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Life cycle assessment of the use of marine biocides in antifouling paint

A comparison of the environmental profiles between conventional copper-based and innovative Selektope paint

Master of Science Thesis

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Thesis in *Industrial Ecology* and *Innovative and Sustainable Chemical Engineering*

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Abstract

Cuprous oxide-based antifouling paint is now the most common type in use, especially in the shipping industry. Anti-fouling paints prevent or slow down the growth of organisms attached to the hull, in order to improve a vessel's performance and durability. However, copper is a scarce resource and never can be retrieved or recycled after leaching into the sea. The need to protect sensitive marine areas from elevated levels of copper and to reduce the amount of copper emitted into the environment has led to the search for an alternative. A new product has been developed by I-Tech as a replacement for cuprous oxide in antifouling paint, trademarked as Selektope. It is based on biological knowledge and does not kill the target organism but instead deters it away from attaching to the ship hull. It is an organic synthetic biocide that can degrade in the marine environment and its mode of action makes it effective at very low concentrations (about 0.1% mass of paint). This is in sharp contrast to copper-based paints which need to be 40 – 60% copper by mass.

This master thesis aims to compare the sustainability profiles of the innovative Selektope paint system with traditional copper-based paint. Life-Cycle Assessment (LCA) is performed to analyse and compare the energy demand, global warming potential (GWP), and marine aquatic ecotoxicity potential (MAETP) of the two paint system. The effect of ecotoxicity on the marine environment on the use of cuprous oxide and Selektope has also been studied using MAMPEC model.

Despite some of uncertainties from assumptions and data availability, the results from LCA indicate an overall higher environmental impact from copper-based paint than from Selektope paint, in terms of all impact categories. The production of cuprous oxide appears to be the dominant burden in the life-cycle impact of copper-based paint, except that the release of copper during user phase has a much larger contribution to the MAETP. The impact generated by the Selektope paint has a relatively even distribution among different phases. However, the choice of transportation method can largely influence the result even though it would still be insignificant compared to copper-based paint. The results from the ectoxicological risk analysis show no potential risk in the leaching of both copper and Selektope.

Key words: marine fouling, antifouling paint, cuprous oxide, Selektope, Life-Cycle Assessment (LCA), ecotoxicity, risk assessment

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Contents

Acronyms

(Q)SAR	Quantitative structure activity relationships
1,4-DCB	1,4-dichlorobenzene
AF	Antifouling
CF	Characterisation factor
CML	Centre of Environmental Science of Leiden University
GWP	Global warming potential
IMO	International Maritime Organisation
ISO	International organisation for standardisation
LC50	Lethal concentration 50%
LCA	Life-cycle assessment
LCI	Life-cycle inventory
LCIA	Life-cycle impact assessment
MAETP	Marine aquatic ecotoxicity potential
MAMPEC	Marine antifoulant model to predict environmental concentrations
NOEC	No observed effect concentration
PEC	Predicted environmental concentration
PEM	Polymer electrolyte membrane
PNEC	Predicted no-effect concentration
RQ	Risk quotient
SPC	Self-polishing acrylic copolymer
TBT	Tributyltin
TBTO	Tributyltin oxide
VOC	Volatile organic compounds

1. Background

I-Tech is a Swedish research company focussed on marine paint, founded in 2000 by a group of researchers from University of Gothenburg and Chalmers University of Technology. The company aims to develop antifouling substances and associated technologies, with customers from the paint and chemical industry, boat and ship owners and other relevant industry stakeholders. It is now developing a marine biocide, Selektope ®, to be used in marine antifouling on ship and boat hulls (I-Tech(a), 2014). This chapter presents a brief introduction on antifouling paint, LCA, ecotoxicity and related issues.

1.1 Antifouling paint protection

Marine biological fouling, also known as marine bio-fouling, can be defined as the undesirable accumulation of microorganisms, plants, and animals on artificial surfaces immersed in sea water (Yebra et al., 2004). The negative impact of biological fouling on ships includes high friction resistance, increased frequency of dry-docking operations and introduction of exotic species into environments where they were not naturally present (Yebra et al., 2004). Bio-fouling results in increased weight, speed reduction and loss of manoeuvrability of the ship. It also leads to increased fuel consumption of the vessel which causes increased emissions of harmful compounds. In recent years the antifouling paints applied on ship hulls must not only prevent the fouling of underwater areas but must do this in compliance with emerging regulations and legislation, and are also required to minimise the release of biocides into the sea water. Therefore, research is on-going to find a more sustainable antifouling paint (Almeida et al., 2007).

There are currently two dominant methods for controlling marine fouling on boat hulls. The first is based on the historical method of dispersing a biocide in a binder system while the second type does not use biocides. The biocide dependent method slowly releases the biocide from the coating surface while the non-biocide dependent antifouling relies on the coating surface having non-stick properties (also referred as foul release technology) (Anderson, 2012).

Coatings to prevent fouling have been applied since antiquity as shown in table 1 (Dafforn, et al., 2011). Some of the disadvantages associated with marine bio-fouling have been known for years and several attempts have been made to solve these problems (Hellio & Yebra, 2009).

After the Second World War, several changes took place in the antifouling paint industry. These changes included the appearance of new synthetic petroleum-based resins, the abandonment of organo-mercurials and organo-arsenicals and the introduction of airless spraying. Also during this period, the addition of extremely toxic organotins like tributyltin oxide (TBTO) to rosin-based soluble matrix paints constituted a major step in terms of antifouling performance (Hellio & Yebra, 2009)

However, despite the high efficiency and cost-effectiveness provided by the tribultyltin (TBT) anti-fouling paints, environmental studies showed evidence of the persistence of organotin compounds in water and in sediments, killing sea-life other than that attached to the hulls of ships and possibly entering the food chain (International Maritime Organization, 2002). TBT was specifically shown to cause shell deformations in oysters, sex changes in whelks and immune response, neurotoxic and genetic effects in other marine species (International Maritime Organization, 2002). This problem was first discovered in the early 1980s, when several oyster farms in France experienced major declines due to reduced oyster spat-fall, anomalies in larval development, and shell malformation affecting 80–100% of individual oysters' (Dafforn et al., 2011).

Period	**Events**
1500–300 BC	Use of lead and copper sheets on wooden vessels
1800–1900s	Heavy metals (copper, arsenic, mercury) incorporated into coatings
1800s - present	Continued use of copper in anti-fouling coatings
1960s	Development of TBT conventional coatings
1974	Oyster farmers report abnormal shell growth
1977	First foul release antifouling (AF) patent
1980s	Development of TBT SPC coatings allowed control of biocide release rates
1980s	TBT linked to shell abnormalities in oysters *Crassostreagigas* and imposex in dogwhelks *Nucella lapillus*
1987–90	TBT coatings prohibited on vessels <25 m in France, UK, USA, Canada, Australia, EU, NZ and Japan
1990s–present	Copper release rate restrictions introduced in Denmark and considered elsewhere e.g. California, USA
2000s	Research into environmentally friendly AF alternatives increases
2001	International Maritime Organisation (IMO) adopts ''AFS Convention'' to eliminate TBT from AF coatings from vessels through:
2003	prohibition of further application of TBT
2008	prohibition of active TBT presence
2008	IMO ‘‘AFS Convention’’ entered-into-force

Table 1: Summary of the historical development of antifouling paint (Dafforn, et al., 2011)

Tin-free technologies have been on the increase after prohibition of active TBT presence in antifouling paint. Most vessels are dry docking with intervals of up to 36 month use antifouling systems that rely on the economical rosin-based control depletions paints or hybrid ablative self- polishing systems (Hellio & Yebra, 2009). The majority of this paint system comprises of Cu2O and algaecide co-biocides, such as, Irgarol 1051, diuron, chlorothalonil, dichlorofuanid and zineb (Hellio & Yebra, 2009). Presently, tin-free technologies are based on the following three patented self-polishing technologies

• silylated acrylate technologies
• metallic acrylate technologies
• acrylic nano capsule technology.

These tin-free paints depend on the controlled formation of seawater soluble sodium-acrylate salts within the paint matrix. It permits the fine-tuning the paint surface erosion under static conditions which is key for the attainment of a constant and sufficient release of biocides throughout the service life of the paint (Hellio & Yebra, 2009)

1.2 Copper and cuprous oxide

According to archaeological evidence, copper has been used by humans for more than 10,000 years. Its first use might have been to make coins, ornaments and decorative shapes (ICSG, 2013).

Copper and copper-based materials play a vital role in modern society’s development. Its corrosion resistance makes it an excellent roofing material for buildings. It is also know to demonstrate natural anti-microbial properties (Kennecott Utah Copper, 2007).

Preliminary statistics in 2012 showed that global copper production from mining reached 16.7 million tonnes per year. In 2012, annual refined copper production increased to 20.1 million tonnes (ICSG, 2013). Refined copper production can be divided into two categories, primary and secondary. Primary copper production refers to those derived from mine production. General processes of primary production are mining (either from drilling, blasting or loading), crushing, concentrating, smelting and refining. Copper scrap collected directly from semi fabrication and production processes is another important source of primary production. Secondary copper production refers to those derived from recycled scrap feed. The production processes are similar to primary production excluding the extraction from mine ores (ICSG, 2013; Kennecott Utah Copper, 2007).

Also, in 2011, it was estimated that at least 30% of the world consumption of copper is from recycled copper, making it one of the most recycled metals (Kennecott Utah Copper, 2007). Copper is 100% recyclable, and does not degrade in the recycling process, which means it can retain its chemical and physical properties (ICSG, 2013). In the United States almost as much copper is recycled from end-of-life products as is extracted from mining.

Cuprous oxide is an inorganic copper compound, and is one of the principal oxides of copper. The largest commercial use of cuprous oxide is as biocide pigment, fungicide and antifouling agent for marine paints due to its effectiveness to deter barnacles and algae (Richardson, 2003). The leaching rate, referring to the release of biocide from a given area in a given time, is expressed as μg/cm2/day and depends on the technology of the binder system. The binder technology for cuprous oxide-based antifouling is categorised as self-polishing acrylic copolymer (SPC). In addition to cuprous oxide as the main biocide, boosting biocide such as copper pyrithione is also needed to provide a better antifouling function against algae. The copper content released from the paint surface can form complexes with organic and inorganic substances in the seawater and ends up in the sediment (Anderson, 2012).

Cuprous oxide can be produced by a variety of methods. When pyrometallurgical methods are applied, copper powder is heated in air above 1030℃. It is also common to blend copper (II) oxide with carbon and heat them to 750℃ in an inert atmosphere (Richardson, 2003). In industrial practices, cuprous oxide powder is often made by electrolytic process under 25℃, from which the powder is characterized as particles with fine dispersivity (Bai, et al., 2001). The sum of the reaction formula for this electrolysis process is presented below (Equation 1).

$$2Cu\ (s) + H_2O\ (l) \rightarrow H_2\ (g) + Cu_2O\ (s)$$

Equation 1: Chemical formula of the electrolytic Cu2O production

1.3 Selektope

With increased use of cuprous oxide as biocide in antifouling paint systems, it is observed that the levels of dissolved copper in water and in sediments in certain areas are exceeding the limits set by water quality standards (I-Tech(b), 2014).

Selektope can be used to replace or greatly reduce the amount of copper required in marine paint at the same time protecting ships and boat hulls from fouling organisms. As given in IUPAC format, it is called 4-[1-(2,3-dimethylphenyl)ethyl]-1H-imidazole.

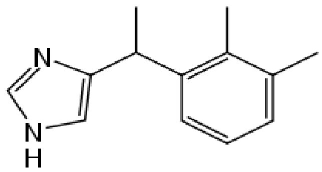
CAS-No.	86347-14-0
IUPAC Name	4-[1-(2,3-dimethylphenyl)ethyl]-1H-imidazole
Other common name	Medetomidine
Molecular formula	$C_{13}H_{16}N_2$
Structural formula	
Molecular weight (g/mol)	200,28 g/mol

Table 2: General information on Selektope (I-Tech, 2014)

Colour	White to almost white
Physical state	Crystalline powder
Odour	Odourless
Melting point	110-116°C
Boiling point	386°C (DSC, 1013 mbar) but decomposition starts at about 150°C resulting in a brownish melt
Relative density	1.113g/cm^3
Vapour pressure	3.5 x 10^{-6} Pa at 20°C, 8.3 x 10^{-6} Pa at 25°C
Dissociation constant	pKb = 6.9
Partition coefficient	Log P_{ow} = 3.1
Solubility in water 25°C	Buffer pH 5.1, 19.8g/l Buffer pH 7.9, 0.2g/l Buffer pH 9.0, 0.16g/
Solubility in organic solvents 25°C	p-Xylene 3.3g/l Acetone 65g/l 1-methoxy-2-propanol 341g/l

Table 3: Physical and Chemical properties of Selektope (I-Tech, 2014)

Concentrations as low as 1 nM in water has been found to stop barnacle larvae from settling. For effective coating, about 0.1% weight of Selektope to wet paint is usually required (I-Tech(b), 2014).

