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Survey of naphthalene

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Sources must be acknowledged.

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Preface

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

Over the period 2012-2015 all 40 substances and substance groups on LOUS will be surveyed. The surveys include collection of available information on the use and occurrence of the substances, internationally and in Denmark, information on environmental and health effects, on alternatives to the substances, on existing regulation, on 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 naphthalene (CAS 91-20-3). This substance was neither included in the first list in 1998 nor the second list in 2000, but was included in the third list in 2004 and has remained on the list since that time (i.e. also included in the fourth list in 2009). The main reason for its inclusion in LOUS is due to its harmonised classification as:

- Acute Tox. 4 H302: Harmful if swallowed
- Carc. 2 H351: Suspected of causing cancer
- Aquatic Acute 1 H400: Very toxic to aquatic life
- Aquatic Chronic 1 H410: Very toxic to aquatic life with long lasting effects

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 FORCE Technology from April to November 2014. The project team was:

- Pia Brunn Poulsen, FORCE Technology, project manager
- Larisa Maya-Drysdale, FORCE Technology, contributor
- Ole Schleicher, FORCE Technology, contributor
- Maria Strandesen, FORCE Technology, quality controller

The work has been followed by an advisory group consisting of:

- Louise Grave Larsen, Danish EPA
- Lone Schou, Danish EPA
- Nikolai Nielsen, Dansk Industri
- Susanne Høyer, Arbejdstilsynet
- Dorte Riis Sørensen, Koppers Denmark ApS
- Pia Brunn Poulsen, FORCE Technology

Data collection

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

Besides, direct enquiries were sent to Danish and European trade organisations and a few key market actors in Denmark.

Summary and conclusion

Classification and most important regulatory aspects
Naphthalene has a harmonised classification of:

- Carcinogenic (Carc. 2, H351 “Suspected of causing cancer”)
- Acutely toxic (Acute Tox 4, H302 “Harmful if swallowed”)
- Very toxic to aquatic life (Aquatic Acute 1, H400 “Very toxic to aquatic life” and Aquatic Chronic 1, H410 “Very toxic to aquatic life with long lasting effects)

As a consequence of the carcinogenic properties of naphthalene, the substance is prohibited for use in cosmetic products. Furthermore, naphthalene is not used in mothballs any more, as no satisfactory application of the use of naphthalene has been made for the Biocidal Products Regulation.

A threshold limit value of 10 ppm or 50 mg/m^3 is set for the working environment regarding naphthalene in the EU (and Denmark)[1]. A limit value of 0.04 mg/m^3 for concentrations of naphthalene in the air, measured at the property line of the companies, has been set for companies in Denmark[2]. A water quality criterion of 2 µg/l has been set as a limit value for naphthalene in water from waterworks and in the drain cock water at consumers in Denmark[3]. The environmental quality standard (EQS) for naphthalene for freshwater is 2.4 µg/l and 1.2 µg/l for marine waters[4].

As a hazardous substance, naphthalene is subject to specific regulation regarding transportation of dangerous goods[5].

Naphthalene has been registered under REACH in a tonnage band of 100,000 – 1,000,000 tonnes per annum (as of May 2014), but it is neither on the Candidate list of substances of very high concern nor on any of ECHA’s Registry of intentions. Naphthalene is on the CoRAP list of substances[6] and was entered on the list in 2014 for evaluation by Germany in 2016, i.e. the evaluation has not started yet (CoRAP, 2014). The initial grounds for concern for naphthalene are listed as:

- Exposure – exposure of workers
- Exposure – high RCR (risk characterisation ratio)
- Exposure – high aggregate tonnage

The Swedish Chemicals Agency has included naphthalene in their PRIO database as a “priority risk reduction substance”, which means that the user of the substance is recommended to review the risk of the envisaged use. Furthermore, naphthalene is found in the SIN List Database developed by ChemSec due to its classification as possible carcinogen and very toxic to the aquatic environment. This means that naphthalene fulfils the SVHC criteria as defined by the REACH Regulation.

Naphthalene is not mentioned directly in any ecolabelling criteria, but will automatically be restricted in any ecolabelling scheme as no chemicals classified as dangerous for the environment or as carcinogenic in general are allowed in ecolabelled products.

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[1] Directive 91/322/EEC and Danish Statutory Order No. 507 of 17.5.2011
[2] Danish Guidance No. 10702 of 19.11.2008
[3] Danish Statutory order No. 292 of 26.3.2014
[4] Danish Statutory order No. 1022 of 25.8.2010
[5] Directive 2008/68/EC
[6] http://echa.europa.eu/information-on-chemicals/evaluation/community-rolling-action-plan/corap-table

Manufacture and use

Manufacturing

The manufacturing of naphthalene is world-wide and is done by two production routes, where the distillation of coal tar and subsequently of naphthalene oil is the most widely applied production route (92% market share of the world). The most widely applied production route consists of two steps. The first step starts with coal tar, produced from coke oven gases, and it is followed by a series of distillation processes where different tar fractions are produced, internally reused or sold externally, with naphthalene as the final product (i.e. crude naphthalene). The second step is applied to produce purer grades of naphthalene and the most common technology used is distillation with solvents. In Denmark, naphthalene is produced by Koppers Denmark ApS and a similar production route as the abovementioned is applied. However Koppers Denmark ApS does not use solvents in the distillation process. Koppers Denmark ApS also imports naphthalene oil in order to match production demand. The final product is 95 – 97% grade naphthalene.

Nowadays, China has nearly half of the naphthalene production capacity and output of the world, although their production configuration is different from that in the EU and Denmark. The EU, the USA and Canada also play an important role in the world production. Twelve companies in the EU are registered as importers and/or producers of naphthalene in the ECHA database (ECHA RSD, 2014), including Koppers Denmark ApS, but it was found that one of them is not in operation any longer. Denmark is the only manufacturer of naphthalene in the Nordic countries.

Manufacturing volumes

It was not possible to find a world estimate on annual production of naphthalene. However, an estimate for the USA was found from 2001 (as the latest), which was 115,000 tonnes/year, and for Canada (for 2006), which was 52,000 tonnes/year. An indicative figure for the EU of 100,000 tonnes/year was found for 2009/2010. This makes for a total estimate of 267,000 tonnes/year of naphthalene produced, which should make up for up to half of the annual production of the world, considering China today has half of the production. However, care should be taken to interpret this figure as it comes from different points in time and from information retrieved from IHS (2013). The trends in production have changed significantly along the past decade. It seems that production of naphthalene has declined in the USA and shifted towards growing productions in other markets instead (China, Russia and Brazil). Similarly, the European production seems to have declined, whereas the Danish production of naphthalen has increased. Denmark currently produces about 30,000 tonnes/year of naphthalene.

Import and export

It was not possible to retrieve publicly available import/export data from the EU. In Denmark the import of naphthalene contained in chemical products has steadily increased during the past 15 years (up to 2011), according to data from the SPIN database. The latest annual registered data for imports is from 2011 (73,739.1 tonnes), which is the total amount of naphthalene imported through chemical products. Information about export of chemical products containing naphthalene is unknown, but according to Koppers Denmark ApS about 30,000 tonnes/year of pure naphthalene is exported. Since all the production of naphthalene in Denmark is exported, it can also be said that all of the naphthalene used in products in Denmark is currently imported.

Use and historical trends

Naphthalene has a track record of being a chemical of many uses, as it has a wide range of technical grades used for different applications. However, the application of purer grades has presented a decrease during the last decade, particularly of grades >90% purity. Furthermore, the fact that naphthalene is no longer used in certain consumer products (mothballs) has also diminished its application and has shifted its use towards a higher use of naphthalene for the manufacturing of intermediates rather than for inclusion in final products. According to data collected from different literature sources, the main applications of naphthalene world-wide are:

- Manufacture of naphthalene sulphonic acids
- Manufacture of phthalic anhydride
- Manufacture of alkylated naphthalene solvents
- Manufacture of azo dyes
- Manufacture of grinding wheels as an artificial pore former (final product)
- Formulation of explosives in pyrotechnics (final product)

The European consumption of naphthalene was around 175,000 tonnes in 2007. The consumption of pure naphthalene in Denmark is expected to be zero as all naphthalene production from Koppers Denmark ApS in Denmark is exported. The naphthalene consumption in Denmark is due to other chemical products containing naphthalene.

According to information retrieved from the SPIN database, the main uses of naphthalene in Denmark and the Nordic countries are for fuel additives and construction materials. As the classification of uses presented in SPIN is more generic, it is assumed that these two major uses relate to the applications world-wide and in particular to the manufacture of naphthalene sulphonic acids (used as plasticiser in concrete mixtures) and phthalic anhydrides (used for e.g. manufacturing of phthalates).

Products containing naphthalene

The unintended presence of naphthalene in a wide range of other products is quite evident. This is because some of these products contain impurities or product distillates from tar-based substances or because naphthalene is a PAH and has therefore been found in products containing mineral oil. A list of examples has been provided, including:

- Tar paints/speciality paints
- Waterproof membranes for floors and walls
- Asphalt
- Rubber and plastic products, including a list of consumer products
- Creosote treated wood

Furthermore, naphthalene has also been found in emissions of some consumer products, for example in emissions from CFL light bulbs and from cigarette smoke.

Waste management

Waste contaminated with naphthalene is handled as hazardous waste in Denmark and the EU. This is typically sent for incineration and thermal treatment. Traces of naphthalene have been found in the flue gases and emissions of the incinerators to ambient air. This is assumed to come not from the burning of naphthalene itself, but from other waste fractions that release PAHs during combustion. No direct release of naphthalene to water is likely to occur from incineration and emissions to soil may happen if traces of naphthalene occur in the bottom ash.

Products containing small amounts of naphthalene will enter into the waste stream through municipal collection of domestic waste. It is expected that most rubber and plastic consumer articles will be incinerated in Denmark, whereas waste in the form of chemical mixtures will be treated as hazardous waste and incinerated.

The largest amount of waste containing naphthalene is assumed to be creosote treated wood which is expected to be around 12,000 tonnes each year in Denmark. The total naphthalene content in creosote treated wood is below 1%. Burning naphthalene (contained in the waste products) will result in the formation of carbon dioxide and water and thus will not result in the release of any hazardous emission in the flue gas or bottom ash.

Environmental effects and fate

Naphthalene has a harmonised classification for environmental effects of:

- Aquatic Acute 1 H400: Very toxic to aquatic life
- Aquatic Chronic 1 H410: Very toxic to aquatic life with long lasting effects

Naphthalene is regarded as persistent. Naphthalene may be readily biodegradable under aerobic conditions, but only in oil-polluted waters. Under normal conditions and under anaerobic conditions biodegradation does not seem to occur. Naphthalene seems to be persistent in sediment and soil, but not in the aqueous environment under aerobic conditions. Naphthalene has a low bioconcentration potential and overall the substance cannot be considered a PBT substance (P, but not B and T) even though naphtalene is 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". This is due to the differences in the effect levels for criteria for the PBT assessment and the classification criteria.

As naphthalene is a PAH, the largest environmental releases (estimated to be 88% of the environmental releases by the European Chemicals Bureau (ECB, 2003)) are due to incomplete combustion of organic material. For this reason naphthalene may also be present in small amount (impurity levels) in consumer products made of plastics or rubber where softeners or carbon black is used. Release to the environment of naphthalene may also occur from production sites or from industrial use of naphthalene as an intermediate chemical. It is, however, the formation of naphthalene from indirect emissions, especially incomplete combustion that seems to be the major source of naphthalene in the environment. Examples of indirect emissions of naphthalene are:

- Release from the use of products which naturally contain naphthalene
- Release from the production of substances using raw materials or ancillaries which naturally contain naphthalene
- Release from oil production
- Release from use of transport vehicles
- Release from coal combustion
- Release from coal carbonisation and gasification

Based on the available monitoring data on naphthalene, it is not expected that naphthalene in general will cause adverse effects in the aquatic or terrestrial environment. However, point source pollution has shown concentrations that are much higher than the calculated predicted no effect concentrations (PNEC), which means that there may be situations which may have an environmental effect, e.g. point releases to the environment or contaminated soil due to release of naphthalene from creosote treated wood[7]. Predicted environmental effect concentration (PNEC) could not be calculated for the atmosphere. Therefore an assessment of the environmental effects of naphthalene to air has not been made (in spite of the fact that most naphthalene is released to air). However, the atmospheric half-life of naphthalene is less than one day, and when released to the air about 90% of this naphthalene will remain in the air. In the air naphthalene will be transformed to 1-naphtol[8], 2-naphtol[9] and 2-nitronaphthalene[10] as the major constituents by photochemical reaction. Two of these reaction products are also classified as toxic to the environment, but with a less toxic classification compared to the environmental classification of naphthalene.

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[7] The production of creosote treated wood is no longer allowed in Denmark, but creosote treated wood may still be in use in Denmark.

[8] Harmonised classification as Acute Tox. 4, H302, H312; Skin Irrit. 2, H315; Eye Dam. 1, H318; STOT SE 3, H335.

[9] Harmonised classification as Acute Tox. 4, H302, H332; Aquatic Acute 1, H400.

[10] Harmonised classification as Carc. 1B, H350; Aquatic Chronic 2, H411.

Human health effects

Toxicokinetics, absorption, distribution, metabolism and excretion

Exposure to naphthalene may occur through inhalation, ingestion or dermal contact. The information available on the toxicokinetics of naphthalene in humans is limited. However, the information available indicates that naphthalene is readily absorbed by all routes of exposure and that almost complete and rapid absorption occurs following ingestion. The urine is the main route of rapid excretion in humans and in animals. Extensive metabolism occurs and elimination from the body is rapid (ECB, 2003; ECHA RSD, 2014).

Human health hazard

Naphthalene has a moderate oral acute toxicity (Acute Tox. 4, H302 "Harmful if swallowed"), and can in human and dogs cause haemolytic anaemia (abnormal breakdown of red blood cells), which may be fatal. There is no information on the effects of naphthalene following acute inhalation or dermal exposure in humans.

No conclusions can be drawn regarding the irritant properties of naphthalene from studies in humans. However, data from animal studies indicates that naphthalene is only a slight skin and eye irritant – insufficient to warrant classification. Absence of case reports on sensitisation in humans suggests that naphthalene is not a skin or respiratory sensitizer.

Animal studies on repeated dose toxicity reveal species differences in response to naphthalene. The effects seen in rodents do not seem to be relevant for humans and the effect seen in humans (and dogs) - haemolytic anaemia - has not been observed in rodents. In general there are no epidemiological studies on the human health effects of naphthalene except for a limited number of case reports on haemolytic anaemia.

No exact NOAEL was identified and no evidence of systemic toxicity was found in the inhalation studies, but a LOAEL of 5 mg/m^3 could be set for repeated inhalation toxicity.

Naphthalene is suspected of being carcinogenic and is classified as Carc. 2, H351 "Suspected of causing cancer". This classification is based on clear evidence of nasal tumours found in rats (at 50 mg/m^3) and clear evidence of lung tumours found in mice. However, the naphthalene-induced lung tumours in mice are unlikely to be of relevance for humans, whereas the relevance for humans of the rat nasal tumours is unclear. It has been discussed intensely whether the occupational threshold limit value of 50 mg/m^3 should be lowered as the nasal tumour study on rats lead to increased tumour incidences at this concentration. Preuss et al. (2003) suggests lowering the occupational threshold limit value to 1.5 mg/m^3 based on the measurement results at international workplaces. However, the occupational threshold limit value for naphthalene has not been lowered yet.

Naphthalene is not genotoxic, i.e. the mode of action for naphthalene for causing cancer is not caused by a genotoxic event, but by another unknown mode of action. Naphthalene has not been found to be fetotoxic nor an endocrine disruptor.

Exposure sources

Inhalation is the route of exposure that is most relevant for naphthalene. The major direct exposure sources to naphthalene are for workers occupational exposure when working with naphthalene and for consumers (primarily the do-it-your-self consumers) exposure to waterproof membranes containing naphthalene used for floors and walls. Occupational exposure is the largest and most significant exposure to humans. The general population is indirectly exposed to naphthalene primarily via indoor air, where cigarette smoke is the largest contributor.

Human health impact

Historically the main health impact being reported for humans is the acute effect haemolytic anaemia as a result of exposure to (sucking on) mothballs. However, this exposure is no longer relevant as the use of naphthalene in mothballs is no longer supported in the EU.

The acute effect haemolytic anaemia may still be of concern for both workers and consumers, as no NOAEL or dose-response characteristics can be derived from the available data for humans. Animal data (in dogs) suggests that an oral dose in the mg/kg range could produce the acute effect haemolytic anaemia in humans. Based on these data, the only consumer exposure that possibly could be of concern is in the situation of laying and post laying of waterproof membranes for do-it-your-self consumers, especially if carried out in unventilated rooms, but a further investigation about the actual exposure and effect in these situations as well as the frequency of use of naphthalene in waterproof membranes may be needed. It is not expected that do-it-your-self consumers will be exposed to naphthalene on a long term basis.

The presented monitoring data for the working environment suggests that most exposure levels are well below the occupational exposure limit (OEL) value of 50 mg/m^3. However, a LOAEL value of 5 mg/m^3 for repeated inhalation toxicity has started a debate about whether the OEL value should be lowered. Preuss et al. (2003) calls for more examination in this area and a lowering of the occupational threshold limit value to 1.5 mg/m^3.

The human health impact from naphthalene residues in rubber and plastic articles is regarded as being insignificant. Nevertheless, the exposure to carcinogenic substances should in general be lowered as much as possible, especially in products for children. It is, however, expected that the adopted restriction on 8 specific PAHs (even though naphthalene is not included) in rubber and plastic products that come into direct contact (long-term and short-term repetitive contact) with the human skin will have an influence on the level of naphthalene impurities in consumer products as well. The restriction will enter into force by December 2015.

The major indirect exposure to naphthalene is due to indoor air and primarily cigarette smoke. However, when adding the total exposure from indirect exposure (air and food), consumer products and occupational exposure, it is not expected that the total exposure from indirect exposure and consumer products will cause concerns regarding human impacts in general. In the following situations humans may be exposed to higher naphthalene concentrations that may be of concern:

- All occupational exposure/workers working with naphthalene.
- Do-it-yourself consumers using waterproof membrane products containing naphthalene – both laying and post laying may be of concern.

Alternatives

Naphthalene is used both as an intermediate in the production of other chemicals as well as in end-use products. Alternatives for both uses have been considered.

Alternatives to naphthalene were found in some uses and to a varying extent. The naphthalene based plasticiser NSF to concrete mixtures, representing the largest use of naphthalene globally, seems to have been subject to most considerations in regard to alternatives with polycarboxylate increasingly gaining more acceptances in the market. Polycarboxylate is accessible on the market and represents a better structurally performing alternative to naphthalene based plasticisers in cement. Furthermore, polycarboxylate has a better health and environmental classification compared to naphthalene.

Phthalic anhydride is also produced today by use of o-xylene and could therefore potentially substitute the use of naphthalene for this purpose entirely. The classification of o-xylene is to some degree better than the classification of naphthalene (i.e. no Carc classification) and could thereby present a somewhat better alternative compared to naphthalene.

Alternatives to phthalic anhydride have not been found to be in the commercial production in spite of the known hazard to health of phthalic anhydride and its representation in major growing industries such as construction, automotive, electrical & electronics and paints & coatings. Phthalic anhydride has been prohibited in certain end-use products, which has created an incentive in the chemical industry to find future alternatives such as the bio-based replacements. Furthermore, the Danish EPA has concluded that alternatives exist technically, but with no realistic opportunities to influence current product compositions from international suppliers.

A desktop research showed that there is increasing public attention to the health risks related with azo dyes in clothing[11]. Furthermore, certain azo dyes are restricted in textile and leather articles according to REACH Annex XVII. It could therefore be assumed that the use of azo dyes globally will decline. Alternatives to azo dyes in textile fibres cotton and cellulose in form of other types of dyes do exist.

In some cases, the incentive to develop substitutions for naphthalene may be due to the increasing awareness of health and safety risks, in others due to environmental concerns, or both issues may play an equally important role. The use of naphthalene globally is predicted to continue to increase by 2 % annually, with expected growth between 2-4 % in growing economies in the Pacific Asia, whilst the use in the European and North American regions is predicted to increase in a slower rate than 2 % and gradually stagnating.

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[11] http://www.abc.net.au/news/2014-05-28/govt-considers-banning-carcinogenic-dyes-more-found-in-clothing/5482040

Sammenfatning og konklusion

Klassificering og de vigtigste lovgivningsmæssige aspekter
Naftalen har en harmoniseret klassifikation som:

- H351: Mistænkt for at fremkalde kræft
- H302: Farlig ved indtagelse
- H400: Meget giftig for vandlevende organismer
- H410: Meget giftig med langvarige virkninger for vandlevende organismer

Som en konsekvens af naftalens kræftfremkaldende egenskaber er det forbudt at anvende stoffet i kosmetiske produkter. Desuden anvendes naftalen ikke længere i mølkugler, da der ikke er blevet indsendt en fyldestgørende ansøgning vedrørende brugen af naftalen i henhold til forordningen om biocidholdige produkter. Dette betyder, at naftalen i dag ikke er tilladt at anvende i mølkugler.

I EU (og Danmark)[12] er der fastsat en grænseværdi på 10 ppm eller 50 mg/m^3 i arbejdsmiljøet. For virksomheder i Danmark[13] er der fastsat en grænseværdi på 0,04 mg/m^3 for koncentrationer af naftalen i luften, målt ved virksomhedernes skel. For tappevandet hos forbrugerne i Danmark[14], samt for vand fra vandværker er der fastsat et vandkvalitetskriterium for indholdet af naftalen på 2 µg/l. Den miljømæssige kvalitetsstandard (EQS) for naftalen er 2,4 µg/l for ferskvand og 1,2 µg/l for havvand[15].

