the East Coast as well as on the West Coast, but higher concentrations are generally allowed on the West Coast, and no antifouling paint is approved for use in the Gulf of Bothnia north of Örskär [KEMI, 2011]. Neither copper(II)sulphate nor copper(I)chloride is approved for use in Swedish waters.

In the United States (US), antifouling paints are governed by the Federal Insecticide, Fungicide, and Rodenticide Act. Approval of antifouling paints by the US EPA is needed before application or sale within the US. Once approved by the US EPA, the product goes through further examination to be registered by individual states. There are currently no bans on the use of copper hull paints in the United States [US EPA, 2011].

The State of California recently issued a decision to re-evaluate all registered copper hull paint products [CADPR, 2010].

In the state of Washington, USA, the use of copper in antifouling paint on recreational vessels will be restricted as follows [Washington, 2011]:
- Beginning January 1, 2018, no manufacturer, wholesaler, retailer, or distributor may sell or offer for sale in this state any new recreational water vessel manufactured on or after January 1, 2018, with antifouling paint containing copper.
- Beginning January 1, 2020, no antifouling paint that is intended for use on a recreational water vessel and that contains more than 0.5 percent copper may be offered for sale in this state.
- Beginning January 1, 2020, no antifouling paint containing more than 0.5 percent copper may be applied to a recreational water vessel in this state.

According to NZ [2011], copper is registered for antifouling in Australia, USA, Canada, Hong Kong and Japan, as well as several EU countries. Information on the actual compounds and other rules are not available.
2.6 Eco-labels

The use of copper compounds is only addressed by a few eco-labels. Table 6 below gives an overview of how copper(I)oxide, copper(II)sulphates and copper(I)chloride are addressed by the EU and the Nordic eco-label schemes. The table lists the product types for which the presence of copper compounds (including copper(I)oxide, copper(II)sulphates and copper(I)chloride), as well as chemicals with aquatic toxicity similar to copper compounds, is restricted. It shows that the use of such compounds are not allowed by eco-labels for products made of wood for outdoor purposes, as well as for certain chemical products, incl. boat care products and paint for outdoor purposes.

TABLE 6
ECO-LABELS TARGETING COPPER(I)OXIDE, COPPER(II)SULPHATE AND COPPER(I)CHLORIDE

<table>
<thead>
<tr>
<th>Eco-label</th>
<th>Substances</th>
<th>Mixtures and articles</th>
<th>Document title</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nordic Swan</td>
<td>Toxic substances</td>
<td>Content of substances classified as aquatic acute toxic 1 or aquatic chronic toxic 1 are severely limited. *1,2</td>
<td>Nordic Ecolabelling of Car and boat care products</td>
</tr>
<tr>
<td></td>
<td>Copper compounds and other biocides</td>
<td>Copper compounds and other biocides must not be used</td>
<td>Nordic Ecolabelling of Durable wood— Alternative to conventionally impregnated wood</td>
</tr>
<tr>
<td>Nordic Swan</td>
<td>Toxic compounds</td>
<td>Substances classified as acute or chronic toxic in the aquatic environment are severely limited. *1,2</td>
<td>Nordic Ecolabelling of Chemical building products</td>
</tr>
<tr>
<td>Nordic Swan</td>
<td>Copper and copper compounds</td>
<td>Copper and copper compounds must not be a part of the products</td>
<td>Nordic Ecolabelling of Outdoor furniture and playground equipment</td>
</tr>
<tr>
<td>EU Flower</td>
<td>Toxic substances</td>
<td>Outdoor paints and varnishes: Substances classified as acute or chronic toxic in the aquatic environment must not exceed 2% of the product mass. *1</td>
<td>COMMISSION DECISION of 13 August 2008 establishing the ecological criteria for the award of the Community eco-label to outdoor paints and varnishes</td>
</tr>
</tbody>
</table>

*1 As stated in Table 4, both copper(I)oxide, copper(II)sulphate and copper(I)chloride are classified as acute and chronic toxic in the aquatic environment and are therefore covered by the requirements listed.

*2 The phrase "severely limited" cannot easily be elaborated – it is advised to consult the criteria documents for more information.

2.7 Summary

Regulation specifically addressing copper(I)oxide, copper(II)sulphates and copper(I)chloride is limited to regulation of biocidal products, and regulation of feed and food as copper(II)sulphate pentahydrate is allowed as an additive to feed and food. Other relevant regulation is focused on copper as an element and not on specific copper compounds.

Currently the only applications of copper(I)oxide, copper(II)sulphates and copper(I)chloride allowed in Denmark as biocides is the use of copper(II)sulphate, pentahydrate within the product
type of "Private area and public health area disinfectants and other biocidal products" (PT2) and the use of copper(I)oxide within the product type "Antifouling products" (PT21). For both applications the use of copper compounds is still subject to an EU review process. For copper(II)sulphate, pentahydrate a decision on the approval/non-approval for the product type stated is anticipated to be reached by late September 2013.

Currently none of the active substances covered by this survey has been approved by EU for any product type. The use of copper(II)sulphate for the product types of "Human hygiene biocidal products" (PT1), and "Food and feed area disinfectants" (PT4) was phased out by 1. February 2013, while the use of copper(I)oxide and copper(II)sulphate for the product type "Wood preservatives" (PT8) was phased out by 1. September 2006.

In Denmark, special restrictions on the use of copper for antifouling paint exist. These restrictions address pleasure boats only. No specific Danish restrictions exist with respect to commercial ships and boats. Based on the EU rules, Risk Assessment of antifouling paint for pleasure boats and commercial ships will take place in the years to come, when the ongoing EU review process for product type 21 under the Biocidal Products Regulation has been finished.

Regarding supply of copper to agricultural soils, restrictions exist for the content in waste products (incl. sewage sludge), but not for content in manure and other residues from domestic animals, despite the fact that residues from domestic animals are a far more important source for supply of copper to agricultural soils than sewage sludge and similar waste products.

Copper(I)oxide, copper(II)sulphates and copper(I)chloride are addressed by the OSPAR and The HELCOM Conventions and the Basel Convention. The substances are furthermore addressed by eco-labels for products made of wood for outdoor purposes, as well as for certain chemical products, incl. boat care products and paint for outdoor purposes.
3. Manufacture and uses

3.1 Manufacturing

3.1.1 Manufacturing processes
Manufacturing of copper(I)oxide, copper(II)sulphates and copper(I)chloride is based on metallic copper.

Copper(I)oxide is manufactured by reacting copper metal with oxygen in the presence of catalysts, forming the product cuprous oxide, according to:

\[ 2 \text{Cu (metal)} + \frac{1}{2} \text{O}_2 \rightarrow \text{Cu}_2\text{O}. \]

The reaction takes place in an aqueous medium and the product is obtained as a suspension, which is de-watered by pressure filtration [ECI, 2008].

Copper(II)sulphate pentahydrate is manufactured by heating Cu metal (with a purity of at least 99.5%) with steam and adding sulphuric acid together with a solution of water/copper sulphate, leading to the formation of a saturated solution of copper(II)sulphate pentahydrate:

\[ \text{Cu (metal)} + \text{H}_2\text{SO}_4 + 5 \text{H}_2\text{O} \rightarrow \text{CuSO}_4 \cdot 5 \text{H}_2\text{O} + 2\text{H}. \]

The crystallisation of copper(II)sulphate pentahydrate can be effectuated in different ways, depending on the size of crystals desired [ECI, 2008].

Copper(II)sulphate pentahydrate is the stable basic form of copper(II)sulphate with room temperature. Other forms, such as the monohydrate or the anhydrate, may be formed by dehydration, e.g. by heating [Richardson 2012]. Manufacturing of the monohydrate compound requires heating to 120–150˚C, while the anhydrate compound requires heating to 2150˚C [Richardson 2012].

Copper(I)chloride is manufactured by reacting heated metallic copper with Cl2 gas:

\[ 2 \text{Cu (metal)} + \text{Cl}_2 \rightarrow 2\text{CuCl} \ [\text{OECD, 2005; Richardson, 2012}]. \]

3.1.2 Manufacturing sites
According to ECI [2008], copper(I)oxide is manufactured in Europe in Germany and Norway, while copper(II)sulphate is manufactured in Italy and Spain.

Based on EUROSTAT [Eurostat, 2013], the countries from which significant export to EU27 takes place is as follows for copper oxides and –hydroxides (listed in order of importance): USA, Australia, Norway and Chile.

For copper sulphates the following countries from which significant export from EU occur (listed in order of importance) are as follows: The Russian Federation, Uzbekistan, Chile, Peru and China.
In OECD [2005], it is claimed with reference to [SPIN] that 2.7 tons of copper(I)chloride was manufactured in Denmark in 2003. The statement must be due to a misunderstanding, as [SPIN] is stating that 2.7 tons of copper(I)chloride was used in preparations in Denmark in 2003.

### 3.1.3 Manufacturing and consumption volumes - internationally

Total consumption of copper chemicals in the EU was 32,400 tons in 1999 [ECI 2008]. More recent figures, as well as data on the manufacturing and consumption of individual copper chemicals in the EU, are not available. Some indication may, however, be found in Figure 1 below.

According to ECI [2008], the important end-uses of copper chemicals in the EU are agricultural applications (animal feeds, fungicides, seed dressing), and as active ingredients in antifouling paint and wood preservatives. It must be assumed that the phrase “Cattle feed” in the figure below covers feed additives for all animals inclusive of pigs, cattle and sheep.

![Figure 1: Consumption of Copper Chemicals in EU in 1999](image)

Minor uses stated by ECI [2008] include the use as a dietary supplement (copper is an essential element in baby food) as well as in vitamins and mineral tonics. Copper chemicals are further used as stains to produce copper ruby glass, as catalysts and in photoelectric cells.

Information on the manufacturing and consumption of the copper compounds in focus for this survey was requested from the European Copper Institute, but no further data has been available on the manufacturing and consumption in the EU, nor at a global level.

Some data are, however, available for individual countries. Data available for Sweden regarding import and manufacture of chemical products containing copper compounds is presented in Table 7 below.

Export of chemical products is estimated at 322 tons compound in total, but not divided into product types [KEMI, 2013]. It is noted that consumption of copper compounds as feed additives is not included in Table 7.
TABLE 7
IMPORT AND MANUFACTURE OF CHEMICAL PRODUCTS THAT CONTAIN INORGANIC COPPER COMPOUNDS IN SWEDEN 2009 [KEMI]

<table>
<thead>
<tr>
<th>Product type</th>
<th>Imported tons compound</th>
<th>Manufactured tons compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood preservative coatings</td>
<td>823</td>
<td>471</td>
</tr>
<tr>
<td>Antifouling paints</td>
<td>183</td>
<td>- *1</td>
</tr>
<tr>
<td>Metal surface treatment agents</td>
<td>4</td>
<td>59</td>
</tr>
<tr>
<td>Dyestuffs, pigments</td>
<td>44</td>
<td>0</td>
</tr>
<tr>
<td>Fertilizers</td>
<td>25</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Raw materials (metal manufacture)</td>
<td>24</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Paints, others</td>
<td>3</td>
<td>12</td>
</tr>
<tr>
<td>Catalytic agents</td>
<td>12</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Disinfectants, slimicides</td>
<td>11</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Lubricants</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>Preservatives</td>
<td>2</td>
<td>&lt; 0,1</td>
</tr>
<tr>
<td>Surface treatment agent for wood, textile, paper</td>
<td>&lt; 1</td>
<td>- *1</td>
</tr>
<tr>
<td>Other types of products</td>
<td>3</td>
<td>&lt; 1</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>Ca. 1140</strong></td>
<td>*<em>Ca. 550 <em>2</em></em></td>
</tr>
</tbody>
</table>

*1 The meaning of the symbol is not indicated by the source. May indicate that data is not available.

*2 The figure may be underestimated, as not all data may be available.

In Table 8, the tonnage band for copper(I)oxide, copper(II)sulphates and copper(I)chloride in the EU, registered by ECHA, is presented. As noted, copper(I)oxide and copper(I)chloride are registered in a total quantity larger than 1,000 tons/year but less than 10,000 tons/year, while copper(II)sulphate is registered in a total quantity larger than 10,000 tons/year but less than 100,000 tons/year. The data confirms the general picture of copper(II)sulphates being the compounds representing by far the highest volume.

TABLE 8
TONNAGE BAND FOR COPPER(I)OXIDE, COPPER(II)SULPHATES AND COPPER(I)CHLORIDE REGISTERED UNDER THE REACH REGULATION BY ECHA

<table>
<thead>
<tr>
<th>Tons/year</th>
<th>Copper(I)oxide</th>
<th>Copper(II)sulphate *2</th>
<th>Copper(I)chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAS No</td>
<td>1317-39-1</td>
<td>7758-98-7</td>
<td>7758-89-6</td>
</tr>
<tr>
<td>Registered, tonnage band (t/y) *1</td>
<td>1,000-10,000</td>
<td>10,000 – 100,000</td>
<td>1,000-10,000</td>
</tr>
</tbody>
</table>

*1 As indicated in the lists of preregistered and registered substances at ECHA’s website. For each separate registration the registered tonnage is indicated.

*2 No separate data is given for the monohydrate compound (CAS No. 10257-69-1) and the pentahydrate compound (CAS No. 7758-99-8). It is therefore assumed that the data stated for copper(II)sulphate covers all relevant compounds inclusive of the monohydrate and the pentahydrate.

Regarding the manufacture of copper sulphate compounds, it is stated by Richardson [2012] that copper(II)sulphate pentahydrate is the dominant compound being manufactured and used. Cop-
per(II)sulphate monohydrate is used for the same purposes as the pentahydrate compound, but less than 5% of copper(II)sulphate (on copper basis) is marketed in the monohydrate form. Copper(II)sulphate anhydride has little commercial use, but can be used as a desiccant for removing water from organic solvents.

3.2 Import and export

3.2.1 Import and export of the copper compounds in question in Denmark
Copper(I)oxide, copper(II)sulphates and copper(I)chloride are not manufactured in Denmark. Some import and export of such goods takes place. Existing statistical data is presented in Table 9. No data on registration of import and export of copper chlorides are available, as copper chlorides are registered together with many other chlorides in the statistical CN-code system, and it is therefore not possible to obtain data on import and export of copper(I)chloride.

From Table 9 it should be noted that the import of copper oxides and –hydroxides to Denmark has been reduced significantly in recent years (actually since 2009 [DS, 2012]), while the import and export of copper sulphates is rather stable. The import of copper sulphates in 2012 has, however, increased by 26% compared to the average for 2007-2011.

<table>
<thead>
<tr>
<th>CN code</th>
<th>Product</th>
<th>Import, tons/year</th>
<th>Export, tons/year</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Average 2007-2011</td>
<td>2012</td>
</tr>
<tr>
<td>28250000</td>
<td>Copper oxides and –hydroxides</td>
<td>500.0</td>
<td>4.7</td>
</tr>
<tr>
<td>28332500</td>
<td>Copper sulphates</td>
<td>2312.0</td>
<td>2917.0</td>
</tr>
</tbody>
</table>

*1. Copper chlorides are in the CN-code system registered together with many other chlorides, and it is thus not possible to obtain data on import and export of copper(I)chloride.

3.2.2 Import and export of the copper compounds in question in EU
Available statistical data on manufacture and import/export of the copper compounds in question at the EU27 level is presented in Table 10. No data on registration of import and export of copper chlorides are available, as copper chlorides are registered together with many other chlorides in the statistical CN-code system, and it is therefore not possible to obtain data on import and export of copper(I)chloride. Furthermore, No statistical data exist for manufacture of copper compounds in EU27.

The figures in Table 10 illustrate that international trade with non-EU countries is important for at least copper oxides and copper sulphates, and that significant import takes place to the EU. The countries from which this import originates are listed in Section 3.1.2.

<table>
<thead>
<tr>
<th>CN code</th>
<th>Product</th>
<th>Import, tons/year</th>
<th>Export, tons/year</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Average 2007-2011</td>
<td>2012</td>
</tr>
<tr>
<td>28250000</td>
<td>Copper oxides and –hydroxides</td>
<td>12081</td>
<td>11887</td>
</tr>
<tr>
<td>28332500</td>
<td>Copper sulphates</td>
<td>37519</td>
<td>35309</td>
</tr>
</tbody>
</table>
*1. Copper chlorides are registered together with many other chlorides in the CN-code system, and it is therefore not possible to obtain data on import and export of copper(I)chloride.