The Selektope molecule acts by targeting the octopamin receptor specifically in the barnacle larva. The receptor triggers a flight behaviour which makes the larva swim away from the Selektope treated surface.

Selektope mainly targets barnacles. It is also effective against other hard fouling organisms to some degree. At the predicted environmental concentration (PEC) it has no effect on non-target species, however at higher concentration above PEC exposed fish can become pale in colour, which is due to the accumulation of pigment on the fish scale and the effect is completely reversible (I-Tech(b), 2014).

Selektope is used in paint in addition to one or more algaecides in order to obtain complete protection against fouling organisms. When Selektope reacts with some common paint ingredients, ionic and acid-base interaction is possible with polymers and rosin containing acidic groups such as carboxylic acids (I-Tech(b), 2014).

Selektope will combine with metal ions and metal oxide such as zinc oxide and cuprous oxide while interacting with paint ingredient (I-Tech(b), 2014). This way it is able to effectively control the release of the active and prevent premature depletion of the paint film. Selektope is said to be released at the same rate as the carrier is dissolved or hydrolysed. It is not corrosive and can be used on all kind of substrates (e.g. aluminium).

1.4 Ecotoxicity

Ecotoxicity is the study of chemical hazards to fish, wildlife, plants, and other wild organisms. In most cases chemical and pesticide producers are required to submit ecotoxicity studies to regulatory authorities to support their registration and/or approval of their products (AltTox, 2007). The goal of ecotoxicity studies is to understand the concentration of chemicals at which organisms in the environment will be affected. This concentration should be avoided or be reduced to the barest minimum in order to protect the environment (Procter & Gamble, 2014).

Certain chemicals can persist for a long period of time in the environment and can travel an extensive distance thousands of kilometres (Mackay et al., 2011). They can also migrate from one medium to another such as air, fresh water and marine waters, soils, sediments, vegetation and other biota, including humans. Due to dynamic nature of the environment, the fate of substances is also subject to change. Hence, it is even difficult to know the fate of chemicals accurately but with the availability of sufficient information such as vital chemical and environmental properties their fate can be understood and even predicted (Mackay et al., 2011). These properties vary from chemical to chemical, in some cases by a factor of a million or even more. Also the environmental conditions show variability in temperature, sunlight intensity, rainfall and soil and vegetation types (Mackay et al., 2011).

Some of the attributes of these chemicals can be measured directly for example concentration while others cannot be measured directly for example fluxes such as evaporation rates, persistence and distance travelled. They are usually estimated by the use of models. These models can act as a calculating tool for receiving data input, processing them and giving relevant output (Mackay et al., 2011).

1.4.1 Ecotoxicity of Copper

Copper plays a vital role in enzyme activity necessary for a healthy metabolic functioning as well as the growth and metamorphosis of many organisms. However the accumulation of copper in the environment or marine bodies becomes toxic when, in a bioavailable form, it exceeds the threshold of an organism's tolerance. Copper toxicity is also affected by the environmental factors that govern copper speciation and its bioavailability (Dafforn et al., 2011).

Natural concentrations of copper in seawater are usually estimated between 0.5 and 3 µg/L, but concentrations of up to 21 µg/L of copper have also been found in contaminated areas. Experimental studies are usually used to determine the toxic effect of copper on a particular species, for example 1.2 µg/L of copper reduces the filtration rate of marine bivalve while 20 µg/L of copper impairs the settlement of coral larvae. Diatoms on the other hand show 50% reduced growth rate and oxidative stress when exposed to 100 µg/L of copper. This can also result in the abnormality of cell. Furthermore, the toxic effects of copper can also impact on infaunal population by reducing benthic recruitment when it is bound to sediments. In the Antarctic area, sediments contaminated with copper (at about 30 µg /g) were found to reduce infaunal diversity (Dafforn, et al., 2011).

A number of factors such as the difficulty in isolating the effects of copper from other contaminants as well as the challenges in assessing the toxic concentration of copper at different trophic levels make it difficult in attributing the effects of copper contamination directly to organism's (Zirino & Seligman, 2002). However according to Dafforn et al (2011), a recent risk assessment on the use of copper as a biocide in antifouling paints systems considering its concentration, speciation and effects of copper on marine environment concluded that copper toxicity was a potential problem in isolated water bodies such as marinas and harbours with little water exchange and high levels of boating.

1.4.2 Toxicity of volatile organic compounds

Volatile Organic Compounds (VOC) is contained in the solvent fraction of paints and cleaning solvents (Malherbe & Mandin, 2007) and (Celebi & Vardar, 2008). They are released into the air through diffuse emissions during painting, paint drying and the use of cleaning solvents (Malherbe & Mandin, 2007). Organic solvents in marine paint typically include toluene, ethyl benzene, xylene, methyl ethyl ketone, ethylene glycol, n-hexane and acetone (Malherbe & Mandin, 2007) and (Celebi & Vardar, 2008). The most popular of these constituents are xylene, methyl-isobutylketone and toluene.

A significant portion of emission VOCs, are generated during painting operations of ships (Celebi & Vardar, 2008). The transfer of VOCs to the environment is dependent on the physico-chemical properties of the solvent constituents and on the environmental hydrodynamic conditions. The density of pure solvents is about 800 g/ and about 100 g/L is present in thinned paints (Malherbe & Mandin, 2007).

Several methods are used for calculating VOC emissions from surface coating operations. The best method to use is dependent upon data availability and resources, and the degree of accuracy required for the estimation. Examples of such estimations include direct measurement, material balance, source testing, continuous emission monitoring system data and predictive emission monitoring (Celebi & Vardar, 2008).

1.4.3 Testing for toxic effects

The following three specific chemical properties are used to describe potential hazards on aquatic environment: aquatic toxicity, degradability and bioaccumulation (AltTox, 2007).

Testing on animals or plants is mainly used to determine whether environmental samples such as soil, sediment, or effluents contain toxic compounds.

The animal test is typically based on toxicity test data for fish, crustacea and algae. Toxicity data obtained from freshwater and marine species are considered to be equivalent, although this is not true for all substances. The fish test is used for testing both acute and chronic toxic effects. The fish 96-hour LC50 (lethal concentration 50%)

test is the standard for obtaining acute toxicity data. However, many scientists question the technical and scientific merit of using short term fish lethality for determining the environmental impact and fate of chemicals released into the aquatic environment. Chronic toxicity may include a number of other endpoints. Unfortunately, the required data is often not available, and a combination of acute toxicity, degradability, and bioaccumulation may be used to determine the potential for chronic aquatic toxicity (AltTox, 2007).

The non-animal methods include cell-based assays, toxicogenomic microarrays, and (Q)SAR [Quantitative Structure Activity Relationships] models for predicting toxic effects on aquatic organisms (Procter & Gamble, 2014).

1.4.4 Life Cycle Assessment of Pesticides

Pesticides can be seen as biologically active substances that are released directly to the environment during the use phase of their life cycle (Hellweg & Geisler, 2003). Pesticides are mainly used in agriculture but their persistence and dispersion creates risks to human via food, drinking water and breathing. “The fate of a pesticide compound is governed by its decomposition/degradation, its adsorption onto the solid phase of the soil, its dissolution in the liquid phase with subsequent movement by leaching, and its volatilization to the gas phase with subsequent diffusion through soil pores and/or emission to the atmosphere. (Ashworth et al., 2013)” These fate processes are in turn modulated by environmental variables such as temperature, soil moisture content, soil type and structure and the physical and chemical properties of individual pesticides.

A number of methods have been identified for the estimation of the environmental impact of pesticides use. Most of these methods focus on the pesticide fate within single environmental compartments such as ground water resources (Müller et al., 2010). On the other hand multimedia fate models consider the persistence of pesticides and their transfer between the different environmental compartments on a global scale. These methods can be adjusted for regulatory risk assessment so as to simulate worst case scenarios i.e. conservative estimates of potential pesticide impacts. However, most of the methods have strong limitations according to (Margni et al., 2002). The limitations range from a lack in detailed definition of the environmental impact of pesticide and neglect in some vital fate processes, toxicology information or the amount of pesticide applied.

One advantage of the use of LCA in pesticide is that “it is well suited to compare the severity of different exposure pathways to pesticides” (Hellweg & Geisler, 2003). A drawback being faced by the use of LCA in the analysis of pesticide use is the underlying assumptions made. Also the performance of the model needs verification and validation (Hellweg & Geisler, 2003).

1.4.5 Models for ecotoxicity

Several models have been developed depending on the task to be addressed. Most common of these models are the compartment box (or "Eulerian" models), Lagrangian models and diffusion models.

Box models are used to assess the environmental fate of chemicals in risk assessment and life cycle analysis (Klepper & Hollander, 1999). The environment here is divided into a number of volumes or boxes, which are fixed in space and are assumed to be homogeneous (Mackay et al., 2011). In this model only one concentration is defined per box. Another advantage of the box model is its simplicity for decision making. Also, the box models have the advantage of simultaneously treating the various fluxes either in a time-dependent or steady state fashion. It requires the solution of a set of equations with a size equal to the number of boxes (Klepper & Hollander, 1999). For regulatory purposes the compartmental box models are commonly applied (Mackay et al., 2011).

Lagrangian models are used for modelling the atmosphere and river where a parcel of air or water and the chemical in the parcel moves from place to place (Mackay, et al., 2011).

When describing chemical migration in sediments and soils where there is marked heterogeneity in concentration, it is preferable to use diffusion differential equations and solve them either numerically or analytically. This method can also be applied to atmospheric dispersion, aquatic and oceanic systems. Diffusion models are mainly used when considering an overall picture of chemical fate in the global atmosphere or oceans, or when estimating the near-source dispersion of emitted chemicals (Mackay et al., 2011).

A recent approach used in LCA is for the use of pesticides is IMPACT 2012, this model works with midpoint and damage categories. It makes use of a life cycle assessment criterion of food commodities which includes the pesticide use together with global-warming potential, primary energy use, land requirement, and others (Müller et al., 2010).

USEtox model

Another model for ecotoxicity analysis in an LCA framework is the USEtox model. This model accounts for direct exposure of freshwater and marine ecosystems at various spatial scales by applying the concept of spatial scale nesting (Henderson et al., 2011). It incorporates a matrix framework for multimedia modelling, allowing separation of fate, exposure, and ecotoxicity effects in the determination of an overall characterisation factor for use in life cycle impact assessment (Henderson et al., 2011). For marine systems, the fate modelling needed for determination of characterisation factors for ecotoxicity impacts in the marine compartment is already part of USEtox. A drawback to this is that the exposure and effect modelling in this system has been considered immature for inclusion, due to the lack of specific data for chemical behaviour and effects on organisms in these domains. Therefore, characterisation factors are not yet provided for effects on marine systems (Henderson et al., 2011)

Most modern models like USEtox depend strongly on compartment specific emissions (Quantis, 2013). Therefore, in other to meet the requirements of those models, there is need for inventory models that can predict emissions that are compartment specific.

PestLCI

PestLCI is a Life Cycle Inventory model for evaluating the fate of pesticides applied on agricultural fields (Quantis, 2013). This model calculates the fractions of applied pesticide that are taken up by the plant or that reach the environmental compartments such as air, surface water; and groundwater for agricultural life cycle analyses (LCAs) (Hellweg & Geisler, 2003) and (Müller et al., 2010). The PESTLCI model is used for the analysis of emission pathways. It could be used for the analysis of the following path: the settling of pesticide on leaves and soil, emission to air by wind drift, evaporation, degradation and plant uptake (Hellweg & Geisler, 2003). The agricultural field described in PestLCI is modelled as a box covering a distance of 100 meters in the air, 1 meter below the ground level in the soil and horizontally following the physical borders of the field. These emissions can be seen as direct emissions to surface water or air, but not soil. Emissions to soil take place indirectly through other compartments such surface water or air. The PESTLCI model also quantifies emissions to the groundwater compartments but these emissions cannot be characterized at the moment (Quantis, 2013).

Prior to the development of the PESTLCI model, regulatory risk assessment models were used to simulate worst case scenarios which provided conservative estimates of the potential impacts of pesticide (Müller et al., 2010). These scenarios were further simulated using two leaching models called Pelmo and Macro to predict pesticide losses to surface and ground water. The result obtained showed that ground water leaching was more sensitive to the substance properties of the pesticides and, to a lesser extent, to spatial parameters.