Naftalen er som et farligt stof underlagt særlige bestemmelser med hensyn til transport af farligt gods[16].

Naphtalen er registreret under REACH i et tonnagebånd på 100.000 – 1.000.000 ton pr. år (maj 2014), men det er hverken på Kandidatlisten eller på ECHA's Register over hensigter (Registry of intensions). Naftalen er på CoRAP (Community Rolling Action Plan)[17] og kom på listen i 2014 til vurdering af Tyskland i 2016, dvs. vurderingen er ikke startet endnu (CoRAP, 2014). De oprindelige årsager til bekymring over naftalen er opført som:

- Eksponering – eksponering af arbejdere (arbejdsmiljø)
- Eksponering – høj RCR (risk characterisation ratio)
- Eksponering – høj tonnage

Kemikalieinspektionen i Sverige har inkluderet naftalen i deres PRIO-database som et "priority risk reduction substance", hvilket betyder, at brugeren af stoffet anbefales at undersøge risikoen ved brugen af stoffet. Naftalen er desuden på SIN Listen (udviklet af ChemSec) på grund af dets klassifikation som mulig kræftfremkaldende og meget giftig for vandlevende organismer. Dette betyder, at naftalen opfylder SVHC-kriteriet som defineret af REACH-bestemmelserne.

Naftalen er ikke direkte nævnt i kriterier for miljømærkning, men vil være begrænset i ethvert miljømærket produkt, da ingen kemikalier, som er klassificeret som farligt for miljøet eller som kræftfremkaldende, er tilladt i miljømærkede produkter.

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[12] Directive 91/322/EEC and Danish Statutory Order No. 507 of 17.5.2011
[13] Danish Guidance No. 10702 of 19.11.2008
[14] Danish Statutory order No. 292 of 26.3.2014
[15] Danish Statutory order No. 1022 of 25.8.2010
[16] Directive 2008/68/EC
[17] http://echa.europa.eu/information-on-chemicals/evaluation/community-rolling-action-plan/corap-table

Fremstilling og brug

Fremstilling

Fremstillingen af naftalen finder sted verden over via to produktionsmetoder, hvor destillationen af stenkulstjære og herefter af naftalenolie er den mest udbredte produktionsmetode (92 % markedsandel i verden). Den mest udbredte produktionsmetode består af to trin. Første trin starter med stenkulstjære, som er produceret af koksgasser, og det efterfølges af en serie af destillationsprocesser, hvor forskellige tjærefraktioner produceres, genbruges internt eller sælges eksternt, med naftalen som slutproduktet (dvs. rånaftalen). Det andet trin anvendes til at få renere naftalen, og den mest almindelige teknologi, som anvendes, er destillation med opløsningsmidler. I Danmark produceres naftalen af Koppers Danmark ApS, og en lignende produktionsvej som ovennævnte anvendes. Dog bruger Koppers Danmark ApS ikke opløsningsmidler i destillationsprocessen. Koppers Danmark ApS importerer også naftalenolie for at kunne klare produktionsefterspørgslen. Det endelige produkt er 95-97 % rent naftalen.

I dag har Kina næsten halvdelen af produktionskapaciteten af naftalen i verden, skønt deres produktionsstruktur er forskellig fra den i EU og Danmark. EU, USA og Canada spiller også en vigtig rolle i verdensproduktionen. Tolv virksomheder i EU er registreret som importører og/eller producenter af naftalen i ECHA-databasen (ECHA RSD, 2014), deriblandt Koppers Danmark ApS, men det har vist sig, at en af de 12 virksomheder ikke længere producerer naftalen. Danmark er den eneste producent af naftalen i de nordiske lande.

Produktionsvolumen

Det har ikke været ikke muligt at finde et nyere estimat for den årlige produktion af naftalen på verdensplan. Der findes ældre estimater af årlig produktion fra forskellige lande/verdensdele. Disse er: 115.000 ton/år for USA (2001), 52.000 ton/år for Canada (2006) og 100.000 ton/år for EU (2009/2010). Dette giver et samlet estimat på 267.000 ton/år for produktion af naftalen, som burde være op til halvdelen af den årlige produktion i verden, når der anvendes den information, at Kina i dag har halvdelen af produktionen (IHS, 2013). Dog bør man være forsigtig med at anvende dette tal, da det er baseret på data fra forskellige tidspunkter og på information om fordeling af produktionsvolumen i Østen og Vesten fra i dag (2013). Tendenserne i produktionen har ændret sig markant i løbet af det seneste årti. Det ser ud til at produktionen af naftalen har været faldende i USA, men til gengæld har været stigende på andre markeder (Kina, Rusland og Brasilien). Tilsvarende ser det ud til at produktionen i Europa har været faldende, hvorimod den danske produktion har været stigende. Danmark producerer for tiden ca. 30.000 ton/år af naftalen.

Import og eksport

Det var ikke muligt at finde offentlig tilgængelige import/eksport-data for EU. I Danmark er importen af naftalen, som er indeholdt i kemiske produkter, steget støt gennem de sidste 15 år (op til 2011) ifølge data fra SPIN-databasen. De seneste årlige registrerede data for import er fra 2011 (73.739,1 ton), som er den samlede mængde naftalen importeret som indhold i kemiske produkter. Information om eksport af kemiske produkter, der indeholder naftalen, er ikke kendt, men ifølge Koppers Danmark ApS eksporterer de årligt 30.000 ton ren naftalen. Da hele produktionen af naftalen i Danmark eksporteres, kan man dermed også konkludere, at alt det naftalen, der anvendes i kemiske produkter i Danmark, importeres.

Anvendelse og historiske tendenser

Naftalen er historisk set et kemikalie til mange anvendelser, da det findes i mange forskellige tekniske renheder til forskellige anvendelser. Dog har der været et fald i anvendelsen af renere fraktioner gennem det seneste årti, især for fraktioner med mere end 90 % renhed. Desuden har det faktum, at naftalen ikke længere bruges i visse forbrugerprodukter (mølkugler), også reduceret dets anvendelse. Brugsmønsteret er dermed ændret, så der i dag ses en større anvendelse af naftalen til fremstillingen af mellemstoffer frem for anvendelse i slutprodukter. Ifølge data, der er samlet fra forskellige litteraturkilder, er de vigtigste anvendelser af naftalen verden over:

- Fremstilling af naftalensulfonsyrer
- Fremstilling af ftalsyre anhydrid
- Fremstilling af alkylerede opløsningsmidler
- Fremstilling af azofarvestoffer
- Fremstilling af slibeskiver som en kunstig pore former (slutprodukt)
- Udarbejdelse af sprængstoffer i fyrværkeri (slutprodukt)

Det europæiske forbrug af naftalen var ca. 175.000 ton i 2007. Forbruget af ren naftalen i Danmark forventes at være nul, da al produktion af naftalen fra Koppers Danmark ApS i Danmark eksporteres. Forbruget af naftalen i Danmark skyldes import og brug af andre kemiske produkter, der indeholder naftalen.

Ifølge information fra SPIN-databasen er de vigtigste anvendelser af naftalen i Danmark og de nordiske lande til brændselsadditiver og byggematerialer. Da disse grupperinger af anvendelser i SPIN er mere generelle, antages det, at disse to større anvendelser relaterer til anvendelser verden over og især til fremstilling af naftalen sulfonsyrer (anvendes som blødgører i betonblandinger) og ftalsyre anhydrider (anvendes til fx fremstilling af ftalater).

Produkter der indeholder naftalen
Naftalen findes utilsigtet i en lang række andre produkter. Dette skyldes, at nogle af disse produkter indeholder urenheder eller destillater fra tjære-baserede stoffer, eller at naftalen er en PAH og derfor kan forekomme i produkter, der indeholder mineralolie. En liste med eksempler er:

- Tjærefarver/specialfarver
- Vandtætte membraner til gulve og vægge
- Asfalt
- Gummi- og plastikprodukter, inklusive forbrugerprodukter
- Kreosot-behandlet træ

Desuden er naftalen også fundet i afgasninger fra nogle forbrugerprodukter, som for eksempel i afgasning fra el-sparepærer og fra cigaretrøg.

Affaldsbehandling

Affald, der er forurenet med naftalen, behandles som farligt affald i Danmark og EU. Det sendes typisk til forbrænding og termisk behandling. Der er blevet fundet spor af naftalen i røggasser og emissioner fra forbrændingsanlæggene til den omgivende luft. Det formodes ikke at komme fra afbrændingen af selve naftalenen, men derimod fra andre affaldsfraktioner, som frigør PAH'er under forbrænding. Det er ikke sandsynligt, at der sker nogen direkte frigørelse af naftalen til vand fra forbrændingen. Udledning til jord kan ske, hvis der forekommer spor af naftalen i bundasken.

Produkter, der indeholder små mængder naftalen, vil komme ind i affaldsstrømmen gennem den kommunale indsamlingsordning for affald. Det antages at de fleste forbrugerprodukter af gummi og plast vil blive brændt i Danmark, hvorimod affald i form af kemiske blandinger vil blive behandlet som farligt affald og brændt.

Den største mængde affald, der indeholder naftalen, forventes at være kreosot-behandlet træ, som forventes at være ca. 12.000 ton årligt i Danmark. Det totale indhold af naftalen i kreosot-behandlet træ er under 1 %. Afbrænding af naftalen (indeholdt i affaldsprodukter) vil resultere i dannelse af kuldioxid og vand, og vil derfor ikke medføre farlige emissioner via hverken røggas eller bundaske.

Miljømæssige effekter og skæbne

Naftalen har en harmoniseret klassificering for miljømæssige effekter som:

- H400: Meget giftig for vandlevende organismer
- H410: Meget giftig med langvarige virkninger for vandlevende organismer

Naftalen betragtes som værende persistent. Naftalen kan være hurtigt biologisk nedbrydeligt under aerobe forhold, men kun i olieforurenet vand. Under normale forhold og under anaerobe forhold ser det ikke ud til, at der forekommer biologisk nedbrydning. Naftalen ser ud til at være persistent i sediment og jord, men ikke i vandmiljøet under aerobe forhold. Naftalen har et lavt biokoncentrationspotentiale, og overordnet kan stoffet ikke betragtes som et PBT-stof (persistent (P), men ikke bioakkumulerbart (B) eller giftigt (T)). På grund af forskellige i de kriterier, der ligger til grund for PBT vurderingen og klassificering af stoffer, så skal naftalen klassificeres som H400 ”Meget giftig for vandlevende organismer” og H410 ”Meget giftig med langvarige virkninger for vandlevende organismer”, uden at de tilgængelige data understøtter en vurdering som B eller T.

Da naftalen er en PAH, skyldes de største miljømæssige emissioner at være ufuldstændig forbrænding af organisk materiale (anslået at være 88 % af de totale emissioner (ECB, 2003)). Af denne årsag kan naftalen også være til stede i små mængder (på forureningsniveau) i forbrugerprodukter lavet af plastik eller gummi, hvor blødgørere eller carbon black (kønrøg) anvendes. Frigørelse af naftalen til miljøet kan også forekomme fra produktionssteder eller fra industriel brug af naftalen som et mellemkemikalie. Det er dog dannelsen af naftalen fra indirekte emissioner, især ufuldstændig forbrænding, der ser ud til at være den største kilde til naftalen i miljøet. Eksempler på indirekte emissioner af naftalen er:

- Emission fra brugen af produkter som naturligt indeholder naftalen
- Emission fra produktionen af stoffer, der bruger råmaterialer eller hjælpestoffer, som naturligt indeholder naftalen
- Emission fra olieproduktion
- Emission fra brug af transportkøretøjer
- Emission fra kulforbrænding
- Emission fra kulkarbonisering og forgasning

Baseret på de tilgængelige data for naftalen forventes det ikke, at naftalen generelt vil forårsage uønskede effekter i vand- eller landmiljøet. Punktkildeforurening har dog vist koncentrationer, som er meget højere end de beregnede forventede koncentrationer med ingen effekt (PNEC). Det betyder, at der kan være situationer, som kan have en miljømæssig effekt, dvs. punktfrigørelser til miljøet eller forurenet jord pga. frigørelse af naftalen fra kreosot-behandlet træ[18]. En tilsvarende PNEC kunne ikke beregnes for luftmiljøet. Derfor er en vurdering af de miljømæssige effekter af naftalen til luft ikke blevet foretaget (til trods for at naftalen primært frigøres til luft). Den atmosfæriske halveringstid for naftalen er mindre end en dag, og når det er frigjort til luften, vil 90 % af denne naftalen forblive i luften. Naftalen vil i luften blive omdannet til 1-naphtol[19], 2-naphtol[20] og 2-nitronaftalen[21] som de vigtigste indholdsstoffer ved fotokemisk reaktion. To af disse reaktionsprodukter er også klassificeret som giftige for miljøet, men med en mindre giftig klassificering sammenlignet med den miljømæssige klassificering for naftalen.

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[18] The production of creosote treated wood is no longer allowed in Denmark, but creosote treated wood may still be in use in Denmark.

[19] Harmonised classification as Acute Tox. 4, H302, H312; Skin Irrit. 2, H315; Eye Dam. 1, H318; STOT SE 3, H335.

[20] Harmonised classification as Acute Tox. 4, H302, H332; Aquatic Acute 1, H400.

[21] Harmonised classification as Carc. 1B, H350; Aquatic Chronic 2, H411.

Effekter på menneskers sundhed

Toksikokinetik, absorption, distribution, metabolisme og udskillelse

Eksponering for naftalen kan ske gennem inhalation, indtagelse eller hudkontakt. Den tilgængelige information om toksikokinetikken for naftalen i mennesker er begrænset. Den tilgængelige information indikerer dog, at naftalen absorberes hurtigt via alle eksponeringsveje, og at der efter indtagelse sker næsten fuldstændig og hurtig absorption. Urinen er den primære udskillelsesvej i mennesker og i dyr. Omfattende metabolisme forekommer, og udskillelsen fra kroppen er hurtig (ECB, 2003; ECHA RSD, 2014).

Sundhedsrisiko for mennesker

Naftalen har en moderat oral akut giftighed (H302 ”Farlig ved indtagelse”) og kan hos mennesker og hunde forårsage hæmolytisk anæmi (abnorm nedbrydning af røde blodceller), som kan være dødelig. Der er ikke nogen information om effekterne fra naftalen efter akut inhalation eller hudeksponering hos mennesker.

Der kan ikke drages nogen konklusioner med hensyn til de irritative egenskaber for naftalen for mennesker. Data fra dyrestudier indikerer dog, at naftalen kun er lidt irriterende for hud og øjne – men utilstrækkelig til en klassificering som irriterende. Mangel på rapportering om tilfælde af sensibilisering i mennesker antyder, at naftalen ikke er sensibiliserende for hverken hud eller luftveje.

Dyrestudier med gentagen dosering viser, at der er forskelle mellem arterne mht. effekterne af naftalen. Effekterne, som er set i gnavere, ser ikke ud til at være relevante for mennesker, og hæmolytisk anæmi, som er set i mennesker (og hund) er ikke blevet observeret i gnavere. Generelt er der ikke nogen epidemiologiske studier af naftalens effekter på menneskers sundhed med undtagelse af et begrænset antal rapporter om tilfælde af hæmolytisk anæmi.

Ingen præcis NOAEL blev identificeret, og der blev ikke fundet tegn på systemisk toksicitet i inhalationsstudierne. En LOAEL på 5 mg/m^3 kunne fastsættes for inhalations toksicitet ved gentagen dosering.

Naftalen er mistænkt for at være kræftfremkaldende og er klassificeret som H351 ”Mistænkt for at fremkalde kræft”. Denne klassificering er baseret på nasale tumorer fundet i rotter (ved 50 mg/m^3) og på lungetumorer fundet i mus. Det er usandsynligt, at effekten med lungetumorer i mus, vil være relevant for mennesker, hvorimod relevansen for mennesker er uklar med hensyn til nasale tumorer i rotter. Det er blevet diskuteret intenst, om grænseværdien for arbejdsmiljøet på 50 mg/m^3 skulle sættes ned, da studiet om nasale tumorer på rotter førte til øget tumorforekomster ved denne koncentration. Preuss et al. (2003) foreslår at sænke grænseværdien for arbejdsmiljøet til 1,5 mg/m^3 baseret på måleresultater på internationale arbejdspladser. Grænseværdien for arbejdsmiljøet for naftalen er dog ikke blevet sænket endnu.

Naftalen er ikke genotoksisk, dvs. årsagen til at naftalen forårsager kræft ikke er forårsaget af en genotoksisk mekanisme, men af en anden ukendt virkningsmekanisme. Naftalen ser ikke ud til at være hverken føtotoksisk eller hormonforstyrrende.

Eksponeringskilder

Inhalation er den eksponeringsrute, der er mest relevant for naftalen. De største direkte eksponeringskilder for naftalen er i arbejdsmiljøet og for forbrugere (primært gør-det-selv-forbrugerne) ved brug af vandtætte membraner (der indeholder naftalen) til brug på gulve og vægge. Eksponering i forbindelse med arbejdet er den største og mest markante eksponering for mennesker. Den generelle befolkning er indirekte eksponeret for naftalen, primært via indendørsluften, hvor cigaretrøg er den største bidragsyder.

Effekter på menneskers sundhed
Historisk set er den væsentligste effekt, der er blevet rapporteret for mennesker, den akutte effekt hæmolytisk anæmi som et resultat af eksponering for (sutning på) mølkugler. Denne eksponering er dog ikke længere relevant, da brugen af naftalen i mølkugler ikke længere er tilladt i EU.

Den akutte effekt hæmolytisk anæmi kan dog stadig være årsag til bekymring for både arbejdere og forbrugere, da man ikke kan aflede nogen NOAEL eller dosis-respons karakteristika fra de tilgængelige data for mennesker. Data for dyr (i hunde) antyder, at en oral dosis i mg/kg-området kunne frembringe den akutte effekt hæmolytisk anæmi i mennesker. Baseret på disse data er den eneste eksponering for forbrugere, der kunne være bekymrende, situationen, hvor gør-det-selv-forbrugere lægger vandtætte membraner indeholdende naftalen (og i perioden efter de vandtætte membraner er lagt) – især hvis arbejdet udføres i uventilerede rum. Yderligere undersøgelse af den aktuelle eksponering og effekt i disse situationer, samt frekvensen af anvendelsen af naftalen i vandtætte membraner kan være nødvendig for at fastslå om denne eksponering giver anledning til bekymring. Det forventes dog ikke, at gør-det-selv-forbrugerne vil blive eksponeret for naftalen i længere tid.

De eksisterende data for arbejdsmiljøet antyder, at de fleste eksponeringsniveauer er pænt under grænseværdien for arbejdsmiljøet på 50 mg/m^3. Dog har en LOAEL-værdi på 5 mg/m^3 for gentaget inhalationstoksicitet startet en debat, om grænseværdien for arbejdsmiljøet burde sænkes. Preuss et al. (2003) kræver yderligere undersøgelse på dette område og en sænkning af grænseværdien for arbejdsmiljøet til 1,5 mg/m^3.

Effekter på menneskers sundhed fra naftalenrester i gummi- og plastikartikler betragtes som værende ubetydelig. Ikke desto mindre bør udsættelse for kræftfremkaldende stoffer generelt sænkes så meget som muligt, især i produkter til børn. Det forventes dog, at den indførte begrænsning for 8 specifikke PAH'er (selvom naftalen ikke er blandt disse otte) i gummi- og plastikprodukter, som kommer i direkte kontakt (både ved kontakt i lang tid og gentagne gange i kort tid) med menneskers hud, også vil have en indflydelse på niveauet af naftalenurenheder i forbrugerprodukter. Begrænsningen træder i kraft i december 2015.

Den største indirekte eksponering for naftalen skyldes indendørsluft og primært cigaretrøg. Når man lægger den totale eksponering fra indirekte eksponering (luft og fødevarer), forbrugerprodukter og arbejdseksponering sammen, forventes det dog ikke, at den samlede eksponering fra indirekte eksponering og forbrugerprodukter generelt vil give anledning til bekymring med hensyn til effekter på mennesker. I de følgende situationer kan mennesker blive eksponeret for højere koncentrationer af naftalen, som kan give anledning til bekymring:

- Al eksponering i arbejdsmiljøet/arbejdere, der arbejder med naftalen.
- Gør-det-selv-forbrugere, der anvender vandtætte membranprodukter, som indeholder naftalen – både lægning og i perioden efter lægning

Alternativer
Naftalen anvendes både som et mellemstof i produktionen af andre kemikalier såvel som i slutprodukter. Alternativer for begge anvendelser er blevet undersøgt.

Alternativer til naftalen blev identificeret i nogle anvendelser og i et varierende omfang. Den naftalen-baserede blødgører NSF (naftalen sulfonsyre) til betonblandinger, som repræsenterer den største anvendelse af naftalen på verdensplan, ser ud til at have været genstand for flest undersøgelser med hensyn til alternativer. Her er det polycarboxylat, der i stigende grad vinder mere accept på markedet. Polycarboxylat er tilgængeligt på markedet og præsterer strukturmæssigt bedre som alternativ til de naftalen-baserede blødgører anvendt i cement. Desuden har polycarboxylat en bedre miljø- og sundhedsklassificering sammenlignet med naftalen.

Ftalsyre anhydrid produceres også i dag ved brug af o-xylen og kunne derfor muligvis helt erstatte anvendelsen af naftalen til dette formål. Klassificeringen af o-xylen er til en vis grad bedre end klassificeringen af naftalen (dvs. ingen klassificering som kræftfremkaldende) og kunne derved udgøre et noget bedre alternativ sammenlignet med naftalen.