3.3 Use

3.3.1 Registered uses by ECHA

Registered uses of copper(I)oxide, copper(II)sulphate and copper(I)chloride by ECHA are listed in Table 11. The list is rather detailed but does not necessarily cover all relevant applications. The functions of copper compounds for the different applications are, however, not clearly described and many of the uses listed must be assumed to be fairly insignificant, responsible for limited consumption of copper only.

TABLE 11
USES ACCORDING TO REGISTRATIONS AT ECHA’S WEBSITE (ECHA, 2013B)

<table>
<thead>
<tr>
<th>CAS No</th>
<th>Substance</th>
<th>Registered (identified) uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>1317-39-1</td>
<td>Copper(I)oxide</td>
<td>Electroplating and Galvanic (e.g. use in electronics)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Catalysts</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Brazing paste</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ceramics (e.g. use in brick-making)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Coatings, inks</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fertilizer</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pigments</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Powder metals</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Putties, fillers, construction chemicals</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pyrotechnics (including fireworks)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Rubber and plastics</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Thermit welding</td>
</tr>
<tr>
<td>7758-98-7</td>
<td>Copper(II)sulphate</td>
<td>Adsorbents</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Catalysts</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ceramics</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Coatings, inks</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cosmetics</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Electroplating and Galvanic (including use in electronics, printed wiring boards, engraving/lithography, metal surface treatment, wire coating)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fertilizer</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Glass</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Laboratory chemicals</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Lubricants and greases</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Leather dyes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Minerals and flotation</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pigments</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Processing aids</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Putties, fillers, construction chemicals</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Polishes and waxes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Raw material for non-ferrous smelting</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Raw materials for production of other compounds and fine chemicals</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Rubber and plastics</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Textile dyes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Adhesives</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Photochemicals</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Washing and cleaning products</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Water treatment</td>
</tr>
</tbody>
</table>
Table 11 does not include applications covered by other legislation than REACH. Such applications include antifouling and slimicides for copper(I)oxide, while for copper(II)sulphates e.g. nutrients, feed additives, disinfectants (e.g. for wash of infected laundry [France, 2013]) are not included.

For copper(I)chloride the applications not covered by Table 11 include surface treatment and intermediate for blue colorants as C.I. Reactive Blue 19, C.I. Acid Blue 40 and C.I. Acid Blue 62 [OECD 2005]. Other specific uses of copper(I)chloride include denitration of cellulose, gas analysis to absorb carbon monoxide, catalyst for organic reactions, decolorizer and desulfuring agent petroleum industry and condensing agent for soaps, fats and oil [OECD, 2005].

### 3.3.2 Registrations by the Danish Product Register

Data on copper(I)oxide, copper(II)sulphates and copper(I)chlorides in preparations registered in the Danish Product Register are summarised in Table 12. The figures presented indicate the quantities of the different compounds for the applications in question placed on the Danish market in 2010-2012.

According to the data available, the dominant use of copper(I)oxide is for antifouling. Another important application may be slimicides, but it appears that a significant export of copper(I)oxide for slimicides is also taking place. It is therefore not known with certainty whether copper(I)oxide was actually used as slimicide in Denmark in 2010-2012.

<table>
<thead>
<tr>
<th>Use area</th>
<th>Substance</th>
<th>Copper tons/year</th>
<th>Copper compound tons/year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antifouling</td>
<td>Copper(I)oxide</td>
<td>46 - 85</td>
<td>52 - 95</td>
</tr>
<tr>
<td>Other uses</td>
<td>Copper(I)oxide</td>
<td>26 - 32</td>
<td>29 - 36</td>
</tr>
<tr>
<td>Total</td>
<td>Copper(I)oxide</td>
<td>72 - 117</td>
<td>81 - 131</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Use area</th>
<th>Substance</th>
<th>Copper tons/year</th>
<th>Copper compound tons/year</th>
</tr>
</thead>
<tbody>
<tr>
<td>All uses</td>
<td>Copper(II)sulphate, mono- and pentahydrate</td>
<td>1 - 28</td>
<td>3 - 91</td>
</tr>
<tr>
<td>All uses</td>
<td>Copper(I)chloride</td>
<td>0.3 - 0.5</td>
<td>0.5 - 0.7</td>
</tr>
</tbody>
</table>
**1.** The figures presented are a mix of 2010 and 2012 data. The figures are registered as tons of compound per year, and here for comparison recalculated as tons of copper per year. The figures are given as an interval, as they are estimated based on concentration intervals for de-registered products.

**2.** It is assumed that compounds registered for paint etc. actually are used for antifouling, as copper(I)oxide to the best of our knowledge is not used for other types of paint in Denmark [Dahl, 2013].

**3.** Includes slimicides (product type 12 in BPD), which cover chemicals and products used for the prevention or control of slime growth on materials, equipment and structures used in industrial processes, e.g. on wood and paper pulp, porous sand strata in oil extraction. A significant export of slimicides containing copper(I)oxide has furthermore been registered.

Due to the rules of the Danish Product Register, it is not possible to divide the consumption of copper(II)sulphates and copper(I)chloride further by application. However, it is registered that in terms of copper(II)sulphate applications, additives for food and feed, together with non-agricultural pesticides and preservatives and process regulators are important uses. Minor consumption is also registered for products belonging to BPD product types 3, 6, 8, 12 and 21 (reference is made to Section 2.1.1).

Similarly for copper(I)chloride, important applications include intermediates and non-agricultural pesticides and preservatives, while minor consumption is also registered for products belonging to BPD product types 12 and 21 (reference is made to Section 2.1.1).

### 3.3.3 Substance flow analysis

In Table 13 the outcome of the substance flow analysis undertaken as part of a larger project in Denmark is presented for metallic copper as well as copper compounds. The figures presented are from 1992 and therefore relatively old, while the list of applications may still be partly valid. The information presented covers the estimated yearly consumption for the most important applications, as well as the knowledge available on the copper compounds used for different applications.

<table>
<thead>
<tr>
<th>Application</th>
<th>Tons Cu/year</th>
<th>Most important copper compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed additives</td>
<td>300 - 400</td>
<td>Copper sulphate, copper oxide</td>
</tr>
<tr>
<td>Wood preservation (pressure preservation)</td>
<td>200 - 250</td>
<td>Cuprioxide, Cuprisulphate, Cuprinaphthenate</td>
</tr>
<tr>
<td>Fertilizer</td>
<td>125 - 140</td>
<td>Copper sulphate</td>
</tr>
<tr>
<td>Pigments and colorants</td>
<td>100 - 200</td>
<td>Many different compounds</td>
</tr>
<tr>
<td>Plating (metals and plastics)</td>
<td>12 - 18</td>
<td>Copper sulphate, copper cyanide</td>
</tr>
<tr>
<td>Antifouling</td>
<td>27 - 40</td>
<td>No data *1</td>
</tr>
<tr>
<td>Fungicides and wildlife repellants</td>
<td>8 - 11</td>
<td>Cuprihydroxycyanide, Cuprinaphthenate</td>
</tr>
<tr>
<td>Catalysts</td>
<td>2 - 5</td>
<td>Copper oxide</td>
</tr>
<tr>
<td>Other applications</td>
<td>&lt;10</td>
<td>Many different compounds</td>
</tr>
<tr>
<td>Total</td>
<td>874 - 1074</td>
<td></td>
</tr>
</tbody>
</table>

*1 The copper compounds used is not stated by Lassen et al. [1996]. Based on [Madsen et al 1998], it is deemed realistic to assume that the copper compounds used in 1992 was either copper(I)oxide, copper thiocyanate or copper metal powder.
It may be noted that the copper compounds in focus for this survey have not been approved as pesticides for plant protection in Denmark as long as an approval system for pesticides has existed in Denmark [Gondolf, 2013].

### 3.3.4 Updated assessment of consumption

For the most important applications, figures on the consumption in Denmark in 2012 have been collected and presented in Table 14.

<table>
<thead>
<tr>
<th>Application</th>
<th>Tons Cu/year</th>
<th>Comment – reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed additive</td>
<td>365</td>
<td>Copper(II)sulphate pentahydrate *1</td>
</tr>
<tr>
<td>Antifouling</td>
<td>46 - 85</td>
<td>Copper(I)oxide – reference to Table 12</td>
</tr>
<tr>
<td>Wood preservation (pressure</td>
<td>47</td>
<td>Cupricarbonate, alkaline [MST, 2012]</td>
</tr>
<tr>
<td>preservation)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fertilizer</td>
<td>32</td>
<td>Mostly coppersulphate, but also a little copper</td>
</tr>
<tr>
<td></td>
<td></td>
<td>peroxychloride [NaturErhvervsstyrelsen, 2013; Broesbol-Jensen, 2013]</td>
</tr>
<tr>
<td>Plating (metals and plastics)</td>
<td>&lt;2</td>
<td>Copper cyanide, copper chloride, copper sulphate *2</td>
</tr>
<tr>
<td>Other applications *3</td>
<td>No data</td>
<td></td>
</tr>
<tr>
<td>Total *4</td>
<td>490 - 531</td>
<td></td>
</tr>
</tbody>
</table>

*1 Based on [Kjeldsen, 2013]. Estimated consumption for all types of domestic animals in Denmark. A reexport of approx. 750 tons copper(I)sulphate is assumed. All figures on copper(II)sulphate are assumed to represent copper(II)sulphate pentahydrate.

*2 Based on data from the Danish Product Register.

*3 May include slimicides and other minor applications etc. (see text). To the best of our knowledge, copper(I)oxide, copper(II)sulphate and copper(I)chloride are not used in paint or dyes [Sørensen, 2013].

*4 Other applications are not included.

The use of copper(II)sulphate as feed additive is by far the dominant use of copper compounds in Denmark. Copper is an essential nutrient to animals. In animal feed for pigs (in particular for piglets), the addition of copper sulphate also has a preventive effect on diarrhoea and thereby indirectly promotes growth. According to Kjeldsen [2013], feed additives for pigs are the largest field of application, consuming about 260 tons of copper (or 1020 tons of copper(II)sulphate), while feed additives for cattle and poultry consumes about 66 tons of copper (in 260 tons of copper(II)sulphate) and 29 tons copper (in 113 tons of copper(II)sulphate), respectively. Small amounts are furthermore used for mink, horses, pets and fish. The total consumption of feed additives for all types of domestic animals may be summed at 365 tons copper per year. These figures of consumption should be assumed to indicate the correct order of magnitude, although they suffer from some uncertainty.

Copper(II)sulphate is reexported from Denmark in premixes of vitamins and minerals for feed. This reexport counts for approximately 191 tons of copper (or 750 tons of copper(II)sulphate) annually [Kjeldsen, 2013].
Copper(I)oxide is regulated and used for antifouling in Denmark. The quantity of copper used is estimated based on data from the Danish Product Register. Antifouling paint containing copper compounds is no longer manufactured in Denmark [Dahl, 2013].

Copper is still used for pressure preservation of wood in Denmark. The only copper compound approved for this purpose today is cupricarbonate [MST, 2013a]. To best of our knowledge, copper(I)oxide is not used anymore. It is noted that an import of copper(II)sulphates for wood preservation is registered by the Danish Product Register. This import is compensated by a similar export, indicating that no use of copper(II)sulphates for wood preservation actually takes place in Denmark.

The nutrient effect is the reason for the use of copper sulphates in mineral fertilisers. Such fertilizers are used in copper-deficient soil (e.g. sandy soil, soil with high content of organic matter and on land cultivated without adding manure for a period of a couple of years). Winter wheat, potatoes and peas are sensitive to lack of copper.

Copper(II)sulphate is also used in the process of copper plating of metals and plastics for decorative purposes or corrosion protection. It is generally used as a basis for subsequent nickel and chromium plating due to the strong attachment of copper to the metal or plastic below.

Regarding other applications, the registrations in the Danish Product Register (Section 3.3.2) indicate that copper(I)oxide, copper(II)sulphates and copper(I)chloride may be used for other purposes in Denmark, inclusive of slimicides and additives for food and feed, alongside non-agricultural pesticides and preservatives, process regulators and for products belonging to BPD product types 3, 6, 8, 12 and 21 (reference is made to Section 2.1.1). No detailed information is available on these applications, and it is not known whether the consumption actually is taking place, or the registration represents an error.

### 3.4 Historical trends in use

No detailed studies on the trends in use of copper compounds are available. In this section, the trends are described to the extent possible based on the picture presented by Tables 13 and 14, supplemented by data available in the Nordic SPIN database on the use of Substances in Products in the Nordic countries. The database is based on data from the Product Registries of Norway, Sweden, Denmark and Finland [SPIN].

Considering feed additives, no significant development in overall consumption of copper compounds from 1992 to 2012 is observed (see Table 13 and 14).

Use of copper(I)oxide for antifouling paint has increased from less than 27-40 tons Cu/year in 1992 to 46-85 tons Cu/year in 2012 (see Table 13 and 14). However, this overall trend may cover significant fluctuation. According to the SPIN database, the consumption of copper(I)oxide in antifouling paint in Denmark was registered at about 364 tons in 2001, 492 tons in 2002 and 88 tons in 2011. No registrations in antifouling paint have been published for other years [SPIN]. The consumption figures for 2001 and 2002 seem very high and it is not known whether the figure is due to database errors or natural variation.

The overall development regarding the consumption of copper(I)oxide in Denmark as registered by SPIN is a decline from approximately 1400 tons in 2002 to 77 tons in 2011 (no explanation on the difference between 77 tons and the 88 tons mentioned above is available) [SPIN]. The rationale behind this large decline has not been investigated, and it is not known whether the decline to some extent is due to database errors.

Survey of copper(I)oxide, copper(II)sulphates and copper(I)chloride
It may be that the trend for use for copper(I)oxide is influenced by the ongoing evaluation of biocides under the EU Biocidal Products Regulation. The same may be the case for use of copper(II)sulphates. Both copper(I)oxide and copper(II)sulphates were “not-included for use” under the BPD for wood preservation in 2006, and currently the use of e.g. copper(I)oxide for antifouling is being evaluated. Use of copper(II)sulphates for “hoof baths” for cattle was banned in 2006 [AVV, 2013]. Copper(I)oxide and copper(II)sulphates are, furthermore, assessed as “not-included for use” for a number of product types under the BPD (product types 1, 4 and 8 - reference is made to Section 2.1.1), which would naturally eliminate the consumption of copper(I)oxide and copper(II)sulphates for these applications.

Regarding other applications such as pressure preservation of wood, fertilizers and plating, the overall trend from 1992 to 2012 is a significant decline in the consumption of copper compounds. The rationale behind this development has not been investigated. It is, however, known that the use of copper(II)sulphate for copper plating in Denmark has been much reduced due to outsourcing and competition from abroad [Sørensen, 2013].

3.5 Summary and conclusions
No detailed studies on the use of copper(I)oxide, copper(II)sulphates and copper(I)chloride are available and information related to use and consumption internationally (in EU and globally) are old and not very detailed.

Based on the information available, the dominant uses in Denmark are assessed as the use of copper(II)sulphate pentahydrate as feed additive, followed by the use of copper(I)oxide for antifouling and the use of copper(II)sulphates in fertilizers. Other uses appear to be insignificant, but detailed data are not available. Compared to the use of copper(I)oxide and copper(II)sulphates, the use of copper(I)chloride is insignificant. For pressure preserved wood, the copper compound used today is cupricarbonate. The total consumption of copper(I)oxide, copper(II)sulphates and copper(I)chloride is estimated at 490-530 tons copper per year in 2012. This figure includes consumption of cupricarbonate for pressure preservation of wood, but does not include a number of minor applications.

The general trend in recent years for the use of copper(I)oxide is a clear decline in consumption. The consumption of copper(I)oxide for antifouling has, however, increased from less than 27-40 tons Cu/year in 1992 to 46-85 tons Cu/year in 2012. No significant development regarding the consumption of copper(II)sulphate as feed additive from 1992 to 2012 is observed. The consumption has been rather steady in the range of 300-400 tons Cu/year. It may be noted that the import of copper(II)sulphate, raised by 26% from 2312 tons/year (average for 2007-2011) to 2912 tons/year in 2012.

The use for copper(I)oxide and copper(II)sulphates may have been influenced by the ongoing evaluation of biocides under the EU Biocidal Products Directive (now replaced by the Biocidal Products Regulation). Both copper(I)oxide and copper(II)sulphate are assessed as “not-included for use” for a number of product types under the BPD inclusive of “Human hygiene biocidal products” (PT1), “Food and feed area disinfectants” (PT4) and “Wood preservatives” (PT8). These decisions will naturally eliminate the consumption of copper(I)oxide and copper(II)sulphate for these applications.