MAMPEC model for antifoulants

The prediction of environmental concentration of antifouling products in the marine system can be estimated with the use of MAMPEC model. This model was first developed by Vrije University and Delft hydraulics in the Netherlands. It can be used for calculating the predicted environmental concentration (PEC) of a specific chemical substance, based on inputs including emission rate, substance properties and the marine processes (Hattum et al., 2002; Wang et al., 2014). For a defined water body, the model utilizes the DELWAQ and SILTHAR modules to compute the hydrological and chemical fate calculations, the water exchange volumes, and the transport of particulate. A mass balance is calculated of the input, outflow, settling, volatilisation and decomposition of the biocide, in order to determine the chemical fate in the water column. When computing the concentration in the sediment, it takes into account the biocide input by settled matter as well as the biocide degradation in the sediment layer (Mukherjee et al., 2009).

The parameters needed for the modelling process, i.e. emission factor, substance properties, marine processes, can be either input by hand or loaded directly with preset data in the MAMPEC software.

1.5 Life cycle assessment

In developed society policies regarding the environment are made on the basis of sustainable production and consumption patterns. In order to see how industries and consumers influence or impact the environment, knowledge on environmental impact of production and consumption is very important. Life Cycle Assessment (LCA) is one of the tools for assessing such impact. The idea behind using this tool is to get "a full picture of a product's impacts in order to find the best solutions for their improvement without shifting the impact to other field" (Guinée & Heijungs, 2005)

LCA as defined in ISO 14040, is a ''compilation and evaluation of the inputs and outputs and the potential environmental impacts of a product system throughout its life cycle'' (Guinée, 2004). This means that the impact of a product is followed from the extraction of raw material "cradle", from natural resources through the production, product parts and the product itself, and the use of the product to the management after it is discarded, either by reuse, recycling or final disposal, "grave" (Baumann & Tillman, 2004).

Relevance of LCA

One basic reason for carrying out LCA is due to the environmental concern expressed by the public, political bodies and industries (Baumann & Tillman, 2004). The object of this concern may range from the availability or use of resources to the health of living organisms and even the natural environment. Hence, there is a need for an assessment tool such as LCA for the environmental assessment of products.

The strength of LCA according to Bauman and Tillman is that it studies a whole product system, which implies that it covers all activities related to a product or function; stating its effects anywhere in the world; covering all relevant substances as well as environmental themes; and having a long-time horizon (Guinée & Heijungs, 2005). This prevents problem shifting that may occur when only one activity, area, substance, environmental problem, or limited period of time is focused on (Baumann & Tillman, 2004; Guinée & Heijungs, 2005). It is also seen as an engineering tool for supporting different technological options that fulfils a certain function by compiling and evaluating the environmental consequences of these options (Guinée & Heijungs, 2005).

Conducting an LCA for a product involves several elements (Guinée & Heijungs, 2005):

1. Data collection on the production, use and disposal of the product that the materials are made from and the energy requirement, etc.

2. A method of combining the data in the appropriate way.

3. Software in which all these methodological rules have been implemented.

4. A procedural context in which the process of doing LCA and using its results is embedded.

According to ISO 14040, an international standard for conducting LCA, the method can be applied to the following areas;

1. Identification of improvement possibilities

2. Decision making

3. Choice of environmental performance indicator and

4. Evaluation of market claims

Others areas LCA could be applied according to Baumann and Tillman is in the area of learning, that is exploring the environmental properties of the product system under study and learning about the relationship of the production system (Baumann & Tillman, 2004).

The LCA Procedure or methodological framework

To carry out an LCA, several procedures have been established by the ISO standard. The standard distinguishes four phases of an LCA study, namely

1. Goal and scope definition

2. Life-cycle inventory (LCI)

3. Life-cycle impact assessment (LCIA)

4. Interpretation of results

LCA begins with setting up of the goal and scope definition of the product to be studied and the purpose of the LCA. This comprises of the intended goal of study, the functional unit, the reference flow, the product system under study, and the breadth and depth of the study in relation to the goal.

Thereafter the inventory analysis is carried out. This according to Bauman and Tillman implies the construction of the life cycle model and the calculation of the emission produced and resources used during the life cycle. This entails setting up economy or environmental boundaries, designing of the process flow diagrams, collecting data for each of the process and performing allocation for multifunctional processes (Guinée, 2004).

The life cycle impact assessment according to ISO 14040, is a ‘‘phase of LCA aimed at understanding and evaluating the magnitude and significance of the potential environmental impacts of the product system’’. It is the step where results from the inventory analysis is processed further and interpreted in terms of environmental impacts and societal preferences (Guinée, 2004). Also, a list of the impact category is defined and models for relating them to a suitable impact indicator are selected through the act of classification and characterisation (Baumann & Tillman, 2004) and (Guinée, 2004) The several steps involve in the impact assessment phase are summarize below

1. Selection of impact categories.

2. Selection of characterisation methods: category indicators, characterisation models, and factors.

3. Classification (assignment of inventory results to impact categories).

4. Characterisation.

5. Normalisation.

6. Grouping.

7. Weighting.

The fourth aspect of an LCA procedure involves the evaluation and analysis of the results obtained from both the inventory analysis and Impact assessment. Finally, conclusions are drawn up and suggestions made.

2. Methods

In this chapter, information concerning the paint system is described in detail. In order to carry out the study, several parameters and scenarios should be decided based on the available data. Models and approaches for the analysis of ecotoxicity need to be selected. The software openLCA is used for computing LCA results and MAMPEC3 (Deltares, 2012) is used for modelling the emission of copper/Selektope into the marine water system.

2.1 Goal and scope definition

The goal of this LCA is to compare the environmental profile of an innovative antifouling paint system based on Selektope with the conventional copper-based biocide (cuprous oxide) alternative. LCA is used to identify environmental hotspots in terms of energy demands, global warming potential (GWP) and marine aquatic ecotoxicity potential (MAETP) of the two paint systems (containing cuprous oxide or Selektope). The result of the LCA is intended to be used by I-Tech as a cornerstone in the company's internal work in documenting the environmental performance of Selektope and part of the future market strategy.

This study aims at assessing the environmental performance of different key components used in an antifouling paint system. Therefore a change oriented LCA is performed. This will affect the data collection for the inventory analysis and will be later on described in *scenarios and assumptions*.

Functional unit

The general function of antifouling paints is to cover the ship surface in order to prevent the accumulation of unwanted organisms. Therefore coverage can be used in defining the functional unit for the LCA. The functional unit of this study is defined as 1 m^2 paint covering and protecting the ship surface. This is the basis for comparison and that all relevant flows are scaled to it. It is also used later on as the basis for the modelling of predicted marine concentrations.

The durability (life time) of paint is between 3 and 5 years, depending on the age of the ship. Ships older than 10 years will be applied with paint with 3-year durability, while younger ships will be applied with 5-year paint. This will affect the thickness and consequentially the amount of paint needed for the functional unit, which will be varied in different scenarios further described in the *scenarios and assumptions* part.

System boundary

A cradle-to-grave analysis is performed in this study. The overall geographical boundary is set in a global scenario, but for the baseline scenario, the location of the manufacturing, application and end-of-life treatment of paint is assumed within

Europe, due to the availability of data. This will be further explained in the *scenarios and assumptions* part.

Process flowchart

The main life cycle processes of an antifouling paint are illustrated in Figure 1. This includes everything from the extraction of raw material to the end-of-life stage. A more detailed flowchart covering all the sub-processes will be shown in the *technical system* part.

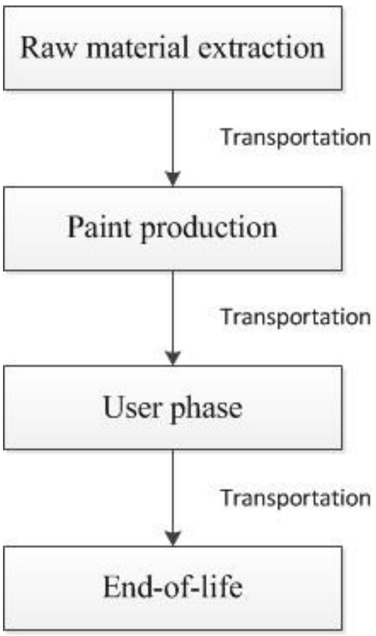


Figure 1: Main process flowchart for the life cycle of antifouling paint

Life-cycle impact analysis

The CML 2001 method is applied for the characterisation of environmental impacts, among which the impacts on global warming potential (GWP) and marine aquatic ecotoxicity potential (MAETP) are further analysed. The "cumulative energy demand" method is used to determine the non-renewable energy demand for the paint life cycle. Both computing methods are provided by EcoInvent version 2.2 using the OpenLCA software (EcoInvent, n.d.).

2.2 Technical system

The life cycle of the targeted antifouling paints can be divided into raw material extraction (for the biocide and other paint components respectively), production of the alternative biocide (either cuprous oxide or Selektope), production of paint, coating of paint on to ships, user phase, sandblasting process to remove paint from ships after the service life of the paint, and final incineration. Figure 2 illustrates the life cycle including all the stages mentioned above. The circled box at the left represents the processes for using Selektope, while the one on the right represents the processes for using cuprous oxide. The alternative processes for using cuprous oxide as the biocide include mining and refining of copper, production of cuprous oxide from refined copper anode, and the raw material extraction and production of other paint components. The alternative processes for using Selektope as the biocide include raw material extraction and production of Selektope and other paint components.

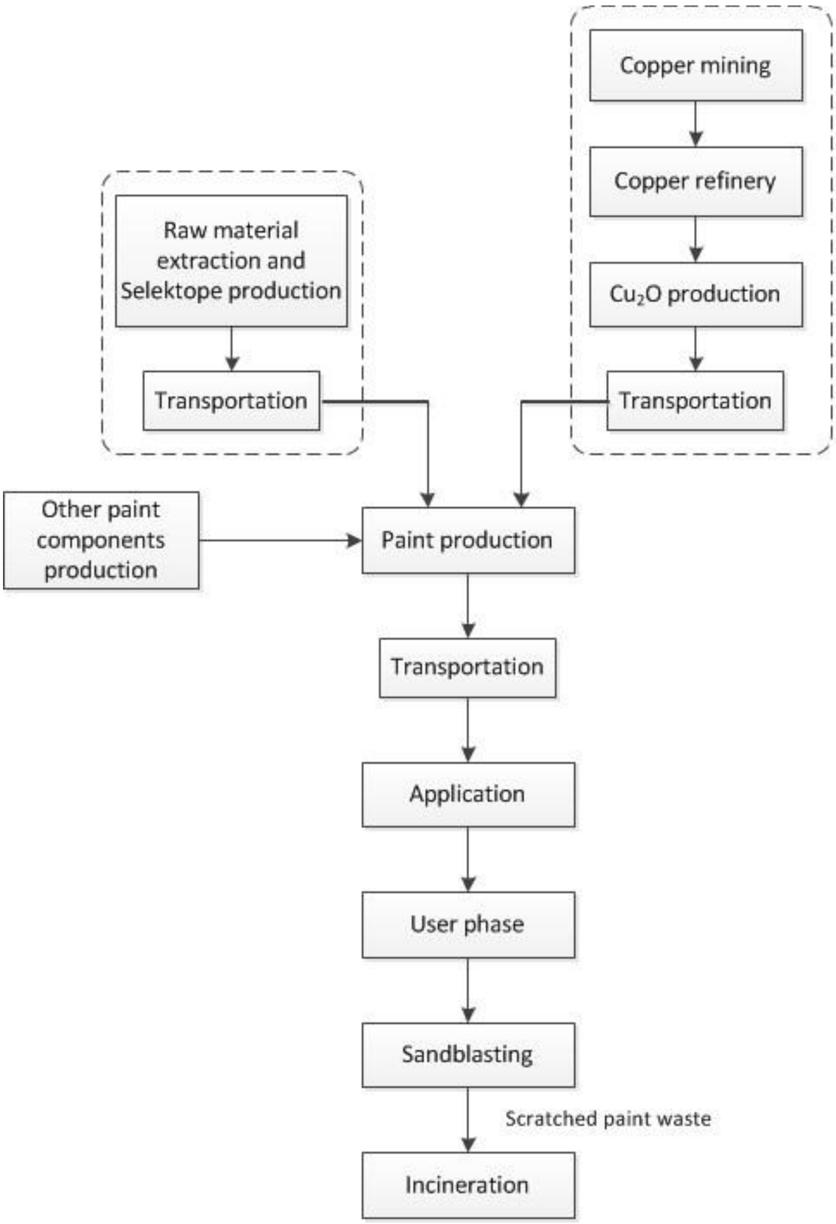


Figure 2: Detailed process flowchart for the antifouling paint system

As can be seen from the flowchart, all the other processes from the production of paint are the same for both biocide alternatives and will not be affected by the composition of paint.