Alternativer til ftalsyre anhydrid ser ikke ud til at være i kommerciel produktion til trods for den kendte risiko for sundheden ved ftalsyre anhydrid og dens tilstedeværelse i større voksende industrier fx indenfor byggeri, bilproduktion, elektronik og malinger/overfladebehandlinger. Ftalsyre anhydrid har været forbudt i visse slutprodukter, hvilket har skabt en tilskyndelse i den kemiske industri til at finde fremtidige alternativer som fx bio-baserede erstatninger. Desuden har Miljøstyrelsen konkluderet, at tekniske alternativer eksisterer, men uden nogle realistiske muligheder for at få indflydelse på de nuværende produktsammensætninger fra internationale leverandører.

En litteratursøgning viste, at der er stigende offentlig opmærksomhed overfor sundhedsrisici med azofarvestoffer i tøj[22]. Desuden er visse azofarvestoffer begrænset i tekstil- og læderartikler i henhold til REACH Annex XVII. Derfor kunne det antages, at anvendelsen af azofarvestoffer vil falde globalt. Der findes alternativer til azofarvestoffer i tekstilfibre og cellulose i form af andre typer farver.

Tilskyndelsen til at udvikle substitutter for naftalen kan skyldes den voksende opmærksomhed omkring sundhed og sikkerhedsrisici, og i andre tilfælde miljømæssige bekymringer - eller begge dele kan spille en vigtig rolle. Anvendelsen af naftalen globalt forventes at fortsætte med at stige med 2 % om året, med en forventet vækst på mellem 2-4 % i de voksende økonomier i Asien og Stillehavsområdet, mens anvendelsen i de europæiske og nordamerikanske regioner forudsiges at stige i et langsommere tempo end 2 % og gradvist stagnere.

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[22] http://www.abc.net.au/news/2014-05-28/govt-considers-banning-carcinogenic-dyes-more-found-in-clothing/5482040

1. Introduction to naphthalene

Naphthalene, also called antimite, naphthalin, naphthene or tar camphor, is an aromatic hydrocarbon with the molecular formula $C_{10}H_8$, which is found as a colourless to brown solid depending on its manufacture and purity (ECB, 2003). When pure, it is found at room temperature in the form of white crystalline flakes or powder, it is water insoluble and it has a characteristic smell of tar or mothballs (Emergency Management Agency, 2013; Schleicher et al., 2009; US EPA, 1998).

Naphthalene is used as precursor to chemical synthesis in large scale, similarly as the basis for the production of dyes and colorants, pesticides and chemical rubbers (Schleicher et al., 2009). More details on its application are listed in chapter 3. Its production is based on two sources: coal tar and petroleum, and coal tar is so far the largest utilised basis of production of naphthalene world-wide (ECB, 2003; US EPA, 1998). The production of naphthalene from coal tar is done by distillation and crystallisation.

Naphthalene has also been documented to be found as by-product emission from combustion processes, therefore typically found as an outdoor emission. Furthermore, it has also been found in significant amounts as indoor emission from consumer products and in pacifiers (Won et al., 2012; Jia C. and Batterman S., 2010; German Federal Institute for Risk Assessment, 2012).

Naphthalene has a harmonised classification as amongst others of Carc. 2, H351 (suspected of causing cancer), Aquatic Acute 1, H400 (very toxic to aquatic life) and Aquatic Chronic 1, H410 (very toxic to aquatic life with long lasting effects). This classification is the primary reason for inclusion on the Danish EPA's list of undesirable substances (LOUS). For further information regarding environmental and health aspects, please see chapter 5 and 6.

Definition and physical-chemical properties of naphthalene are given in Table 1 and Table 2 on the next pages.

1.1 Definition of the substance

	Naphthalene
EC Number	202-049-5
CAS Number	91-20-3
Synonyms	Tar camphor, naphthene, naphthalin, naphthaline, mothballs, moth flakes, white tar, antimite
Molecular weight	128,17 g/mol

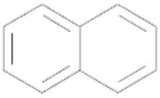
Molecular formula and structure	$C_{10}H_8$ 
Degree of purity	>90% (w/w)
Major impurities	Quinoline (C_9H_7N), Phenol (C_6H_6O)

TABLE 1
NAME AND OTHER IDENTIFIERS OF NAPHTHALENE (ECHA, 2014; CHEMICAL BOOK, 2014; JIA C. AND BATTERMAN S., 2010; ECB, 2003; US EPA, 1998)

1.2 Physical and chemical properties

The physical and chemical properties of naphthalene are given in Table 2 below. Naphthalene is a solid at room temperature, but sublimes slowly at room temperature (ECB, 2003), which means that naphthalene undergoes a phase transition directly from solid to the gas phase without passing through an intermediate liquid phase.

Naphthalene has a moderate vapour pressure (7.2 Pa at 20 °C), which is just below the 10 Pa cut-off value often used to define volatile organic compounds (VOCs), (Jia and Batterman, 2010). Naphthalene is hence one of the least volatile VOCs – and is therefore also characterised as a semi-volatile organic compound (SVOC). Naphthalene is, however, considered to be the most volatile PAH (polyaromatic hydrocarbon), (Jia and Batterman, 2010). A definition of PAHs can be found below in section 1.3. “Naphthalene and PAHs”.

According to Jia and Batterman (2010) naphthalene has often been excluded in both VOC and PAH studies, as naphthalene is a borderline substances both with respect to VOC (least volatile VOC) and PAH (most volatile PAH).

Property		Reference
Physical state	Solid in the form of flakes, granules or powder at 20°C and 1013 hPa	ECHA RSD, 2014
Colour	White	ECHA RSD, 2014
Odour	Characteristic of aromatic compounds	ECHA RSD, 2014
Substance type	Organic	ECHA RSD, 2014
Melting point	78.9 to 80,3 °C	ECHA RSD, 2014
Boiling point	218.1 °C at 1013 hPa	ECHA RSD, 2014
Flash point	78.5 °C at 990 hPa (experimental) 79 °C at 1010 hPa (experimental) 79 – 99 °C at 1013 hPa (literature)	ECHA RSD, 2014
Autoflammability/ self-ignition temperature	526 to 587 °C at 1013 hPa (literature) 540 °C at 1013 hPa (measured)	ECHA RSD, 2014

Property		Reference
Explosiveness	Explosive at vapor from 0.9% (vol) to 5.9% (vol), lower limit 48 g/m^3, upper limit 315 g/m^3	ECHA RSD, 2014
Relative density	1.069 g/cm^3 at 20 & 24,7 °C (technical quality) 1.085 g/cm^3 at 20 & 24,7 °C (pure)	ECHA RSD, 2014
Viscosity	1 mm^2/s at 80 °C (technical quality) 1,03 & 1,05 mm^2/s at 85 & 81,5 °C respectively (pure)	ECHA RSD, 2014
Vapour pressure	7.2 Pa at 20 °C 10.5 Pa at 25 °C 768 Pa at 75 °C 2500 Pa at 100 °C	ECHA RSD, 2014
Water solubility	30.8 – 34.4 mg/l at 25 °C 31.7 mg/l at 25 °C Slightly soluble (0,1 – 100 mg/l)	ECHA RSD, 2014
Log P (octanol/water) **Log K_{ow}**	3.4 at 25 °C (experimental result) 3.33 – 3.45 at 22 °C (experimental result) 3.7 at 25 °C (experimental result)	ECHA RSD, 2014
Odour threshold	Approx. 0.08 ppm (mL/m3)	ECHA RSD, 2014
Henry's law constant	44.86 Pa · m^3/mol (modelled)	ECB, 2003

TABLE 2
PHYSICAL-CHEMICAL PROPERTIES FOR NAPHTHALENE (REFERENCE: MOST DATA IS TAKEN FROM ECHA REGISTERED SUBSTANCES DATABASE (ECHA, 2014))

1.3 Naphthalene and PAHs

PAHs are described in details in this section as PAHs (polyaromatic hydrocarbons) are a large group of chemicals – some with more problematic health effects than others – that are formatted during incomplete combustion of organic material. Naphthalene is considered to be a PAH and it is therefore of importance to address this issue, when describing the release of naphthalene to the environment.

1.3.1 Definition of PAHs

The term "polycyclic aromatic hydrocarbons (PAHs)" refers to a ubiquitous group of several hundred chemically-related and environmentally persistent organic compounds of various structures and varied toxicity. Many PAHs are suspected of being carcinogenic, but 15 of the PAHs were considered as having sufficient evidence for a carcinogenic effect (Carc 1A or 1B) in 2002 (European Commission, 2002).

PAHs are hydrocarbons containing only carbon and hydrogen that consist of at least two *fused* aromatic rings that share one or more sides, with no substituent and branching on any of the ring structures. In organic chemistry, rings are *fused* if they share two or more atoms[23] (Jensen & Blinksbjerg, 2000).

Though poly- literally means "many", there is precedence in nomenclature for defining the first and most simple PAH, as the one with two ring cases. Thus **naphthalene would be the first and most simple PAH.** However, the ‘two-ring PAH’ is not considered to be a ‘true’ PAH. PAH with three or more rings are considered to be ‘true’ PAH, e.g. anthracene and phenanthrene.

According to the International Union of Pure and Applied Chemistry (IUPAC), the simplest PAHs are phenanthrene and anthracene which both contain three fused aromatic rings. Smaller molecules, such as naphthalene which consist of two coplanar six-membered rings sharing an edge, is not a ‘true’ PAH, though it is referred to as a bicyclic aromatic hydrocarbon[24]. However, according to US EPA Test Methods (no. 0610, 8100, 8310 from 1986), naphthalene is one of the 16 PAH normally analyzed according to these methods, and naphthalene is thereby considered to be a PAH by the US EPA. In Jensen & Blinksbjerg (2000) naphthalene is described as the simplest PAH, which, however, is not always considered to be a PAH as described in this section.

1.3.2 General characteristics of PAHs

The general characteristics of PAHs are high melting and boiling points (therefore they are solid), low vapour pressure and very low aqueous solubility, which both tend to decrease with increasing molecular weight, whereas resistance to oxidation and reduction increases. PAHs are highly lipophilic and therefore very soluble in various organic solvents. Aqueous solubility decreases for each additional ring[25]. Naphthalene being the most simple PAH, even though not by all considered to be a ‘true’ PAH, is therefore the PAH with the highest aqueous solubility, the highest vapour pressure and the PAH, which is most likely to oxidise in chemical reactions.

Emission sources

PAHs are natural constituents of mineral oil (petrogenic PAHs) or are generated during combustion (pyrogenic PAHs). More or less the same PAHs will be present whether the source is pyrogenic or petrogenic, but the relative composition of the mixture of PAHs is different depending on the source (Lassen et al., 2011). Mixtures of PAHs are formed in incomplete combustion processes and pyrolysis of organic matter. PAHs are emitted to the environment either in the form of vapour or as particle matter. PAHs are in general mainly associated to particle matter because of the generally low volatility of PAHs (Jensen & Blinksbjerg, 2000). However, as naphthalene is the most volatile PAH, most naphthalene will be emitted in the form of vapour (> 95%), (Jia and Batterman, 2010).

1.3.3 Differences in PAHs included in chemical analysis

The most often used standard blend of PAHs is 16 PAHs chosen by the US EPA (listed as EPA Method 660 in the table). Naphthalene is included in these 16 PAHs. Table 3 below illustrates different definitions of PAHs used in different methods for chemical analysis or by different countries (Jensen & Blinksbjerg, 2000). From Table 3 it can be concluded that naphthalene is not always included in the range of PAHs that are analysed.

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[23] http://www.toxipedia.org/display/toxipedia/Polycyclic+Aromatic+Hydrocarbons+(PAHs)+-+Abridged

[24] http://www.toxipedia.org/display/toxipedia/Polycyclic+Aromatic+Hydrocarbons+(PAHs)+-+Abridged

[25] http://www.toxipedia.org/display/toxipedia/Polycyclic+Aromatic+Hydrocarbons+(PAHs)+-+Abridged

PAH compound	EPA Method 610	ISO GC/MS	Italy 1990	France	UK	Germany
Acenaphthene	x	x			x	x
Acenaphthylene	x	x			x	x
Anthracene	x	x			x	x
Benz[a]anthracene	x	x	x	x	x	x
Benzo[b]fluoranthene	x	x	x	x	x	x
Benzo[j]fluoranthene			x		x	
Benzo[k]fluoranthene	x	x	x	x	x	x
Benzo[ghi]perylene	x	x		x	x	x
Benzo[a]pyrene	x	x	x	x	x	x
Benzo[e]pyrene		x				
Chrysene	x	x			x	x
Coronene		x			x	
Cyclopenteno[cd]pyrene		x				
Dibenz[a,h]acridine			x			
Dibenz[a,h]anthracene	x	x	x	x	x	x
Dibenzo[a,e]pyrene			x		x	
Dibenzo[a,h]pyrene			x		x	
Dibenzo[a,i]pyrene			x		x	
Dibenzo[a,l]pyrene			x		x	
Fluoranthene	x	x		(x)	x	x
Fluorene	x	x		(x)	x	x
Indeno[1,2,3-cd]pyrene	x	x		x	x	x
5-Methylchrysene					x	
Naphthalene	**x**	**x**				**x**

PAH compound	EPA Method 610	ISO GC/MS	Italy 1990	France	UK	Germany
Perylene		x				
Phenanthrene	x	x			x	x
Pyrene	x	x			x	x

TABLE 3
DIFFERENT DEFINITIONS OF PAH BLENDS USED FOR CHEMICAL ANALYSIS OF PAHS IN DIFFERENT COUNTRIES (SOURCE: JENSEN & BLINKSBJERG, 2000)

1.3.4 Danish emission regulation of PAHs

The Danish emission regulation for PAHs (Danish EPA, 2001) is based on the principle of regulating the emission by toxicity. This is carried out by linking a toxicity factor to the toxicity of the PAH benz[a]pyrene. For each of the PAHs the concentration is multiplied by the toxicity factor, and summarised to one value, with the unit “mg benz[a]pyrenequivalences/m³”.

The PAHs included cover 15 of the 16 PAH according to US EPA method, excluding naphthalene. Naphthalene is apparently excluded because it is less harmful than the other 15 PAH and it is consequently classified differently, having its own emission limit value. The toxicity factor system is based on all the 15 PAH being considered either as carcinogenic or able to promote the carcinogenic effect for other PAH.

1.3.5 Naphthalene is the most abundant of the PAHs

According to Jensen & Blinksbjerg (2000), naphthalene is normally found in much higher concentrations in PAH emissions compared to the other PAHs. This is illustrated by Image 1, which shows that naphthalene emissions from an asphalt factory consisted of 58% of the total PAH emission.

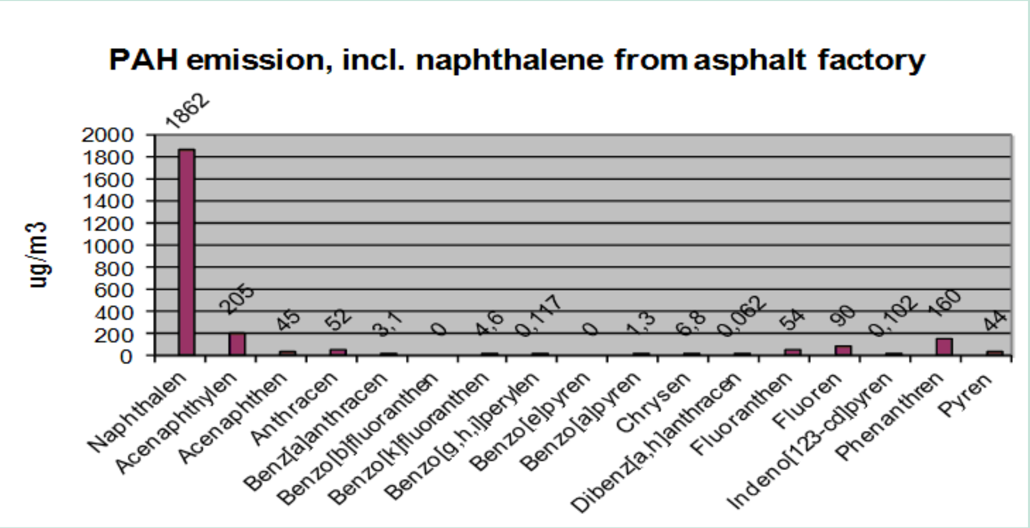
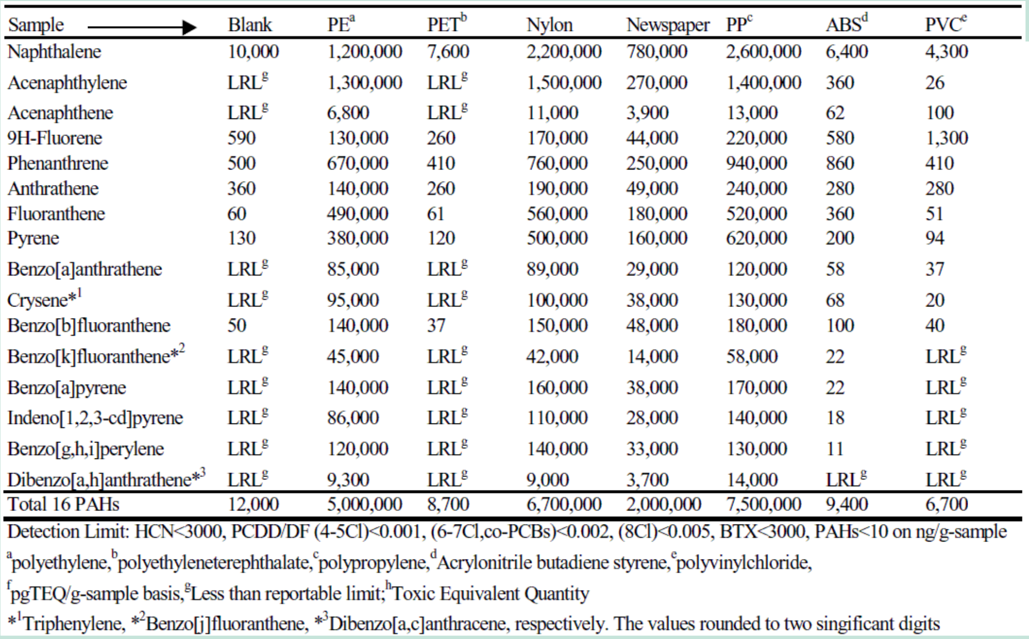


IMAGE 1
EXAMPLE OF PAH EMISSIONS FROM A DANISH ASPHALT FACTORY. DATA ARE FROM 1999. (SOURCE: JENSEN & BLINKSBJERG, 2000)

Another example of naphthalene being the most abundant PAH in emissions of PAHs can be found in Image 2 below. Here the emissions of PAHs have been investigated for combustion of some plastic materials and newspaper.



Sample →	Blank	PE[a]	PET[b]	Nylon	Newspaper	PP[c]	ABS[d]	PVC[e]
Naphthalene	10,000	1,200,000	7,600	2,200,000	780,000	2,600,000	6,400	4,300
Acenaphthylene	LRL[g]	1,300,000	LRL[g]	1,500,000	270,000	1,400,000	360	26
Acenaphthene	LRL[g]	6,800	LRL[g]	11,000	3,900	13,000	62	100
9H-Fluorene	590	130,000	260	170,000	44,000	220,000	580	1,300
Phenanthrene	500	670,000	410	760,000	250,000	940,000	860	410
Anthrathene	360	140,000	260	190,000	49,000	240,000	280	280
Fluoranthene	60	490,000	61	560,000	180,000	520,000	360	51
Pyrene	130	380,000	120	500,000	160,000	620,000	200	94
Benzo[a]anthrathene	LRL[g]	85,000	LRL[g]	89,000	29,000	120,000	58	37
Crysene*[1]	LRL[g]	95,000	LRL[g]	100,000	38,000	130,000	68	20
Benzo[b]fluoranthene	50	140,000	37	150,000	48,000	180,000	100	40
Benzo[k]fluoranthene*[2]	LRL[g]	45,000	LRL[g]	42,000	14,000	58,000	22	LRL[g]
Benzo[a]pyrene	LRL[g]	140,000	LRL[g]	160,000	38,000	170,000	22	LRL[g]
Indeno[1,2,3-cd]pyrene	LRL[g]	86,000	LRL[g]	110,000	28,000	140,000	18	LRL[g]
Benzo[g,h,i]perylene	LRL[g]	120,000	LRL[g]	140,000	33,000	130,000	11	LRL[g]
Dibenzo[a,h]anthrathene*[3]	LRL[g]	9,300	LRL[g]	9,000	3,700	14,000	LRL[g]	LRL[g]
Total 16 PAHs	12,000	5,000,000	8,700	6,700,000	2,000,000	7,500,000	9,400	6,700

Detection Limit: HCN<3000, PCDD/DF (4-5Cl)<0.001, (6-7Cl,co-PCBs)<0.002, (8Cl)<0.005, BTX<3000, PAHs<10 on ng/g-sample

[a]polyethylene,[b]polyethyleneterephthalate,[c]polypropylene,[d]Acrylonitrile butadiene styrene,[e]polyvinylchloride,

[f]pgTEQ/g-sample basis,[g]Less than reportable limit;[h]Toxic Equivalent Quantity

*[1]Triphenylene, *[2]Benzo[j]fluoranthene, *[3]Dibenzo[a,c]anthracene, respectively. The values rounded to two significant digits

IMAGE 2
EXAMPLE OF PAH EMISSIONS FROM COMBUSTION OF SOME PLASTIC MATERIALS AND NEWSPAPER (SOURCE: TAKASUGA, 2003)

The formation of PAHs – and hereby also naphthalene – by incomplete combustion of organic material, is hence important to include in the overall picture for naphthalene manufacturing, use, environmental release etc.

2. Regulatory framework

This chapter gives an overview of how naphthalene is addressed in existing and upcoming EU and Danish legislation, international agreements, and ecolabel criteria.