It should be noted that copper(II)sulphate covers several compounds, of which copper(II)sulphate pentahydrate is the dominant compound being manufactured and used. Copper(II)sulphate monohydrate has limited use compared with copper(II)sulphate pentahydrate, while copper(II)sulphate anhydride has little commercial use.

Survey of copper(I)oxide, copper(II)sulphates and copper(I)chloride
4. Waste management

In considering the fate of copper compounds in the waste management part of the life cycle, it must be recognised that many uses are minor and not well described. This description is therefore focused on the main applications of copper(I)oxide, copper(II)sulphate and copper(I)chloride known to take place in Denmark, and for which knowledge on actual use and disposal patterns is available. It has, however, been decided to include wood preservation in the considerations as well, as copper oxides and copper sulphates have historically been used in this context (mainly for pressure preservation). The applications to be focused on therefore include:

- Antifouling paint;
- Feed additives;
- Mineral fertilizers, and
- Pressure preservation of wood.

For other applications, the available data on the applications and disposal of waste products are too scarce to be addressed.

4.1 Waste from manufacture and use of copper(I)oxide, copper(II)sulphates and copper(I)chloride etc.

Manufacture of copper compounds, mixtures and articles (materials and products) based on copper(I)oxide, copper(II)sulphate and copper(I)chloride does not take place in Denmark.

4.2 Waste products from the use of copper(I)oxide, copper(II)sulphate and copper(I)chloride in mixtures and articles

Waste products from use of antifouling paint are generated with construction of new ships and boat as well as with maintenance and repair. The waste products must be assumed to include packaging with residues of paint, and dust as well as other residues from grinding, sandblasting or high pressure washing processes intended to remove old paint from boats and ships before new paint is applied. No recent studies on generation or disposal of residues from these processes are available. It is known that antifouling paint may contain between 3 and 50% copper(I)oxide on a weight basis depending on the type of paint [Hempel, 2013a; Hempel, 2013b]. According to [MIM, 2012], all waste products classified as hazardous waste must be collected and treated as hazardous waste.

The amount of paint being lost to surface water, sewage treatment or soil has, however, been estimated in the EU Emission Scenario Document for Antifouling Products [Plassche and Aa, 2004]. According to this document, application of paint on commercial ships in shipyards will result in a typical loss of paint to surface water of 7.5%, while a worst case scenario may result in a loss of 35%. For pleasure boats, losses to sewage treatment plants and soil of typically up to 2.5% and up to 6% in worst case scenarios are anticipated, respectively. Considering removal of old paint layer by either high pressure water washing or abrasion in shipyards, or by normal washing or abrasion in boat yards, the Emission Scenario Document states that losses of 5% up to 30% (worst case scenario) should be assumed [Plassche and Aa, 2004]. Disposal will take place to surface water for shipyards and to surface water, sewage treatment plants and soil for boatyards. Although no recent surveys are available for Denmark, the emission factors quoted from the EU Emission Scenario...
Document clearly show that application of antifouling paint and removal of old paint are considered activities responsible for significant losses of copper compounds and other active ingredients in antifouling paint to the environment if risk mitigation measures are not used. According to Gondolf [2013], risk mitigation measures have high priority in the ongoing EU review of the active substances within product type 21.

Regarding waste products from pressure preservation of wood in Denmark, no recent studies on disposal are available. According to Hansen et al. [1997], waste products are limited to contaminated sludge. The sludge is classified as chemical waste and must be disposed of as such. Through use (cutting, drilling etc.) of pressure preserved wood, dust and small pieces of wood are generated that will partly end up in soil and partly be collected as solid waste. No recent studies on the quantities of copper being disposed of by these routes are available.

Old pressure preserved wood being disposed as waste must be landfilled unless the supervising authority after a concrete assessment finds that the wood is suitable for material recovery or incineration [MIM, 2012]. The majority of Danish pressure preserved wood is exported for incineration at approved facilities in Germany. So far no plant or facilities approved for treatment of pressure preserved wood exist in Denmark.

Depending on the applications, waste products from other uses of copper(I)oxide, copper(II)sulphate and copper(I)chloride may be assumed to be recycled or end up as chemical waste in municipal waste, in waste water or sewage sludge, or be dispersed in the environment. No recent studies on the circulation of copper in the Danish society are available.

End products manufactured in Denmark using copper compounds include feed, fertilizer and pressure preserved wood. The following data illustrate the content of copper or copper compounds in these end products:

- **Feed**: 0.0015-0.0170% Cu as copper sulphate (see Table 3)
- **Fertilizer**: up to 0.1% Cu as e.g. copper sulphate [Lassen et al., 1996]
- **Wood pressure preserved**: 0.05-0.36% copper (freshly preserved [Hansen et al., 1997]).

Disposal of waste from manufacture of end products depends on the concentration of copper compounds in the waste. Waste exceeding certain thresholds is treated as hazardous waste. The lowest threshold for characterization as hazardous waste is related to copper sulphate [MIM, 2012]. In this case, a threshold of 20% of the waste weight is prescribed. For copper(I)oxide and copper chloride, the threshold is 25% of the waste weight. These thresholds address the toxicity of the copper compounds towards humans and not their toxicity in aquatic environments.

If toxicity in the aquatic environment is taken into account, which it is in some European countries and some Danish municipalities, waste containing the copper substances in question is considered hazardous above a threshold of 0.25% [Astrup, 2013].

### 4.3 Releases of copper(I)oxide, copper(II)sulphate and copper(I)chloride from waste disposal

Feed is supplied to livestock, and residues in the form of manure are applied to farmland. The only study illustrating the circulation of copper in Danish agriculture is rather old (reference is made to [Hansen and Tjell, 1981]) and should preferably be updated.

While copper in itself is an element and cannot be destroyed by waste treatment, the fate of chemical compounds such as copper(I)oxide, copper(II)sulphate and copper(I)chloride are more uncertain. As described in Section 5.2., the copper ion (Cu⁺) in cuprous substances such as copper(I)oxide
and copper(I)chloride are unstable in aqueous environments and tend to transform to the cupric ion (Cu$^{2+}$), while copper(II)sulphate is hydrolytically stable, not biodegradable and characterised by strong adsorption to organic carbon and to inorganics such as aluminium, manganese and iron oxides.

All the substances in question should be assumed to be decomposed to their basic components (e.g. ionic copper) by thermal or chemical treatment, while their fate by biological treatment as composting or landfilling may depend strongly on the humidity of the environment. In a humid environment copper(I)oxide and copper(I)chloride should be expected to transform into other substances, while they may remain unchanged in a dry environment. During biological treatment, copper(II)sulphate will likely remain unchanged and strongly attached to soil particles. From landfills it may slowly be washed out as part of the leachate.

4.4 Summary and conclusions

In Denmark, waste is generated from use of mixtures and articles containing copper compounds and from used products being discarded as waste, including packaging with residuals. Waste from manufacture of copper compounds and mixtures and articles based on copper(I)oxide, copper(II)sulphates and copper(I)chloride is not generated in Denmark.

The chapter is focused on waste products from the use of copper compounds for antifouling, feed additives, fertilizer and wood pressure preservation. Other uses are insignificant and not well described. However, also with respect to the uses in focus, no recent studies on generation or disposal of residues from waste generating processes are available. Based on the knowledge available, it may be concluded:

- The concentration of copper compounds in some products as e.g. antifouling paint is so high that residues qualify for characterisation as hazardous waste. Waste products classified as hazardous waste must be collected and treated as such.

- Emission factors quoted from the EU Emission Scenario Document for Antifouling Products clearly show that internationally application of antifouling paint and removal of old paint are considered activities responsible for significant losses of copper compounds to the environment if risk mitigation measures are not used.

- Waste products from wood pressure preservation are limited to contaminated sludge. By shaping of pressure preserved wood, dust etc. containing copper will end up in soil and solid waste. In Denmark, old pressure preserved wood being disposed of as waste may be directed to landfill or exported for treatment abroad, as no facilities approved for treatment of pressure preserved wood exist in Denmark.

- All the copper compounds in question must be assumed to be decomposed to their basic components (e.g. ionic copper) by thermal and chemical treatment, while their fate by biological treatment and landfilling may differ depending on the amount of water they are exposed to.
Survey of copper(I)oxide, copper(II)sulphates and copper(I)chloride
5. Environmental effects and exposure

Numerous studies on the environmental toxicity, behaviour and fate of copper and copper compounds have been reported in the scientific literature and in various reports. A Voluntary Risk Assessment Report (VRAR) for copper, copper(II)sulphate pentahydrate, copper(I)oxide, copper(II)oxide and copper chloride trihydroxide was prepared in 2008 for the European copper industry by the European Copper Institute [ECI, 2008]. The VRAR has been reviewed and commented on by the European Commission’s (DG JRC) Technical Committee on New and Existing Substances (TC NES) and by the Commission’s (DG SANCO) Scientific Committee on Health and Environmental Risks (SCHER), which found the overall quality of the report to be good.

This report summarises and evaluates all the main environmental effect and fate studies on copper with the overall purpose being the development of no-effect concentrations (PNECs) suitable for Risk Assessment of copper in a number of relevant European environmental exposure scenarios. The ECI [2008] data review of environmental fate and effects of copper forms the backbone of the data used in the PT2 assessment report for copper(II)sulphate pentahydrate under the Biocides Product Directive (98/8/EC). France was the Rapporteur Member State (RMS) [France, 2013]. Much of the description in the following is based on this data review.

5.1 Environmental Hazard

5.1.1 Classification

As can be seen from the overview of existing legislation (Chapter 0), both copper(I)oxide, copper(II)sulphate and copper(I)chloride are subject to EU harmonised classification and labelling. All of these compounds are classified for acute and chronic hazards to the aquatic environment in Category 1, according to Annex VI of Regulation (EC) No 1272/2008 (CLP Regulation) (see Table 15).

<table>
<thead>
<tr>
<th>CLP Index No</th>
<th>International chemical identification</th>
<th>CAS No</th>
<th>Classification</th>
<th>Hazard Class and Category Code(s) *1</th>
<th>Hazard statement Code(s) *1</th>
</tr>
</thead>
<tbody>
<tr>
<td>029-002-00-x</td>
<td>Copper (I)oxide</td>
<td>1317-39-1</td>
<td>Aquatic Acute 1 Aquatic Chronic 1</td>
<td>H400 H410</td>
<td></td>
</tr>
<tr>
<td>029-004-00-0</td>
<td>Copper (II)sulphate,</td>
<td>7758-98-7</td>
<td>Aquatic Acute 1 Aquatic Chronic 1</td>
<td>H400 H410</td>
<td></td>
</tr>
<tr>
<td>029-001-00-4</td>
<td>Copper(I)chloride</td>
<td>7758-89-6</td>
<td>Aquatic Acute 1 Aquatic Chronic 1</td>
<td>H400 H410</td>
<td></td>
</tr>
</tbody>
</table>

*1 Aquatic acute toxicity Category 1/H400: Very toxic to aquatic life.
Aquatic chronic toxicity Category 1/H 410: Very toxic to aquatic life with long lasting effects.
These classifications apply to substances that are "very toxic to aquatic life" (H400), i.e. exert 50% acutely lethal or other significant toxic effects (LC50/EC50) on aquatic organisms at concentrations below 1 mg/l (Acute Category 1), or are "very toxic to aquatic life with long lasting effects" (H410). In this category, in addition to the high acute toxicity, the above mentioned copper compounds are either not rapidly degradable in the aquatic environment or they have a potential for bioaccumulation (Chronic Category 1).

5.1.2 Toxicity in the aquatic environment
The following summary of the acute and chronic toxicity of copper (compounds) is considered valid for all the copper compounds selected for this study, as it is widely accepted that it is the copper ion that determines the overall toxicity.

**Acute/short-term toxicity**
The acute toxicity of copper (compounds) is not used for the derivation of predicted no-effect values (PNECs) but is relevant for the assessment of risk for acute effects and for establishing the environmental classification of copper compounds.

The VRAR for copper [ECI, 2008] summarises in an appendix (K1) the valid data on acute/short-term toxicity to aquatic organisms and reports a lowest acute LC50 = 2.8 µg/l for rainbow trout (*Onchorhynchus mykiss*) and EC50 = 7.0 µg/l for *Daphnia magna*. The geometric means of all data on these two species were 73.4 µg/l and 62.0 µg/l, respectively.

ECHA [2013] provides information on publically available toxicity studies used for the registration and assessment of copper which include acute/short-term studies on its website. The review on copper by EHC [1998] also summarises acute/short-term ecotoxicological studies on aquatic species. The key studies in the two data sources are, however, the same.

It is noted that most data on the aquatic toxicity of copper (compounds) are relatively old, published 20-40 years ago. It is also apparent that the observed toxicity of copper compounds is due to the toxicity of free copper (II) ions and therefore depends significantly more on the ambient conditions in the test media (not least pH and water hardness) than on the specific test substance, which is most commonly the sulphate or the chloride.

The sum of data indicate that salmonid fish species tend to be more susceptible to copper (ions) than other common test species. The acute toxicity to salmonid fish appears to be approximately the same as the toxicity to invertebrates (crustacea, primarily *D. magna*) and algae.

The acute toxicity of copper to a number of marine species has also been tested; however, the data indicate that marine species are not more sensitive than freshwater species. The most sensitive marine species and acute endpoints reported by EHC [1998] are LC50 = 60 µg/l (copper sulfate) for Chinook salmon (*Onchorhynchus tshawytscha*), EC50 = 17 µg/l for the mysid shrimp *Holmesinysis costata* (copper sulfate) and EC50 = 50 µg/l for the alga *Chlamydomonas bullosa* (copper chloride).

**Chronic toxicity**
The VRAR for copper [ECI, 2008] identified 139 individual chronic NOEC values originating from high quality studies considered acceptable as the basis for the (pelagic) aquatic Risk Assessment of copper. These 139 values resulted in derivation of 27 species-specific NOEC values covering eight different trophic levels.

For freshwater fish, the "species mean" NOEC values ranged from 11.6 µg/l for *Onchorhynchus mykiss* (rainbow trout) to 120 µg/l for *Noemacheilus barbatulus* (loach) (endpoints growth and mortality, respectively). Almost all data on fish originated from studies with salmonids and minnows. The most sensitive individual NOEC for fish was 2.2 µg/l for *O. mykiss*.
For freshwater invertebrates the identified “species mean” values as reported in the literature ranged from 6.0 µg/l for the snail *Juga plicifera* to 50.3 µg/l for the amphipod *Hyalella azteca* (both based on endpoint mortality). Most data on aquatic invertebrates were available for the crustaceans *Daphnia magna*, *Daphnia pulex* and *Ceriodaphnia dubia* (water fleas). The most sensitive NOEC was 4 µg/l for *D. magna* and *C. dubia*.

The “species mean” NOEC for algae ranged from 43 µg/l for the green algae *Pseudokirchneriella subcapitata* (formerly *Selenastrum capricornutum*) to 138 µg/l for *Chlorella vulgaris* (endpoint growth for both). The lowest identified NOEC was 15.7 µg/l for *P. subcapitata*.

The individual single species data showed a very large intra-species variability, which was significantly influenced by test media characteristics, e.g. pH, dissolved organic carbon and water hardness. Therefore, for the aquatic risk assessment, the original NOEC values were normalised with regard to bioavailability in a number of typical European exposure scenarios using chronic copper bioavailability models (Biotic Ligand Models, BLM) developed and validated for three taxonomic groups: fish, invertebrates and algae. The species-specific BLM-normalized NOECs were then used for derivation of log-normal Species Sensitivity Distributions (SSD) and defining the HC5-50 (HC = Hazardous Concentration (threshold) and HC5-50 = the median 5th percentile of the SSD), using statistical extrapolation methods [ECI, 2008].

**PNEC derivation**

Based on this approach, as described above, it was suggested to use the HC5-50 of 7.8 µg/l as a “reasonable worst case PNEC freshwater for Europe in a generic context in absence of site-specific information on bioavailability parameters (pH, DOC, water hardness)” [France, 2013], i.e. this value was used for the risk assessment. In consideration of the very large volume of available data including a number of mesocosm studies, it was found acceptable not to apply any additional Assessment Factor (AF) to compensate for residual uncertainty (i.e. AF = 1).

If, instead of the statistical distribution method, the traditional assessment factor method is applied for derivation of the PNEC using the lowest identified chronic NOEC (2.2 µg/l for the fish *O. mykiss* (rainbow trout)) and an AF = 10 (standard, considering the amount of available data), the PNEC becomes 0.8 µg/l. This value is within the range of background copper levels in European freshwater environments [ECI, 2008].