Most paints, including antifouling paints, are prepared using similar manufacturing processes. The manufacturing processes usually involve two or more of the following steps: raw material blending, extruding, grinding, mixing, filling, control and packaging (US National Center for Manufacturing Sciences, 2011). In this study, the production processes for antifouling paints are simplified as dispersing, stirring and canning for the purpose of data collection.

In the application process, electricity is needed for airless spray guns to apply the paint onto the ships, after that the applied paint is attached to the ship and the water surface during its lifetime. The user phase of paint is divided into two parts, the application of paint and the new “user phase” when coated ships travel around the globe. The new “user phase” implies the period when the coated paint is protecting the ship’s underwater surface. It is assumed that the two types of paint have the same performance during the user phase.

When the paint has reached its expected life time, the ship is sent to the shipyard to be repainted. Around 90% of the original paint is lost during use and released into the aquatic system. Before the repainting process, the ship is sandblasted to remove the paint left on the surface. The waste from the sandblasting process must be handled properly, according to the EU directive on port reception facilities for ship-generated waste and cargo residues (European Commission, 2010). It is important to use appropriate waste treatment methods for paint waste so as to reduce the environmental impacts arising from the end-of-life phase (Zuin et al., 2014). In Sweden, over 90% of all water based paints are incinerated (Lindberg, 2014). Although the paint studied in this project is solvent based, the VOCs in the paint content are evaporated after the application to the ship, which leaves mainly inorganic components in the paint waste. The incineration process is therefore selected as the waste treatment method for this analysis.

2.3 Data collection

The data collection of necessary information for the implementation of LCA in this thesis is generally from three types of sources. Most of the knowledge regarding paint production is from unpublished sources, i.e. interviews with I-Tech employees. Documented sources are also included in the data gathering, using information from books and articles. Finally estimations and assumptions are applied where data are lacking.

LCI and LCIA

Life cycle inventory data from the EcoInvent database version 2.2, are used when constructing the models for the impact analysis.

The copper-based antifouling paint studied in this assessment is the SeaQuantum Classic manufactured by the paint company Jotun. Data sheet regarding the chemical composition of SeaQuantum Classic can be found in the appendix. Information regarding paint composition, ingredients and production process for Selektope is confidential to I-Tech. Therefore these data will not be presented in detail in the report.

According to I-Tech, Selektope, does not have negative effects on non-target species at the predicted environmental concentration (PEC). Fish exposed to very high concentrations can go pale, a chromatic effect which is completely reversible. Considering that it is also 100% degradable in the aquatic system (final form as carbon dioxide), acting as an energy source for the bacteria in the water, it is therefore recognized to be environmental friendly regarding ecotoxicity (I-Tech, 2014). Nevertheless, in order to make a quantitative comparison with copper-based paint, the effect of Selektope emitted in user phase needs to be studied even though it might be very small. Current characterisation methods for MAETP do not include Selektope as one of the target substances, so a proxy calculation (equation 1) is proposed to develop a characterisation factor (CF) for Selektope compared to 1,4-dichlorobenzene (1,4-DCB), the chemical applied in presenting MAETP. The emission of copper ion into ocean has a CF of 25360 kg 1,4-DCB/kg copper as described in the CML method for MAETP.

$$\mathrm{CF} = \frac{\text{PNEC for 1,4}-\text{DCB}}{\text{PNEC for Selektope}}$$

Equation 2: Proxy calculation of characterization factor for MAETP

The PNEC value for 1,4-DCB used in this study is defined by Boutonnet et al., (2004) as 20 μg/L, based on acute and chronic toxicity studies with no distinction between marine and freshwater taxa. The PNEC value for Selektope is decided based on a series of studies on acute and chronic toxicity data for aquatic organism. The documented no observed effect concentrations (NOEC): 0.01 mg/l for *Oncorhyncus mykiss*, 0.12 mg/l for *Scenedesmus subspicatus*, 0.253 mg/l for *Skeletonema costatum*, and 0.001 mg/l for *Cyprinodon variegatus* (Maunder et al., 2012; Bätscher, 2007; Maunder & Vaughan, 2011; Vaughan & Hutchinson, 2011). In this case the lowest value, 0.001 mg/l is selected as the PNEC value for Selektope.

MAMPEC model and risk assessment of antifoulants

The leaching rate of copper and Selektope into the aquatic system during user phase is calculated based on the functional unit. An average value is applied through dividing the amount of total leached substance (90% of the amount applied in paint) by the number of days of the selected time span.

When performing the calculation of predicted environmental concentration of chemicals (PEC) in MAMPEC 3.0, one needs to choose from different environment and emission scenarios. In this study, the OECD-EU commercial harbor and marina are selected. In the MAMPEC model, a background concentration can be added into the calculation. For the case of copper, background concentrations within estuarine and coastal area range from 0.5 to 3μg/L according to Hellio et al., (2009). A geometric mean value of 1.53μg/L is applied in the calculation, according to the data for marinas/harbours provided by Hall et al., (1999). For the case of Selektope, the background level is assumed to be zero (0), since Selektope is a newly developed synthetic chemical, and has not been widely employed yet.

The calculated maximums in predicted concentrations are used in determining the environmental risk of copper/Selektope. This is done by applying a risk quotient (RQ) approach, which is determined by the equation shown below (equation 3).

$$RQ = \frac{\text{Predicted environmental concentration (PEC)}}{\text{Predicted no effect concentration (PNEC)}}\text{, if RQ>1 there exist risk}$$

Equation 3: Calculation of risk quotient

When deciding the predicted no effect concentration (PNEC) for copper, a value with a 95% protection level for all species is used, which is 5.6 μg/L (Hellio & Yebra, 2009). The PNEC for Selektope according to I-Tech is 1μg/L for *Cyprinodon variegates* (I-Tech(c), 2014).

2.4 Scenarios and assumptions

The baseline scenario in this LCA is defined as antifouling paint with expected durability of three years. The difference between a 3-year and 5-year life time of paint is merely the amount of paint coated on the ship surface. Based on this scenario, two sub-scenarios are developed regarding different waste treatment data. The EcoInvent database includes an incineration process for hazardous paint waste. However, this process takes no account of the actual paint composition, and only documents the emission from the incineration process rather than the emission of incinerated paint content, e.g. gases, small particles, residues etc. For this thesis a simplified incineration process is also created in order to study the impacts from incinerated paint content, assuming all the organic components be emitted as gaseous oxides (e.g. CO2, NOx etc…) into the atmosphere and all the metal and non-metal inorganic components would stay in the ash residue after incineration. No energy input or other necessary processes for incineration are included in this case, due to lack of sufficient data. The two waste treatment scenarios are studied for both copper-based and Selektope paints. From now on, the scenarios using incineration process provided by EcoInvent are defined as Scenario A, and the ones with simplified incineration process are referred as Scenario B.

Due to the scope and the time and information available, many assumptions and exclusions are made in this study, which are listed as follows:

- It is estimated that more than 40% of the copper used in Europe comes from recycling, and recycling can save up to 85% of the energy required for primary production (European copper institute, 2014). However, production of copper from secondary sources (recycling) is not included due to availability of sufficient inventory data.
- Methods other than electrolysis used for preparing cuprous oxide for antifouling paint are not considered in order to simplify the analysis.

- The energy input in producing cuprous oxide is calculated based on the entropy change in the chemical reaction, multiplied by an assumed efficiency flow factor, which will be later explained in the inventory analysis.
- Paint components, other than cuprous oxide and Selektope, which make up less than 10% (except for silylacrylate and magnesite due to lack of sufficient information) of total paint by weight are not included in the inventory analysis.
- Material losses during the coating process are included: about 25% of the final applied amount as described by I-Tech.
- The production of packaging material is not included in the study, since it is similar by amount for both types of paint. This exclusion was also made in an LCA study of the carbon footprint of paints, stating that components contributing to less than 2 percent of total inputs may be excluded (dcarbon8, 2008).
- The production of copper and cuprous oxide is assumed to take place in Chile, one of the main copper producers for copper in the world. The production of Selektope is assumed to be in the Swedish city, Karlskoga. The production of the paint is assumed to take place in the Netherlands for copper-paint and Norway for Selektope paint. The shipyard where coating is done is assumed to be in Gdansk, Poland.
- For the baseline scenarios, road transport is applied except for the shipping of cuprous oxide from Chile to the Netherlands by container ships. Air transport is applied in a sensitivity analysis for the shipping of Selektope paint, because this is described by I-Tech as the current method in use.
- The energy required in the sandblasting process is assumed to be the same with coating process in terms of amount per mass of paint.
- One allocation challenge occurring in this study is the incineration process for paint waste, because there will be surplus heat produced to the district heating system, thus less heat is needed from alternative energy sources. As described in the incineration process by EcoInvent, the net energy produced in incineration is 17.11MJ/kg electric energy and 1.27MJ/kg thermal energy. The standard allocation settings in this case are used as defined in EcoInvent 2.2 already. However, this incineration process provided by EcoInvent may not well represent the situation that happens in Gdansk today, and can only be used as a reference.

3. Inventory analysis

In this chapter, the inventory data for the paint systems is presented and further explained. A summary of input included inventory under different life phases with ready-made incineration process is listed in Table 4 and Table 5 for copper-based and Selektope paint respectively.

Phase	Process	Resource	Input	Unit	Reference
Mining	**Copper ore extraction**	Diesel fuel	0.002	t/t ore	Norgate, 2001
		Electricity	13	kWh/t ore	
		Mine drainage	0.78	t/t ore	
		Waste rock	0.18	t/t ore	
Mineral processing	**Copper refining**	Electricity	31	kWh/t ore	
		Grinding	0.001	t/t ore	
Copper production	**Smelting & converting**	Natural gas	24	kg/t concentrate	
		Coal	17	kg /t concentrate	
		Oil	7	kg/t concentrate	
		Electricity	1143	kWh/t Cu	
		Oxygen	834	kg/t Cu	
		Silica	130	kg/t concentrate	
		Limestone	21	kg/t concentrate	
	Refining	Electricity	323	kWh/t Cu	
		Steam	230	kg/t Cu	
Cuprous Oxide Production	**Electrolysis**	Energy	1.81	MJ/g Cu_2O	Research assumption
Transportation	**San Antonio to Amsterdam**	Ship	14000	km	I-Tech(b), 2014
Paint production	**Biocide**	Cuprous oxide	48.4	%w/paint w	
	Other paint components	Xylene	22.9	%w/paint w	
		Zinc Oxide	8.2	%w/paint w	
	Turrax	Energy	0.018	kWh/kg paint	
	Stirrer	Energy	0.032	kWh/kg paint	
	Canning	Energy	0.001	kWh/kg paint	
Transportation	**Amsterdam to Gdansk**	Truck	1000	km	
Coating	**Spray gun**	Electricity (max)	19	kWh/vessel	
		Electricity (min)	7.4	kWh/vessel	
Sandblasting	**Sandblasting**	Electricity	0.004	kWh/kg paint	Assumption
End-of-life	**Waste treatment**	As defined in EcoInvent database			

Table 4: Input inventory for copper-based paint

Phase	Process	Resource	Input	Unit	Reference
Raw material extraction	**Reactants for Selektope**	Ethyl acetate	32778	kg/t prod.	I-Tech(b), 2014
		Toluene	20035	kg/t prod.	
		Isopropanol	17613	kg/t prod.	
		Acetonitrile	10770	kg/t prod.	
		HCl 37% (aq)	10396	kg/t prod.	
		Acetone	10233	kg/t prod.	
Selektope production	**Chemical production**	Electricity	0.467	MWh/kg prod.	
		Steam	0.617	MWh/kg prod.	
Transportation	**Karlskoga to major EU ports**	Truck	500	km	
Paint production	**Biocide**	Selektope	0.1	%w/paint w	
	Other chemicals	Xylene	22.9	%w/paint w	
		ZnO	16	%w/paint w	
		Talc	15	%w/paint w	
		Dolomite	10	%w/paint w	
	Turrax	Energy	0.018	kWh/kg paint	
	Stirrer	Energy	0.032	kWh/kg paint	
	Canning	Energy	0.001	kWh/kg paint	
Transportation	**Oslo to major EU ports**	Truck	660	km	
Coating	**Spray gun**	Electricity (max)	19	kWh/vessel	
		Electricity (min)	7.4	kWh/vessel	
Sandblasting	**Sandblasting**	Electricity	0.0072	kWh/kg paint	Assumption
End-of-life	**Waste treatment**	As defined in EcoInvent database			

Table 5: Input inventory for Selektope paint

The inventory data regarding the mining and production of copper is from a previous study on different copper production methods by CSIRO in 2001 (Norgate, 2001). The production process selected in the study is categorised under pyrometallurgy, which is a traditional and yet currently dominant method in cathode copper production (Eltringham, 1997; Moskalyk & Alfantazi, 2003).