For readers not accustomed with legislative issues, Appendix 2: provides an overview of the different legislatives instruments in the EU and Denmark. The appendix also gives a brief introduction to the chemicals legislation, it explains the lists referred to in this chapter, and it provides a brief introduction to international agreements and selected ecolabel schemes.

2.1 Legislation

This section lists existing legislation addressing naphthalene, the classification of naphthalene, and finally aspects concerning REACH.

2.1.1 Existing legislation

Table 4 provides an overview of existing legislation addressing naphthalene. For each area of legislation, the table lists the relevant legislation ('Legal instrument') – whether this is a Directive, Regulation or Danish Statutory Order. Furthermore, it is noted whether the legislation covers the EU, Denmark or both and a short description of the aspects concerning naphthalene is provided in each case. It should be noted that national rules (i.e. Statutory Orders) will only be described in case the Danish rules differ from the related EU Directive.

Legal instrument	EU/DK	Requirements which concern naphthalene
Regulation addressing chemicals		
REGULATION (EC) No. 1272/2008 of 16 December 2008 on classification, labelling and packaging of substances and mixtures (CLP)	EU/DK	The CLP Regulation where naphthalene is listed in Annex VI of the Regulation with the harmonised classification. See Table 5 in this report. http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CONSLEG:2008R1272:20110419:EN:PDF
REGULATION (EC) No. 1907/2006 of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)	EU/DK	Naphthalene is not listed directly in the REACH Regulation, but the requirements listed in REACH concerning registration, evaluation, authorisation and restriction apply for naphthalene as well. http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CONSLEG:2006R1907:20130421:EN:PDF

Legal instrument	EU/DK	Requirements which concern naphthalene
REGULATION (EC) No. 1048/2005 amending Regulation No 2032/2003 on the second phase of the 10-year work programme referred to in Article 16(2) of Directive 98/8/EC concerning the placing of biocidal products on the market REGULATION (EC) No 1451/2007 of 4 December 2007 on the second phase of the 10-year work programme referred to in Article 16(2) of Directive 98/8/EC of the European Parliament and of the Council concerning the placing of biocidal products on the market	EU/DK	Naphthalene is listed in Annex I "Active substances identified as existing". This means that naphthalene is regarded as an existing active substance (biocidal product) available on the market before 14 May 2000. Naphthalene is also listed in Annex II "Active substances to be examined under the review programme" as product type 19 ("Repellent and attractants"). This means that a complete dossier for naphthalene must be sent to the competent authority of the UK from November 1 2005 to 30 April 2006. However, no satisfactory application of the use of naphthalene within the product type 19 was made, which means that naphthalene is not allowed to be used in mothballs today (see Commission Decision below). http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:02005R1048-20050729&qid=1400758584853&from=EN http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:02007R1451-20130901&from=EN
COMMISSION DECISION of 28 July 2008 concerning the non-inclusion of certain substances in Annex I, IA or IB to Directive 98/8/EC concerning the placing of biocidal products on the market	EU/DK	Naphthalene is listed in the Annex of this Commission Decision meaning that naphthalene for product type 19 ("Repellent and attractants") cannot be included in Annex I, IA or IB to the biocidal products directive. This means that naphthalene from 29 July 2008 was no longer allowed to be used in mothballs in the EU. http://eur-lex.europa.eu/legal-content/en/TXT/PDF/?uri=CELEX:32008D0681&rid=3
REGULATION (EEC) No. 793/93 on the evaluation and control of the risks of existing substances	EU/DK	Naphthalene is listed in Annex I "List of existing substances produced or imported within the community in quantities exceeding 1,000 tonnes per year". For substances in this Annex I the importer or manufacturer must have submitted certain data on classification, use, toxicity, environmental fate, etc. to the Commission. If new uses or new data is obtained on the substances, the updated information must be sent to the Commission. Member States draw up a Priority List based on the data received on the potential effects on man or the environment of the substances. http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:01993R0793-

Legal instrument	EU/DK	Requirements which concern naphthalene
		20031120&from=EN The REACH Regulation No. 1907/2006 will supersede this legislation.
REGULATION (EC) No. 1179/94 of 25 May 1994 concerning the first list of priority substances as foreseen under Council Regulation No 793/93	EU/DK	Naphthalene is listed in the Annex, which means that naphthalene is considered to be a 'priority substance' for which an evaluation of the substance must be performed for the designated Member State (here UK). http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:31994R1179&from=EN
Regulation addressing products		
REGULATION (EC) No. 1223/2009 of 30 November 2009 on cosmetic products	EU/DK	Naphthalene is listed as entry no. 1167 in Annex II: "List of substances prohibited in cosmetic products". This means that naphthalene must not be used as an ingredient in cosmetic products. http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CONSLEG:2009R1223:20130711:EN:PDF
Regulation addressing waste		
DIRECTIVE 2008/98/EC of 19 November 2008 on waste and repealing certain directives	EU	General legislation on waste and description of the waste hierarchies. Naphthalene is not mentioned directly, but it is stated in annex III that waste is considered to be dangerous when it contains ecotoxic substances (thus it indirectly covers naphthalene). http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2008:312:0003:0030:EN:PDF
STATUTORY ORDER No. 1309 of 18.12.2012 on waste	DK	General legislation on waste based on the EU legislation on waste. Naphthalene is not mentioned directly, but it is stated in annex 4 that waste is considered to be dangerous if it contains 1% or more of a chemical substance considered to be carcinogenic Carc. 2, H351 as is the case with naphthalene. https://www.retsinformation.dk/Forms/R0710.aspx?id=144826#Bil4

Legal instrument	EU/DK	Requirements which concern naphthalene
Regulation addressing emissions to the environment		
DIRECTIVE 2008/105/EC of 16 December 2008 on environmental quality standards in the field of water policy amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC DIRECTIVE 2013/39/EU of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy DIRECTIVE 2000/60/EC of 23 October 2000 establishing a framework for Community action in the field of water policy	EU	Environmental quality standards (EQS) are laid down for a long list of substances including naphthalene. The purpose of the Directives is to establish a framework for the protection of inland surface waters, transitional waters, coastal waters and groundwater. Limit values have been listed for a number of priority substances. Naphthalene is included in the list of priority substances. The listed environmental quality standards (EQS) for naphthalene have effect from 22 December 2015. The requirements listed for naphthalene in Annex II "Environmental Quality Standards for Priority Substances and Certain Other Pollutants", Part A "Environmental Quality Standards (EQS)" are: - AA-EQS (annual average) for inland and other surface waters: 2 µg/l - MAC-EQS (maximum allowable concentration) for inland and other surface waters: 130 µg/l http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:02008L0105-20130913&qid=1401540113061&from=EN http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32013L0039&from=EN http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:02000L0060-20140101&qid=1401539851953
STATUTORY ORDER No. 1022 of 25.8.2010 concerning environmental quality standards for water areas and requirements for discharge of pollutants to streams, lakes or the ocean	DK	Naphthalene is listed as entry no. 22 in Annex B "List of prioritised substances within the EU water policy". Naphthalene is listed with a general EQS (environmental quality standard) of 2.4 µg/l for freshwater and 1.2 µg/l for marine waters. https://www.retsinformation.dk/Forms/R0710.aspx?id=132956
STATUTORY ORDER No. 292 of 26.3.2014 concerning water quality and supervision on water supply plants		In this statutory order the quality criteria is listed for drinking water in Denmark. Naphthalene is listed with the following water quality criteria: - Limit value at departure from waterworks: 2 µg/l - Limit value at entrance to property: 2 µg/l - Limit value in drain cock at consumer: 2 µg/l

Legal instrument	EU/DK	Requirements which concern naphthalene
		It is stated that naphthalene is an indicator for the presence of oil and gasoline products as well as tar products. https://www.retsinformation.dk/forms/R0710.aspx?id=160400
GUIDANCE No. 9696 of 1.11.2010 on reporting and approval of water supply data	DK	In this statutory order naphthalene is listed in Annex 1c with the code 0649 which is to be used when performing the mandatory reporting on water quality. https://www.retsinformation.dk/forms/R0710.aspx?id=134415
REGULATION No. 166/2006 of 18 January 2006 concerning the establishment of an European Pollutant Release and Transfer Register amending Council Directives 91/689/EEC and 91/61/EC DECISION of 2 December 2005 on the conclusion, on behalf of the European Community, of the UN-ECE Protocol on Pollutant Release and Transfer Registers STATUTORY ORDER No. 210 of 3.3.2010 concerning certain companies' submission of environmental information	EU/DK	This regulation establishes an integrated pollutant release and transfer register at EU level (the European PRTR or E-PRTR), which is a publicly available accessible database. The European PRTR includes information on releases of pollutants by operators as well as releases of pollutants from diffuse sources where available. Activities listed in Annex I (e.g. energy sector, chemical industry etc.) with releases to air, water and land of any of the pollutants specified in Annex II above the applicable threshold values specified in Annex II must be reported to the authorities. Pollutants are defined as substances listen in Annex II. Naphthalene is listed as entry no. 68 in Annex II. However, pollutants are only to be registered if above the given capacity thresholds as listed in Annex II. The capacity thresholds listed for naphthalene are: - Threshold for release to air: 100 kg/year - Threshold for release to water: 10 kg/year - Threshold for release to land: 10 kg/year - Threshold for off-site transfer of pollutants: 100 kg/year - Manufacture, process or use threshold: 10,000 kg/year http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:02006R0166-20090807&qid=1401555335531&from=EN http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=OJ:JOL_2006_032_R_0054_01&from=EN https://www.retsinformation.dk/forms/R0710.aspx?id=128761

Legal instrument	EU/DK	Requirements which concern naphthalene
GUIDANCE no. 10702 of 19.11.2008 on B values (B-værdier) GUIDANCE no. 2, 2001 from the Danish EPA – Guidance on air (“Luftvejledningen”)	DK	Naphthalene is listed with a B value (contribution value) of 0.04 mg/m^3. The B value is low because it is based more on odour than toxicological aspects. The B-value is the permitted contribution to the outdoor concentration of the compound outside the company boundary, calculated by the OML computer model based on the measured total emission from the company. Naphthalene is listed as main group 2, table 7, and class II. A special background document has been made for the substance in 1992. https://www.retsinformation.dk/Forms/R0710.aspx?id=135894 http://www2.mst.dk/udgiv/publikationer/2001/87-7944-625-6/pdf/87-7944-625-6.pdf
CONSOLIDATED ACT No. 879 of 26.6.210 on environmental protection	EU/DK	The above guidance document concerning B values is based on the Danish consolidated act concerning environmental protection, which is based on several EU directives. https://www.retsinformation.dk/Forms/R0710.aspx?id=132218
GUIDANCE No. 9810 of 31.5.2006 on connection of industrial discharge water to public sewage treatment plants	DK	Naphthalene is rated as a C* substance, i.e. a category C substance which has only been assessed according to the ecotoxic properties. Naphthalene is listed as a substance especially selected by the EU. The water quality requirement for naphthalene is 1 µg/l according to Table 1.1 of Annex 1. https://www.retsinformation.dk/forms/R0710.aspx?id=12944
CONSOLIDATED ACT No. 879 of 26.6.210 on environmental protection	EU/DK	The above guidance document concerning industrial discharge water is based on the Danish consolidated act concerning environmental protection which is based on several EU directives. https://www.retsinformation.dk/Forms/R0710.aspx?id=132218
STATUTORY ORDER No. 8 of 29.5.2008 of annex to protocol of 2 November 1973 concerning remedial action on the open sea at pollution of the sea of other substances than oil	DK	Naphthalene is listed in Appendix 2 of this Danish Statutory order. This means that naphthalene is considered as a harmful substance that will pollute the sea and the environment if accidents should happen at sea. Spillage of naphthalene at sea therefore results in remedial actions to be taken. https://www.retsinformation.dk/Forms/R0710.aspx?id=114936

Legal instrument	EU/DK	Requirements which concern naphthalene
DIRECTIVE 2010/75/EU of 24 November 2010 on industrial emissions (integrated pollution prevention and control)	EU	The industrial emissions directive (IED) is unifying seven existing directives on the area of environmental pollution. Companies which manufacture or emit a range of specific hazardous substances have to apply for an environmental permit and have to report on their emissions to air, water and soil.
LAW No. 446 of 23.5.2012 on changes of law on environmental protection (implementing the EU Directive on industrial emissions)	DK	One company in Denmark manufactures naphthalene. Furthermore, the directive may be relevant for emissions of naphthalene to air as VOCs are listed in Annex II "List of polluting substances" of the directive for air. http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2010:334:0017:0119:en:PDF https://www.retsinformation.dk/forms/R0710.aspx?id=141738
Regulation addressing emissions to the working environment		
DIRECTIVE 91/322/EEC of 29 May 1991 on establishing indicative limit values by implementing Council Directive 80/1107/EEC on the protection of workers from the risks related to exposure to chemical, physical and biological agents at work DIRECTIVE 2000/39/EC of 8 June 2000 establishing a first list of indicative occupational exposure limit values in implementing Directive 98/24/EC on the protection of the health and safety of workers from the risks related to chemical agents at work	EU	The threshold limit value for naphthalene in the working environment in Denmark and the EU is 10 ppm or 50 mg/m^3. Naphthalene is marked with E and K which means that the substance has an EU threshold limit (E) and that the substance is regarded as being carcinogenic (K). http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:01991L0322-20060301&qid=1400838425354&from=EN
STATUTORY ORDER no. 507 of 17.5.2011 on threshold limit values for substances and materials - and subsequent changes (e.g. 986 of 11.10.2012)	DK	Same as above. https://www.retsinformation.dk/Forms/R0710.aspx?id=143596 https://www.retsinformation.dk/Forms/R0710.aspx?id=136417

Legal instrument	**EU/DK**	**Requirements which concern naphthalene**
DIRECTIVE 2004/37/EC of 29 April 2004 on the protection of workers from the risks related to exposure to carcinogens or mutagens at work DIRECTIVE 98/24/EC of 7 April 1998 on the protection of the health and safety of workers from the risks related to chemical agents at work STATUTORY ORDER no. 908 of 27.9.2005 on measures to prevent the risk of cancer when working with substances and materials - and subsequent changes (e.g. 1175 of 11.10.2007)	EU DK	Because of the carcinogenic properties of naphthalene, the substance is covered by this Danish statutory order if the concentration of naphthalene in chemical preparations is 0.1% or higher (and for some applications in concentrations of 10% or higher). Special provisions are valid for naphthalene when it comes to laboratory work (§17), industrial use (§17), and other applications such as paint, lacquers, impregnating agents, glue, fillers, lubricants etc. (§29-32). §17 states that for these working processes (i.e. laboratory work and industrial use) naphthalene may only be used in closed processes or if no release of the substance occurs. If this is not possible the substance shall not be used, and if this is not possible suitable personal protection equipment should be used. §29-32 state that for these other applications/uses an authorisation must be granted from the Danish Working Environment Authority before work with naphthalene is allowed. https://www.retsinformation.dk/Forms/R0710.aspx?id=30283 https://www.retsinformation.dk/Forms/R0710.aspx?id=31334
STATUTORY ORDER no. 1246 of 11.12.2009 on announcement from The Danish Maritime Authority concerning working environment on ships	DK	According to this Danish Statutory order (Annex 1, section A), it is not allowed to use chemical preparations with a content of naphthalene of above 0.1-10% on ships. https://www.retsinformation.dk/Forms/R0710.aspx?id=129083
Regulation addressing transportation of chemicals		
DIRECTIVE 2008/68/EC of 24 September 2008 on the inland transport of dangerous goods STATUTORY ORDER no. 788 of 27.6.2013 on road transport of dangerous goods	EU DK	Naphthalene is listed with UN no. 1334, Hazard Class 6.1 in the Annex of this Danish Statutory order. This means that naphthalene is covered by the rules concerning transportation of dangerous goods and should be labelled and handled accordingly. The UN no. should be used during transportation. https://www.retsinformation.dk/Forms/R0710.aspx?id=152738

TABLE 4
EU AND DANISH LEGISLATION ADDRESSING NAPHTHALENE (AS OF MAY 2014)

2.1.2 Upcoming legislation

A search has been performed in the EUR-Lex database concerning preparatory documents regarding naphthalene. No upcoming legislation regarding naphthalene was identified.

2.1.3 Classification and labelling

2.1.3.1 Harmonised classification in the EU

The EU harmonised classification of naphthalene is presented in Table 5 below. It shows that naphthalene is classified as carcinogenic (Carc. 2, H351 “Suspected of causing cancer”), acutely toxic (H302 “Harmful if swallowed”) and very toxic to aquatic life (Aquatic Acute 1, H400 “Very toxic to aquatic life” and Aquatic Chronic 1, H410 “Very toxic to aquatic life with long lasting effects).

Index No	International chemical identification	CAS No	Classification	
			Hazard Class and Category Codes	Hazard Statement Codes
601-052-00-2	naphthalene	91-20-3	Acute Tox. 4 Carc. 2 Aquatic Acute 1 Aquatic Chronic 1	H302 H351 H400 H410

H302: Harmful if swallowed, H351: Suspected of causing cancer, H400: Very toxic to aquatic life, H410: Very toxic to aquatic life with long lasting effects

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

2.1.3.2 Self-classification in the EU

According to the current CLP regulation, companies which place chemical substances or chemical mixtures on the market in the EU are obliged to notify the classification (they apply for) to the European Chemicals Agency, ECHA. The classifications used (and notified) by the companies can be seen at the ECHA website in the Classification & Labelling (C&L) Inventory database. ECHA maintains the Inventory, but does not verify the accuracy of the information. The notified classifications for naphthalene can be found in Appendix 3.

The most important information derived from the notifications is the fact that the majority of the companies (1017 out of 1665) used the harmonised classification, while the majority of the remaining companies used notifications very similar to the harmonised classification but with additional classification as Flam. Sol. 2 (H228: Flammable solid). Only a few companies have notified other/additional effects, such as STOT RE 1 (H373: May cause damage to organs through prolonged or repeated exposure), Skin Irrit. 2 (H315: Causes skin irritation), Asp. Tox. 1 (H304: May be fatal if swallowed and enters airways) or Acute Tox. 2 (H330: Fatal if inhaled).

2.1.4 REACH

2.1.4.1 Registration

Naphthalene has been registered under REACH in a tonnage band of 100,000 – 1,000,000 tonnes per annum (as of May 2014).

2.1.4.2 Candidate list

Naphthalene is not listed on the ECHA Candidate list of substances of very high concern (SVHC) for authorisation (as of May 2014).

2.1.4.3 Authorisation list / REACH Annex XIV

Naphthalene is not listed on the ECHA Authorisation list (as of May 2014).

2.1.4.4 Restrictions concerning certain dangerous substances – Annex XVII

Naphthalene is not restricted in Annex XVII of REACH which contains restrictions on the manufacture, placing on the market and the use of certain dangerous substances, mixtures and articles.

2.1.4.5 Community rolling action plan (CoRAP)

The Community Rolling Action Plan is a list of substances to be evaluated by the Member States during the next three years. Naphthalene is on the CoRAP list of substances[26] and was entered on the list in 2014 for evaluation by Germany in 2016, i.e. the evaluation has not started yet (CoRAP, 2014). The initial grounds for concern for naphthalene are listed as:

- Exposure – exposure of workers
- Exposure – high RCR (risk characterisation ratio)
- Exposure – high aggregate tonnage

2.1.4.6 Registry of intentions

Naphthalene is not on any of ECHA's Registry of intentions (i.e. SVHC intentions, Harmonised Classification and Labelling intentions or Restriction proposal intentions) as of May 2014.

2.1.5 Other legislation/initiatives

No other legislation/initiatives have been identified for naphthalene.

2.2 International agreements

A search for international agreements concerning naphthalene was performed. The following international agreements concerning naphthalene (directly or indirectly) were found.

2.2.1 Basel Convention

Protection of human health and the environment against the adverse effects of hazardous waste is covered by the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal. Details on the Basel Convention can be found in Appendix 2: "Background information on regulation" to this report. Naphthalene is not directly mentioned in the Basel Convention, but is covered by Annex III of the Convention text: "Annex III – List of hazardous characteristics". In Annex III wastes which have "ecotoxic" characteristics (as naphthalene), are according to the convention text regarded as being hazardous waste if the waste is generated from special production (listed in Annex I) or if the waste is considered to be hazardous waste by national legislation. Waste containing naphthalene is thereby covered by the Basel Convention.

2.2.2 International Conventions regarding safety and pollution at sea

The International Convention for the Safety of Life at Sea, 1974 (SOLAS), as amended, deals with various aspects of maritime safety and contains the mandatory provisions governing the carriage of dangerous goods in packaged form or in solid form in bulk. The carriage of dangerous goods is prohibited except in accordance with the relevant provisions of chapter VII which are amplified by the International Maritime Dangerous Goods (IMDG) Code.

The International Convention for the Prevention of Pollution from Ships, 1973, as modified by the Protocol of 1978 (MARPOL), deals with various aspects of prevention of marine pollution and contains in its Annex III the mandatory provisions for the prevention of pollution by harmful

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[26] http://echa.europa.eu/information-on-chemicals/evaluation/community-rolling-action-plan/corap-table

substances carried by sea in packaged form. Regulation 1(2) prohibits the carriage of harmful substances in ships except in accordance with the provisions of Annex III which are also amplified by the IMDG Code.

The IMDG Code lists naphthalene with the UN No. 1334, transportation class 4.1 (i.e. flammable solids) and lists the special provisions, packaging instructions, proper shipping name etc. for naphthalene (IMDG Code, 2012).

2.3 Ecolabels

Naphthalene is not mentioned directly in any Eco labelling criteria (the Nordic Swan, the European Flower or the Blue Angel). However, as naphthalene is classified as being carcinogenic (Carc. 2), naphthalene will in many cases automatically be restricted in Eco labelling products as no carcinogenic substances in general are allowed in ecolabelled products. Furthermore, naphthalene is classified as very toxic to aquatic life (Aquatic Acute 1 and Aquatic Chronic 1) and in many cases it will also automatically be restricted in Eco labelling products because of this classification.