Using the lowest NOEAEC (No Observed Ecologically Adverse Effect Concentration) observed in mesocosm/field studies and an AF = 1 as an alternative data basis of the assessment, the resulting PNEC becomes 3.6 µg/l [ECI, 2008].

For PNEC sediment the HC5-50 value of 1741 mg Cu/kg OC (corresponding to 87 mg Cu/kg dry weight) was proposed for generic Risk Assessment at European level using an AF = 1 [France, 2013].

The PNEC for Sewage Treatment Plants (STPs) - based on the most sensitive endpoint, which was inhibition of respiration - was determined to be 0.23 mg/l (AF = 1) [France, 2013].

The VRAR by ECI [2008] has been reviewed and commented on partly by the European Commission’s (DG JRC) Technical Committee on New and Existing Substances (TC NES) and partly by the Commission’s (DG SANCO) Scientific Committee on Health and Environmental Risks (SCHER).

TC NES [DG JRC, 2008] concluded that the Voluntary Risk Assessment Report (VRAR) had been conducted in line with the methodology described in the Technical Guidance Document (TGD), expanded by the use of the BLM concept for deriving PNEC values. Overall, TC NES found the con-
Survey of copper(I)oxide, copper(II)sulphates and copper(I)chloride

Inclusions of the VRA plausible and they were supported by the majority of the Committee. The SCHER [DG SANCO, 2009] also accepted the proposed conclusions on risk characterisation.

5.1.3 Effects in the terrestrial environment
Similar to the aquatic environment the toxicity of copper compounds in the terrestrial environment is considered to be determined by the copper ion and, hence, the below summary is valid for all the copper compounds selected for this study.

Specific data on ecotoxicological endpoints in the soil environment indicate that effects on growth and reproduction of earthworms and other soil macro-organisms occur at a copper level of less than 100 mg/kg dw [EHC, 1998; ECHA, 2013]. EHC [1998] report a one-week acute EC$_{50}$ for the earthworm Eisenia fetida of 62 mg Cu/kg soil and a 56 day chronic NOEC for reproduction of the same species = 32 mg/kg. A four-week EC$_{50}$ (reproduction) = 51 mg Cu/kg soil was reported for the earthworm Allolobophora chlorotica and 68 mg Cu/kg for the earthworm Aporrectodea caliginosa.

ECHA [2013] report for A. caliginosa, a 14 day NOEC (reproduction) = 50 mg Cu/kg and a 56 day NOEC = 70 mg/kg. A 40 day NOEC for litter decomposition = 50 mg Cu/kg soil is also reported.

PNEC derivation
For the terrestrial environment a dataset of 252 individual chronic NOEC/EC$_{10}$ values from 28 species and processes representing different trophic levels (decomposers, primary producers, primary consumers) were identified as valid and useful for the risk characterisation of copper (II)sulphate pentahydrate under the review programme for biocidal active substances [France, 2013]. The Risk Assessment approach was the same as described for the aquatic compartment, i.e. use of bioavailability-normalized chronic NOECs for derivation of PNECs based on statistically derived HC$_{5}$-50 values.

Using this approach and an AF = 1, the HC$_{5}$-50 of 45.6 mg Cu/kg soil dw was proposed as PNEC for the Risk Assessment of copper (sulphate) under the Biocide Products Directive as “reasonable worst case PNECsoil for Europe in absence of site-specific information on soil properties”.

Development of resistant bacteria
A special concern in relation to copper seems to be the possible release of copper-resistant bacteria in the environment, primarily in connection with the spreading of copper-containing (pig) manure on agricultural soils. EFSA [2012] reports that "high dietary copper induces an increase in copper-resistant bacteria" and find e.g. that genetically the copper resistance gene in Enterococcus faecium is located at the same plasmid that codes for erythromycin (and macrolide antibiotics in general), thus making co-transfer plausible. Other examples are also mentioned and EFSA [2012] further reports that data from soil bacterial isolates confirm a principal correlation between the development of resistance to copper and resistance to various antibiotics. However, at present the available data does according to EFSA [2012] not allow any estimate of the practical relevance of these findings.

The issue of possible development and transfer of bacterial resistance related to copper (and other contaminants) in the soil environment is currently being addressed in a Danish research project at the University of Copenhagen, Denmark [Dechesne et al., 2013].

5.2 Environmental fate and behaviour
Copper, an element regarded as belonging to the “heavy metals” group, is a transition metal with oxidation state I (cuprous, Cu$^+$) and II as (cupric, Cu$^{2+}$) as the principal forms. Being an element, copper does not degrade like organic compounds, but it does undergo transformation in the environment through different types of reactions. Copper is an essential element to all living organisms...
The below description of the environmental fate and behaviour of copper (compounds) is considered valid for all the copper compounds selected for this study. It is widely accepted that it is the copper ion that determines the overall bioavailability and thereby potential for toxic effects.

**Behaviour in the aquatic environment**

The cuprous ion, Cu⁺, is unstable in aqueous media and forms Cu²⁺ ions or compounds or precipitate as copper solids through a redox reaction. However, Cu(I) cations are only susceptible to such transformation when they are not chemically bound in insoluble compounds or stabilised in complexed forms. The cupric ion, Cu²⁺, typically binds to inorganic and organic ligands contained within water, soil and sediments. In water, Cu(II) binds to dissolved organic matter such as humic or fulvic acids and forms stable complexes with −NH₂, −SH and −OH in these organic acids. Cu(II) will also bind with varying affinities to inorganic and organic compounds in sediments and soils [ECI, 2008].

Free cupric ions are the biologically most active copper species; therefore, total copper concentrations do not necessarily directly reflect the potential for ecological effects as the actual exposure to and bioavailability of copper is affected by processes such as precipitation, dissolution, adsorption/desorption, complexation and competition for biological adsorption sites (biotic ligands).

Thus, in natural environments, more than 90% of the total copper is complexed and one study has shown that 99.8% of copper in aquatic systems can be bound to humic acids [ECI, 2008].

Precipitation will be more important in alkaline than in acid media. In aerobic environments, the most probable precipitates that can form are copper hydroxide (Cu(OH)₂), malachite (Cu(CO₃)(OH)₂) and azurite (Cu₃(CO₃)₂(OH)₂). In anaerobic, biologically active sediments, the solubility of copper is reduced due to formation of highly stable, sulphide-containing Cu(I) and Cu(II) minerals [ECI, 2008].

In accordance with this, it is found in the OECD SIDS on copper monochloride [OECD, 2005] that the copper (I) ion is unstable in the aquatic environment and tends to transform either to copper (II), to copper metal or to precipitate as the sulphide, cyanide or fluoride, respectively, unless a stabilizing ligand is present.

With regard to copper(II)sulphate pentahydrate, the EU Draft Assessment Report [France, 2013] describes the substance as non-volatile, hydrolytically stable, not biodegradable and characterised by strong adsorption to organic carbon and to inorganics such as aluminium, manganese and iron oxides.

**Adsorption to sediment and soil**

Adsorption to sediments, colloids and suspended particles is an important process in relation to the behaviour of copper in the aquatic environment. Both inorganic particles (clay minerals, iron, manganese, aluminium oxides) and organic materials are important adsorbents. In the Voluntary Risk Assessment Report for copper [ECI, 2008], the following partitioning coefficients (50th percentile) have been derived for copper and copper compounds:

- Partition coefficient in suspended matter: $K_{p_{\text{susp}}} = 30,246 \text{ l/kg (log } K_{p_{\text{susp}}} = 4.48)$
- Partition coefficient in sediment: $K_{p_{\text{sed}}} = 24,409 \text{ l/kg (log } K_{p_{\text{sed}}} = 4.39)$

In the terrestrial environment the processes are in principle the same as described for the aquatic environment but limitations in transformation rates may occur if soil moisture (pore water) levels...
in the soil are low or under anaerobic conditions. Regarding adsorption of copper (compounds) to soils, a median Kd = 2120 l/kg (average 4799 l/kg) was derived by ECI [2008] together with an empirical regression equation for prediction of Kd for copper in soil:

\[
\text{Log Kd} = 1.75 + 0.21 \text{pH(\text{soil solution})} + 0.51 \log(\text{OC \%}) \quad (R^2 = 0.42).
\]

The equation shows that sorption of copper to soil increases with increasing pH and content of organic matter in the soil.

**Behaviour in the atmosphere**

The atmosphere is not a relevant compartment for the inorganic copper species as demonstrated by their negligible vapour pressure (see Table 2) and as also stated in the VRAR for copper [ECI, 2008] (with copper production processes as an exception).

**PBT and vPvB assessment**

Copper is a metallic element and therefore is in principle not degradable at all. Persistence tests and criteria used in the assessment of organic chemicals are not applicable to inorganic species and elements [France, 2013]. Copper as inorganic metal is excluded from the P assessment taking into account Annex XIII of REACH Regulation 1272/2008. Therefore, the criterion for persistence in soil is not relevant.

Due to the homeostatic regulation of the concentration of the essential element copper in living cells of all kinds and the toxicity above the upper level of this regulation, copper is not considered to bioconcentrate to any appreciable degree. The approach to assess bioaccumulation for organic chemicals is not applicable to metals and inorganic metal compounds. Copper compounds are assessed not to fulfil the B criterion [ECI, 2008; France, 2013].

The effect data presented in section 5.1 (lowest NOEC = 2.2 µg/l) show that copper compounds meet the T criterion (NOEC = 10 µg/l) in the PBT assessment.

In conclusion, none of the copper compounds in this study are considered PBT or vPvB [ECI, 2008; France, 2013].

### 5.3 Environmental exposure

#### 5.3.1 Sources of release

No recent studies of copper emissions to the environment in Denmark are available. The emission pattern disclosed by the most recent study [Lassen et al., 1996] dealing with 1992-figures is presented in Table 16.

**TABLE 16**

<table>
<thead>
<tr>
<th>Process/source</th>
<th>Estimated emission to (tons Cu/year) *1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Air</td>
</tr>
<tr>
<td>Feed/manure</td>
<td>0</td>
</tr>
<tr>
<td>Fertilizer</td>
<td>0</td>
</tr>
<tr>
<td>Antifouling *3</td>
<td>0</td>
</tr>
<tr>
<td>Fungicides and wildlife repellants</td>
<td>0</td>
</tr>
<tr>
<td>Total</td>
<td>0</td>
</tr>
</tbody>
</table>

---

Survey of copper(I)oxide, copper(II)sulphates and copper(I)chloride
Based on the updated consumption figures presented in Table 14, the emission of copper to Danish soil with manure and fertilizer in 2012 can be estimated at 365 tons copper with manure and 32 tons with fertilizer. An emission of copper to the water environment based on the use of antifouling paint also takes place, but cannot be quantified. As part of the ongoing EU assessment of copper(I)oxide as active substance within product type 21 (Antifouling) under the Biocidal Product Regulation a comprehensive Risk Assessment incorporating the newest knowledge available will be prepared. This assessment will also include an exposure assessment. The assessment is anticipated to be available relatively soon.

A balance of copper in Danish agricultural soils was calculated more than 30 years ago [Hansen and Tjell, 1981]. At that time, the total supply of copper to Danish agricultural soils was estimated at 1180 tons/year (700 tons with mineral fertilizers, 400 tons with manure and 80 tons by other sources), while an estimated 30 tons/year were removed by leaching, consumption of livestock and miscellaneous losses. The accumulation of copper in the top soil layer (ploughing layer) was calculated at 1.5%/year as an average for all Danish agricultural soils.

The figures presented in Tables 14 and 16 illustrate that accumulation of copper in the topsoil is an ongoing process. Assuming that the supply is reduced to about 397 tons/year (reference is made to Table 14 – consumption data on feed and fertilizer) corresponding to about 1/3 (397/1180 – please see above) of the supply in 1981, the accumulation of copper in the top soil layer (ploughing layer) will now have been reduced to an average of roughly 0.5% yearly (1/3 of 1.5% - please see above).

The supply of copper with manure to agricultural soils in Denmark is, however, not evenly distributed. As stated in Section 3.2.3, feed for pigs is the dominant use of copper feed additives, followed by feed for cattle. The highest concentrations are used in feed for piglets (see Table 3). It should therefore be expected that agricultural soil subject to supply of manure from pigs, and in particular piglets, will be exposed to a supply of copper significantly exceeding the average supply. The differences are illustrated by the monitoring results of the copper content in manure given in Table 17.

Copper(I)oxide used for antifouling purposes is in Denmark mainly used for commercial marine vessels, as the use for pleasure boats is restricted (see Table 3). It follows that emission in Denmark is predominantly to marine waters, including harbours, shipping lanes and the open sea. Copper(I)oxide is released to marine waters during the service life of the paint and via discharge from shipyards or boatyards as a result of application or maintenance and removal of antifouling paint (see details in Section 4.2). In the water, copper will partly sorb to particles and sediment.

It may be noted that in 2010, dredged materials from e.g. harbours being dumped at sea emitted 16,457 tons copper to the Danish marine environment [OSPAR, 2012]. A fraction of this copper likely originates from antifouling paint use in Denmark.

5.3.2 Monitoring data

Copper as an element is included in the National Monitoring and Assessment Programme for the Aquatic and Terrestrial Environment, NOVANA. This monitoring programme covers point sources (sewage treatment plants) as well as streams, deposition from air and the marine environment.
However, no specific copper compounds, including copper(I)oxide, copper(II)sulphate and copper(I)chloride, are included in the programme. Therefore, the values stated in the tables below are for copper in general (total copper). Table 17, below, shows figures from the NOVANA programme as well as from other relevant Danish monitoring programmes.

**TABLE 17**

MoST recent monitoring data for copper in the environment from the National Environmental Surveillance Programme (NOVANA) and other Relevant monitoring programmes

<table>
<thead>
<tr>
<th>Medium</th>
<th>Number of samples</th>
<th>Median (maximum) concentration</th>
<th>Unit</th>
<th>Year</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Municipal sewage treatment plants – effluent</td>
<td>41</td>
<td>4.4 (60)</td>
<td>µg/L</td>
<td>2011</td>
<td>Naturstyrelsen, 2012</td>
</tr>
<tr>
<td>Sewage sludge</td>
<td>No data</td>
<td>256 (286) *1</td>
<td>Mg/kg dw</td>
<td>2005</td>
<td>Schwærter and Grant, 2003</td>
</tr>
<tr>
<td>Manure from pigs</td>
<td>17</td>
<td>240 (510)</td>
<td>Mg/kg dw</td>
<td>2002</td>
<td>Schwærter and Grant, 2003</td>
</tr>
<tr>
<td>Manure from cattle</td>
<td>17</td>
<td>51 (280)</td>
<td>Mg/kg dw</td>
<td>2002</td>
<td>Schwærter and Grant, 2003</td>
</tr>
<tr>
<td>Air concentration (background)</td>
<td>No data</td>
<td>Approx. 2</td>
<td>µg/m³</td>
<td>2010</td>
<td>DCE, 2012</td>
</tr>
<tr>
<td>Air deposition (background - land)</td>
<td>No data</td>
<td>790</td>
<td>µg/m²</td>
<td>2010</td>
<td>DCE, 2012</td>
</tr>
<tr>
<td>Air deposition (background - territorial waters)</td>
<td>No data</td>
<td>750</td>
<td>µg/m²</td>
<td>2010</td>
<td>DCE, 2012</td>
</tr>
<tr>
<td>Lakes (water)</td>
<td>96</td>
<td>0.57 – 0.66</td>
<td>µg/L</td>
<td>1998-2003</td>
<td>Boutrup et al., 2006</td>
</tr>
<tr>
<td>Streams (water)</td>
<td>&gt; 51</td>
<td>0.67 – 1.1 (7.25)</td>
<td>µg/L</td>
<td>2001</td>
<td>Bøgestrand, 2002</td>
</tr>
<tr>
<td>Marine waters (mussels)</td>
<td>No data</td>
<td>Approx. 10-15 (approx. 50)</td>
<td>mg/kg dw</td>
<td>2003</td>
<td>Boutrup et al., 2006</td>
</tr>
<tr>
<td>Ground water</td>
<td>No data</td>
<td>0.2-2 (1000)</td>
<td>µg/L</td>
<td>1998-2003</td>
<td>Boutrup et al., 2006</td>
</tr>
<tr>
<td>Sediments – Egå marina, Århus</td>
<td>No data</td>
<td>53-600 *2</td>
<td>Mg/kg dw</td>
<td>Before 1997</td>
<td>Madsen et al., 2000</td>
</tr>
<tr>
<td>Sediments - Århus Fishing Port</td>
<td>No data</td>
<td>100 – 2400 *2</td>
<td>Mg/kg dw</td>
<td>Before 1997</td>
<td>Madsen et al., 2000</td>
</tr>
<tr>
<td>Sediments- Bønnerup Harbour - slipways</td>
<td>No data</td>
<td>7000 – 8000 *2</td>
<td>Mg/kg dw</td>
<td>Before 1997</td>
<td>Madsen et al., 2000</td>
</tr>
<tr>
<td>Sediments - Bønnerup Harbour – bassins</td>
<td>No data</td>
<td>15 – 70 *2</td>
<td>Mg/kg dw</td>
<td>Before 1997</td>
<td>Madsen et al., 2000</td>
</tr>
<tr>
<td>Sediments - Århus Bay - sediments</td>
<td>No data</td>
<td>25- 50 *2</td>
<td>Mg/kg dw</td>
<td>Before 1997</td>
<td>Madsen et al., 2000</td>
</tr>
</tbody>
</table>
Survey of copper(I)oxide, copper(II)sulphates and copper(I)chloride

In Table 18, the outcome of the only existing comprehensive investigation of the content of copper in Danish agricultural soils is presented. The investigation dates back to the beginning of the 1990’s. The overall median concentration was determined as 7.0 mg/kg. The concentration in agricultural soils was higher, and highest in soil being subject to sludge application. In undisturbed nature and forest soils, levels were as low as 0.9 mg/kg.