The energy demand for the electrolysis process is calculated through multiplying the molar entropy change of the reaction by an energy efficiency factor, as described in scenarios and assumptions. The efficiency factor applied in this study is assumed as 10, which is based on a review of different electrolysis methods for hydrogen production by (Bhandari, et al., 2013). In the review article, the net energy demand for the electrolytic hydrogen production is provided for two different methods, alkaline electrolysers and polymer electrolyte membrane (PEM) electrolysers. The energy efficiency factor for the two electrolytic methods is therefore calculated, 6 for alkaline electrolysers and 11 for PEM electrolysers. The assumed efficiency factor 10 for electrolytic cuprous oxide production is then within the suggested range of 6~11, and is also simple in calculation. A sensitivity test on the selection of efficiency factor is later performed to study its influence on the LCIA results.

After coating, VOC components in the paint are vaporize when the paint is dried. Therefore it is included as the emission from the coating process.

The released Selektope in the aquatic system is gradually degraded with a half-life of 50 days (I-Tech(c), 2014), and ends in the form of carbon dioxide, which is included as the emissions from the user phase (I-Tech(b), 2014).

A summary of amount of paint needed per functional unit for both 3-year and 5-year period is presented in Table 6. The amount of cuprous oxide used accounts for about 48.4% of total paint by weight. Considering an average purity of 92% for cuprous oxide, the actual concentration of cuprous oxide in the paint is about 44.5% by weight. The concentration of Selektope in the paint is 0.1% by weight. The difference in weight between copper-based and Selektope paint is due to their different density, which is 1.75 g/cm3 for copper-based and 1.31g/cm3 for Selektope. The difference in weight between different time spans is simply because a longer durability needs more paint applied to the surface.

Time span	**3-year**	**5-year**
Copper-based paint	0.485 kg	0.607 kg
Selektope paint	0.365 kg	0.455 kg

Table 6: Amount of wet paint (kg) needed per functional unit

4. Results

The results obtained from the life cycle inventory analysis are presented in this section. Firstly a comparison is made for the two paint system in terms of their environmental impact. Hotspots for the various process streams in the production of antifouling paint are identified and analysed. Furthermore, a sensitivity analysis in relation to the geographical boundary and electrolysis efficiency used for estimating energy demand for producing cuprous is made. Finally, a normalised environmental impact of the Selektope released is presented and the risk analysis associated with the copper and Selektope leaching is also made.

Comparison of the two paint systems

The calculation results of the cumulative non-renewable energy demand for all the scenarios are presented in Figure 3 below.

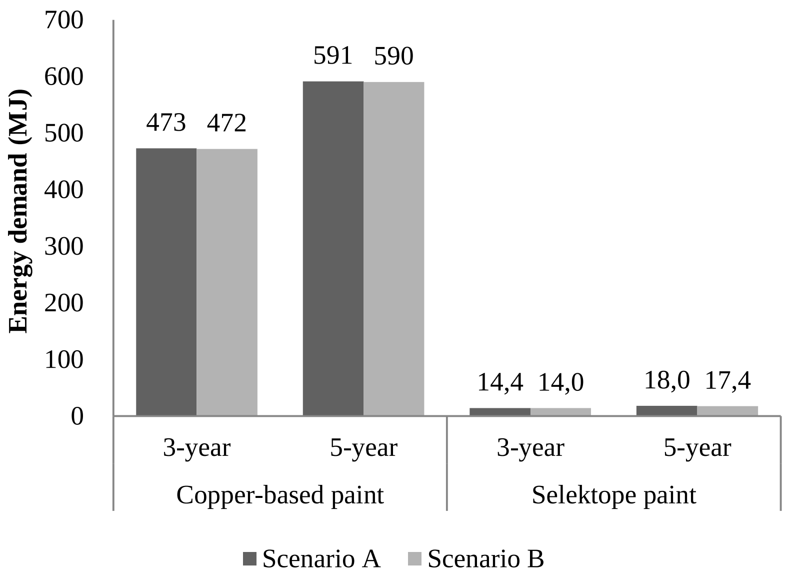


Figure 3: Cumulative non-renewable energy demand (MJ) for the two paint system

For the baseline scenarios (scenario A with 3-year time span), the copper-based paint has a much larger demand for non-renewable energy (473 MJ) than the Selektope paint (14.4 MJ). All 5-year scenarios have a higher result than 3-year scenarios, mainly because there is more paint needed for a longer durability.

There is rather big difference between the two paint systems, with a gap of almost 600 MJ in a 5-year scenario, which is equivalent to the heat value of about 15 litres of diesel fuel (World Nuclear Association, 2010). With the average combined fuel economy for today’s mid-size cars around 25-35 MPG (miles per gallon), this means a mileage at about 160-220 km for a diesel car (U.S. Department of Energy, 2014).

The contribution of each process from scenario A is presented in Figure 4 for copper-based paint and in Figure 5 for Selektope paint.

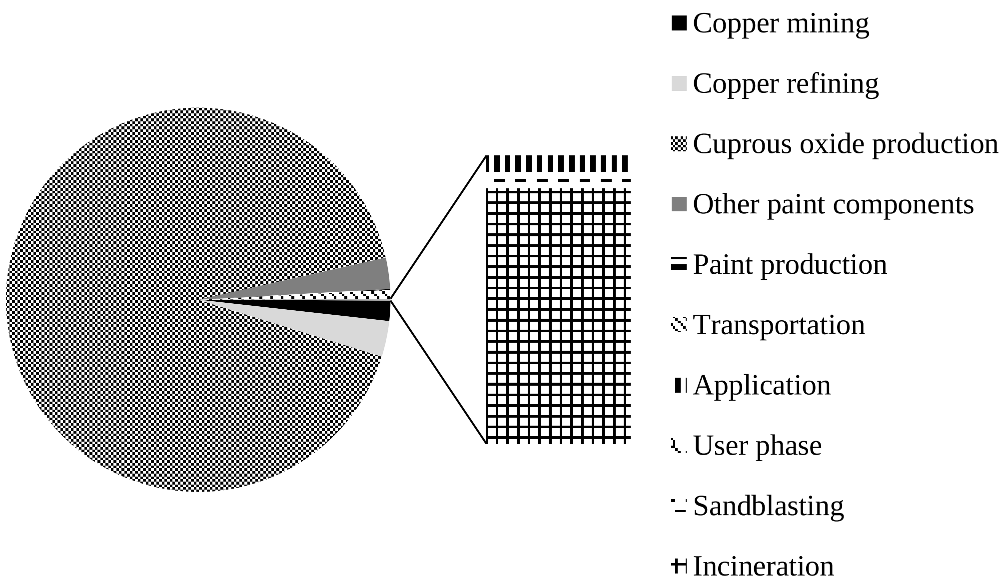


Figure 4: Process contribution to energy demand for copper-based paint

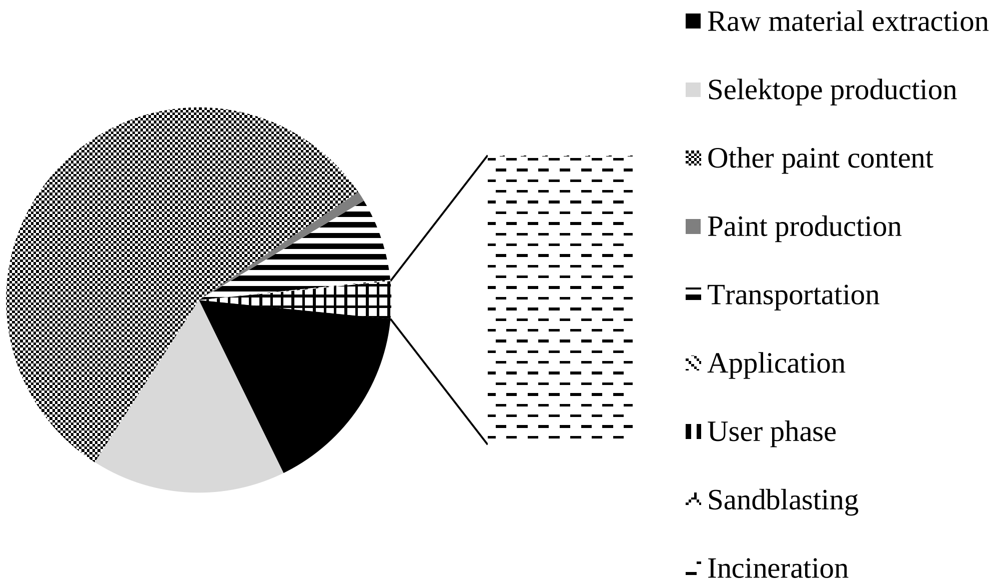


Figure 5: Process contribution to energy demand for Selektope paint

It can be concluded from the figures that the production process of cuprous oxide appears to be the major burden (more than 90%) in the energy demand for copper-based paint, while the production process of other paint content plays a major role (about 56%) in the Selektope system, followed by raw material extraction and production of Selektope (both around 16%).

To get a general idea of the difference of the two types of paint regarding their impact on GWP and MAETP both over 100-year interval, the results from scenario A are presented in Figure 6 and 7.

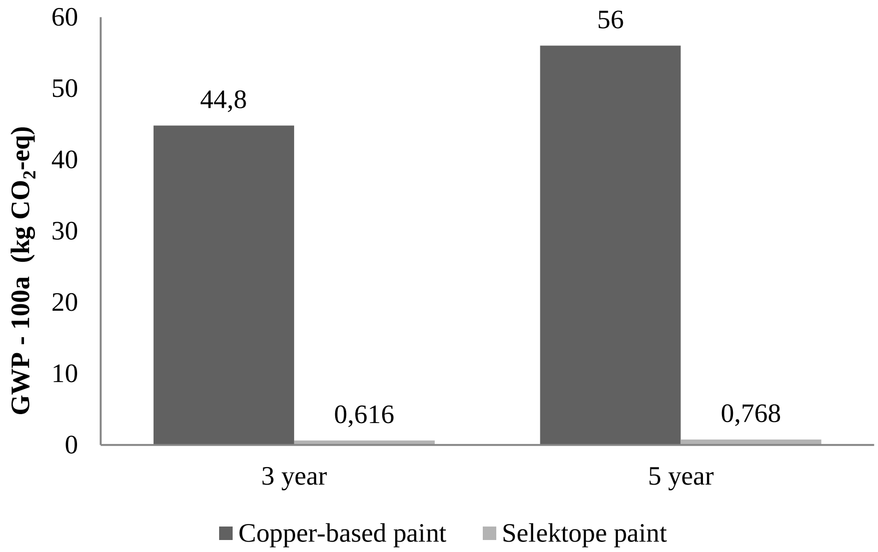


Figure 6: The impact on GWP (kg CO_2-eq) per functional unit for two paint systems, scenario A

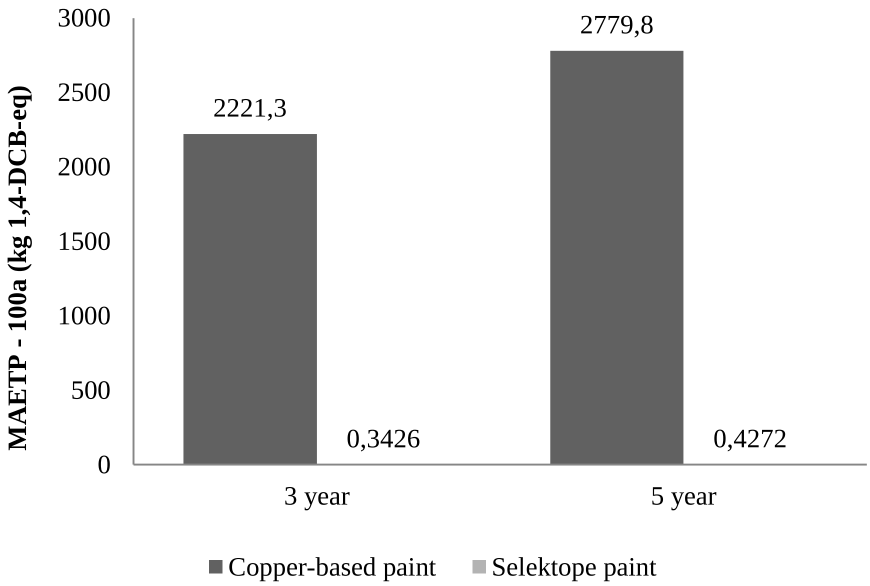


Figure 7: The impact per functional unit on MAETP (kg 1,4-DCB-eq) for two paint systems, scenario A

It can be concluded that the copper paint system makes a larger contribution to both GWP and MAETP than the Selektope paint. This result is in consistence with the different energy demand by the two paint systems as described in Figure 3. Since the inventory for process from paint production to end-of-life is almost the same for both paints, the difference between the production of cuprous oxide and Selektope plays a major role in the environmental impacts, which will be analysed in the *hot spots for antifouling paints.*

For different expected life time of the paint, the results for a 5-year period are about 10~20% higher than a 3-year period. This is because more paint is used for a 5-year durability.