2.4 Other lists

Naphthalene is found in the *SIN List Database developed by the International Chemicals Secretariat (ChemSec)*[27] in Sweden (data search May, 2014). The SIN List includes substances which are identified by ChemSec as fulfilling the criteria for Substances of Very High Concern (SVHC) as defined by the REACH Regulation. Naphthalene was included in the first SIN List (1.0) in September 2008 due to its classification as possible carcinogen and as very toxic to aquatic organisms.

Naphthalene is also included in the *PRIO database*[28] *developed by KEMI (the Swedish Chemical Agency)*. The PRIO database is a web-based tool which contains 4,658 substances (May 2014) with properties hazardous to health and the environment that should be prioritised in risk reduction work. Naphthalene is included in the PRIO database due to the fact that it is environmentally hazardous with long term effects and is listed as a "priority risk reduction substance" which means that the user of the substance is recommended to review the risk of the envisaged use. "I.e. manufacturers, importers, suppliers and users of chemical products and other articles should conduct a risk assessment to aid identification of necessary risk reduction measures and to ensure that the substance does not pose unacceptable risks at any stage of handling".

Naphthalene is not included in the EU list of 194 potential endocrine disruptors (Danish EPA, 2014).

2.5 Summary and conclusions

Naphthalene has a harmonised classification of

- Acute Tox. 4, H302 (Harmful if swallowed)
- Carc. 2, H351 (Suspected of causing cancer)
- Aquatic Acute 1, H400 (Very toxic to aquatic life)
- Aquatic Chronic 1, H410 (Very toxic to aquatic life with long lasting effects)

As a consequence of the carcinogenic properties of naphthalene, the substance is prohibited for use in cosmetic products. Furthermore, the use of naphthalene in mothballs is no longer supported.

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[27] http://www.chemsec.org/what-we-do/sin-list
[28] http://www2.kemi.se/templates/PRIOEngframes____4144.aspx

A threshold limit value of 10 ppm or 50 mg/m^3 is set for the working environment regarding naphthalene in the EU (and Denmark)[29]. A limit value of 0.04 mg/m^3 for concentrations of naphthalene in the air, measured at the property line of the companies, has been set for companies in Denmark[30]. A water quality criterion of 2 µg/l has been set as a limit value for naphthalene in water from waterworks and in the drain cock water at consumers in Denmark[31]. The environmental quality standard (EQS) for naphthalene for freshwater is 2.4 µg/l and 1.2 µg/l for marine waters.

As a hazardous substance, naphthalene is subject to specific regulation regarding transportation of dangerous goods[32].

Naphthalene has been registered under REACH in a tonnage band of 100,000 – 1,000,000 tonnes per annum (as of May 2014), but it is neither on the Candidate list of substances of very high concern nor on any of ECHA's Registry of intentions. Naphthalene is on the CoRAP list of substances[33] and was entered on the list in 2014 for evaluation by Germany in 2016, i.e. the evaluation has not started yet (CoRAP, 2014). The initial grounds for concern for naphthalene are listed as:

- Exposure – exposure of workers
- Exposure – high RCR (risk characterisation ratio)
- Exposure – high aggregate tonnage

The Swedish Chemicals Agency has included naphthalene in their PRIO database as a "priority risk reduction substance", which means that the user of the substance is recommended to review the risk of the envisaged use. Furthermore, naphthalene is found in the SIN List Database developed by ChemSec due to its classification as possible carcinogen and very toxic to the aquatic environment. This means that naphthalene fulfils the SVHC criteria as defined by the REACH Regulation.

Naphthalene is not mentioned directly in any Eco labelling criteria, but will automatically be restricted in any Eco labelling scheme as no chemicals classified as dangerous for the environment or as carcinogenic in general are allowed in eco-labelled products.

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[29] Directive 91/322/EEC and Danish Statutory Order No. 507 of 17.5.2011
[30] Danish Guidance No. 10702 of 19.11.2008
[31] Danish Statutory Order No. 1022 of 25.8.2010
[32] Directive 2008/68/EC
[33] http://echa.europa.eu/information-on-chemicals/evaluation/community-rolling-action-plan/corap-table

3. Manufacture and uses

An overview of the manufacturing routes of naphthalene including the most widely applied world-wide and in Denmark is presented next. Also, a description of the imports and exports of naphthalene and its major applications is presented, including historical trends. Finally, an overview of the unintended presence of naphthalene in a range of industrial and consumer products is also provided.

Information from a wide range of literature sources, including scientific reports and articles, databases and commercial reports was used to elaborate this chapter. In Denmark, information from the only producer of naphthalene was also included. The information is provided in four sections, starting with the manufacturing, imports and exports, use and historical trends of naphthalene.

3.1 Manufacturing

There are two production routes for the manufacture of naphthalene (ECB, 2003; Preuss et al., 2003):

- **From coal tar**, which usually comes in various fractions containing different contents of naphthalene. Coal tar is produced from coke oven gases by condensation and separation; once the coal tar fractions are available, they are distilled and crystallised to produce naphthalene of different purities. This route accounts for the majority of the production in the European Union and world-wide.
- **From petroleum** which also presents various naphthalene-containing fractions, including the by-product of cracking processes (as methylnaphthalene). The production of naphthalene from this source occurs as recovery of naphthalene.

According to IHS Chemical (2013), over 92% of the naphthalene production of the world in 2012 was produced from coal tar. Koppers Denmark ApS, the only Danish naphthalene producer, produces naphthalene from coal tar. Petroleum naphthalene capacity is concentrated in China, the United States and Western Europe.

3.1.1 Manufacturing process

From coal tar

The first step is to produce coal tar from coke oven gases by condensation and separation, with a yield of 38 l tar/tonne coal. Naphthalene is then produced from coal tar by distillation and for higher purity also crystallisation, with an overall yield of 4.8 kg crude naphthalene/l tar (ECB, 2003).

The **distillation** occurs from different tar fractions after it has been dried (see Image 3), and the produced **crude naphthalene** can either be used directly for some applications (e.g. manufacture of phthalic anhydride) or **processed/distilled further** to produce **purer grades** of **naphthalene** (this next distillation step is not illustrated in Image 3).

The middle fraction of crude naphthalene (naphthalene oil) is the most abundant source of naphthalene, containing about 70% available. After distillation this fraction is further processed in several ways, depending on the final application and its demand for purity in the final product (ECB, 2003):

- **Additional distillation** to produce a crude grade with a crystallisation point of 74°C to 78°C: suitable for applications such as the manufacture of phthalic anhydride.

- **Treating** the naphthalene oil **with sulphuric acid** followed by **neutralisation and re-distillation**, to give a product with a crystallising point of over 79°C.

- **Crystallisation** of the naphthalene oil in shallow pans to produce a pure grade that does not contain thionaphthalene and other impurities: suitable for applications such as insecticides and mothballs.

Drained oils remaining from these purification processes may be blended for use in creosote oils or if not suitable they can be used in the manufacture of carbon black.

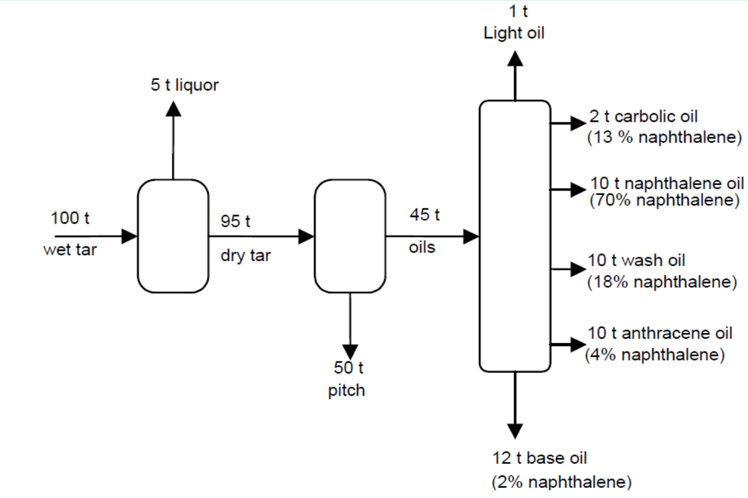

IMAGE 3
MASS BALANCE AND SCHEMATIC REPRESENTATION OF CRUDE NAPHTHALENE DISTILLATION (FROM ECB, 2003).

According to ECB (2003) and as shown in Image 3, various other distilled fractions are also produced from crude naphthalene production. Apart from liquor and pitch, all the other fractions contain naphthalene and an additional tar residue with 10% naphthalene content is as well produced from distillation.

These oil fractions are further processed to separate commercially viable chemicals, such as primarily creosote oil or carbon black feedstock or to a smaller extent to anthracene from anthracene oil. Alternatively they are used in blends, for example in base oil, which previously has been used for road tar production. However, this is no longer allowed in the EU.

Drained oils remaining from the further processing of these distilled fractions are then blended to produce creosote, which may contain up to 25% naphthalene according to ECB (2003). However, according to Koppers Denmark ApS the usual content of naphthalene in creosote is around 5%[34]. Any remaining oils containing about 4% naphthalene may be sold for the manufacture of carbon black. Furthermore, some producers may supply heating oil containing up to 10% naphthalene (ECB, 2003).

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[34] Personal communication with Koppers Denmark ApS in June 2014.

Danish naphthalene production

Koppers Denmark ApS is the only Danish producer of naphthalene. They produce naphthalene from coal tar, as most other naphthalene producers. Their production process is specified in the figure below, consisting of two steps:

1. Distillation from coal tar – this step produces:
    - Naphthalene oil
    - Creosote oil
    - Carbon Black Feed stock / Antracene oil high
    - Water
    - Pitch
2. Distillation of naphthalene oil – this step produces:
    - Naphthalene
    - Naphthalene still residue / Wash oil
    - Solvent / light oil

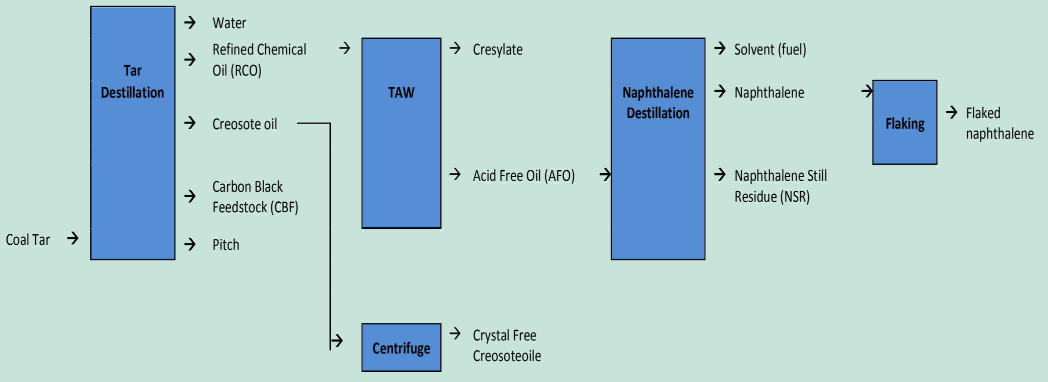

IMAGE 4
PRODUCTION PROCESS FOR NAPHTHALENE CARRIED OUT AT KOPPERS DENMARK APS (SOURCE: KOPPERS DENMARK APS)

Koppers Denmark ApS produces naphthalene oil themselves by distillation of coal tar, but they also import naphthalene oil from other EU countries. The total amount of naphthalene oil is distilled (step 2 above) to produce naphthalene. The naphthalene produced is 95-97% pure naphthalene.

From petroleum

Production of naphthalene from petroleum is less common in the European Union, and there was only one producer who uses this manufacturing process that was identified by the time the ECB conducted an investigation (ECB, 2003). No information about the practice of this manufacturer was possible to collect as its identity was not disclosed in the abovementioned reference. But according to a literature study presented therein, the production from petroleum comprehends three principal steps:

1. **Hydroaromatisation** or **cyclisation** of petroleum fractions high in methylnaphthalenes to aromatic oil, by boiling the petroleum in the naphthalene/alkylnaphthalene range.

2. **Dealkylation** of the produced aromatic oil either thermally or catalytically, and carried out at high temperature and pressure and in the presence of hydrogen.

3. **Fractional distillation and crystallisation**, recovering naphthalene as high quality product (99% pure and low in sulphur).

Naphthalene is also recovered from the stream of methylnaphthalenes formed in cracking of heavy liquids (naphthas and gas oils) for ethylene production (ECB, 2003; Preuss et al., 2003).

3.1.2 Manufacturing sites

World-wide

According to Guidechem (2014), there are about 103 suppliers of naphthalene around the world registered in their database: 55% from China, 16% from India, 12% from the USA, 4% from Japan, 2% from Germany, 2% from South Korea, 1% from Taiwan, 1% from the United Arab Emirates, 1% from Pakistan, 1% from Spain and 5% from other countries. This indicates that the trading of naphthalene is quite diversified amongst different countries, although the majority of the suppliers are located in China. Furthermore, the top suppliers registered (i.e. those selling the largest volumes) are also Chinese.

According to IHS Chemical (2013), China has nearly half of the world naphthalene capacity and output. However, China's naphthalene industry consists of medium-sized to small production plants that are not very well interlinked with each other so available coal tar feed stocks are not easily supplied resulting in less-than-optimal operating rates.

From an additional literature source (Environment Canada, 2008a), Canada also stands as manufacturer despite it is not mentioned in the suppliers' list provided by Guidechem (2014). Canada reported 13 manufacturers and 18 importers of naphthalene with about the half of the manufacturing volume registered compared to that registered by the USA. By not being listed as a supplier in Guidechem (2014), it may indicate that Canadian manufacturers do not trade their products themselves, or simply that it does not trade much with other countries under this trading service (Guidechem, 2014).

As earlier described, over 92% of the world naphthalene production in 2012 was produced from coal tar. Petroleum naphthalene capacity is concentrated in China, the United States and Western Europe (IHS Chemical, 2013).

The European Union (EU)

According to ECHA's website (ECHA RSD, 2014)[35], the following twelve companies have registered naphthalene under REACH and thereby they are either producers or importers of naphthalene:

- LUYTEN SA, in Belgium
- RÜTGERS Belgium N.V., in Belgium
- DEZA a.s., in Czech Republic
- Unipetrol RPA, in Czech Republic
- NAM & NAM Europe GmbH, in Germany
- RÜTGERS Basic Aromatics GmbH, in Germany
- BILBAINA DE ALQUITRANES, S.A., in Spain
- Industrial Quimica del Nalon, S.A. , in Spain
- Koppers Denmark ApS , in Denmark
- Metinvest International Italia Srl, in Italy
- Koppers Netherlands B.V., in the Netherlands[36] (production of naphthalene has ceased)
- Allied Carbon Trading Ltd., in the UK

According to Guidechem (2014), five additional suppliers of naphthalene trade in the EU, compared to the abovementioned ECHA list:

- Campro Scientific GmbH, in Germany

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[35] http://echa.europa.eu/en/information-on-chemicals/registered-substances

[36] Production has ceased as of 1. April 2014. Personal communication with Koppers Denmark ApS in June 2014

- Eastern Chemicals S.A., in Spain
- Cindu Chemicals BV, in the Netherlands
- Fisher Scientific, in the UK
- CDF Chimie-Societe Chimique des Charbonnages, in France

However, these suppliers may only be traders and therefore simply receive the chemical product from one of the manufacturing/importing sites mentioned in ECHA RSD (2014). Another reason for them not to be included in the ECHA list is that their trading volume may be lower than the minimum required for registration (i.e. 1 tonne/year). However, according to the ECB (2003), manufacturers in France and Austria (amongst others) were also found at the time of the study. This indicates that all companies are neither registered in ECHA (due to their low import and/or production) nor that these companies registered in 2003 do not operate any longer.

In the EU, the ECB (2003) found from their survey only one company which produced naphthalene from both coal tar and petroleum, whilst the rest produced it only from coal tar.

Denmark and the Nordic countries
According to the list of manufacturers mentioned (ECHA RSD, 2014), Koppers Denmark ApS is the only manufacturer of naphthalene in the Nordic countries. Schleicher et al. (2009) did an investigation of the application, production and emissions of naphthalene in Denmark, and found that Koppers Denmark A/S produced naphthalene from imported oil containing 60 to 100% of naphthalene. Also today (2014) Koppers Denmark ApS imports naphthalene oil (see Image 2) which they use to produce purer grades of naphthalene by additional distillation (see section 3.1.1 for further explanation about this process). Koppers Denmark ApS informs that their entire production of naphthalene is exported – most of the production is exported to countries outside the EU. Koppers Denmark ApS informs that their produced naphthalene is used for the applications listed in section 3.3 ”Use”, but primarily for use as intermediate in other production processes.

3.1.3 Manufacturing volumes

World-wide
Only manufacturing volumes data for the USA and Canada were found, apart from those from the EU (Environment Canada, 2008a; Preuss et al., 2003; NTP, 2000). The latest data for the US production is from 2001 which is 115,000 tonnes/year. The US production experienced a peak in the late 60s (409,000 tonnes/year), finding its bottom point around 1996 with 109,000 tonnes/year and slowly increasing by the early 2000s. On the other hand, Canada reports the latest manufacturing volume in 2006 with 52,000 tonnes/year. It is suspected that the decrease in production in the US is due to the shift of production in other areas of the world (first Western Europe and later on China and India amongst others), and the diversification of intermediates used to produce industrial chemicals which previously came from fewer sources like naphthalene. China has nearly half of the world naphthalene capacity and output today (2012) (IHS Chemical, 2013).

As naphthalene is mainly produced from coal tar the distilled volumes of coal tar have been investigated as well. According to Rütgers Chemicals (a Canadian player on the market), the amount of coal tar distilled in North American has declined from around 1,150,000 million tonnes in 2000 to around 800,000 million tonnes in 2003 to 2007. However, according to Rütgers Chemicals new coal tar players are on the market; these are situated in China, Russia and Brazil (Rütgers Chemicals, 2008).

The European Union (EU)
According to ECHA Registered Substance Database (2014), a tonnage band of 100,000 – 1,000,000 tonnes/year is registered for naphthalene in the European Union, which are imported from abroad or produced in the EU. No up-to-date specific information publicly available that gives a better

indication of its current use could be found. However, there are indications that the production of naphthalene in the EU in 2009/2010 is much closer to the low end of the tonnage band (100,000 tonnes) than to the high end of the tonnage band.

According to the ECB (2003), the total EU annual production known by 2003 was between 199,000 to 204,000 tonnes/year. This includes both the production of crude naphthalene (i.e. naphthalene oil) and pure naphthalene. Naphthalene at lower grades, i.e. <=60%, has a separate CAS number and was therefore not quantified in the study. Furthermore, naphthalene present in distillates used for the production of creosote (about 10,000 tonnes/year) and naphthalene present as constituent of oil used for carbon black manufacture and heating oils (volume not established) was not included either. Individual production figures for manufacturers in the EU ranged from 4,000 to 70,000 tonnes/year in 2003.

Denmark
Production volume from Koppers Denmark ApS was 21,500 tonnes in 2006 which was about 10% of the total produced in the EU in 2003 (Schleicher et al., 2009). As mentioned previously, this was pure naphthalene at unknown grades which used about 14,500 tonnes of naphthalene oil and all production was exported (Schleicher et al., 2009). Current information from Koppers Denmark ApS[37] (2013) states that their annual capacity and production of naphthalene is 30,000 tonnes, which makes about 15% of the total annual EU production in 2003.

Koppers Denmark ApS imports each year around 150,000 – 170,000 tonnes coal tar containing around 10-15% naphthalene. This coal tar is used in the production of naphthalene - distillation of coal tar to produce pure naphthalene, which is described in Image 4.

3.2 Import and export

According to Regulation No. 927/2012 concerning statistical nomenclature and the common customs tariff, naphthalene does not have a specific CN code (combined nomenclature), but is grouped together with anthracene under the CN code 29029010 "*Naphthalene and anthracene*". However, this CN code was only effective until 2008 – from 2009 and until today "naphthalene and anthracene" has been merged into one large CN code 29029000 named "Other cyclic hydrocarbons excluding cyclanes, cyclenes, benzene, toluene, xylenes, styrene, ethylbenzene and cumene". Actually the following former CN codes have been merged together into the overall CN code 29029000:

- 29029010 – Naphthalene and anthracene
- 29029030 – Biphenyls and terphenyls
- 29029050 – Vinyltoluenes
- 29020960 – 1,3-Diisopropylbenzene
- 29029080 – Cyclic hydrocarbons (excluding cyclane, cyclenes, benzene, toluene, xylenes, styrene, ethylbenzene, cumene, naphthalene, anthracene, biphenyl, terphenyls, vinyltoluenes and 1,3-diisopropylbenzene
- 29029090 – Cyclic hydrocarbons (excluding cyclane, cyclenes, benzene, toluene, xylenes, styrene, ethylbenzene, cumene, naphthalene, anthracene, biphenyl and terphenyls

As there is no specific CN code for naphthalene (only an overall CN code covering other cyclic hydrocarbons), no import and export statistics can be elaborated as they will not provide a realistic picture of the import and export of naphthalene in Denmark or the EU. However, an indication of the import into Denmark can be established from the SPIN database (see next section), and an indication of the import/export/use of naphthalene is given in section 3.2.2 based on literature sources from 2003 at latest.

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[37] Personal communication with Koppers Denmark ApS in June 2014

3.2.1 Import and export of naphthalene in Denmark

A data retrieve from the SPIN database (Substances in Preparations in Nordic countries) demonstrates that the use of naphthalene in chemical preparations in Denmark has steadily increased since 2000. Due to the fact that the only producer in the country is Koppers Danmark ApS, and knowing that all their production is exported, it can be concluded that all the use of naphthalene in Denmark is imported. See an overview in Image 5.