**Table 18** MONITORING OF COPPER IN DANISH SOILS

<table>
<thead>
<tr>
<th>Medium</th>
<th>Number of samples</th>
<th>Median concentration (variation) *1</th>
<th>Unit</th>
<th>Year</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil – all</td>
<td>393</td>
<td>7.0 (0.8; 15.9)</td>
<td>mg/kg</td>
<td>1992-93</td>
<td>Jensen et al., 1996</td>
</tr>
<tr>
<td>Soil – agricultural, not sludge amended *2</td>
<td>311</td>
<td>7.8</td>
<td>mg/kg</td>
<td>1992-93</td>
<td>Jensen et al., 1996</td>
</tr>
<tr>
<td>Soil – agricultural, sludge amended *2</td>
<td>20</td>
<td>10.4</td>
<td>mg/kg</td>
<td>1992-93</td>
<td>Jensen et al., 1996</td>
</tr>
<tr>
<td>Soil – undisturbed nature and forests</td>
<td>12 – 34</td>
<td>0.9 – 5.6</td>
<td>mg/kg</td>
<td>1992-93</td>
<td>Jensen et al., 1996</td>
</tr>
</tbody>
</table>

*1 Figures in brackets represent 5%-fractile and 95%-fractile, respectively.

*2 Sludge amended means that municipal sewage sludge has been supplied to the soil.

The content of copper in Danish agricultural soils reported as the copper figure is, however, monitored yearly by the Danish Knowledge Center for Agriculture. The copper figure (1 Cut) is defined as 1 mg of copper soluble in EDTA per 1 kg soil, corresponding to approximately 2.5 kg Cu/ha in the top soil layer (ploughing layer) [AVV, 2013]. Yearly, about 10,000 soil samples from locations all over Denmark are analysed. The results available cover the period of 1987 to 2012. The average copper figures per year for this period are approximately 3 Cut and slowly increasing. The percentage of copper figures per year exceeding 10 Cut is increasing as well [AVV, 2013]. Assuming that the relation between the copper figure and the content of copper in soil is reasonably solid, these data thus confirms the anticipated accumulation of copper in the top soil layer presented in Section 5.3.1 above.

An issue calling for attention in recent years has been the “Funen roe deer disease”. It has been suggested that this disease was caused by copper supplied to agricultural soils by application of manure. Investigations of the content of copper in liver samples from healthy and sick roe deer have
been carried out in order to examine this hypothesis. The outcome of these investigations are summarised in Table 19 [Chriël et al., 2012] and discussed in Section 5.4.

**TABLE 19**

<table>
<thead>
<tr>
<th>Origin</th>
<th>Number of samples</th>
<th>Average (min.-max.) concentration</th>
<th>Unit</th>
<th>Year</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Funen – sick deer</td>
<td>23</td>
<td>20.5 (2-205)</td>
<td>Mg/kg ww</td>
<td>2009-2010</td>
<td>Chriël et al., 2012</td>
</tr>
<tr>
<td>Bornholm – healthy deer</td>
<td>12</td>
<td>43 (5-116)</td>
<td>Mg/kg ww</td>
<td>2009-2010</td>
<td>Chriël et al., 2012</td>
</tr>
<tr>
<td>Bornholm – healthy deer</td>
<td>18</td>
<td>20.3 (0.03-82)</td>
<td>Mg/kg ww</td>
<td>2009-2010</td>
<td>Chriël et al., 2012</td>
</tr>
<tr>
<td>Funen – healthy deer</td>
<td>18</td>
<td>15.2(3-60)</td>
<td>Mg/kg ww</td>
<td>2009-2010</td>
<td>Chriël et al., 2012</td>
</tr>
<tr>
<td>Funen – sick deer</td>
<td>17</td>
<td>35(3-186)</td>
<td>Mg/kg ww</td>
<td>2009-2010</td>
<td>Chriël et al., 2012</td>
</tr>
<tr>
<td>Funen – deer found dead</td>
<td>7</td>
<td>20.3(2-52)</td>
<td>Mg/kg ww</td>
<td>2009-2010</td>
<td>Chriël et al., 2012</td>
</tr>
</tbody>
</table>

5.3.3 **Comparison of PEC with PNEC**

The monitoring data presented in Table 17 and Table 18 above can be regarded as indicative of the environmental concentrations occurring in various sub-compartments of the Danish environment. Therefore, they can replace “PEC” in a comparison with the PNEC values presented in Sections 5.1.2 and 5.1.3, i.e. an indicative PEC-PNEC assessment of copper in the Danish environment. It is important to stress that the monitoring data represent the combined environmental exposure from all sources of copper and copper compounds, not only the specific compounds otherwise being addressed in this report.

With this in mind, the levels of (total) copper in fresh and marine surface waters in Denmark appear to be in the range 0.5-1.5 µg/l (Table 17), which is roughly 5-15 times lower than the PNEC value of 7.8 µg/l for water proposed by France [2013] while they are of the same magnitude as the more conservative value of 0.8 µg/l resulting from the traditional assessment factor approach (the official Danish EQS for (dissolved) copper is 1.0 µg/l, see Table 3), i.e. PEC/PNEC ≈ 1.

In marine sediments not polluted by point sources, copper levels are 25-35 mg/kg dw while the proposed PNECsed is 87 mg/kg dw [France, 2013]. This gives a PEC/PNEC ≈ 0.3–0.4. In polluted harbour sediments the PEC/PNEC ratio will exceed 1 considerably.

Regarding possible impacts of copper on STP processes, the influent levels to STPs, which are the relevant levels for this assessment, are no longer included in the NOVANA programme but Kjølholt et al. [2011] have, based on an analysis of national monitoring data from 1998-2009, shown that they are roughly 10 times higher than the effluent levels. Therefore, an estimated median influent level to STPs will be around 35 µg/l compared to the proposed PNEC of 230 µg/l [France, 2013], i.e. the median PEC/PNEC ratio will be approx. 0.15.

In agricultural soils having been amended with sewage sludge the average copper concentration is 10.4 mg/kg dw and in soils without such amendment 7.8 mg/kg dw. In natural soils, copper concen-
lations have been found in the range 0.9–5.6 mg/kg dw. Comparing this to the proposed PNEC of 45.6 mg/kg dw [France, 2013], the PEC/PNEC ratio for sludge amended soils will be less than 0.25, while for other soils it will be even lower.

5.4 Environmental impact

The increasing content of copper in Danish agricultural soils
As stated in Section 5.3, an accumulation of copper in the top soil layer (ploughing layer) in Danish agricultural soils has been going on since at least the 1980’s. The current rate of accumulation is assessed roughly at 0.5% yearly. Considering that the median content of copper in Danish agricultural soil was determined at 7.8 mg/kg by 1996 [Jensen et al., 1996] and that the eco-toxicological soil quality criterion for copper was established as 30 mg/kg [Scott-Fordsmand et al., 1995], it can be calculated that the time needed for the median content of Danish agricultural soils to reach a level corresponding to the eco-toxicological soil quality criterion exceeds 500 years

As stated above, it is expected that agricultural soil subject to supply of manure from pigs, and in particular piglets, will be exposed to a supply of copper significantly exceeding the average supply, and the variation in the content of copper in soil may consequently also be significant. In Poulsen [1998], calculations have been made showing that if the maximum allowable addition of copper to piglets is utilized and a soil quality criterion of 40 mg/kg is adopted, the criterion will be reached in only 110 years. It follows, that if the criterion is reduced to 30 mg/kg, it will be reached in less than 100 years.

The Funen roe deer disease
Focusing on the "Funen roe deer disease" and the hypothesis that this disease was caused by copper supplied to agricultural soils by application of manure, the study referred to above concluded that the study results did not confirm the hypothesis. The study also concluded that the methods had some design weaknesses and it was recommended that further and more extensive investigations be carried out as the quantities of copper supplied to agricultural soils, combined with the sensitivity of certain wildlife species, called for concern [Chriël et al., 2012].

In this context, attention is drawn to the significant variation in the content of copper in roe deer as presented in Table 19. An issue not clarified is how roe deer and other wildlife are actually exposed to copper, as copper, due to the homeostatic regulation of the concentration of the essential element copper in living cells, is not considered to bioconcentrate in plants to any appreciable degree. It may be noted that chronic poisoning has been reported in sheep grazing on herbage dressed with liquid manure from pigs fed copper supplemented diets [Poulsen, 1998].

Voluntary Risk Assessment Report (VRAR) of copper compounds [ECI, 2008]
The overall result of the risk characterization in the VRAR by ECI [2008] is that there is no concern for most of the industrial sectors assessed, i.e. no further risk reduction measures are required beyond those already applied. For chemical industry it was, however, concluded that additional information on emissions and the bioavailability corrections that had been used is needed for the subsequent process of developing risk reduction measures. Waste water from landfills and incineration sites being lead to a sewage treatment plant was found to be of no environmental concern while for direct discharges to surface waters from waste incineration plants additional information similar to that described above is needed. For road borders a potential risk to the terrestrial environment in the immediate vicinity (1-2 metres) of urban roads was identified and it was concluded that the bioavailability correction used in the VRAR should be incorporated when developing risk reduction measures.

3 Calculated as 0.5% of 7.8 mg/kg = 0.039 mg per year, and (30 mg/kg-7.8 mg/kg)/0.039 mg/year = 569 years.
EFSA assessment of copper(II)sulphate pentahydrate as feed additive

EFSA [2012] concluded in its Risk Assessment of the use of copper(II)sulphate pentahydrate that the use of this chemical is safe for all animal species up to the maximum total copper content authorised in feed. For the environment, it was found that “there might be a potential concern related to sediment contamination” whereas the use of copper compounds in aquaculture is not expected to pose a risk. The issue of possible development of bacterial co-resistance to copper and certain antibiotics is discussed, but EFSA finds that data are currently insufficient for a quantification of the risk.

Concerning the terrestrial environment, potential risks to soil organisms have been identified by model calculations as a result of application of piglet manure [EFSA, 2012]. There may also be a potential environmental concern related to contamination of sediment owing to drainage and the run-off of copper to surface water [EFSA, 2012]. The statement is elaborated on by Monteiro et al. [2010], who state that while "livestock evaluations indicated that environmental risks are acceptable at the current time but in the future risks could occur in some systems. The systems most vulnerable to metal input in manure were clearly acid sandy soils, represented in the scenarios. The distribution of these scenarios within Europe is largely in Flanders, the Netherlands, north western Germany and Denmark. There is a clear need to better establish whether such soils are as sensitive to metal inputs as is predicted here. Since problems of high metal concentrations in drain flow and runoff, once established, would be difficult to remediate, it is important to proactively assess soil sensitivity before setting policy on manure application". This assessment is based on model calculations that integrate the physicochemical and hydrological processes determining the accumulation and leaching of metals in soil. According to [EFSA, 2012], final conclusions must await further model validation and additional data.

Antifouling

According to Madsen et al. [2000], the concentrations at which effects of copper are measured in laboratory tests will generally be higher than the background concentrations observed for copper in the marine environment in Denmark. However, concentrations measured in and in the vicinity of harbours are at the same level as or higher than concentrations at which effects have been measured. The measurements available of the content of copper in the marine environments in Denmark are, however, old, and more recent and updated measurements have so far not been published.

5.5 Summary and conclusions

Copper(I)oxide, copper(II)sulphate and copper(I)chloride are all subject to EU harmonised classification. They are classified as Aquatic Acute 1 H400 (very toxic to aquatic life) and Aquatic Chronic 1 H410 (very toxic to aquatic life with long lasting effects). Neither of these compounds, however, qualifies for being classified as PBT-substances or vPvB, as the P and B criterion in the PBT is not considered applicable to copper. The toxicity of all the copper species in this report is largely due to the toxicity of the copper (II) ion.

An accumulation of copper in the top soil layer (ploughing layer) in Danish agricultural soils has been going on at least since the 1980’s. The current average rate of accumulation is roughly estimated to about 0.5% yearly. The supply of copper to Danish agricultural soils is, however, not evenly distributed and areas exposed to supply of manure from pigs (in particular piglets) will be exposed to a supply of copper significantly exceeding the average supply. It is estimated that the soil concentration of copper for areas supplied with manure from piglets may reach the Danish ecotoxicological soil quality criterion for copper of 30 mg/kg in less than 100 years.

The hypothesis has been presented that the "Funen roe deer disease" was caused by copper supplied to agricultural soils by application of manure. Existing studies have not confirmed the hypothesis. It was also concluded from the studies that further and more extensive investigations are needed as
the quantities of copper supplied to agricultural soils combined with the sensitivity of certain wild-
life species called for concern.

EU Model calculations have shown potential risks to soil organisms as a result of application of
piglet manure. Potential environmental concern is also related to the contamination of sediment
owing to drainage and the run-off of copper to surface water. Calculations have shown that the
systems most vulnerable were clearly acid sandy soils, distributed largely in Flanders, The Nether-
lands, north-western Germany and Denmark. According to EFSA, final conclusions must await
further model validation and additional data.

A special concern in relation to copper seems to be the possible release of copper-resistant bacteria
in the environment, primarily in connection with the spreading of copper-containing (pig) manure
on agricultural soils, and a correlation between the development of resistance to copper and re-
sistance to various antibiotics. This concern is currently being addressed in a Danish research pro-
ject at the University of Copenhagen, Denmark. At present, EFSA finds that the available data does
not allow any estimate of the practical relevance of these findings.

Considering impacts of copper used for antifouling, concentrations of copper measured in and
around the vicinity of harbours are at the same level or higher than concentrations at which effects
have been measured. In other cases, the concentrations at which effects of copper are measured are
generally higher than the background concentrations observed for copper in the marine environ-
ment in Denmark. The measurements available of the content of copper in the marine environ-
ments in Denmark are, however, old. An emission of copper to the water environment based on the
use of antifouling paint also takes place, but cannot be quantified. As part of the ongoing EU as-
essment of copper(I)oxide as active substance within product type 21 (Antifouling) under the Bio-
cidal Product Regulation a comprehensive Risk Assessment incorporating the newest knowledge
available will be prepared. The assessment is anticipated to be available relatively soon.
Survey of copper(I)oxide, copper(II)sulphates and copper(I)chloride
6. Human health effects and exposure

6.1 Human health hazards
As mentioned in Chapter 5 a Voluntary Risk Assessment Report (VRAR) for copper, copper(II)sulphate pentahydrate, copper(I)oxide, copper(II)oxide and copper chloride trihydroxide was prepared by the European Copper Institute [ECI, 2007] and submitted to ECHA on behalf of the European copper industry consortium. The VRAR was developed as a response to the discussions regarding the health and environmental effects of copper and to prepare for the entry into force of REACH in July 2007. The Risk Assessment was completed in 2008. However, with regard to the Chapter 4 on human health, only the draft version from 1 June 2007 is available on ECHA's website and not the final version from June 2008 as it is the case for the Chapter 3 on environmental effects.

Both the European Commission’s (DG JRC) Technical Committee on New and Existing Substances (TC NES) and the Commission’s (DG SANCO) Scientific Committee on Health and Environmental Risks (SCHER), have agreed to the overall conclusions in the VRAR in their review [TC NES, 2008; SCHER, 2008].