Comparison of the two waste incineration scenarios

In order to know how the choice of incineration process during modelling would affect the final results, the comparison between scenario A and B is presented in Figure 8 for GWP and Figure 9 for MAETP.

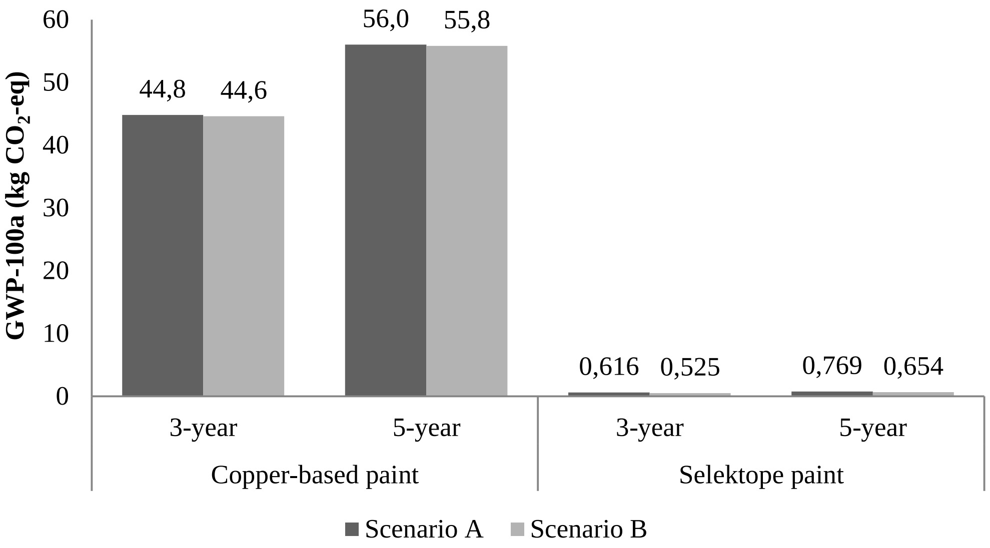


Figure 8: Comparison of the GWP for the scenario A and B

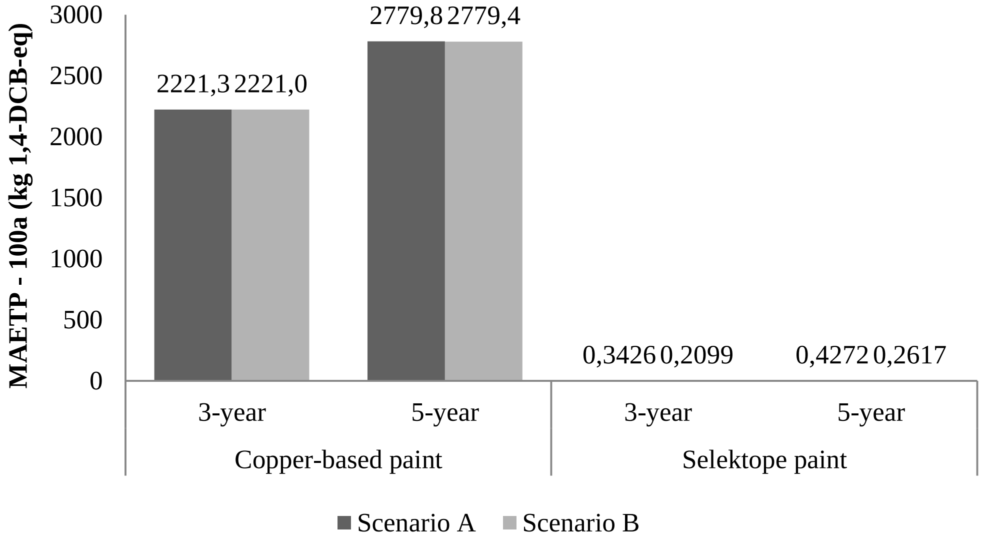


Figure 9: Comparison of the MAETP for scenario A and B

It can be seen from Figure 8 that the differences between the two scenarios are quite small for the copper paint’s impact on GWP, while that for Selektope is slightly higher for the 3 year period than for the 5 year period. The result for MAETP shows the same trend (in Figure 9) for both paint system, with an even sharper difference in the Selektope paint for scenario A and B for the 5 year period. The reason is that the incineration process from Ecoinvent applied in scenario A is much more sophisticated than the simplified incineration process, including more emissions that will be calculated in the impact analysis.

Hotspots for antifouling paints

The environmental impacts are further analysed for the life cycle phases of antifouling paint based on scenario A. The contribution of each phase is calculated for each of the two impact categories for both copper-based paint and Selektope paint, and is presented in Figures 6 to 9 respectively. Results for scenario B are presented in the appendix.

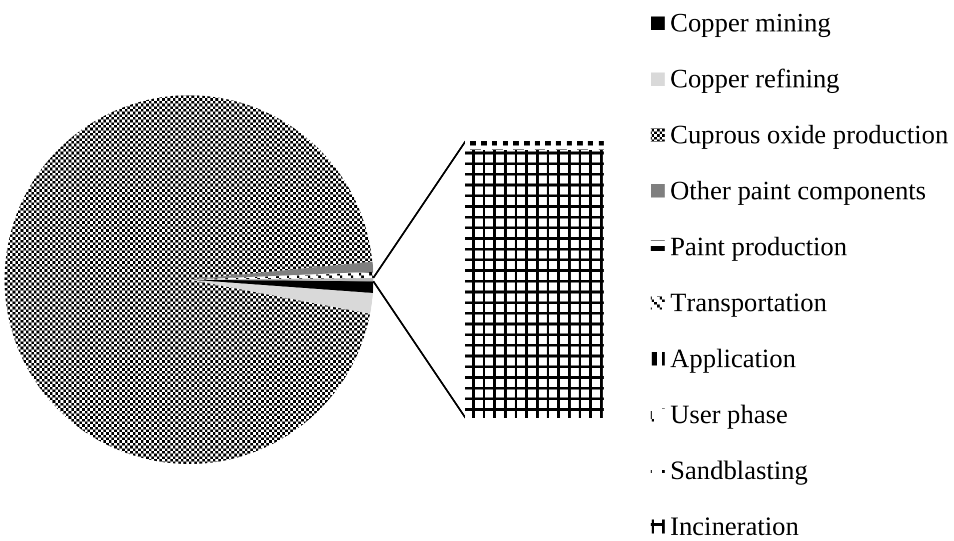


Figure 10: Identification of the hotspots in GWP for copper-based paint

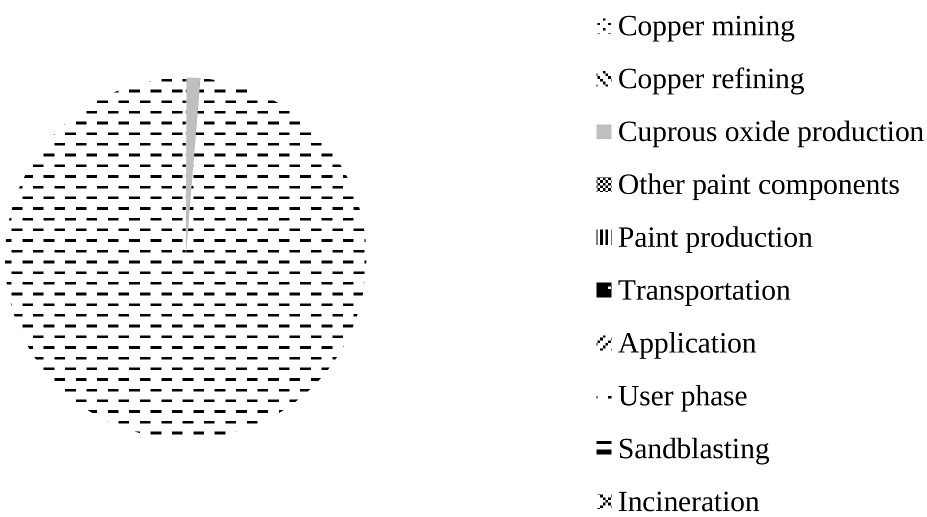


Figure 11: Identification of the hotspots in MAETP for copper-based paint

Judging from Figure 10, the majority (more than 95%) of the environmental impact on GWP for copper-based paint arises from the production process of cuprous oxide, which is related to the energy demand for the electrolysis process. While for MAETP, the impact from cuprous oxide production accounts for just 1.23% of the total, with more than 98% of the contribution coming from the user phase. This is due to the copper emission to the ocean from the paint leachate during use. Other processes not mentioned above show less influence on both impact categories.

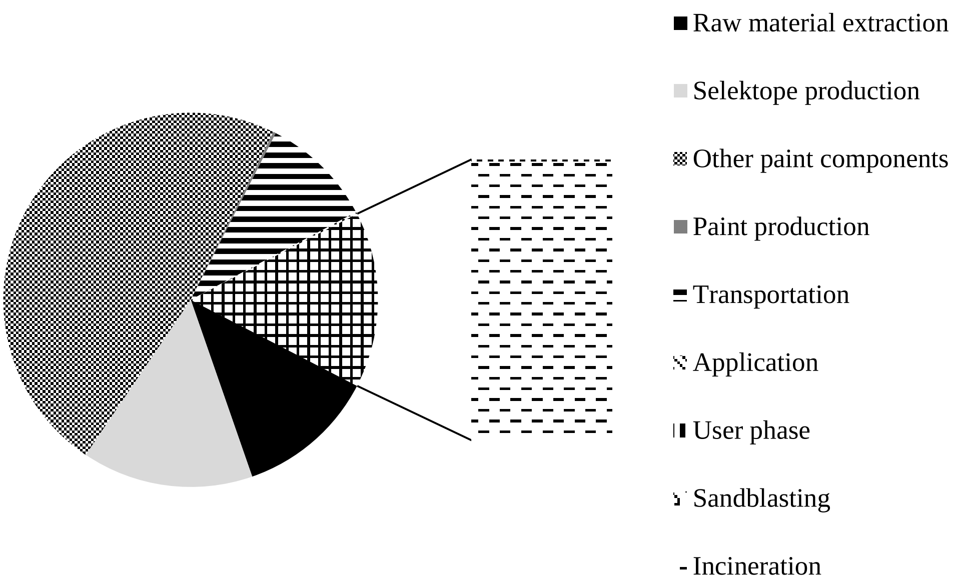


Figure 12: Identification of the hotspots in GWP for Selektope-based paint

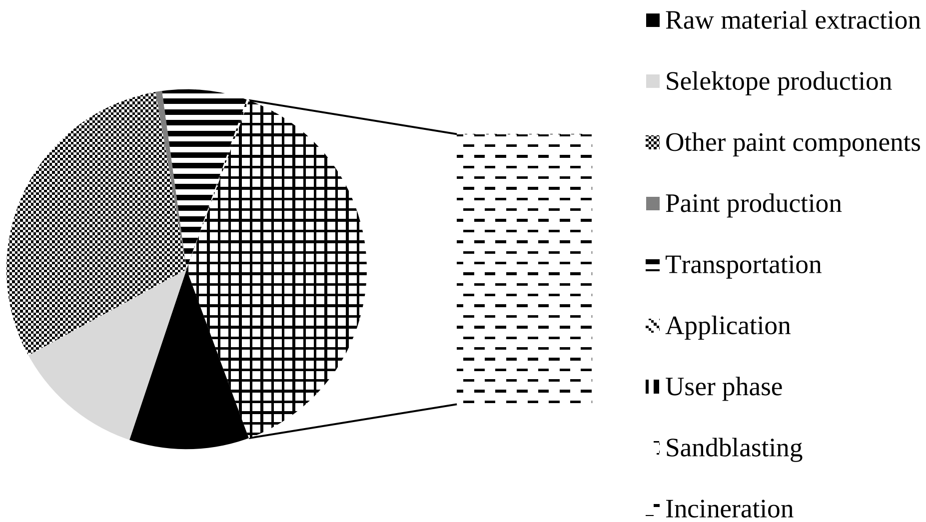


Figure 13: Identification of the hotspots in MAETP for Selektope based paint

Contrary to the result on copper-based paint, Figure 12 and Figure 13 indicate a much different contribution by percentage of each phase in the Selektope paint's life cycle, showing the production of other paint components to be the biggest component

(47.8%) of the GWP. Regarding MAETP, the major contribution comes from the incineration process (38.7%), following by the production of other paint components (30.2%). Transportation plays a minor but non-negligible part for Selektope paint, 9.7% of the GWP and 7.6% of the MAETP, which will be further assessed in *assessing the sensitivity of geographical parameters and electrolysis efficiency*.