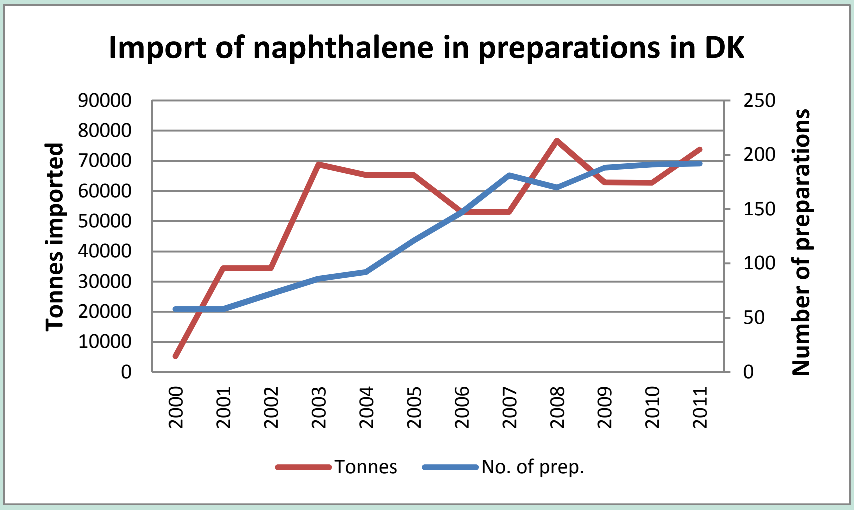

IMAGE 5
IMPORT OF NAPHTHALENE IN CHEMICAL PREPARATIONS IN DENMARK FROM 2000 TO 2011

According to Image 5, the imported amount of naphthalene in preparations (including coal tar) has steadily increased by the same rate as the number of preparations imported, reaching the highest peak in tonnes in 2008 (76,591.7), and in number of preparations in 2011 (192). Although the number of preparations was lower in 2003 (86), the annual tonnage was one of the highest since 2000 until 2008 (68,786.3). Afterwards it was observed a steady decrease until 2007, even though the number of preparations continued to increase.

More details on the use/import pattern can be found in Appendix 4, including the uses for each of the years registered. Generally, it can be said that the number of preparations does not correlate to the annual tonnage in early stages (from 2003 to 2005), but from 2005 the use of naphthalene appears to have increased by tonnage corresponding to a more diversified use (see Appendix 4).

3.2.2 Import and export of naphthalene in the EU

According to the ECB (2003), the demand of naphthalene in the EU by then did not exceed 127,000 tonnes/year. Due to a higher production volume (between 199,000 and 204,000 tonnes/year – see section 3.1.3) and up to a 25% higher export, it was estimated that only small amounts were imported. The study thus determines that by 2003 about 140,000 to 150,000 tonnes/year were used within the EU borders. From this, it is also possible to conclude that about 50,000 tonnes/year were exported from the EU.

3.3 Use

The world consumption of naphthalene is shown in Image 6, showing China as the largest consumer of naphthalene in the world (in 2012). According to Rütgers Chemicals (2008), the North American consumption of naphthalene has declined from around 110,000 tonnes in the year 2000 to around 89,000 tonnes in 2007. Rütgers Chemicals expect a continued decline in the North American consumption of naphthalene. On the other hand, the European consumption of naphthalene has been rather constant from a consumption of around 180,000 tonnes in 2000 to around 195,000 tonnes in 2004 to around 175,000 tonnes in 2007 (Rütgers Chemical, 2008).

Naphthalene is a chemical of many uses as previously discussed, and its many different applications are related to the technical grade (i.e. how pure it is). In this study the focus is on the grades higher than 60% as these grades refer to the CAS number evaluated.

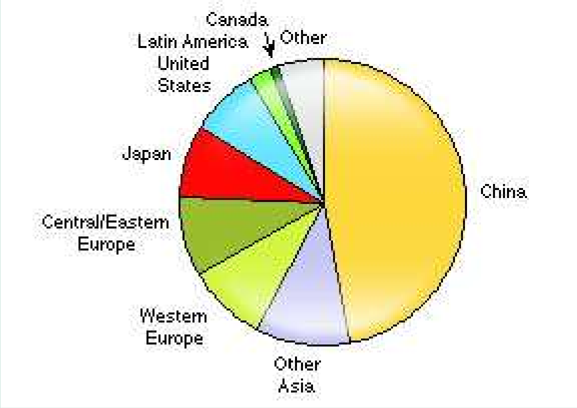

IMAGE 6
WORLD CONSUMPTION OF NAPHTHALENE 2012 (SOURCE: IHS CHEMICALS, 2013)

According to several references (SPIN database, 2014; ECHA RSD, 2014; Chemical Book, 2014; Won et al., 2012; European Commission, 2010; ECB, 2003; US EPA, 1998), the main applications of naphthalene are:

- **As final product:**
    - Manufacture of mothballs as moth repellent and of other fumigants
    - Manufacture of theatrical pyrotechnics, either together with other components or only itself used in an explosive container
    - Manufacture of grinding wheels, as an artificial pore former
    - Used as deodorizer for diaper pails and toilets
    - Used as ancillary material (as high purified reagent) in industry (e.g. abrasive) and laboratories

- **As an intermediate:**
    - Manufacture of phthalic anhydride, which is used for the production of phthalate plasticizers, resins, dyes and insect repellents
    - Manufacture of naphthalene sulphonic acids, which is for the production of plasticisers for concrete, sulfonates and dispersants in synthetic and natural rubbers and in tanning agents for the leather industry
    - Manufacture of azo dyes (i.e. dyestuffs) intermediates, such as 2-naphthol
    - Manufacture of alkylated naphthalene solvents
    - Other uses for the manufacturing of miscellaneous products, from various chemicals to pharmaceuticals
    - Manufacture of insecticides (e.g. Carbaryl & Sevin)

According to Rütgers Chemicals (2008), the major markets in Europe (in 2007) are the following:

- Naphthalene sulphonates – 47%
- Phthalic anhydride – 40%
- Other – 7%
- Pesticides – 6%

However, as the use of naphthalene as pesticide has ceased within Europe from around 2008 the above picture will be somewhat different today.

The ECB (2003) and Preuss et al. (2003) provide more details about the most important usages of naphthalene in the EU in terms of volumes and locations. In the next paragraphs a summary is provided.

Manufacture of mothballs and other fumigants

Naphthalene was used vastly for the manufacture of fumigants in the EU until 1986, but it has since decreased due to the introduction of chlorinated compounds such as p-dichlorobenzene. Its use in the manufacture of mothballs was still active in the EU, reaching about 1,000 tonnes/year by the time of these studies (2003). However, the use of naphthalene in mothballs is no longer supported in the EU since 2008. Minor uses as fumigant still occur in museums for the protection of old articles from pests. By 2003, the use of naphthalene in mothballs production was carried out by one company in Belgium which distributed world-wide.

Manufacture of pyrotechnics

By 2003, about 15 tonnes/year of naphthalene were used for the manufacturing of pyrotechnics in the EU. A few manufacturers were found, four in the UK, two in Germany, one in France and one in Italy. The one UK manufacturer was accountable for about 10% of the total use in the EU.

Manufacture of grinding wheels

A precise accounting of the usage volume for this application could not be done, as it was not possible to determine the total number of manufacturing plants in the EU. However, p-dichlorobenzene may also be used for the same purpose. Three companies were identified which use naphthalene in the manufacture of grinding wheels, with a total usage of about 350 tonnes/year. The location of these sites was not disclosed in the literature sources.

Manufacture of phthalic anhydride

The amount of naphthalene used for this application depends on its relative market price compared to that of o-xylene, which has caused the use of naphthalene to fall over the recent years (from 56,000 tonnes/year in 1982 to 40,000 tonnes/year in 2003). However, the increased demand of phthalic anhydride in more recent years may change this trend oppositely irrespective of the price of naphthalene (Preuss et al., 2003). According to these literature sources (ECB, 2003; Preuss et al., 2003), three plants using naphthalene to manufacture phthalic anhydride were located in the EU at the time of these studies: one in the UK, one in Belgium and one in Italy.

According to IHS Chemical (2013), the manufacture of phthalic anhydride is the second-largest end use for naphthalene today globally (2012), and according to Rütgers Chemicals (2008) it is also the second-largest end use market in Europe. However, in countries such as Japan, Russia and the Republic of Korea the phthalic anhydride production accounted for more than 80% of the total naphthalene demand.

Manufacture of naphthalene sulphonic acids

According to literature sources, the latest data on usage of naphthalene for this application is from 1986 and was reported to be 24 000 tonnes/year. However, it was also indicated in these sources that this figure could be underestimated as naphthalene usage is expected to increase by a rate of 7-9% per annum in the USA, which somehow it is expected to influence usage in the EU. According to the ECB (2003), about 12-17 companies in the EU used naphthalene for this purpose by that time.

According to IHS Chemical (2013), this is the major use of naphthalene nowadays, influencing largely China’s recent expansion on the demand of this substance for the production of naphthalene sulphonate formaldehyde condensate (NSF). NSF is used as plasticiser in concrete mixtures (ECB, 2003), and in 2011 this application accounted for an estimated 50% of the total demand of naphthalene of the world (70% of China's demand). This market continues to exhibit the strongest growth globally, at about 2.5% per year (IHS, 2013). According to Rütgers Chemicals (2008), the manufacture of naphthalene sulphonic acids is the largest end use for naphthalene.

Manufacture of azo dyes (dyestuffs)

The latest data on usage of naphthalene for this application is also from 1986, which was 46,000 tonnes/year. However, Preuss et al. (2003) present the annual use of naphthalene for 2-naphthol specifically which was 12,000 tonnes by then. Information about manufacturers in the EU using naphthalene for manufacturing dyestuffs was not available.

Manufacture of alkylated naphthalene solvents

By 2003, an estimated use of naphthalene of 15,000 tonnes/year was done by only one company in Germany to produce these products.

3.3.1 Main uses of naphthalene in Denmark and the other Nordic countries

According to the SPIN database, the main applications of naphthalene from 2000 to 2011 in both Denmark and other Nordic countries have been as listed below. The listed amounts are for Denmark only:

- Fuel additives – 25.3 tonnes in 2011 in 40 different preparations
- Construction materials – 21.0 tonnes in 2011 in 4 different preparations
- Fuels – 2.2 tonnes in 2011 in 30 different preparations
- Corrosion inhibitors – 2.1 tonnes in 2011 in 7 different preparations
- Solvents – high use in Finland primarily or in earlier years in Denmark
- Lubricants and additives – 0.1 tonnes in 2011 in 21 different preparations
- Non-agricultural pesticides and preservatives – use below 0.0 tonnes in 2011
- Other uses

For other uses in Denmark, see Appendix 4, where all the applications from 2000 to 2011 are listed.

3.3.2 Products containing naphthalene

Besides the above listed uses of naphthalene, the substance is also contained in the following type of products due impurities or due to the products containing distillates of e.g. coal tar which contain naphthalene:

- Creosote treated wood (ECB, 2003). According to ECB (2003) creosote oil consists of 5-25% naphthalene. According to Koppers Denmark ApS, their creosote oil contains up to 5% naphthalene
- Tar paints/specialist paints used by the building trade industry (ECB, 2003)
- Waterproof membranes for floors and walls (ECB, 2003)
- Asphalt (ATSDR, 2005)
- PAH containing products, as naphthalene is regarded as a PAH. PAH is mainly found in:
  - Extender oils – found in rubber and plastic products
  - Carbon black - found in rubber and plastic products (Lassen et al., 2011)

Furthermore, naphthalene has been found to be emitted from the following products:

- In emissions from CFL light bulbs (ALAB, 2011)
- Cigarette smoke (HPA, 2007)

Some of the products are described in more details in the paragraphs below.

Creosote treated wood

According to the ECB (2003), creosote consists of 5-25% naphthalene dependant on the type creosote used. In the European Chemical Bureau report (2003) it is estimated that about 100,000 tonnes of creosote were used in the EU at the time of the preparation of the report (1996-2003) and that 10% of this amount therefore represented the level of naphthalene used in this industry. Creosote is no longer used for treatment of wood in Denmark (it has been restricted since 1997). However, creosote treated wood may still be imported and creosote treated wood may still be in use in Denmark (Hansen et al., 2008).

Tar paints/specialist paints

Tar containing about 1-2% naphthalene has been used in some specialist paints. However, according to the European Chemical Bureau (2003), the Scandinavian market was moving away from a use of these tar paints at the time of the preparation of the European Chemical Bureau report. Therefore, it is expected that these products are not used any more in Denmark. This is in line with information from the SPIN database where the use of naphthalene in "paints, lacquers and varnishes" was 0.0 tonnes (i.e. below 50 kg) in 2011.

Waterproof membranes

Tar containing about 1% naphthalene is used in waterproof membranes. The waterproof membranes are generally used by the building industry and are used to waterproof floors and walls. The European Chemical Bureau (2003) estimated that these waterproof systems accounted for 10% of the waterproofing market at the time of the preparation of the European Chemical Bureau report (i.e. 1996-2001).

Asphalt

Naphthalene is present in asphalt according to ATSDR (2005) and may therefore evaporate especially from slow curing asphalt (Jia and Batterman, 2010).

PAH containing products – rubber and plastic products

As described in section 1.3 "Naphthalene and PAHs", naphthalene is often considered to be a PAH, but is not included in the standard Danish measurements of PAHs (they include 15 PAHs, but not naphthalene). Naphthalene is neither included as one of the 8 PAHs that are restricted in tyres according to the REACH Annex XVII restriction. PAHs are natural constituents of mineral oil (petrogenic PAHs) or are generated during combustion (pyrogenic PAHs). More or less the same PAHs will be present whether the source is pyrogenic or petrogenic, but the relative composition of the mixture of PAHs is different depending on the source (Lassen et al., 2011).

At least two types of additives are known to contain PAHs: extender oils and carbon black. Extender oils are mineral oil products which are derived from crude oil (petrogenic PAHs) whereas carbon black is a material produced by the incomplete combustion or thermal decomposition of heavy petroleum such as e.g. coal tar (mainly pyrogenic PAHs). Carbon black is used as a pigment and reinforcement in rubber and plastic products. Extender oils in the rubber and plastic industry are mainly used by (Lassen et al., 2011):

- Manufacturers of soften polymers
- Manufacturers of finished rubber products in order to aid processing (the main function of the extender oil is here to swell the polymer and to function as lubricant). A major use of extender oils is as an additive in rubber tyres.

Processes to extract the PAHs from the oil have been developed, which then produce 'cleaner' oil products in general for use in e.g. consumer products. Therefore, the amount of PAHs in the mineral oils and carbon black will depend on the origin and the production process. Carbon black is also used as an additive and even though PAHs are removed to some extend during the production of carbon black, PAH residues are still expected to be present (Lassen et al., 2011).

For consumer products the main source of PAHs is considered to be different mineral oils which are used in the productions of the used materials, mainly as additives. Consumer products consisting of the following materials or additives are considered to have potential PAH contamination (Lassen et al., 2011):

- Rubber and flexible plastics (e.g. PVC): softeners and carbon black as e.g. pigment
- Plastics: black carbon used as e.g. black pigment

The German Federal Institute for Occupational Safety and Health (BAuA) has in connection with a proposal for a restriction of PAHs in consumer products under the REACH Regulation summarised a number of investigations of PAHs in consumer products. They summarised the data of the content of more than 5300 samples and found that PAHs could be found in the following types of consumer products (BAuA, 2010):

4. Electrical devices such as cable insulations, plugs, chinch-plugs, covers of domestic electrical appliances or compressors, printers, switches, adapters, remote controls, handheld electrical tools, rubber sleeves on electrical devices, cable sheathings.
5. Grips: grips/handles made of rubber or plastic, e.g. of tools (hammer, screwdriver, knives, pliers), bicycles, gardening tools, buggies, stationary bicycles, walking frames, torches, handle coatings.
6. Skin contact areas of sports equipment or other consumer products: mostly grips and handles of sports equipment, e. g. a dumb-bell set.
7. Toys: balls, figures, toy cars, run bikes, coloured pencils, shuttlecocks, toy guns, electrical parts of toy train set.
8. Materials with close contact to the body: shoes, gloves, underwear, working clothes, flip-flops.
9. Other products with skin contact: e.g. ski goggles, headphones, pulse monitors, eye-cups, desk pads, bracelets, steering wheel covers, computer mice, mouse pads, furniture handles, watch straps.
10. Tyres and rolls: e.g. car tyres, tyre cover, transport wheel, rolls of transport aid.
11. Other products: O-ring-seals, seals for sanitary devices, doormats, door stopper, plastic hook coating, measuring tape, rubber hems, foam, rubber band, bulb horn, rubber lips.

BAuA (2010) gives detailed information about the level of PAHs measured in the different type of products, but it is the sum of PAHs that is listed. Hence, it is not possible to see the level of naphthalene in the different types of products.

Lassen et al. (2011) states, that no precise data on the content of PAHs in different extender oils is available. Examples of a naphthalene content between 2.3 and 8.68 mg/kg (ppm) in carbon black are given (Lassen et al., 2011).

Furthermore, no information on which extender oils or carbon black products that are used in different rubber and plastic materials is available. Therefore, it is impossible in general to state a general content of PAHs and thereby of naphthalene in different product types. However, some examples of naphthalene levels found in consumer products are listed below.

Examples of naphthalene levels found in consumer products

For the past 13 years, the Danish EPA has investigated chemicals used in consumer products[38]. Based on these surveys on chemicals in consumer products, a database has been made of the findings (based on chemical analysis of consumer products). These findings are presented in Table 6 below. Some information about other products containing naphthalene has been added to Table 6 as well.

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[38] http://eng.mst.dk/topics/chemicals/consumers-consumer-products/danish-surveys-on-consumer-products/

Product type	Amount	Reference
Window colours (glass colours)	5.7-11 mg/kg in red paint	Mikkelsen et al., 2004
Toothbrush	5.3 µg/toothbrush 0.04 – 0.53 µg/g Migration: 0.29 – 2.60 µg/toothbrush	Svendsen et al., 2004
Incense (smoke)	403 µg/m^3	Eggert and Hansen, 2004
Printed matter	18 – 90 µg/m^3 emitted 122 – 389 µg/kg	Hansen and Eggert, 2003
Textiles	0.04-2.4 mg/kg	Laursen et al., 2003
Rubber shoes	< 0.2 mg/kg	Lassen et al., 2011
Bathing shoes	0.2-0.5 mg/kg	Lassen et al., 2011
Bracelet	< 0.2 mg/kg	Lassen et al., 2011
Tyre of bicycles	0.5 -1.0 mg/kg	Lassen et al., 2011
Handle, scooter	< 0.2 mg/kg	Lassen et al., 2011
Handle, bicycle	< 0.2 mg/kg	Lassen et al., 2011
Eraser	< 0,2 mg/kg	Lassen et al., 2011
Rubber figurine	0.2-0.5 mg/kg	Lassen et al., 2011
Ball	< 0.2 – 0.5 mg/kg	Lassen et al. 2011
Doll	< 0.2 mg/kg	Lassen et al., 2011
Teething ring	< 0.2 mg/kg	Lassen et al., 2011
Swimming equipment	< 0.2 mg/kg	Lassen et al., 2011
Bib	< 0.2 mg/kg	Lassen et al., 2011
Bags	< 0.2 mg/kg	Lassen et al., 2011
Balloons	0.2-0.5 mg/kg	Lassen et al., 2011
Toy car	0.2-0.5 mg/kg	Lassen et al., 2011
Alarm horn	< 0.2 mg/kg	Lassen et al., 2011
Pen	< 0.2 mg/kg	Lassen et al., 2011

Product type	Amount	Reference
Tattoo color (black)	0.8-81 µg/g	Jacobsen et al., 2012
Tattoo color (blue)	1.9-2.8 µg/g	Jacobsen et al., 2012
Tattoo color (red)	1.6 µg/g	Jacobsen et al., 2012
Tattoo color (orange)	1.3 µg/g	Jacobsen et al., 2012
Wood tar	510 mg/kg	Hansen and Steen, 2012
Gags	0.11 g/kg	Nilsson et al., 2006
Silicone based pacifiers	> 0.1 mg/kg	Öko-Test 8, 2012

TABLE 6
NAPHTHALENE IN CONSUMER PRODUCTS – LEVELS FOUND IN PRODUCTS (PRIMARY SOURCE: DANISH EPA: CHEMICALS IN CONSUMER PRODUCTS DATABASE, 2014)

Silicone based pacifiers
In 2012, the German test magazine, Öko-Test, has tested silicone based pacifiers and found small levels of PAHs including naphthalene in concentrations above 0.1 mg/kg (ppm) in six out of 17 tested silicone based pacifiers (Öko-Test 8, 2012).

Emission from CFL light bulbs
In 2014, the Danish EPA has initiated a survey of chemicals emitting from CFL light bulbs. This project is currently ongoing and no report has been published yet. However, the findings of this project illustrate that naphthalene can be emitted from CFL light bulbs. In 2014, the German laboratory ALAB tested 14 different CFL light bulbs and found that naphthalene emitted from 12 of the 14 tested CFL light bulbs in concentrations between 0.1 and 18.8 µg/m^3. Most measured emissions (for 11 of the CFL light bulbs) were in the range of 0.1-0.7 µg/m^3. The emission rate was measured to be between 0.001 – 0.205 µg per light bulb per hour (and mostly in the range of 0.001 – 0.008 µg per light bulb per hour), (ALAB, 2011).