Copper(II)sulphate pentahydrate has been evaluated as an active substance within product type 2 under the EU review programme for biocidal active substances provided for in Article 16(2) of Directive 98/8/EC concerning the placing of biocidal products on the market [France, 2013]. The determination of a systemic NOAEL in the health assessment of the report has been EU harmonised with the EU VRAR. The Assessment Report is carried out in the context of the work programme for the review of existing active substances.

6.1.1 Classification
As can be seen from the overview of existing legislation (Chapter 0) copper(I)oxide, copper(II)sulphate and copper(I)chloride are all subject to EU harmonised classification and labelling. All of these compounds are classified for acute oral toxicity, while copper(II)sulphate also is classified for skin and eye irritation in category 2.
### TABLE 20
EU HARMONISED CLASSIFICATIONS - HUMAN HEALTH

<table>
<thead>
<tr>
<th>CLP Index No</th>
<th>International chemical identification</th>
<th>CAS No</th>
<th>Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Hazard Class and Category Code(s) *1</td>
</tr>
<tr>
<td>029-002-00-x</td>
<td>Copper (I)oxide</td>
<td>1317-39-1</td>
<td>Acute Tox.4*</td>
</tr>
<tr>
<td>029-004-00-0</td>
<td>Copper (II)sulphate,</td>
<td>7758-98-7</td>
<td>Acute Tox.4*</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Eye Irrit. 2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Skin Irrit. 2</td>
</tr>
<tr>
<td>029-001-00-4</td>
<td>Copper(I)chloride</td>
<td>7758-89-6</td>
<td>Acute Tox.4*</td>
</tr>
</tbody>
</table>

*1 Acute toxicity category 4/ H302: Harmful if swallowed.
Eye irritation category 2/H319: Causes serious eye irritation.
Skin irritation category 2/H315: Causes skin irritation.
Use of ‘*’ in connection with a hazard category (e.g. Acute Tox. 4 * ) implies that the category stated shall be considered as a minimum classification.

Copper(II)sulphate pentahydrate does not have an EU harmonised classification but is notified to ECHA with different suggestions for health classifications as shown in Table 21:

### TABLE 21
NOTIFIED CLASSIFICATIONS OF COPPER(II)SULPHATE PENTAHYDRATE – HUMAN HEALTH (AS OF 09/2013)

<table>
<thead>
<tr>
<th>Hazard Class and Category Code(s)</th>
<th>Hazard statement text</th>
<th>No. of notifiers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Not classified</td>
<td>-</td>
<td>1004</td>
</tr>
<tr>
<td>Acute tox. 4</td>
<td>H302 - Harmful if swallowed</td>
<td>266*1</td>
</tr>
<tr>
<td>Acute tox. 3</td>
<td>H301 - Toxic if swallowed</td>
<td>28</td>
</tr>
<tr>
<td>Skin irrit. 2</td>
<td>H315 - Causes skin irritation</td>
<td>199*1</td>
</tr>
<tr>
<td>Eye irrit. 2</td>
<td>H319 - Causes serious eye irritation</td>
<td>199*1</td>
</tr>
<tr>
<td>Eye Dam. 1</td>
<td>H318 - Causes serious eye damage</td>
<td>2</td>
</tr>
<tr>
<td>Skin Sens. 1</td>
<td>H317 - May cause an allergic skin reaction</td>
<td>3</td>
</tr>
<tr>
<td>Resp Sens. 1</td>
<td>H334 - May cause allergy or asthma symptoms or breathing difficulties if inhaled</td>
<td>2</td>
</tr>
<tr>
<td>Muta. 2</td>
<td>H341 - Suspected of causing genetic defects</td>
<td>3</td>
</tr>
<tr>
<td>Repr. 2</td>
<td>H361 - Suspected of damaging fertility or the unborn child</td>
<td>3</td>
</tr>
<tr>
<td>STOT SE 1</td>
<td>H370 - Causes damage to organs</td>
<td>3</td>
</tr>
<tr>
<td>STOT RE 2</td>
<td>H373 - May cause damage to organs through prolonged or repeated exposure</td>
<td>3</td>
</tr>
</tbody>
</table>

*1 In addition 28 notifiers have notified without indicating the hazard class, rather only the corresponding hazard statement.

As can be seen from the table, most notifiers have notified with "not classified" whereas the major part of the remaining notifiers suggest a classification similar to copper(II)sulphate (Cas. no. 7758-98-7) as shown in Table 21. Three notifiers out of 1326 have classified the substance as Muta. 2 and Repr. 2, but there is no documentation for the classification available in the Classification & Label-
ling (C&L) Inventory on the ECHA homepage. The hazard identification and assessment presented in Section 6.1.2 does not support classification in these two hazard classes.

In the draft Assessment Report [France, 2013] evaluating the active substance copper(II)sulphate pentahydrate for product type 2 (private area and public health area disinfectants and other biocidal products), the health classification is suggested as Acute tox. 4/H302 (Harmful if swallowed) and Eye Dam. 1/H318 (Causes serious eye damage).

6.1.2 Health hazard assessment

Homeostasis
Copper is a micronutrient and plays as such an essential role in human physiology. Copper is also potentially toxic and its homeostasis is carefully regulated through a system of protein transporters enabling the body to maintain the balance between dietary copper intake and excretion that allows normal physiological processes to take place [France, 2013]. The major control mechanism is gastrointestinal absorption with the liver as the main organ involved in copper distribution and copper homeostasis and biliary excretion into faeces as the main route of elimination [SCHER, 2008]. Adverse effects may result from both copper deficiency and excess copper, with the most severe effects seen in relation to deficiencies. Copper is critical to foetal/infant development and growth, immune function, brain development and function, bone and collagen strength, haematopoiesis, iron metabolism, cholesterol and glucose metabolism, myocardial contractility, maintenance of hair and skin, and pigment formation [ECI, 2007]. Copper status is not easy to determine, and the mechanisms that control copper distribution and metabolism are not completely understood [EFSA, 2012]. Based on a review of the evidence for deficiency and copper balance studies, the VRAR indicates that intakes below 1 mg/day may be insufficient to maintain copper status.

Toxicokinetics
Data on toxicokinetics evaluated in the VRAR are primarily from studies with copper(II)sulphate (not further specified) which is the most soluble of the copper compounds included in the survey. It is assumed that the copper administered by the oral route at least in part will be available in the ionic form in the gastrointestinal tract where absorption takes place [ECI, 2007]. Orally administered copper is absorbed from the stomach and small intestine by active and passive processes, and copper in the ionic form is complexed with plasma proteins and transported via the portal blood to the liver. Here copper is incorporated into copper-requiring enzymes and proteins which are stored in the liver and kidney, and subsequently secreted into the blood and transported to other tissues, or secreted in the bile and excreted in faeces. The liver and brain have been shown to contain the highest concentrations of copper. Copper is tightly regulated at the cellular level, involving protective species to protect the accumulation of potentially toxic, free copper ions within the cell [ECI, 2007].

Absorption and availability may be influenced by the carbohydrate content of the diet [EFSA, 2012]. According to the VRAR it is not possible to conclude about bioavailability of different copper compounds based on the solubility of the substance. Different absorption rates have been reported from studies of varying quality. Based on the available data on true absorption, an oral absorption factor of 25% is suggested as the best estimate of true absorption in rats at high copper intakes [ECI, 2007]. In the Assessment Report evaluating copper(II)sulphate pentahydrate for product type 2 under the Biocidal Products Directive a percentage of 25% of the administered copper(II)sulphate pentahydrate available for absorption is used in rats and 36% in humans [France, 2013].

No data are available on dermal absorption of copper in animals. Based on in vitro studies a dermal absorption factor of 0.3% is proposed for insoluble copper substances in solution or suspension and for soluble substances as well, as there is no consistent evidence to show that dermal absorption is
greater for soluble than for insoluble substances [ECI, 2007]. The VRAR suggests a dermal absorption factor of 0.03% for dry exposure scenarios.

According to the VRAR inhaled copper deposited in the upper respiratory tract is assumed to be translocated to the gut and subject to intake-dependent absorption along with dietary copper. A default absorption factor of 100% is applied to the pulmonary fraction.

**Acute toxicity**
Copper(I)oxide, copper(II)sulphate and copper(I)chloride are all classified for acute oral toxicity, and the majority of notifiers classifying copper(II)sulphate pentahydrate are also self-classifying this substance as harmful if swallowed (H302). The liver is the main target organ and ingestion of large amounts of copper(II)sulphate as in cases of self-poisoning has been shown to produce severe hepatotoxicity, nephrotoxicity and gastrointestinal effects typical for food poisoning [ECI, 2007; WHO, 2004]. An increase in gastro-intestinal symptoms is associated with single oral exposure to copper via drinking water. The VRAR suggests an external NOAEL of 4 mg Cu/L drinking water for acute oral toxicity. Dermal toxicity is considered low and potential inhalation toxicity of copper(II)sulphate is considered less relevant partly due to the large particle size of the current products.

According to the Screening Information dataset (SIDS) for High Volume Chemicals on copper(I)chloride [OECD, 2005], there are no studies available on acute oral or inhalation toxicity.

The acute lethal dose for adults lies between 4 and 400 mg Cu$^{2+}$-ion/kg bw based on information from accidental ingestion and suicide cases with copper(II)sulphate [WHO, 2004].

**Irritation and sensitisation**
Only copper(II)sulphate has an EU harmonised classification as an eye and skin irritant but is like the other copper compounds not considered a skin sensitizer. Based on available animal data the VRAR suggests that copper(I)oxide should also be classified for eye irritation with R36. Regarding copper(II)sulphate pentahydrate, the VRAR suggests that the substance should be classified for severe eye irritation with R41 but not for skin irritation which is agreed by EFSA [EFSA, 2012]. With reference to the American Conference of Industrial Hygienists (ACGIH) and the International Programme on Chemical Safety (IPCS) the EFSA notes that copper or copper salts may induce allergic contact dermatitis in susceptible individuals producing itching and eczema. Respiratory sensitisation is not known [SCHER, 2008].

The VRAR concludes that copper(II)sulphate pentahydrate is an irritant to the eye, is not at skin irritant, and is not considered a skin sensitizer. In the EFSA scientific opinion it is noted that copper and copper salts may induce allergic contact dermatitis in susceptible individuals producing cutaneous itching and eczema.

According to the SIDS report on copper monochloride [OECD, 2005] there are no studies available on skin or eye irritation, but observations from an acute dermal study suggests that copper monochloride has a skin irritation potential. No information is available on skin sensitisation.

**Repeated dose toxicity**
Repeated dose toxicity data for the oral route are primarily available for copper(II)sulphate pentahydrate from studies in rats. The liver, forestomach and kidneys are target organs and the VRAR suggests an external NOAEL of 16.3 mg Cu/kg bw corresponding to an internal NOAEL of 4.075 mg Cu/kg bw using a 25% absorption factor. This internal NOAEL is used for the risk characterisation in the VRAR irrespective of the copper compound considered.
Repeated oral gavage dosing of copper monochloride resulted in squamous cell hyperplasia of the forestomach considered to be local, non-systemic effect. A NOAEL of 5 mg/kg bw/day for male rats and 1.3 mg/kg bw/day for female rats were derived from the study [OECD, 2005].

**Mutagenicity and cancer**

Based on available data copper(I)oxide and copper(II)sulphate /copper(II)sulphate pentahydrate are not considered mutagenic *in vitro* or *in vivo* following peroral exposure and the substances are also not considered carcinogenic by the VRAR.

Copper monochloride did not show mutagenic activity in bacteria strains of Salmonella typhimurium (±S9). Clastogenic potential was observed in an *in vitro* chromosome aberration study using Chinese Hamster Lung cells (CHL) but no induction of micronuclei was observed in an *in vivo* mammalian erythrocyte micronucleus test. No results were available on carcinogenicity [OECD, 2005].

SCHER [2008] agrees that carcinogenicity is not a concern for copper.

**Reproductive and developmental effects**

Available data do not suggest that copper and its compounds result in reproductive or developmental toxicity. Developmental effects are only seen when the normal uptake and distribution mechanisms are bypassed through intraperitoneal or intravenous administration [France, 2013].

In a reproductive toxicity study for copper(I)chloride on toxicity to fertility the NOAEL was 80 mg/kg bw/day which also represented the highest test dose. In a developmental toxicity study NOAEL was reported to be 20 mg/kg bw/day in a guideline study where the animals were tested up to 80 mg/kg bw/day [OECD, 2005].

**Endocrine disruption**

Based on the available data evaluated in the Assessment Report of copper(II)sulphate pentahydrate for product type 2 it is concluded that no alert on the endocrine disruption was observed. In the toxicity tests with mammals there were no effects in test animals which could be related to possible endocrine disruption [France, 2013].

**Bacteria resistance to copper**

As mentioned in the previous chapter on environmental effects and exposure, Section 5.1.3, there is a specific concern in relation to development of bacterial co-resistance to copper and certain antibiotics in the environment which is currently being investigated. Increasing occurrence of multidrug-resistant pathogenic bacteria constitutes a threat to public health.

**Conclusion on health hazards**

The VRAR concludes that acute toxicity (gastro-intestinal symptoms) and repeated dose toxicity (liver effects) represent the most significant end-points in relation to human health for copper substances (including copper(I)oxide and copper(II)sulphate). The oral and inhalation routes represent the most significant routes of exposure [ECI, 2007].

### 6.2 Human exposure

#### 6.2.1 Direct exposure

No monitoring data on occupational exposure for the four copper compounds in Denmark have been identified. However, occupational exposure to copper(II)sulphates used for feed additives and fertilizers in Denmark and copper(I)oxide for antifouling may give rise to occupational exposures.
Data on the direct exposure of Danish consumers to the copper compounds are also not available. In addition, no particular consumer uses of the copper compounds have been identified. In the Voluntary Risk Assessment from the European Copper Institute [ECI, 2007], direct consumer exposure to copper (compound not specified) is mentioned in relation to cosmetics and coins, and by smoking cigarettes. Secondary exposure from grinding and maintaining pleasure boats treated with copper(I)oxide antifouling products may also result in exposure.

6.2.2 Indirect exposure
Indirect exposure to copper via the environment can occur from soil, water (surface water, groundwater, seawater and drinking water) and airborne dust (wind dispersed particulate matter), indoor air and through food which is the principal source of indirect copper exposure for humans.

According to WHO [2004], the copper intakes from food in the Scandinavian countries are in the range of 1.0–2.0 mg/day for adults, 2 mg/day for lactovegetarians and 3.5 mg/day for vegans based on references from the 1990’s[4].

Based on duplicate diet studies, the VRAR estimates the mean dietary intake for men aged 30-34 years in Denmark and representing three geographical areas and different socio-economic groups at 1.2 mg/day (median intake was 1.1 mg/day).

For Risk Assessment purposes a 90 percentile (RWC) of 2.0 mg/day and a 10 percentile RWC of 0.6 mg/day are carried forward for the Risk Assessment in the VRAR.

The Danish Food Composition Database contains information about 1049 foods [DTU Food, Sept. 2013]. A search for the component copper results in a list of 812 foods containing copper in concentrations up to 7.93 mg/100 g food.

No information on copper-content in soil or drinking water has been identified, but it is assumed that the soil and drinking water quality criteria for copper are observed.

6.3 Bio-monitoring data
No human biomonitoring data for Denmark have been identified. Copper is in general not considered a highly relevant biomarker due to strong inter-individual variability and limited health risks. In a report on Biomonitoring-based indicators of exposure to chemical substances[5] it is also mentioned that even though the substance can in principle be easily measured in urine, no appropriate effect marker has been identified that could be used for untargeted screening methods [WHO, 2012].

6.4 Human health impact
The risk characterisation related to occupational exposure performed as part of the VRAR has its focus on exposure from activities performed during production of copper in the massive form, melting and casting, further processing, and production of copper powder and copper compounds [ECI, 2007]. The end-points of concern are acute effects and repeat dose effects.

The Scientific Committee on Health and Environmental Risks [SCHER, 2008] agreed on a VRAR regarding risk characterisation for workers. It concluded that "there is at present no need for further information and/or testing and no need for risk reduction measures beyond those which are being applied already". This corresponds to "conclusion (ii). The Risk Assessment was carried out using the Margin of Safety approach (MOS) and included using the internal/absorbed doses includ-

---


ing the sum of oral, inhalation and dermal doses. Only in relation to acute effects in production of copper powder and copper compounds and maintenance operations without Respiratory Protective Equipment (RPE) in melting and casting, the conclusion is that "there is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account" [ECI, 2007; SCHER, 2008]. This corresponds to "conclusion (iii)". This conclusion was also reached for repeated dose effects in some sites of copper powder production. For the sites which have not provided data, it was concluded, that there is a need for further information and/or testing (Conclusion (i)).