A summary of Figures 4, 5, 10 to 13 with percentage values is presented in Table 8 below.

System	Process	Contribution		
		GWP-100a	MAETP-100a	Energy demand
Copper	Copper mining	1.02%	0.01%	1.71%
	Copper refining	1.81%	0.05%	3.01%
	Cuprous oxide production	95.47%	1.23%	91.69%
	Other paint components	0.89%	0.01%	2.62%
	Paint production	0.05%	0.00%	0.07%
	Transportation	0.48%	0.01%	0.75%
	Coating	0.00%	0.00%	0.01%
	User phase	0.00%	98.69%	0.00%
	Sandblasting	0.00%	0.00%	0.01%
	Incineration	0.28%	0.01%	0.13%
Selektope	Raw material extraction	12.08%	10.76%	16.19%
	Selektope production	14.79%	11.93%	16.32%
	Other paint components	47.80%	30.17%	56.45%
	Paint production	0.24%	0.58%	0.86%
	Transportation	9.72%	7.60%	6.94%
	Coating	0.17%	0.20%	0.11%
	User phase	0.11%	0.00%	0.00%
	Sandblasting	0.02%	0.02%	0.01%
	Incineration	15.07%	38.74%	3.13%

Table 7: Summary of the process contribution to GWP, MAETP and cumulative non-renewable energy demand for copper-based and Selektope paint

Assessing the sensitivity of geographical parameters and electrolysis efficiency

After changing the transportation method for Selektope paint from road to air transport, the LCIA results are 0.9423 kg CO_2-eq in GWP and 0.380 kg 1,4-DCB-eq in MAETP (Scenario A, 3-year time span). The increase compared to the original results is about 53% and 11% for GWP and MAETP respectively. The breakdown of process contribution is presented in Figure 14 and Figure 15 below.

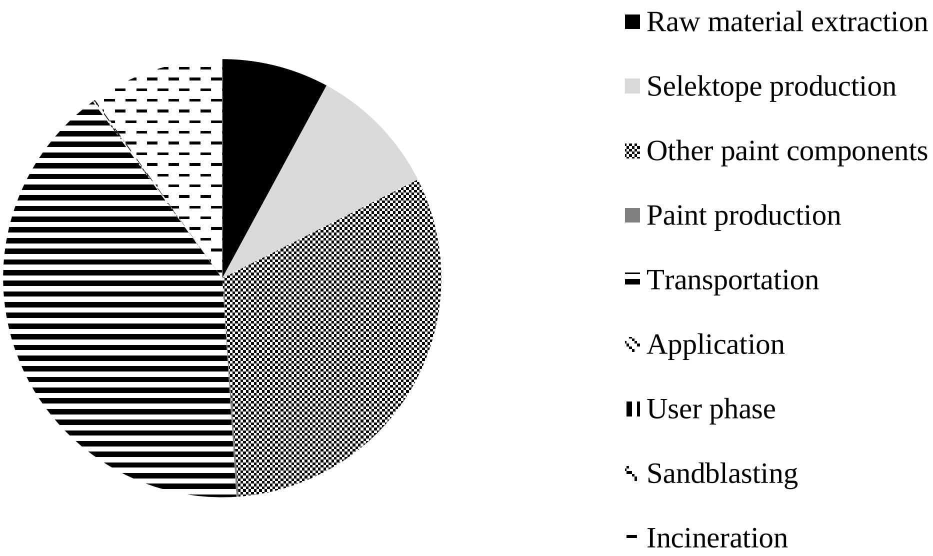


Figure 14: Identification of the hot spots in GWP for Selektope paint after applying air transportation

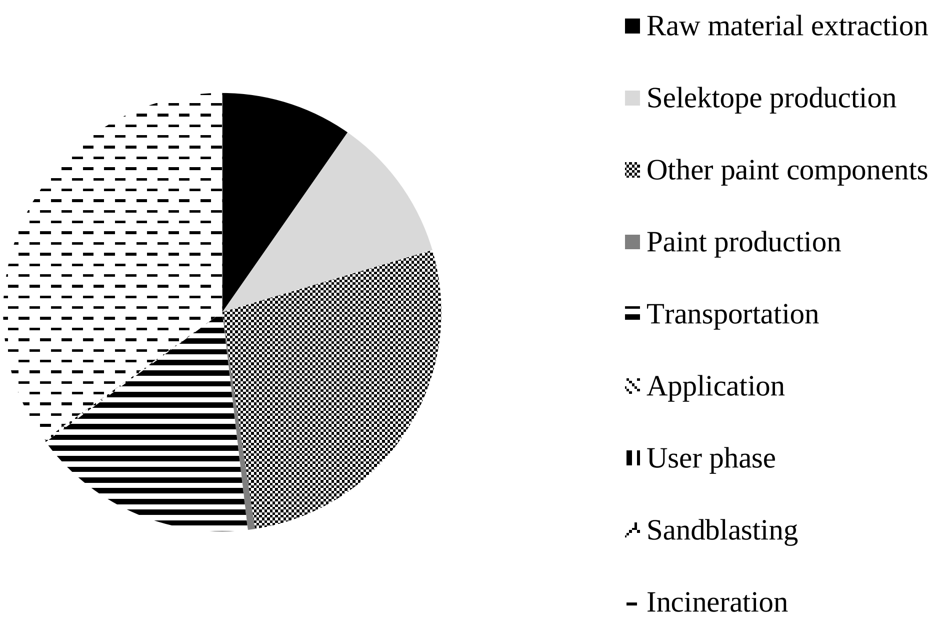


Figure 15: Identification of the hot spots in MAETP for Selektope paint after applying air transportation

Compared with previous results in Figure 12 and Figure 13, it can be seen that the role of transportation has increased from 9.7% to 41.0% of GWP, and from 7.6% to 16.8% of MAETP. Although the total impact is still much lower than the copper-based paint, this increase indicates that the selection of a transportation method can significantly influence the paint's environmental impact.

For the sensitivity of the choice of energy efficiency factor for the production of cuprous oxide, i.e. electrolysis, the results on both impact categories from a 3-year time span are presented for both scenario A and B, in Table 9 below.

Paint system		Copper-based			Selektope	Unit
Efficiency factor		11	6	1	N/A	
Energy demand	Scenario A	834	473	112	14.4	MJ
	Scenario B	833	472	111	14.0	MJ
Scenario A	GWP	49.00	27.65	6.30	0.62	kg CO_2-eq
	MAETP	2223.94	2210.29	2196.64	0.34	kg 1,4-DCB-eq
Scenario B	GWP	48.87	27.52	6.17	0.52	kg CO_2-eq
	MAETP	2223.69	2210.04	2196.39	0.21	kg 1,4-DCB-eq

Table 8: Influence on the LCIA results using different efficiency factor for Cu_2O production

It can be concluded from the above table that the choice of an adequate efficiency factor in the electrolysis process to produce cuprous oxide can largely affect the final environmental impacts of a copper-based paint. However, even in the best case assumption where there is 100% efficiency (efficiency factor = 1), which is impossible to achieve in reality, the results for copper-based paint is still larger than that of Selektope by a factor of 10. Therefore it would not affect the general conclusion that Selektope paint has a better environmental profile.

Assessing the environmental impacts with proposed contribution from released Selektope

As described in chapter 3.3, the integration of the ecotoxicity analysis of the biocide with LCIA results is conducted using a proxy calculation related to the substance's PNEC value. Using the suggested chronic PNEC value for 1,4-DCB in water (no distinction between marine and freshwater taxa), 20 µg /L, and the value for Selektope provided by I-Tech, 1 µg/L, a characterisation factor (regardless of time horizon) on MAETP of Selektope is therefore 20 kg 1,4-DCB/kg Selektope.

For the 3-year paint durability, the amount of total emission into the sea during paint user phase is approximately 0.24 g for Selektope. Thus the MAETP (1,4-DCB$_{eq}$) resulted from the leaching of biocides is 0.0047 kg for Selektope paint.

Adding the proposed contribution from paint leaching, the total MAETP for scenario A in a 3-year time span is 0.3473 kg 1,4-DCB-eq for Selektope. The respective result for a 5-year time span is 0.4331 kg 1,4-DCB-eq.

The increase in MAETP for Selektope is insignificant to the overall conclusion, compared with copper-based paint's values (2221~2279 kg 1,4-DCB-eq).

Overall risk analysis on the leaching of copper and Selektope

The results from MAMPEC software for the predicted environmental concentration (PEC) of copper and Selektope compared with the substances' PNEC value. The risk quotient for each emission is presented in Table 10 below.

Scenario	Marina		Commercial harbour		Background (µg/L)	PNEC (µg/L)	Leaching rate (µg/cm^2/d)
	Harbour	Surroundings	Harbour	Surroundings			
Copper 3-yr	0.70	0.29	0.33	0.28	1.53	5.6	7.799
Selektope 3-yr	0.007	0.0002	0.02	0.001	0	1.0	0.022
Copper 5-yr	0.43	0.28	0.62	0.29	1.53	5.6	5.849
Selektope 5-yr	0.005	0.0002	0.002	0.00007	0	1.0	0.016

Table 9: Risk analysis for the leaching of copper and Selektope

The above Table 10 indicates that there is no risk in the two types of marine environment for all the scenarios analysed regarding the leaching of either copper or Selektope from the ship surface, since none of the calculated risk quotients is larger than 1. Although there's an overall higher risk for copper level than Selektope level, which is mainly due to both the higher background concentration and the leaching rate.

5. Discussion

In this chapter the method used for this study and the results obtained from the life cycle inventory analysis are discussed.

Methodological Approach

The choice of method used in an LCA is very important as there are many areas to which LCA can be applied and this places different requirements on the methodological approach (Baumann & Tillman, 2004). Hence, the method used should be guided by the purpose of the study. The purpose of this study is to aid decision making and market communication for the use of Selektope in antifouling paint in comparison to copper-based paint, thus this study has tried to reflect on the consequences of the continued used of one product in relation to the other and tried to compare both product as "fair" as possible within the boundary of available data by carrying out a sensitivity analyses on these products.

Four critical issues in LCA methodology determine the outcome of an LCA study according to Baumann and Tillman (2004), this are the definition of the functional unit, system boundary and allocation, type of data and impact assessment made.

In this study, the choice of the functional unit has been defined as 1 m^2 paint covering and protecting the ship surface. The reason for this choice is to estimate the coverage of paint used on the ship as well as in modelling the marine concentration of the paint component leached into the marine environment. A global scenario has been considered for the system boundary for this study but due to available data the study has been restricted within the European context. Because of this chosen geographical boundary, the result may be representative from the world average perspective, since nowadays the world shipping industry mainly takes place in Asia, with top 10 world container ports all situated in Asian countries (World Shipping Council, 2014).

In any LCA study the choice of data is very important as this would influence the reliability and workload of the study. Also, the quality of the data used is very important for any LCA study. The quality can be broken down into 3 aspects; relevance, reliability and accessibility (Baumann & Tillman, 2004). Data obtained for this study in relation to Selektope has primarily been obtained from I-Tech either through interviews or documented data and this affects the accessibility of the data due to confidentiality of most of the information obtained. Other relevant data are obtained from literature either from books or articles. In areas where there is lack of documented data, estimations and assumptions have been made. Due to the lack of available data for determining the concentrations of the free copper ions in the marine environment many risk assessments have used modelling tools to determine the predicted environmental concentration (Hellio & Yebra, 2009). For this study the MAMPEC model has been used to determine the PECs of both copper and Selektope in the marine environment. The advantage of using this model is that it takes into account many of the parameters specific to antifouling products such as leaching rate, vessel and compound related factors and processes, physiochemical factors and hydrodynamic processes of typical marine environment (Hellio & Yebra, 2009).

In carrying out an LCA study, it is important to note which environment impacts are to be considered or taken into account. This could be done using three categories: resource use, ecological consequences and human health as stated in ISO 14040 (1997). These categories can be divided into other several sub-categories (Baumann and Tillman, 2004). For example, ecological consequences can be further divided into global warming, acidification, eutrophication and eco-toxicological impacts among others. The goal of this study is to study the environmental profile of Selektope biocide that replaces the conventional copper-based biocide (cuprous oxide) which is related to the ecological consequences. Therefore the environmental profile of these two products has been made in reference to their contribution to global warming potential and their eco-toxicology impact (MAETP).