Emissions from cigarette smoke
Naphthalene is as other PAHs produced upon the burning of organic material, such as fossil fuels, wood and tobacco, and is present in exhaust emissions and also in emissions from cigarette smoke. According to Jia and Batterman (2010), second-hand cigarette smoking is among the largest contributor to personal exposure of naphthalene. Emission factors of naphthalene in the side-stream smoke measured in the laboratory range from 12-15 µg/cigarette. Under realistic conditions, emission factors of naphthalene have been reported between 17 and 54 µg/cigarette and will depend on air exchange rates, furnishing level and smoking conditions. All or most of these emissions are due to the side stream smoke. Jia and Batterman state that the emission factors for cigarettes across different studies are reasonably consistent.

3.4 Historical trends in use

Approximately 70% of naphthalene produced in 1976 was used in the production of phthalic anhydride, which fell over the late 90s. This is mainly due to the alternative feedstock, o-xylene, which showed a cheaper price and therefore an economic benefit. However, due to the increased demand shown over the early 2000s, the ECB (2003) predicted an increased usage of naphthalene for this application. IHS Chemical (2013) reports that a result of the expanding NSF markets (naphthalene sulfonates consumption) as well as phthalic anhydride being produced from o-xylene instead, consumption of phthalic anhydride has gradually declined, which makes it the second largest end use for naphthalene globally. However, naphthalene based production of phthalic anhydride is often preferred to o-xylene due to fluctuating petrochemical (o-xylene) feedstock pricing. Globally, IHS Chemical (2013) predicts an annually growth rate of 2-2.5% during 2011-2017 for phthalic anhydride.

Generally, the use of naphthalene for the manufacturing of intermediates presents volumes a few orders of magnitude higher than its use for the manufacturing of products. However, some figures are outdated (from 1986), when the use of naphthalene in the EU was 20% higher, according to the ECB (2003). Anyhow, this decrease still holds the higher use of naphthalene as intermediate.

Not only does the demand of the applications influence the consumption of naphthalene. Alternatives substances such as o-xylene and p-dichlorobenzene and their relative prices compared to that of naphthalene also influence the usage of naphthalene. However, due a high diversification of its application, the overall demand may remain around the same level of magnitude whilst the relative applications may shift from one usage to another.

IHS Chemical (2013) predicts an overall global naphthalene consumption increase of 2% annually during 2011-2017. This forecast is based on the fact that an increased environmental pressure placed on naphthalene use in pesticides, dyestuff intermediates and solvent applications has contributed to demand declines in most industrialized regions. The United States, Japan and Western Europe are forecasted to experience less than 2% average annual growth through 2017, while developing regions (China, Central and Eastern Europe, and the Middle East) will continue to exhibit the fastest demand growth, ranging between 2% and 4% annually.

3.5 Summary and conclusions

Manufacturing

The manufacturing of naphthalene is world-wide and is done by two production routes, where the distillation of coal tar and subsequently of naphthalene oil is the most widely applied production route (92% market share of the world). The most widely applied production route consists of two steps. The first step starts with coal tar, produced from coke oven gases, and it is followed by a series of distillation processes where different tar fractions are produced, internally reused or sold externally, with naphthalene as the final product (i.e. crude naphthalene). The second step is applied to produce purer grades of naphthalene and the most common technology used is distillation with solvents. In Denmark, naphthalene is produced by Koppers Denmark ApS and a similar production route as the abovementioned is applied. However Koppers Denmark ApS do not use solvents in the distillation process. Koppers Denmark ApS also imports naphthalene oil in order to match production demand. The final product is 95 – 97% grade naphthalene.

China has nowadays nearly half of the naphthalene production capacity and output of the world, although their production configuration is different from that in the EU and Denmark. The EU, the USA and Canada also play an important role in the world production. Twelve companies in the EU are registered as importers and/or producers of naphthalene in the ECHA database (ECHA RSD, 2014), including Koppers Denmark ApS, but it was found that one of them is not in operation any longer. Denmark is the only manufacturer of naphthalene in the Nordic countries.

Manufacturing volumes

It was not possible to find a world estimate on annual production of naphthalene. However, an estimate for the USA was found from 2001 (as the latest), which was 115,000 tonnes/year, and for Canada (for 2006), which was 52,000 tonnes/year. An indicative figure for the EU of 100,000 tonnes/year was found for 2009/2010. This makes for a total estimate of 267,000 tonnes/year of naphthalene produced, which should make up for up to half of the annual production of the world, considering China today has half of the production. However, care should be taken to interpret this figure as it comes from different points in time and from information retrieved from IHS (2013). The trends in production have changed significantly along the past decade. It seems that production of naphthalene has declined in the USA and shifted towards growing production in other markets instead (China, Russia and Brazil). Similarly, the European production seems to have declined, whereas the Danish production of naphthalene has increased. Denmark currently produces about 30,000 tonnes/year of naphthalene.

Import and export
It was not possible to retrieve publicly available import/export data from the EU. In Denmark the import of naphthalene contained in chemical products has steadily increased during the past 15 years (up to 2011), according to data from the SPIN database. The latest annual registered data for imports is from 2011 (73 739.1 tonnes), which is the total amount of naphthalene imported through chemical products. Information about export of chemical products containing naphthalene is unknown, but according to Koppers Denmark ApS about 30,000 tonnes/year of pure naphthalene is exported. Since all the production of naphthalene in Denmark is exported, it can also be said that all of the naphthalene used in products in Denmark is currently imported.

Use and historical trends
Naphthalene has a track record of being a chemical of many uses, as it has a wide range of technical grades used for different applications. However, the application of purer grades has presented a decrease during the last decade, particularly of grades >90% purity. Furthermore, the fact that naphthalene is no longer used in certain consumer products (mothballs) has also diminished its application and has shifted its use towards a higher use of naphthalene for the manufacturing of intermediates rather than for inclusion in final products. According to data collected from different literature sources, the main applications of naphthalene world-wide are:

- Manufacture of naphthalene sulphonic acids
- Manufacture of phthalic anhydride
- Manufacture of alkylated naphthalene solvents
- Manufacture of azo dyes
- Manufacture of grinding wheels as an artificial pore former (final product)
- Formulation of explosives in pyrotechnics (final product)

The European consumption of naphthalene was around 175,000 tonnes in 2007. The consumption of pure naphthalene in Denmark is expected to be zero as all naphthalene production from Koppers Denmark ApS in Denmark is exported. The naphthalene consumption in Denmark is due to other chemical products containing naphthalene.

According to information retrieved from the SPIN database, the main uses of naphthalene in Denmark and the Nordic countries are for fuel additives and construction materials. As the classification of uses presented in SPIN is more generic, it is assumed that these two major uses relate to the applications world-wide and in particular to the manufacture of naphthalene sulphonic acids (used as plasticiser in concrete mixtures) and phthalic anhydrides (used for e.g. manufacturing of phthalates).

Products containing naphthalene
The unintended presence of naphthalene in a wide range of other products is quite evident. This is because some of these products contain impurities or product distillates from tar-based substances or because naphthalene is a PAH and has therefore been found in products containing mineral oil. A list of examples has been provided, including:

- Tar paints/speciality paints

- Waterproof membranes for floors and walls
- Asphalt
- Rubber and plastic products, including a list of consumer products
- Creosote treated wood

Furthermore, naphthalene has also been found in emissions of some consumer products, for example in emissions from CFL light bulbs and from cigarette smoke.

4. Waste management

Information on waste from the manufacture and use of naphthalene is presented in this section. Most of this information has been retrieved from literature sources, especially from scientific reports and articles where major surveys were conducted at a European level.

4.1 Waste from manufacture and use of naphthalene

Manufacturing of naphthalene occurs in Denmark and in the European Union. Koppers Denmark ApS is the only producer in Denmark, whilst in the EU ten other companies import and/or produce biphenyl according to ECHA's website (ECHA RSD, 2014).

According to the Danish statutory order on waste, waste generated from *manufacture or from industrial use* of naphthalene has to be treated as hazardous waste if the waste contains substances in an amount that according to classification rules for chemical substances and preparations would result in classification for either physical-chemical toxicological or environmental properties (Danish Ministry of Environment, 2012).

According to information from Koppers[39], waste contaminated with naphthalene is treated as hazardous waste and therefore sent to incineration. In Denmark, the company Nord (which is a company authorised to handle hazardous waste) categorises naphthalene as waste category H: Organic chemical waste without halogen or sulphur[40] . Nord disposes of the chemical waste by burning it at a temperature of approximately 1200 °C. Burning naphthalene will result in the formation of carbon dioxide and water and thus will not result in the release of any hazardous emission in the flue gas or bottom ash.

Concerning the use of naphthalene in *final products*, two final products are relevant to mention: *pyrotechnics and grinding wheels*. Concerning *pyrotechnics*, it should be mentioned that naphthalene is used to produce black smoke. Thus it is released during the formulation stage of the explosive and during the use of the product. Concerning *grinding wheels*, EU RAR Addendum (2007) collected information from a BREF document (concerning the ceramics industry) and from a survey to the Federation for European Producers of Abrasives (FEPA). These sources indicated that any naphthalene emitted during the production of grinding wheels was collected for incineration or thermal treatment, thus having little potential for emission to wastewater

Waste from the *final product* creosote treated wood is of relevance as well. It is estimated that impregnated wood as a waste product constitutes around 100,000 tonnes each year in Denmark (Regeringen, 2003). However, this amount is all impregnated wood, i.e. impregnated with CCA (chromium, cupper and arsenic), tin and creosote. Hansen et al. (2008) estimates that the amount of waste for creosote treated wood will be around 12,000 tonnes each year in Denmark. The amount of creosote in creosote treated wood is 15%[41]. If assumed that creosote consists of 5% naphthalene (see chapter 3 for details), the amount of naphthalene in waste in the form of creosote treated wood is therefore around 90 ton each year in Denmark. Waste treatment of creosote treated wood happens in Denmark at special waste treatment plants that are authorised to burn the creosote treated waste. Burning naphthalene (contained in the waste products) will result in the formation of

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[39] Personal communication with Koppers Denmark ApS, in July 2014

[40] http://www.nordgroup.eu/da-DK/Hvorfor-NORD/Gode-r%C3%A5d-om-h%C3%A5ndtering/Sorteringsvejledning.aspx

[41] http://www.rhinehartrailroad.com/Docs/RRC/creosotetreatedwoodrailroadtiemsds.pdf

carbon dioxide and water and thus will not result in the release of any hazardous emission in the flue gas or bottom ash.

4.2 Waste products from the use of naphthalene in mixtures and articles

Due to the use of naphthalene in mixtures and due to the presence of small amounts of naphthalene in rubber and plastic articles, a small amount of waste containing naphthalene may derive from consumer use and professional use. Thus a small amount of naphthalene may go into the municipal collection and treatment of domestic waste. It is expected that most rubber and plastic consumer articles will be incinerated in Denmark, whereas waste in the form of chemical mixtures will be treated as hazardous waste (and handled (incinerated) at the company Nord in Denmark).

4.3 Release of naphthalene from waste disposal

According to information presented in section 3.3, the demand of naphthalene as intermediate is by far higher than that as part of a final product. This means that the potential for release of naphthalene in waste and wastewater from the manufacturing and use of the intermediates listed is also of greater importance than that from final products where naphthalene is intentionally applied. This, particularly from the manufacturing of naphthalene sulphonic acids, phthalic anhydride, alkylated naphthalene solvents and azo dyes (where naphthalene is used as intermediate chemical) which together make it for most of world’s demand of naphthalene.

Waste contaminated with naphthalene is handled as hazardous waste and is either incinerated or subjected to thermal treatment in the EU. Particulate emissions from house hold incinerators have been found to contain naphthalene. It has also been found in samples of flue gas from a hazardous waste incinerator. It is assumed that the naphthalene comes from the combustion of organic matter releasing PAHs. Release of naphthalene to water from waste incineration is not likely to occur. Release to soil may happen from the disposal of ash (no information available on emission values). A study made on incinerators in the UK operating with a throughput of 6-10 tonnes/hour reported an emission factor of 12.3 ng/kg burned fuel (ECB (2003). In spite that no more information was available from the amount of waste incinerated in the rest of Europe by then, it was expected that waste incineration would not be a significant source due to the low estimated emission factor.

Wastewater containing naphthalene is treated before release, and according to ECB (2003) all the wastewater treatment practices in the production sites, covered by their assessment, removed at least 98% of naphthalene in their effluent before being discharged to the environment. The same report presents a list of technologies surveyed. These are:

- Storage of effluent in a tank before sent to an effluent treatment plant;
- Pre-treatment by adsorption, which removes most PAHs prior to treatment in a biological plant;
- Treatment by resin adsorption;
- Release to a municipal treatment plant with no pre-treatment.

4.4 Summary and conclusions

Waste contaminated with naphthalene is handled as hazardous waste in Denmark and the EU. This is typically sent for incineration and thermal treatment. Traces of naphthalene have been found in the flue gases and emissions of the incinerators to ambient air. This is assumed to come not from the burning of naphthalene itself, but from other waste fractions that release PAHs during combustion. No direct release of naphthalene to water is likely to occur from incineration, and emissions to soil may happen if traces of naphthalene occur in the bottom ash.

Products containing small amounts of naphthalene will enter into the waste stream through municipal collection of domestic waste. It is expected that most rubber and plastic consumer articles will be incinerated in Denmark, whereas waste in the form of chemical mixtures will be treated as hazardous waste (and handled (incinerated) at the company Nord in Denmark).

The largest amount of waste containing naphthalene is assumed to be creosote treated wood which is expected to be around 12,000 tonnes each year in Denmark. The total naphthalene content in creosote treated wood is below 1%.

5. Environmental effects and fate

Release of naphthalene into the environment (to air, water and soil) may occur from industrial processing, i.e. during production of naphthalene or other production processes where naphthalene is used as chemical intermediate. Other sources of releases of naphthalene into the environment are accidental spills, emissions from waste incineration, but the largest releases to the air (at least in the USA) are judged to be a result of combustion of wood and fossil fuels (e.g. combustion of gasoline and diesel by vehicles) and the off-gassing of naphthalene-containing moth repellents (ATSDR, 2005; ECB, 2003).

The majority of the data presented in the following sections is based on information from the ATSDR (2005), ECB (2003) and Environment Canada (2008a and 2008b) reports on naphthalene. However, information in the Registered Substances database of ECHA (ECHA RSD, 2014) as well as ECB (2008) and IUCLID datasheets has also been used.

5.1 Environmental hazard

5.1.1 Toxicity to aquatic organisms

Data regarding the toxicity to aquatic organisms (fish and aquatic invertebrates) has been found in the ECB (2003 and 2008) and in ECHA Registered Substances Database (ECHA RSD, 2014). Relevant and reliable data presented in ECHA RSD (2014) is reproduced in Table 7 and Table 8 below. Data from the ECB (2003) has only been included in Table 7 and Table 8 below to supplement the values from ECHA RSD (2014), with higher or lower measurement values.

5.1.1.1 Toxicity to fish

It is stated as a concluding remark in one of the studies reported in ECHA RSD (2014 – Short-term toxicity to fish.003 and 004) that because of the fact that naphthalene volatilises from water, a closed flow-through system for testing is preferable and produces results more representative of the actual toxicity of naphthalene (compared to open static systems used in other studies). This difference in testing conditions could explain the differences in the listed figures in Table 7 below. If static conditions or a flow-through system has been used for testing it is indicated in the column with the values. Similarly, it is stated in the ECB (2003) report that care must be taken when interpreting data from tests based on nominal concentrations (compared to measured concentrations) because naphthalene can be lost from solutions during testing due to evaporation. The data presented in Table 7 below is based on measured concentrations unless otherwise stated.

It can be seen from Table 7 below that the acute toxicity of naphthalene to fish ranges from 0.96 mg/L for rainbow trout to 150 mg/L for mosquito fish. However, the figure of 150 mg/L for mosquito fish stands out by being a factor of ten or more higher than the other data presented. It is emphasised in the ECB (2003) report that this study has been based on nominal concentrations and not measured concentrations. Further testing was made under static conditions making evaporation from the test vessels likely. Therefore a large part of the naphthalene may have evaporated during testing and thereby resulting in a higher LC_{50} value. As a result the lower LC_{50} values between 0.96

mg/L and 7.8 mg/L may therefore be more reliable since they are data from flow through tests with measured concentrations.

In the EU risk assessment report of coal tar pitch, where toxicity data for naphthalene is discussed as well, it is concluded that the lowest usable effect concentration for fish is the EC_{10} value of 0.020 mg/L (ECB, 2008 and 2003).

Test organism	Type of test	Endpoint	Value	Reference
Acute toxicity to fish				
Pimephales promelas (fathead minnow)	Acute (96 h) Acute (72 h) Acute (48 h) Acute (24 h)	LC_{50}	6.08 mg/L 6.08 mg/L 6.35 mg/L 7.76 mg/L (all: flow)	Holcombe et al. (1984) in ECHA RSD (2014, ST.001)
Pimephales promelas (fathead minnow)	Acute (96 h)	LC_{50}	7.9 mg/L (static)	DeGraeve et al. (1982) in ECHA RSD (2014, ST.004)
Pimephales promelas (fathead minnow)	Acute (96 h)	LC_{50}	1.99 mg/L (static)	Millemann et al. (1984) in ECHA RSD (2014, ST.005)
Oncorhynchus gorbuscha (pink salmon fry)	Acute (48 h)	LC_{50}	0.96 mg/L (flow)	Rice and Thomas (1989) in ECHA RSD (2014, ST.002)
Oncorhynchus mykiss (rainbow trout)	Acute (96 h)	LC_{50}	1.6 mg/L (flow)	DeGraeve et al. (1982) in ECHA RSD (2014, ST.003)
Oncorhynchus kisutch (coho salmon)	Acute (96 h)	LC_{50}	2.1 mg/L (flow)	Moles et al. (1981) in ECHA RSD (2014, ST.006)
Gambusia affinis (Mosquito fish)	Acute (96 h)	LC_{50}	150 mg/L (nominal) (static)	Wallen et al. (1957) in ECB (2003)
Chronic toxicity to fish				
Oncorhynchus kisutch (coho salmon)	40 days	NOEC	0.37 mg/L (flow)	Moles et al. (1981) in ECHA RSD (2014, LT.001)
Gadus morrhua – fish eggs	4 days	NOEC	2.78 mg/L (static)	Saetre et al. (1984) in ECHA RSD (2014, LT.005)
Oncorhynchus kisutch (coho	40 days	NOEC	0.12 mg/L (flow)	Moles and Rice (1983) in ECB (2003).

Test organism	Type of test	Endpoint	Value	Reference
salmon)				
Oncorhynchus mykiss (rainbow trout)	4 days	EC_{10}	0.02 mg/L (not stated)	Black et al. (1983) in Europeans Chemicals Bureau (2003 and 2008)

FLOW – FLOW-THROUGH CONDITIONS, I.E. NAPHTHALENE CONCENTRATIONS CONTINOUSLY MAINTAINED
STATIC – STATIC CONDITIONS (WATER UNCHANGED FOR DURATION OF TEST), NAPHTHALENE MAY HAVE EVAPORATED
NOMINAL – NOMINAL CONCENTRATION, I.E. CONCENTRATION HAS NOT BEEN MEASURED. NAPHTHALENE MAY HAVE EVAPORATED.

TABLE 7
EMPIRICAL DATA FOR AQUATIC TOXICITY TO FISH FOR NAPHTHALENE

5.1.1.2 Toxicity to aquatic invertebrates

Some of the data on the acute toxicity of naphthalene to aquatic invertebrates is summarised below in Table 8. The data presented illustrates the range in values for the different dataset. Again, it is stated in the ECB (2003) report that care must be taken when interpreting data from tests based on nominal concentrations (compared to measured concentrations) because naphthalene can be lost from solution during testing due to evaporation. The data presented in Table 8 below is based on measured concentrations unless otherwise stated.

Test organism	Type of test	Endpoint	Value	Reference
Acute toxicity to aquatic invertebrates				
Daphnia magna (water flea)	Acute (48h)	EC_{50}/LC_{50}	2.16 mg/L (static)	Milleman et al. (1984) in ECHA RSD (2014, ST.001)
Daphnia pulex (water flea)	Acute (48h)	LC_{50}	2.92-3.89 mg/L (nominal) (static)	Geiger and Buikema (1982) in ECHA RSD (2014, ST.002)
Daphnia magna (water flea)	Acute (48h) Acute 24h)	LC_{50}	8.6 mg/L 17 mg/L (nominal) (static)	LeBlanc (1980) in ECHA RSD (2014, ST.003)
Daphnia magna (water flea)	Acute (48h) Acute 24h)	LC_{50}	3.4 mg/L 13.2 mg/L (static)	Crider et al. (1982) in ECB (2003)
Daphnia magna (water flea)	Acute (48h)	LC_{50}	22.6 mg/L (nominal) (static)	Eastmond et al. (1984) in ECB (2003)
Eualis suckleyi (kelp shrimp)	Acute (96h)	LC_{50}	1.39 mg/L (flow)	Rice and Thomas (1989) in ECB (2003)

Test organism	Type of test	Endpoint	Value	Reference
Neomysis Americana (mysid)	Acute (96h)	LC_{50}	0.85 mg/L (flow)	Smith and Hargreaves (1983) in ECB (2003)
Scylla serrata (crab)	Acute (48h) Acute (96h)	LC_{50}	20 mg/L 17 mg/L (static)	Kulkami and Masurekar (1983) in ECB (2003)
Chronic toxicity to aquatic invertebrates				
Daphnia pulex (water flea)	125 days	NOEC	0.59 mg/L (static)	Geiger and Buikema (1982) in ECHA RSD (2014, LT.001)
Strongylocentrotus droebachiensis (sea urchin)	4 days	NOEC	1.86 mg/L (static)	Seathre et al. (1984) in ECHA RSD (2014, LT.002)
Eurytemora affinis	10 days	NOEC	>50 µg/L (static)	Berdugo et al. (1977) in ECHA RSD (2014, LT.004)
Rhithropanopeus harrisii (mud crab)	21 days	NOEC	>500 µg/L (static)	Laughlin et al. (1979) in ECHA RSD (2014, LT.005)

FLOW – FLOW-THROUGH CONDITIONS, I.E. NAPHTHALENE CONCENTRATIONS CONTINOUSLY MAINTAINED
STATIC – STATIC CONDITIONS (WATER UNCHANGED FOR DURATION OF TEST), NAPHTHALENE MAY HAVE EVAPORATED
NOMINAL – NOMINAL CONCENTRATION, I.E. CONCENTRATION HAS NOT BEEN MEASURED. NAPHTHALENE MAY HAVE EVAPORATED.