Conclusions regarding consumer exposure and indirect exposure
The risk characterisation for consumers concludes that "there is at present no need for further information and/or testing and no need for risk reduction measures beyond those which are being applied already" (conclusion ii).

The same conclusion was also reached regarding indirect exposure through the environment [ECI, 2007]. This conclusion was accepted by the Scientific Committee on Health and Environmental Risks [SCHER, 2008] but it was noted that the VRAR did not stress enough that the margin of safety at high copper concentrations is low for the acute effects resulting from copper in drinking water leaching from the distribution system.

Conclusions regarding combined exposure
For typical combined exposure of the general population (indirect and consumer exposure) the VRAR concludes that "there is at present no need for further information and/or testing and no need for risk reduction measures beyond those which are being applied already" (conclusion (ii)). This is also the conclusion for reasonable worst case (RWC) scenarios using moderately corrosive drinking water. The same conclusion (ii) was also reached for combined exposure of workers, and typical indirect exposure. However in the production of copper powder work scenario the conclusion was that "there is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account" (conclusion (iii)). These conclusions were also agreed by the Scientific Committee on Health and Environmental Risks [SCHER, 2008] with the previous mentioned note regarding high copper concentrations in drinking water.

With regard to consumer safety, EFSA [2012] states that the Scientific Committee on Food (SCF) in their opinion on the Upper Intake Level of Copper from March 2003, has defined a tolerable upper intake level (UL) of 5 mg/day for adults and 1 mg/day for toddlers (1-3 years). This figure was derived from an overall no observed adverse effect level (NOAEL) of 10 mg Cu/day, applying an uncertainty factor of 2 for potential variability in the normal population. This UL value has been consistently used in the assessments of copper in different forms by different EFSA Scientific Panels.

In the Risk Assessment of copper(II)sulphate pentahydrate for product type 2 a systemic NOAEL of 4.1 mg Cu/kg BW/day has been used for the calculations of AELs (Acceptable Exposure Levels) [France, 2013]. The Risk Assessment concludes that the risk for professional users is acceptable if gloves are used. Unacceptable risks are identified in relation to secondary indirect exposure scenarios involving chronic exposure of adults, children and infants from disinfected clothing and acute, subchronic exposure of infants. These risks are reflected in the proposed decisions regarding the approval and use of the substance for product type 2 biocides and the elements to be taken into account when authorising products containing copper(II)sulphate pentahydrate.

6.5 Summary and conclusions
Copper(I)oxide, copper(II)sulphate and copper(I)chloride are subject to EU harmonised classification and labelling. All of these compounds are classified for acute oral toxicity, while copper(II)sulphate also is classified for skin and eye irritation in category 2. Copper(II)sulphate pentahydrate does not have an EU harmonised classification but is notified to ECHA with different
suggestions for health classifications. Most notifiers have notified with “not classified” whereas the majority of the remaining notifiers suggest a classification similar to copper(II)sulphate (Acute tox. 4, Skin irrit. 2 and Eye irrit. 2).

General systemic toxicity (liver effects) following repeated oral exposure, gastrointestinal symptoms following acute oral exposure and respiratory effects from acute inhalation exposure represent the most significant endpoints in relation to human health for or copper(I)oxide, copper(II)sulphate, copper(II)sulphate pentahydrate, and copper(I)chloride. The oral and the inhalation route present the most significant routes of exposure. Adverse effects arise both in relation to copper deficiencies and excess copper. Copper status in the cells is regulated by mechanisms assisting to protect the cells against accumulation of copper.

For Risk Assessment purposes under the Biocidal Products Directive, it is proposed that 36% of orally administered copper(II)sulphate pentahydrate is available for absorption in humans and that the dermal absorption factor is 0.03% for both insoluble copper substances in solution or suspension and for soluble substances for dry exposure scenarios. The oral and inhalation routes represent the most significant routes of exposure and it is noted that the margin of safety at high copper concentrations is low for the acute effects resulting from copper in drinking water leaching from the distribution system.

According to WHO, the copper intakes from food in the Scandinavian countries are in the range of 1.0–2.0 mg/day for adults, 2 mg/day for lactovegetarians and 3.5 mg/day for vegans based on references from the 1990’s6). The EU Scientific Committee on Food (SCF) has in 2003 defined a tolerable upper intake level (UL) of 5 mg/day for adults and 1 mg/day for toddlers (1-3 years).

The Voluntary Risk Assessment submitted by the European Copper Institute and reviewed by the Technical Committee on New and Existing Substances (TC NES) and the Scientific Committee on Health and Environmental Risks (SCHER) concludes that the copper compounds covered by the assessment do not represent a major human health concern.

In the Voluntary Risk Assessment of copper(II)sulphate pentahydrate conducted by the European Copper Institute [ECI, 2007] it is concluded that the use of copper products is in general safe for the health of European citizens. Risk of occupational exposure is possible at some industrial sites, specifically for workers involved in the production of copper chemicals and powders.

No specific exposure data related to occupational conditions in Denmark or human biomonitoring data have been identified in order to allow a more specific characterisation of the risk. Based on the information available, the use of copper(II)sulphate as feed additive, followed by the use of copper(I)oxide for antifouling and the use of copper(II)sulphates in fertilizers are the main uses in Denmark. None of these uses are expected to result in risks that are significantly different from the EU scenarios.

---

7. Information on alternatives

This description is focused on the main applications of copper(I)oxide, copper(II)sulphate and copper(I)chloride known to take place in Denmark, and for which knowledge on actual use and disposal patterns is available. These applications are antifouling paint, feed additives and mineral fertilizers.

Recognizing that copper is an essential nutrient and the general use of copper(II)sulphate as feed additive and fertilizer is based on the need to supply domestic animals as well as agricultural soils with essential nutrients, the choice is made to limit the discussion on alternatives to applications where options are available without affecting the need for nutrients for animals or plants. Therefore, this chapter is focused on the following applications:

- Antifouling
- Feed additives for piglets.

7.1 Antifouling

Antifouling paint is used to avoid or reduce algae, plants, microorganisms or animals being attached to ship hulls and other submerged parts of ships, boats and aquatic structures. Alternatives to paint using copper(I)oxide as the biocidal ingredient include biocidal alternatives as well as non-biocidal alternatives.

Regarding biocidal alternatives, nine existing active substances are currently being reviewed together with copper(I)oxide for use within product type 21 “Antifouling products” under the Biocidal Products Regulation (see Section 2.1.1). Furthermore, two new substances – tralopyril and medetomidine - are also being EU reviewed for use within this product type. The outcome of the review processes determines which biocidal substances that are allowed to be used in antifouling products in the EU and thereby, which substances that may be approved for antifouling products in Denmark. These active substances are listed in Table 22.

Of the active substances listed in Table 22 only copper thiocyanate, copper, zineb, DCOIT, tralopyril and medetomidine has the same target organisms (hard fouling: barnacles, mussels) as copper(I)oxide [Fink et al 2013; Janssen 2013; Helcom 2008] and may be considered as biocidal alternatives to copper(I)oxide. The target organisms for the other active substances listed are soft fouling (bacteria, fungi and algae) [Fink et al., 2013]. Data on hazard classification is available for all substances apart from medetomidine. It is, however, known, that medetomidine is preventing adhesion of fouling organisms to ship hulls etc. by stimulating larvae swimming behaviour rather than exerting toxic effects [Helcom, 2008].

Briefly comparing the active substances having hard fouling as target organisms it should be noted that zineb is the only substance not classified as Aquatic Acute 1/H400(very toxic to aquatic life). Although data on hazard classification is not available for medetomidine, the information from Helcom [2008] presented above may indicate that medetomidine also are not very toxic in aquatic environments.
**TABLE 22**

CLASSIFICATION OF ACTIVE SUBSTANCES BEING POTENTIAL ALTERNATIVES TO COPPER(I)OXIDE FOR ANTIFOLDING AND CURRENTLY UNDER REVIEW UNDER THE EU BIOCIDAL PRODUCT REGULATION (DATA ON COPPER(I)OXIDE IS INCLUDED FOR REFERENCE).

<table>
<thead>
<tr>
<th>Active substances</th>
<th>CLP Index No. *1</th>
<th>CAS No.</th>
<th>Hazard Class and Category Code(s)</th>
<th>Hazard statement Code(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper(I)oxide</td>
<td>029-002-00-x</td>
<td>1317-39-1</td>
<td>Acute Tox.4*</td>
<td>H302</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Aquatic Acute 1</td>
<td>H400</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Aquatic Chronic 1</td>
<td>H410</td>
</tr>
<tr>
<td>Tolylfluanid *1</td>
<td>613-116-00-7/613-116-01-4</td>
<td>731-27-1</td>
<td>Acute Tox. 2 *</td>
<td>H330</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>STOT RE 1</td>
<td>H372**</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Eye Irrit. 2</td>
<td>H319</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>STOT SE 3</td>
<td>H335</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Skin Irrit. 2</td>
<td>H315</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Skin Sens. 1</td>
<td>H317</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Aquatic Acute 1</td>
<td>H400</td>
</tr>
<tr>
<td>Dichlofluanid *1</td>
<td>616-006-00-7</td>
<td>1085-98-9</td>
<td>Acute Tox. 4 *</td>
<td>H332</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Eye Irrit. 2</td>
<td>H319</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Skin Sens. 1</td>
<td>H317</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Aquatic Acute 1</td>
<td>H400</td>
</tr>
<tr>
<td>Copper thiocyanate *2</td>
<td>No EU harmonised classification</td>
<td>1111-67-7</td>
<td>Acute Tox. 4</td>
<td>H302/H312/H332</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Aquatic Acute 1</td>
<td>H400</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Aquatic Chronic 1</td>
<td>H410</td>
</tr>
<tr>
<td>Copper *2</td>
<td>No EU harmonised classification</td>
<td>7440-50-8</td>
<td>Acute Tox ¾</td>
<td>H301/H302</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Aquatic Acute 1</td>
<td>H400</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Aquatic Chronic 2/3</td>
<td>H311/H312</td>
</tr>
<tr>
<td>Zineb *1</td>
<td>006-078-00-2</td>
<td>12122-67-7</td>
<td>STOT SE 3</td>
<td>H335</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Skin Sens. 1</td>
<td>H317</td>
</tr>
<tr>
<td>Zine pyrithione *2</td>
<td>No EU harmonised classification</td>
<td>13463-41-7</td>
<td>Acute Tox ¾</td>
<td>H301/H302/H331/H332</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Eye Dam. 1</td>
<td>H318</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Aquatic Acute 1</td>
<td>H400</td>
</tr>
<tr>
<td>Copper pyrithione *2</td>
<td>No EU harmonised classification</td>
<td>14915-37-8</td>
<td>Acute Tox. 2/4</td>
<td>H330/H302</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Eye Irrit. 1</td>
<td>H318</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Skin Sens. 2</td>
<td>H315</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Aquatic Acute 1</td>
<td>H400</td>
</tr>
<tr>
<td>Cybutryne *2</td>
<td>No EU harmonised classification</td>
<td>28159-98-0</td>
<td>Skin Sens. 1</td>
<td>H317</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Aquatic Acute 1</td>
<td>H400</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Aquatic Chronic 1</td>
<td>H410</td>
</tr>
<tr>
<td>DCOIT *2</td>
<td>No EU harmonised classification</td>
<td>64359-81-5</td>
<td>Acute Tox. 2/3/4</td>
<td>H330/H331/H302/H312</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Eye Dam. 1</td>
<td>H318</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Skin Corr. 1B/1A</td>
<td>H34</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Skin Sens. 1/1A</td>
<td>H317</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Aquatic Acute 1</td>
<td>H400</td>
</tr>
<tr>
<td>Tralopyril</td>
<td>No EU harmonised classification</td>
<td>122454-29-9</td>
<td>Acute Tox.3</td>
<td>H301/H331</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Aquatic Acute 1</td>
<td>H400</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Aquatic Chronic 1</td>
<td>H410</td>
</tr>
<tr>
<td>Medetomidine</td>
<td>No EU harmonised classification</td>
<td>86347-14-0</td>
<td>No data</td>
<td>No data</td>
</tr>
</tbody>
</table>
According to Annex VI of Regulation (EC) No 1272/2008 (CLP Regulation, 2008). The substance is preregistered under REACH. The hazard classes and codes stated are based on self-classification, and represent the classification made by the dominant number of notifiers. In case there are notifiers of more classes within the same hazard category, all classes are stated (e.g. Acute Tox 2/3/4 covering Acute Tox 2 as well as Acute Tox 3 and Acute Tox 4) together with the corresponding Hazard Statements Codes.

In Denmark significant efforts have been invested in investigating and developing alternatives to copper-based antifouling paint from before 1998 and up to now. The alternatives investigated so far include [Højenvang, 2002; Allermann et al., 2004; Schneider et al., 2007; Højenvang & Bischoff, 2008; Wallström et al., 2012; Nygaard et al., 2012]:

- Antifouling paint being less environmentally harmful inclusive of biocide-free paints with a reduced amount of active substances and paints with "natural" active substances;
- Bottom coatings being less environmentally harmful inclusive of epoxy and silicone coatings;
- Underwater washing systems with brushes or high pressure cleaning;
- Algae cloth (closely fitting sheet that covers the underwater hull);
- Boat lifts (the boat is lifted out of the water, when not used for sailing);
- Mechanical washing on shore.

Considering biocidal alternatives, research has shown that antifouling paint using silicate based encapsulation technologies with a minimised amount of the biocidal active substance and without substances as zinc oxide and copper(I)oxide can give antifouling effects and other technical properties wanted for the use of the paint. The paint will not be more expensive than existing commercial products [Wallström et al., 2012].

According to Fink et al. [2013], the best non-biocidal alternative is a costly siliconized epoxy coating. This results in a very smooth and slippery surface that can prevent foulants from settling permanently on the surface. The solution is commercially available and applicable on ships or boats that sail with a high speed (>15 knots). For slower boats (<15 knots) this solution is not feasible, as the lower sailing speed allows the foulants to settle.

Considering other non-biocidal alternatives, both underwater washing systems, algae cloths, boats lifts and mechanical washing on shore are solutions available and relevant under certain conditions. They, however, each have limitations and are not suitable as general solutions being cost effective for the majority of pleasure boats in Denmark [Højenvang, 2002; MST, 2013b].

Efforts to identify alternatives to copper-based antifouling paints are also invested outside Europe. and many commercially available alternatives have been reviewed by the US EPA [US EPA, 2011; US EPA 2012]. The alternatives may be grouped as given in the table below.
TABLE 23

<table>
<thead>
<tr>
<th>Alternative group</th>
<th>Description</th>
<th>Cost *1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc biocide paints</td>
<td>Generally zinc pyrithione and often zinc oxide *2</td>
<td>More expensive</td>
</tr>
<tr>
<td>Organic biocide paints</td>
<td>Organic biocide is often Econea *3 (alternatively Irgarol *4, Sea Nine or tolyfluanid are used); These biocides are generally combined with zinc oxide *2</td>
<td>More expensive</td>
</tr>
<tr>
<td>Zinc/organic biocide combination paints</td>
<td>Most often contain zinc pyrithione and an organic biocide, usually Econea*3; is generally combined with zinc oxide *2</td>
<td>More expensive</td>
</tr>
<tr>
<td>Zinc oxide only paints</td>
<td>Zinc oxide for photoactive surface producing hydrogen peroxide; contain no biocides</td>
<td>More expensive</td>
</tr>
<tr>
<td>Soft nonbiocide paints</td>
<td>Contain no biocides or zinc oxide; is based on silicon compounds and/or fluoropolymers *2</td>
<td>Comparable costs</td>
</tr>
<tr>
<td>Hard nonbiocide paints</td>
<td>Contain no biocides; generally contain epoxy and sometimes ceramic</td>
<td>Slightly more expensive</td>
</tr>
</tbody>
</table>

*1 Cost analysis over the lifetime of the paint, considering paint, paint procedures, cleaning, paint life time/ frequency of reaplication etc.; compared to traditional copper paints.

*2 The harmonised classification for zinc oxide (CAS 1314-13-2) is Aquatic Acute 1 and Aquatic Chronic 1 with the hazard statements codes H400 and H401 according to Annex VI of Regulation (EC) No 1272/2008 (CLP Regulation, [EC, 2008]). According to Gondolf [2013], it has not been decided yet at EU level if zinc oxide is a biocidal active substance.

*3 The active substance in Econea is tralopyril [Jannsen, 2013].

*4 Irgarol is the same substance as cybutryne.