Analysis of the results

For the two paint systems analysed (Figure 3), it can be seen that the copper based paint has higher impact in both GWP and MAETP categories than the Selektope paint. This huge difference as seen from the several process steps or streams making the whole paint system is connected to the energy required in the production of cuprous oxide and copper. From literature it is found that several methods or processes are used in the production of cuprous oxide, but for this study only the electrolysis process is analysed, as it is described as the most common method used for this process. When determining the energy demand in producing cuprous oxide using the electrolysis process, estimation has been made for the entropy change and these were multiplied by a factor of 10 due to lack of available data for the energy required for the process. Given the result for the baseline scenario that the electrolysis process accounts for up to 95% of the total impacts related to copper-based paint, the actual efficiency factor needs to be further investigated in future work. Although in this study the choice of efficiency factor does not affect the general conclusion that the copper-based paint has a larger environmental impact than the Selektope paint. The impact from using other manufacturing technologies for cuprous oxide may also be studied.

In contrast to the copper-based paint, it can be observed that from the different streams in the production of Selektope, the contribution from the production of other paint ingredients to GWP is much higher than from the production of Selektope. One reason for this difference could be that the amount of Selektope used in the paint is too small (0.1% by weight) to make large influence to the overall result. Another aspect worth noticing is that in the production of 1000 kg Selektope, only raw materials larger than 10,000 kg are included in the inventory analysis, which excludes the possibility of a significantly large impact generated from a rather low mass raw material.

As can be seen from the sensitivity analysis on transportation methods (Figure 10 and 11), the choice of using air transport has a large influence on the result for Selektope (up to 50% increase in terms of GWP). Air transport is considered to be a method with high energy intensity, which leads to high contribution to GWP. Although I-Tech suggests that the delivery of commercialised Selektope paint in the future would still be by air, it is strongly recommended to take into consideration its significant impact on the product's total environmental profile. As the current shipping industry is mainly in the Asia-Pacific region, which entails much longer distances in comparison to the European boundary defined in this study, using container ships for paint delivery would be much more favoured by the environment.

In this study a proxy calculation for the characterisation factor for Selektope was to integrate the impact from leaching Selektope with other contribution to MAETP. Nevertheless, it does not appear to have affected the result that Selektope paint has smaller value of MAETP than copper-based paint. The reliability of this calculation method is worth discussing. The suggested PNEC value for Selektope is only based on the NOECs for four aquatic organisms, while the PNEC value for 1,4-DCB is based on an evaluation of more than 60 marine organisms, which is more complex and comprehensive. Therefore the numeric result showing that Selektope is 20 times worse than 1,4-DCB in MAETP is inevitably worth questioning. Thus there is a need for further work regarding the quantitative relationship in ecotoxicity between Selektope and the MAETP method used in LCA.

There are also uncertainties within the result of risk analysis using MAMPEC model. First of all, although the calculated RQ indicates no potential risk in the aquatic environment for the two scenarios (OECD-EU commercial harbour and marina), there are studies indicating that in certain areas the extreme background copper concentration has already exceeded the environmental quality standard (EQS) for copper, much higher than 5 μg/L (Hellio & Yebra, 2009). Moreover, a study by Mukherjee et al. (2009) indicates when combined with certain booster biocides, there is a synergistic effect in the toxicity of copper being observed. The study also suggests that there are other uncertainties regarding the bioavailability of copper, which depends a lot on other parameters such as pH, hardness, alkalinity and etc. Finally, the MAMPEC model does not take into account the degradation process of Selektope with a rather short half-life of 50 days. This makes the calculated PEC an overestimation assuming all the released Selektope would stay in the aquatic system at least over a one-year period of time.

6. Conclusion

- The overall LCA results indicate a much higher impact from the life-cycle of copper-based paint than Selektope in terms of non-renewable energy demand, global warming potential and marine aquatic ecotoxicity potential. Selektope paint has a better environmental profile in general.

- For copper-based paint system, the production of cuprous oxide appears to be the dominant contributor to GWP, while the user phase is the major burden in terms of MAETP.

- The risk analysis on marine ecotoxicity for the release of the two antifouling biocides shows no potential risk using the leaching rate based on the functional unit for LCA.

- In terms of the commercial use of Selektope paint in the future, it is suggested that the choice of transportation should be handled properly in order to lower the environmental impact.

- Several uncertainties exist such as the assumption of efficiency factor for the electrolysis process, the excluded inventory data of some paint component and raw material in Selektope production, the choice of waste incineration process and the proxy calculation for the characterisation factor for Selektope. However these uncertainties do not seem to have significant influence on the results of analysis.

- Suggestions for future work are made, regarding the study of other processes for producing copper and cuprous oxide, applying a global geographical boundary for the analysis, developing improved ways to assess toxicity in an LCA framework.

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Appendix A – Chemical composition of SeaQuantum Classic

Jotun Quantum Classic

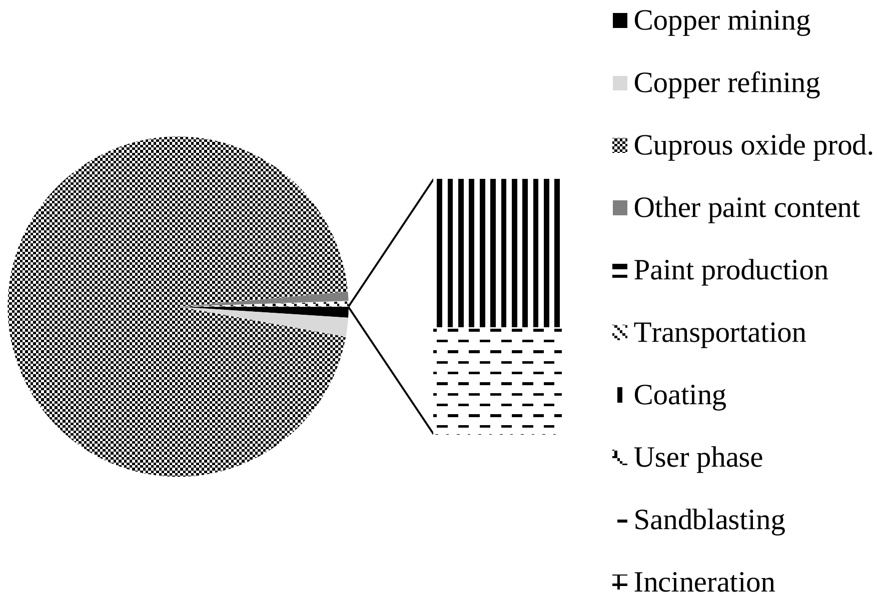
Substances		%w/w
Cu2O		48.4
CuPT		1.48
VOC		27.9
	Xylene	22.9
	Naptha	2.5
	Ethylbenzene	2.5
ZnO		8.2
Talc		1
Choliph.		1
Silylacrylate		10
Iron Oxide Fe2O3		1
Magnesite		1

Appendix B – Chemical composition of SeaQuantum Classic

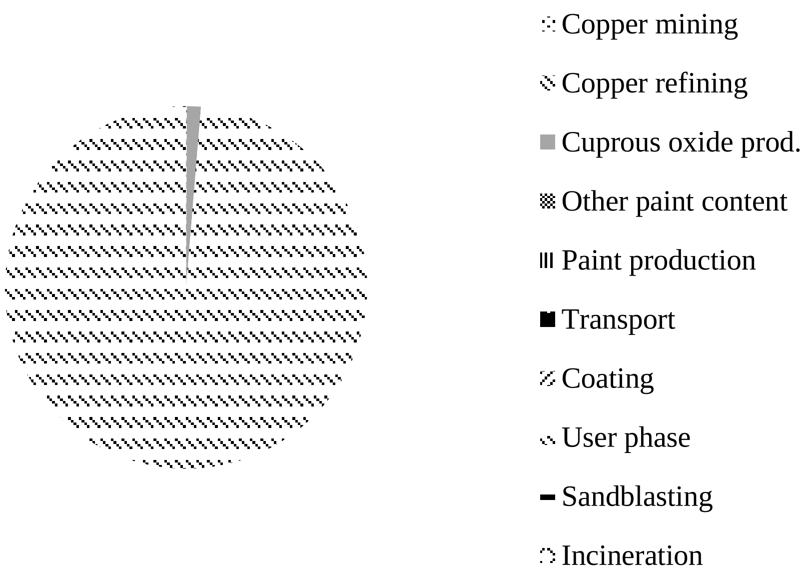
Selektope Classic

Substances		%w/w
Selektope		0.1
CuPT		3
VOC		27.9
	Xylene	22.9
	Naptha	2.5
	Ethylbenzene	2.5
ZnO		16
Talc		15
Sulphates		5
Choliph.		2
Silylacrylate		10
Iron Oxide Fe2O3		1
Magnesite		10

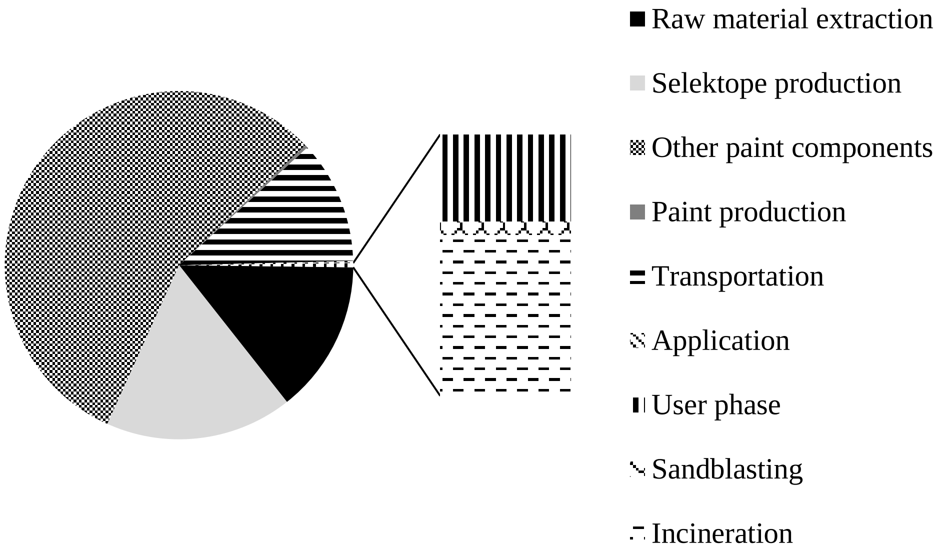
Appendix C – Hotspots for antifouling paints, Scenario B



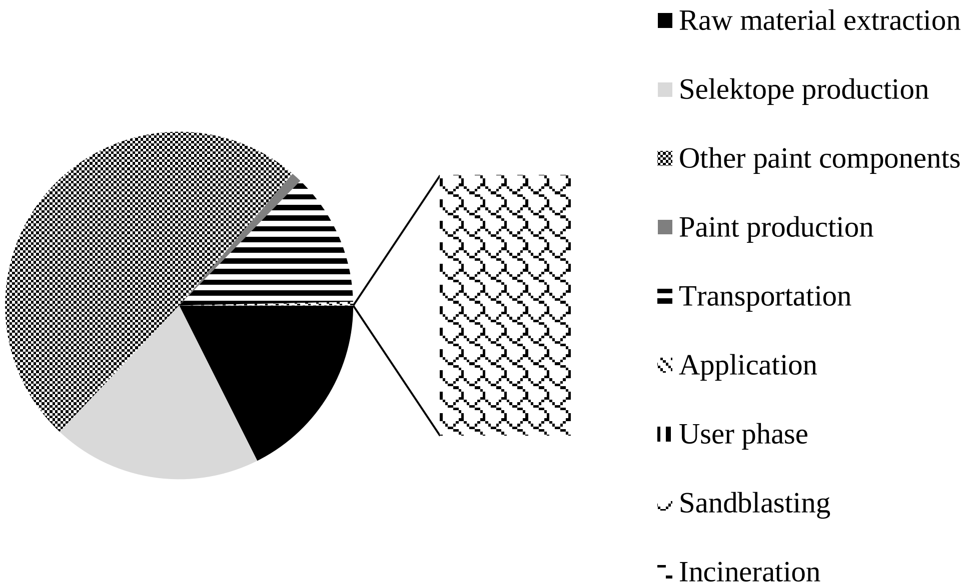
Copper-based paint, GWP-100a



Copper-based paint, MAETP-100a



Selektope paint, GWP-100a



Selektope paint, MAETP-100a