The American studies on soft non-biodegradable coatings identified products that were assessed to perform well (although not as well as a copper coating), to be cost-effective over the long-term and already available on the market [US EPA, 2011]. The products were based on fluoropolymers and silicon. The costs were assessed to be comparable to copper coatings in the long-term perspective. The products were tested on pleasure boats operated with speeds below 8 knots. It should be noted that the outcome of the American studies may not be directly applicable to boats operated and maintained in Danish waters. It should also be noted that one of the tested products claimed to be a non-biocidal coating actually contains the substance dibutyltin dilaurate in a small concentration (below 1% in the final product) [Hempel, 2013c]. Dibutyltin dilaurate is self-classified as Aquatic Acute 1 and Aquatic Chronic 1.

Antifouling paints and coatings should be regarded as a field of ongoing development. Among the concepts currently being evaluated are [Almeida et al., 2007; Chambers et al., 2006]:

- Fibrous surface coatings – commercially available products including paints integrating synthetic microfibers;
- Enzymatic antifouling systems - metabolites of marine organisms used as natural biocides, and
- Microstructured surfaces (such as silicone) inspired by marine animals with surfaces preventing the attachment of marine organisms, multilayer systems, and intelligent polymers.

As a different approach to developing new technologies for the antifouling paint, more efficient underwater mechanical cleaning of fouled surfaces using ultraviolet radiation, ultrasound, laser beams, etc. are being examined. The potential cost of such underwater cleaning may be cheaper than cleaning with high pressure water jets [Almeida et al., 2007].
7.2 Feed additives for piglets
Addition of copper to feed for pigs started in Denmark in the 1960’s. Copper is an essential nutrient to animals and the addition of copper(II)sulphate also has a preventive effect on diarrhoea and thereby indirectly promotes growth. A Danish study has demonstrated significantly increased growth and improved economy of pig production through the use of copper (organic as well as inorganic) as feed additive to piglets [Maribo and Poulsen, 1999]. According to Tjell [2012], the actual mechanisms behind the effect of copper is still debatable; it may be that zinc is the effective substance and that copper contributes to the improved uptake of zinc, thereby improving the resistance of the pig against infections and diarrhoea.

Alternatives to the use of copper(II)sulphate pentahydrate as feed additive for piglets are briefly outlined in Table 24 below. The only alternative that could eliminate supply of copper to agricultural areas would be to postpone the weaning of piglets to a time where no use of copper as feed additive would be needed in order to prevent diarrhoea and other relevant effects. Other alternatives will reduce the consumption of copper, but no data on the size of the reduction to be obtained is available. The alternative of replacing copper(II)sulphates with copper lysine has been included in order to emphasize that the content of copper in manure depends on the amount of copper used and not on the actual compound [Maribo and Poulsen, 1999].

<table>
<thead>
<tr>
<th>Alternative</th>
<th>Description</th>
<th>Cost/consequences *1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduce early weaning for piglets</td>
<td>Expansion of the weaning time from the typical 4 weeks after birth to e.g. 7 weeks or more in order to reduce/avoid excessive use of copper as feed additive for piglets.</td>
<td>Production costs for pigs will increase. Supply of copper to farmland may be eliminated or reduced depending on the action chosen.</td>
</tr>
<tr>
<td>Replace with other copper compounds</td>
<td>Copper(II)sulphate pentahydrate may be replaced with copper lysine.</td>
<td>Production results are similar but production value based on copper sulphate is slightly better than for copper lysine [Maribo and Poulsen, 1999]. Supply of copper to farmland will not decrease.</td>
</tr>
<tr>
<td>Consecutive supplementation of zinc and copper [Jacela et al., 2010]</td>
<td>Zinc has effects similar to the effect of copper supplementation to piglets (essential trace elements; reduce incidences of diarrhoea; promote growth of piglets when supplemented at high dietary levels [EC, 2003; Jacela et al., 2010]). An analysis indicates that feeding high levels of zinc until pigs reached 12 kg, then feeding high levels of copper for the remainder of the nursery period provides the most cost-effective administration strategy of zinc and copper trace elements [Jacela et al., 2010].</td>
<td>Cheaper supply of copper to farmland will be reduced.</td>
</tr>
<tr>
<td>Combination of copper trace elements and organic acids such as benzoic acid [Tybirk, 2013]</td>
<td>Combining copper with organic acids, for example benzoic acid, improves the effect against diarrhoea. Full substitution of copper with organic acids for this effect has not been thoroughly investigated.</td>
<td>Comparable costs. Increased cost due to the addition of organic acids is roughly outweighed by the increase in productivity. Supply of copper to farmland will be reduced.</td>
</tr>
</tbody>
</table>

*1 Lifetime cost analysis, considering nutrient cost and productivity gain.
### 7.3 Summary and conclusions

The information presented on alternatives is focused on antifouling and feed additives for piglets. Regarding alternatives to copper(I)oxide used in antifouling paint, a number of active substances are currently being EU reviewed under the Biocidal Products Regulation together with copper(I)oxide for use in antifouling products. The outcome of this review process determines which biocidal active substances that is allowed to be used in antifouling products in the EU, and thereby which active substances that may be approved for antifouling products in Denmark. Of the active substances being EU reviewed only copper thiocyanate, copper, zineb, DCOIT, tralopyril and me-detomidine has the same target organisms (hard fouling: barnacles, mussels) as copper(I)oxide and may be considered as biocidal alternatives to copper(I)oxide.

Significant efforts have been invested in investigating and developing alternatives to copper-based antifouling paint in Denmark. The alternatives investigated include less toxic antifouling paint as well as other bottom coatings and several mechanical solutions inclusive of washing systems, algae cloths and boat lifts.

The best non-biocidal alternative is a siliconized epoxy coating that gives a very smooth and slippery surface that can prevent foulants from settling permanently on the surface. The solution is commercially available and applicable on ships or boats that sail with a high speed (>15 knots). For slower boats (<15 knots) this solution is not feasible, as the lower sailing speed allows the foulants to settle.

Promising results has been obtained for anti-fouling paint using silicate based encapsulation technologies with a minimised amount of the biocidal active substance and without substances as zinc oxide and copper(I)oxide. Mechanical solutions as washing systems etc. are not suitable for the majority of pleasure boats in Denmark.

American research shows that products based on silicon and fluoropolymers are also available for pleasure boats operated at low speed besides having costs comparable to copper-based products. It is, however, not known with certainty whether these results are applicable to boats operated in Danish waters.

Regarding alternatives to the use of copper(II)sulphate pentahydrate as feed additive for piglets, the basic alternative is to postpone weaning to a time where no use of copper as feed additive would be needed in order to prevent diarrhoea and other relevant effects. The drawback of this alternative will be higher production costs. Other alternatives available could reduce the consumption of copper, but no data on the size of the reduction to be obtained is available.
# Abbreviations and acronyms

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AEL</td>
<td>Acceptable Exposure Level</td>
</tr>
<tr>
<td>BEK</td>
<td>Bekendtgørelse (Statutory Order)</td>
</tr>
<tr>
<td>BLM</td>
<td>Biotic Ligand Models</td>
</tr>
<tr>
<td>BPD</td>
<td>Biocidal Products Directive</td>
</tr>
<tr>
<td>BPR</td>
<td>Biocidal Products Regulation</td>
</tr>
<tr>
<td>Bw</td>
<td>Body weight</td>
</tr>
<tr>
<td>CAS</td>
<td>Chemical Abstracts Service</td>
</tr>
<tr>
<td>C.I.</td>
<td>Colour Index</td>
</tr>
<tr>
<td>Cl</td>
<td>Chloride</td>
</tr>
<tr>
<td>CLP</td>
<td>Classification, labelling and packaging of substances and mixtures (EU regulation)</td>
</tr>
<tr>
<td>C&amp;L</td>
<td>Classification &amp; Labelling</td>
</tr>
<tr>
<td>Cu</td>
<td>Copper</td>
</tr>
<tr>
<td>DEPA</td>
<td>Danish Environmental Protection Agency</td>
</tr>
<tr>
<td>DKK</td>
<td>Danske kroner (Danish currency)</td>
</tr>
<tr>
<td>DTU</td>
<td>Technical University of Denmark</td>
</tr>
<tr>
<td>EC</td>
<td>European Community</td>
</tr>
<tr>
<td>EC50</td>
<td>Half maximal effective concentration</td>
</tr>
<tr>
<td>ECI</td>
<td>European Copper Institute</td>
</tr>
<tr>
<td>ECHA</td>
<td>European Chemicals Agency</td>
</tr>
<tr>
<td>EEC</td>
<td>European Economic Community</td>
</tr>
<tr>
<td>EFSA</td>
<td>European Food Safety Authority</td>
</tr>
<tr>
<td>ESI</td>
<td>ESIS (European chemical Substances information System)</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental Protection Agency</td>
</tr>
<tr>
<td>EU</td>
<td>European Union</td>
</tr>
<tr>
<td>EU27</td>
<td>European Union with 27 Member States</td>
</tr>
<tr>
<td>EUROSTAT</td>
<td>The statistical office of the European Union</td>
</tr>
<tr>
<td>FAO</td>
<td>United Nations Food and Agriculture Organization</td>
</tr>
<tr>
<td>H</td>
<td>Hydrogen</td>
</tr>
<tr>
<td>HELCOM</td>
<td>Helsinki Commission - is the governing body of the Helsinki Convention for the protection of the Marine Environment of the Baltic Sea Area.</td>
</tr>
<tr>
<td>IARC</td>
<td>International Agency for Research on Cancer</td>
</tr>
<tr>
<td>IPCS</td>
<td>International Programme on Chemical Safety</td>
</tr>
<tr>
<td>JEFCA</td>
<td>Joint Food and Agriculture Organization of the United Nations (FAO)/WHO Expert Committee on Food Additives</td>
</tr>
<tr>
<td>KemI</td>
<td>Kemikalie Inspektionen (Sweden)</td>
</tr>
<tr>
<td>KLIF</td>
<td>Klima- og Forureningsdirektoratet</td>
</tr>
<tr>
<td>kPa</td>
<td>Kilo Pascal</td>
</tr>
<tr>
<td>L</td>
<td>Liter</td>
</tr>
<tr>
<td>LC50</td>
<td>Median Lethal Concentration</td>
</tr>
<tr>
<td>LDC</td>
<td>Least Developed Countries</td>
</tr>
<tr>
<td>Log Kow</td>
<td>Octanol-water partition coefficient</td>
</tr>
<tr>
<td>LOUS</td>
<td>List of undesirable substances</td>
</tr>
<tr>
<td>NOEC</td>
<td>No Observed Effect Concentration</td>
</tr>
</tbody>
</table>
Survey of copper(I)oxide, copper(II)sulphates and copper(I)chloride

NOAEL  No Observed Adverse Effect Level
NOEL  No Observed Effect Level
NOEAEAL  No Observed Environmentally Adverse Effect Level
NOVANA  Danish National Monitoring and Assessment Programme for the Aquatic and Terrestrial Environment
O  Oxygen
OECD  Organisation for Economic Co-operation and Development
OSPAR  The OSPAR-Convention covering the marine environment of the North-East Atlantic. OSPAR refers to the 2 conventions (the Oslo Convention and the Paris Convention), which in 1992 were unified into the OSPAR Convention.
PARNCOM  Paris Commission - the governing body of the Paris Convention - reference is made to OSPAR
PBT  Persistent, Bioaccumulative and Toxic (chemical)
PEC  Predicted Environmental Concentration
pH  A measure of acidity level (actually a measure of the activity of the solvated hydrogen ion)
PIC  Prior Informed Consent - reference is made to the Rotterdam Convention
PNEC  Predicted No Effect Concentration
POP  Persistent Organic Pollutants
ppm  parts per million (e.g. mg/kg)
PRODCOM  EU statistical database on the production of manufactured goods. The term comes from the French "PRODuction COMmunautaire" (Community Production)
PROBAS  The database of the Danish Product Register
PRTR  Pollutant Release and Transfer Register
REACH  REACH is the European Community Regulation on chemicals and their safe use. It deals with the Registration, Evaluation, Authorisation and Restriction of Chemical substances
S  Sulfur
SCF  EU Scientific Committee on Food – has been replace by the European Food Safety Authority (EFSA)
SCHER  European Commission's Scientific Committee on Health and Environmental Risks.
SVHC  Substances of Very High Concern
TC NES  European Commission’s Technical Committee on New and Existing Substances.
TWI  Tolerable Weekly Intake
UL  Upper Level – related to intake with food
UNEP  United Nations Environmental Programme
US EPA  United States Environmental Protection Agency
VRAR  Voluntary Risk Assessment Report
WHO  World Health Organisation
vPvB  very Persistent very Bioaccumulative (chemical)
References


84 Survey of copper(I)oxide, copper(II)sulphates and copper(I)chloride


http://www.janssenpmp.com/download/35/antifouling (October 2013)


http://www.epa.govt.nz/Publications/Background information.pdf


SPIN. SPIN –Substances in preparations in the Nordic countries.
http://90.184.2.100/DotNetNuke/default.aspx (June 2013)

Sørensen G. (2013). Personal communication with Gitte Sørensen, Danish Technological Institute, June 2013.


http://www.dn.dk/Files/Filer/PDF/Kobber_i_foder_Tekst_box_Tjell-SWA-120512.pdf


http://www.mst.dk/Publikationer/Publikationer/2012/marts/978-87-92779-79-3.htm

http://apps.leg.wa.gov/RCW/default.aspx?cite=70.300&full=true (August 2013)


Appendix 1: Background information to Chapter 3 on legal framework

The following annex provides some background information on subjects addressed in Chapter 3. The intention is that the reader less familiar with the legal context may read this concurrently with Chapter 3.

EU and Danish legislation
Chemicals are regulated via EU and national legislation, 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 margin for manoeuvering as to the form and means of implementation. However, there are great differences in the space for manoeuvering 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).
- **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.

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 pieces 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.

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

REACH and CLP
The REACH Regulation\(^7\) and the CLP Regulation\(^8\) are the overarching pieces of EU chemicals legislation regulating industrial chemicals. The below briefly summarises the REACH and CLP provisions and gives an overview of ‘pipeline’ procedures, i.e. procedures which may (or may not) result in 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 tons or more per year, carcinogenic, mutagenic or toxic to reproduction substances above 1 ton per year, and substances dangerous to aquatic organisms or the environment above 100 tons per year.
- 31 May 2013: Registration of substances manufactured or imported at 100-1000 tons per year.
- 31 May 2018: Registration of substances manufactured or imported at 1-100 tons 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 their use within a given deadline (sunset date) or apply for authorisation for certain specified uses within an application date.

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

Classification and Labelling
The CLP Regulation implements the United Nations Global EU 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. EU **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 EU harmonised classifications, the annex has taken over the EU 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.

---

\(^7\) Regulation (EC) No 1907/2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)

\(^8\) Regulation (EC) No 1272/2008 on classification, labelling and packaging of substances and mixture
2. **Classification and labelling inventory.** All manufacturers and importers of chemical substances are obliged to classify and label their substances. If no EU 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 publish 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 2 to the main report.

**Ongoing activities - pipeline**
In addition to listing substance 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 are 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 thus subject to Authorisation, it has to go through the following steps:

1. It has to be identified as a SVHC leading to inclusion in the candidate list
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 website)
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 website).
4. The candidate list (substances agreed to possess SVHC properties) and the Authorisation list are published on the ECHA website.

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

- EU 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.

---

*9 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
- 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.

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

Rotterdam Convention
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 is 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 fulfill 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).
Blue Angel (Blauer Engel)
The Blue Angel is a national German eco-label. More information can be found on: http://www.blauer-engel.de/en.
Survey of copper(I)oxide, copper(II)sulphate and copper(I)chloride
This survey is part of the Danish EPA’s review of the substances on the List of Undesirable Substances (LOUS). The report defines the substances and present information on the use and occurrence of copper(I)oxide, copper(II)sulphate and copper(I)chloride internationally and in Denmark, information on existing regulation, on environmental and health effects, on monitoring and exposure, on waste management and on alternatives to the substances.

Kortlægning af kobber(I)oxid, kobber(II)sulfat og kobber(I)klorid
Denne kortlægning er et led i Miljøstyrelsens kortlægninger af stofferne på Listen Over Uønskede Stoffer (LOUS). Rapporten definerer stofferne og indeholder blandt andet en beskrivelse af brugen og forekomsten af kobber(I)oxid, kobber(II)sulfat og kobber(I)klorid internationalt og i Danmark, om eksisterende regulering, en beskrivelse af miljø- og sundhedseffekter af stoffet, af moniteringsdata, af affaldsbehandling samt alternativer til stoffet.