TABLE 8
EMPIRICAL DATA FOR AQUATIC TOXICITY TO INVERTEBRATES FOR NAPHTHALENE

In a chronic toxicity study of effect of naphthalene on *Daphnia pulex,* naphthalene only produced a slight reduction in growth rate at concentrations of 0.33 and 0.6 mg/L. However, Daphnia exposed to naphthalene lived significantly longer and produced equal or more live young than did the controls (Geiger and Buikema (1982) in ECHA RSD, 2014).

Saethre et al. (1984 in ECHA RSD, 2014) exposed fertilised sea urchin (*Strongylocentrotus droebachiensis*) eggs to naphthalene concentrations of between 0.90 and 2.78 mg/l for 4 days. The lower exposure concentration had no effect on the survival of the eggs. The higher concentration killed all the eggs within 2 to 4 days: 60% to 98% of the cells were abnormal within 6 hours of exposure. The authors note that naphthalene was lost from solution very rapidly.

The last two chronic toxicity studies to aquatic invertebrates listed in Table 8 found no toxic effects of naphthalene for the highest concentrations used. It should be noted that all the chronic toxicity tests listed are carried out under static conditions. This means that some naphthalene may be evaporated during the tests. It is not mentioned if or how the naphthalene concentration is maintained constant during the tests.

5.1.1.3 Calculation of Predicted No Effect Concentration (PNEC) for water

The lowest No Observable Effect Concentration **(NOEC) of 0.02 mg/L** listed in Table 7 for *Oncorhynchus mykiss* (4 days) has been used in the ECB (2008) report to calculate a Predicted No

Effect Concentration – **PNEC value of 0.002 mg/L** by using an assessment factor of 10. A PNEC value of 0.0024 mg/L has been reported (and calculated) in the Registered Substance Database of ECHA (ECHA RSD, 2014), which is based on the EU risk assessment report of naphthalene (ECB, 2003). However, the later EU risk assessment report of Coal-Tar Pitch argues for using other data instead (ECB, 2008). ECB (2008) states that the PNEC value of 0.002 mg/L can be used for both freshwater and the marine environment.

5.1.2 Toxicity to microorganisms

Toxicity to microorganisms is shortly described in ECB (2003) and ECHA RSD (2014) which report the same studies:

- Blum and Speece (1991): Inhibition concentration IC_{50} of 29 mg/l for *Nitrosomonas* and IC_{50} of 670 mg/l for aerobic heterotrophs.
- Vaishnav (1986): An EC50, based on maximum observed biodegradation rate, was calculated to be 1,154 mg/l. However, it is concluded that the calculated EC_{50} concentration is very high in this study and that it is expected that EC_{50} values based on respiration activity of all waste water or sediment settling microorganisms will be much lower than the EC_{50} value of 1,154 mg/litre determined in the present study.
- Kiene and Capone (1984) studied the effect of naphthalene (1,000 mg/kg) on methanogenesis, sulphate reduction and carbon dioxide evolution of anaerobic salt marsh sediment over a 7- to 9-day period. Initially, methanogenesis was significantly inhibited but towards the end of the experiment there was significant stimulation of methanogenesis. Sulphate reduction was significantly inhibited and carbon dioxide evolution was only significantly inhibited in one of three experiments. It is emphasised that concentrations used in these experiments were high compared to naturally occurring naphthalene concentrations and the resulting effects on anaerobic sediment settling microorganisms were relatively mild.
- Bauer and Capone (1985) studied aerobic and anaerobic marine sediment microbes exposed to naphthalene concentrations of 1, 10, 100 and 1,000 mg/l. Naphthalene concentrations of 100 and 1,000 mg/l significantly inhibited glucose metabolism and thymidine incorporation in both aerobic and anaerobic sediment.

5.1.3 Toxicity to sediment living organisms

The ECB (2008) lists the only sediment effect concentration available: EC_{50} for the reburial of *Rhepoxynius abronius* after 10 days of exposure is 2,900 mg/kg_{dw}, recalculated to a sediment with an organic carbon content of 10%. The effect concentration is considered to be rather chronic than acute and is used to calculate a **PNEC for sediment of 2.9 mg/kg_{dw}** by using an assessment factor of 1,000. For marine sediment an assessment factor of 10,000 is used resulting in a PNEC for marine sediment of 0.29 mg/kg_{dw}.

In comparison the ECB (2003) calculated a PNEC for sediment of 67.2 µg/kg, but this value was based on the PNEC value for water.

5.1.4 Toxicity to terrestrial organisms

There is only limited data on naphthalene toxicity to terrestrial organisms. The ECB (2003) and ECHA RSD (2014) report the same studies, but most studies are judged to be unreliable and therefore not elaborated here.

Laboratory tests of the growth rate of basidomycete fungi in the presence of naphthalene vapour were carried out (Newell et al., 1987 in ECB (2003)). Nine different basidomycete fungi were grown in the presence of naphthalene vapour for 6 days. All but one of the test fungi showed significant reduction in growth and irregular growth in the presence of naphthalene vapour. The mean reduction in growth compared with the controls varied between 31% and 70%. ECHA RSD (2014) concludes that although the study is not very well-documented and only vapour exposure to fungi under laboratory conditions has been investigated, the results indicate that fungi might be negatively influenced by naphthalene when administered to soil. The used fungi are a very important component in fauna-microflora interactions and the results reported here do cause the concern that exposure to naphthalene would probably affect the composition of fungal communities.

ECB (2008) reports that the lowest usable effect concentration is a NOEC of 10 mg/kg$_{dw}$ for reproduction of the springtail *Folsomia candida* from a 28 day study from 2003. Based on this NOEC, a **PNEC for soil can be calculated to be 1.0 mg/kg$_{dw}$** by use of an assessment factor of 10.

In comparison the ECB (2003) calculated the PNEC for the terrestrial compartment (using the equilibrium partitioning method in the Technical Guidance document because of limited data) to be 53.3 µg/kg using the PNEC calculated for freshwater.

5.1.5 Toxicity to the atmosphere

No information on the biotic or abiotic effects in the atmosphere was identified.

It is noted in the ECB (2003) that it is not possible to calculate a PNEC value for naphthalene in the atmosphere. However, naphthalene is not expected to contribute to global warming nor significantly to stratospheric ozone depletion because of a short atmospheric lifetime of approximately 1 day.

5.1.6 Classification

Naphthalene has the following harmonised classification with respect to environmental effects:

- Aquatic Acute 1 H400: Very toxic to aquatic life
- Aquatic Chronic 1 H410: Very toxic to aquatic life with long lasting effects

Nevertheless, some notifiers have suggested other environmental classifications. Out of a total of 1,665 notifiers, 94 suggested the following 'less severe' environmental classification:

- Aquatic Chronic 2 H411: Toxic to aquatic life with long lasting effects

One single notifier has even suggested the 'less severe' environmental classification of:

- Aquatic Chronic 3 H412: Harmful to aquatic life with long lasting effects

According to the CLP classification (table 4.1.0 in EU Regulation No. 286/2011 (of CLP 1272/2008)), substances with chronic NOEC > 0.1 but ≤ 1.0 mg/l should be classified with "Aquatic Chronic 2; H411 (Toxic to aquatic life with long lasting effects)" if the substance is non-rapidly degradable. The aquatic chronic NOEC of 0.12 mg/l in the 40 day fish test on *Oncorhynchus kisutch* described in ECB (2003) leads to the evaluation that naphthalene fulfils the criteria for classification as "Aquatic Chronic 2; H411 (Toxic to aquatic life with long lasting effects)" which has also been suggested by 94 notifiers. However, hhe NOEC value of 0.12 mg/l is very close to the limit value of ≤ 0.1 mg/l for classification as "Aquatic Chronic 1; H410 (Very toxic to aquatic life with long lasting effects), which is the existing harmonised classification of naphthalene.

5.2 Environmental fate

The environmental fate of naphthalene after release to air, water and soil has been estimated in the Environment Canada (2008b) report. Modelling of the environmental fate (Level III fugacity modelling) indicates that naphthalene will remain in the media to which it is released (see Table 9), although the substance has a tendency to bind to soil (which is also indicated by the relatively high Log K$_{ow}$ value of naphthalene (see Table 2)).

Emission profile	**Distribution (% of total emitted)**			
	Air	**Water**	**Soil**	**Sediment**
Equal parts to air/water/soil	1.03 %	12.8%	85.6%	0.578%
100% to water	2.19 %	93.5%	0.107%	4.23%
100% to air	90.5 %	4.81%	4.44%	0.218%
100% to soil	0.143%	0.379%	99.5%	0.0172%

TABLE 9
ESTIMATED DISTRIBUTION OF NAPHTHALENE AFTER RELEASE TO AIR, WATER AND SOIL (SOURCE: ENVIRONMENT CANADA, 2008B)

The fate of naphthalene in each environmental compartment is summarised briefly below in section 5.2.1 to 5.2.5.

5.2.1 Air

Naphthalene has a moderate vapour pressure (7.2 Pa at 20 °C), which is just below the 10 Pa cut-off value often used to define volatile organic compounds (VOCs), (Jia and Batterman, 2010). The boiling point of naphthalene (218.1 °C at 1013 hPa) is below 250 °C, which by another definition defines a VOC[42]. Therefore naphthalene is classified as a semi-volatile organic compound (SVOC), (Jia and Batterman, 2010). Furthermore, naphthalene sublimes slowly at room temperature (ECB, 2003), which means that naphthalene undergoes a phase transition directly from solid to the gas phase without passing through an intermediate liquid phase.

Naphthalene released to the atmosphere may be transported to surface water and/or soil by wet or dry deposition. Since most airborne naphthalene is in the vapour phase, deposition is expected to be very slow (ATSDR, 2005). This is also indicated by modelling of the environmental fate of naphthalene (Table 9); about 90% of the naphthalene released to air will remain in the air.

The most important atmospheric removal process for naphthalene is reaction with photo chemically produced hydroxyl radicals. The atmospheric half-life for naphthalene based on this reaction is less than 1 day. The major products of this reaction are 1-naphtol[43], 2-naphtol[44] and 2-nitronaphthalene[45]. Two of these reaction products are also classified as toxic to the environment, but with a less toxic classification compared to the environmental classification of naphthalene. Naphthalene also reacts with N_2O_5, nitrate radicals and ozone in the atmosphere (ATSDR, 2005; ECB, 2003).

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[42] The EU "Paint Directive" 2004/42/EC.
[43] Harmonised classification as Acute Tox. 4, H302, H312; Skin Irrit. 2, H315; Eye Dam. 1, H318; STOT SE 3, H335.
[44] Harmonised classification as Acute Tox. 4, H302, H332; Aquatic Acute 1, H400.
[45] Harmonised classification as Carc. 1B, H350; Aquatic Chronic 2, H411.

5.2.2 Water

Inherent biodegradability screening studies of naphthalene suggest that naphthalene is persistent (2% biodegradation after 4 weeks), (ECB, 2003). However, another study illustrates 99.9% biodegradation of naphthalene in 15 days (ECHA RSD, 2014). The explanation could be that biodegradation of naphthalene seems to occur slowly (half-life up to 1,700 days) in unpolluted water, but much more rapidly in oil-polluted water (half-life about 7 days). The biodegradation rate increases with the naphthalene concentration. In an experiment with seawater, the half-life of naphthalene was reported at 0.8 days, mainly due to biodegradation, (ATSDR, 2005). Naphthalene is hence considered to be biodegradable under aerobic conditions, but under anaerobic conditions degradation does not appear to occur, yet naphthalene does degrade under denitrifying conditions (ECB, 2003).

With a moderate vapour pressure (7.2 Pa at 20 °C) and based upon the estimated Henry's Law constant for naphthalene (44.86 Pa · m^3/mol), it is likely that volatilisation will be an important route of naphthalene loss from water. Especially in surface water naphthalene may volatise to the atmosphere (ATSDR, 2005). However, the estimated distribution of naphthalene (see Table 9) indicates a loss of 2.2% of the naphthalene to the air if 100% is released into water.

Based on the log K_{ow} value of naphthalene (3.4 at 25 °C), it is expected that only a small fraction (less than 10%) of naphthalene in surface water will be associated with particulate matter such as suspended solids and sediments (ATSDR, 2005). This is in line with the modelling of the environmental fate of naphthalene (Table 9) where about 4.4% of the naphthalene released to water will end up in the sediment compartment.

Naphthalene is degraded in water by photolysis and biological processes. As naphthalene does not contain chemical groups amenable to hydrolysis (cleavage of chemical bonds by addition of water), hydrolysis is not a removal process for naphthalene. The half-life for photolysis of naphthalene in surface water is estimated to be about 71 hours, but the half-life in deeper water (5 m) is estimated at 550 hours (ECB, 2003).

5.2.3 Sediment

Naphthalene biodegradation rates are about 8-20 times higher in sediment than in the water phase above the sediment. Half-lives reported in sediment include 4.9 hours in oil-contaminated sediment and >88 days in uncontaminated sediment (ATSDR, 2005). This indicates that the biodegradation rate is much slower in unpolluted sediment similar to unpolluted water. Studies reported in ECHA RSD (2014) illustrate that naphthalene is readily biodegradable under aerobic conditions in sediment, but does not biodegrade under aerobic conditions in sediment. Studies on bioaccumulation reported in ECHA RSD (2014) conclude that naphthalene exhibits a low bioconcentration potential in sediment.

Naphthalene is expected to adsorb to sediments to a moderate extent (ECB, 2003). Modelling of the environmental fate of naphthalene (Table 9) shows that about 4.4% of the naphthalene released to water will end up in the sediment compartment.

5.2.4 Soil

According to ATSDR (2005) there is considerable variability in the reported naphthalene soil half-lives. Half-lives are reported from 2-3 days to 3.6 months. Studies on biodegradation of PAHs suggest that adsorption to the organic matter significantly reduces the bioavailability for microorganisms, and thus the biodegradability of PAHs, including naphthalene. Biodegradation studies of naphthalene in soil in ECHA RSD (2014) illustrate that naphthalene is readily biodegraded in soil under aerobic conditions. However, under anaerobic conditions no significant degradation was shown in periods of 50 days. Under denitrification conditions naphthalene was degraded to non-detectable concentrations in 45 days (ECHA RSD, 2014).

Naphthalene is expected to adsorb to soils to a moderate extent (ECB, 2003), which is also indicated by the octanol/water coefficient log K_{ow} of 3.4. According to a study reported in ECAH RSD (2014), the adsorption of naphthalene to soil can be regarded as fast, reaching equilibrium within one day. Desorption experiments showed that only 30-50% of adsorbed naphthalene could be desorbed. Modelling of the environmental fate of naphthalene (Table 9) shows that about 99.5% of the naphthalene released to soil will remain in the soil compartment. Leaching of naphthalene to groundwater could therefore be expected.

5.2.5 Biota

Experimental log K_{OW} values of 3.4 for naphthalene suggest that this chemical has a relatively low potential to bioaccumulate in the environment. Experimental bioconcentration factors (BCF) lie between 2.3 and 1158 L/kg, and a BCF value of 279 has been derived by use of QSAR (ECB, 2014). These BCF values support the low bioconcentration potential of naphthalene and the conclusion in ECHA RSD (2014) is that naphthalene does not have a potential for bioaccumulation.

5.2.6 PBT

A PBT assessment has been performed in an environment addendum to the ECB (2003). The conclusion of the EU RAR Addendum (2007) is that naphthalene meets the screening criteria for persistent (P) and very persistent (vP). The half-life in marine water is estimated at 550 hours (ECB, 2003), which is less than >60 days, which is the requirement for being categorised as persistent and very persistent according to ECHA's Guidance on information requirements and chemical safety assessment, Chapter R.11: PBT Assessment[46]. However, an estimation of the biodegradation half-life of naphthalene in sediment has been estimated to be 230 days (EU RAR Addendum, 2007), which is more than the >180 days requirement for being categorised as persistent and very persistent[47]. Other studies reported in ECHA RSD (2014) also suggest that naphthalene is non-degradable in sediment under anaerobic conditions. Based on the data for sediment, naphthalene is therefore considered to meet the screening criteria for P and vP.

However, naphthalene does not meet the criteria for bioaccumulation (B) of BCF>2000 L/kg nor the very bioaccumulative criterion (vB) of BCF>5000 L/kg, as the highest BCF reported for fish is 1158 L/kg (according to EU RAR Addendum (2007)). Experimental data on BCF for fish is listed in the Environment Canada (2008b) report – the values listed range between 4 and 426 L/kg. The data and statements given in ECHA RSD (2014) also conclude that there is no evidence for bioaccumulation for naphthalene. ECHA RSD (2014) reports of bioaccumulation factors for sediment in the range of 36.5 to 168. Because of differences in the criteria for the PBT assessment and the classification criteria, naphthalene is therefore not regarded as being bioaccumulative (B), but is classified as Aquatic Chronic 1, H410 "Very toxic to aquatic life with long lasting effects".

Naphthalene does not meet the toxicity (T) criterion, as naphthalene does not have the required human health classification to meet the T criterion of Carc 1A or 1B or STOT RE 1 or 2 (the harmonised classification of naphthalene is Acute Tox. 4 H302: Harmful if swallowed and Carc. 2 H351: Suspected of causing cancer). Another toxicity criterion according to ECHA's criteria[48] is that NOEC or EC_{10} values for marine or freshwater organisms should be below 0.01 mg/L. The lowest is an EC_{10} value of 0.02 mg/l as listed in Table 7. Because of differences in the criteria for the PBT assessment and the classification criteria, naphthalene is therefore classified as Aquatic Acute 1, H400 "Very toxic to aquatic life", but it is not so toxic that it meets the toxicity (T) criterion in the PBT assessment.

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[46] Table R.11-1 in ECHA Guidance R.11, 2012
[47] Table R.11-1 in ECHA Guidance R.11, 2012
[48] Table R.11-1 in ECHA Guidance R.11, 2012

Therefore, it is concluded in the EU RAR Addendum (2007) that naphthalene is not a PBT or vPvB substance (EU RAR addendum, 2007).

5.2.7 Conclusion

Naphthalene is regarded as persistent. Naphthalene may be readily biodegradable under aerobic conditions, but only in oil-polluted waters. Under normal conditions and under anaerobic conditions, biodegradation does not seem to occur. Biodegradation of naphthalene seems to occur slowly (half-lives up to 1700 days) in unpolluted water, but much more rapidly in oil-polluted water (half-life about 7 days). Naphthalene does degrade under denitrifying conditions. Naphthalene seems to be persistent in sediment and soil, but not in the aqueous environment under aerobic conditions.

If naphthalene is released into air, water, or soil, it will reside predominantly in the compartment to which it is released, although the substance has a tendency to bind to soil. The atmospheric half-life of naphthalene is less than 1 day, whereas the half-life in surface water is estimated to be about 71 hours, but the half-life in deeper water (5 m) is much longer and estimated to be 550 hours. Half-lives in sediment and soils have been reported from a couple of days to a couple of months, which seems to be dependent on the presence of oxygen. The degradation is much quicker under aerobic conditions.

Naphthalene has a low bioconcentration potential and overall, naphthalene cannot be considered to be a PBT substance (P, but not B and T).

5.3 Environmental exposure

According to the EU risk assessment report of naphthalene (ECB, 2003), emissions to air from the **production** of naphthalene occur during *processing, open handling* and *storage* (as it is stored off-site). Furthermore, some leakage is also expected, especially during open handling and storage. Emissions to wastewater from the production of naphthalene occur mainly from *distillation of coal tar*, rather than from distillation of naphthalene oil (see section 3.1.1 for details on manufacturing process). There is no indication of naphthalene being released to wastewater from other source. There is limited information regarding emissions to soil, but it could happen from leakages and uncontrolled spills, as NTP (2000) has also reported.

Concerning the **use** of naphthalene for the *manufacturing of intermediates*, emissions of naphthalene to air have been identified during the loading and storage stages. Concerning the use of naphthalene in *final products*, two final products were considered in the EU risk assessment report: *pyrotechnics and grinding wheels*. Concerning *pyrotechnics*, it should be mentioned that naphthalene is used to produce black smoke. It is thus released during the formulation stage of the explosive and during the use of the product. Concerning *grinding wheels*, it is stated that any naphthalene emitted during the production of grinding wheels is collected for incineration or thermal treatment, thus having little potential for emission to wastewater (EU RAR Addendum, 2007). Emissions of naphthalene in waste, wastewater and to ambient air and soil from other products where naphthalene is used are expected to be minor, due to the low usage of naphthalene in these products.

5.3.1 Main sources of release

Releases of naphthalene to the environment can be classified in several ways, e.g. based on the generation mechanism, the type of source or an emission inventory perspective.

Based on the generation mechanism, naphthalene is emitted from the following sources (Jia and Batterman, 2010; ECB, 2003):

- As a product of incomplete combustion (e.g. from wood, straw, tobacco, gasoline and diesel combustion) – PAH emissions
- From evaporation or sublimation of naphthalene-containing materials (e.g. coal tar, crude oil, petroleum products, moth repellents (however not relevant in the EU) and air fresheners)
- From production processes using naphthalene (e.g. production of phthalic anhydride, dyes and other chemicals) or production of naphthalene

Releases of naphthalene can also be classified based on the type of source, e.g. (Jia and Batterman, 2010):
- Emissions from natural sources (e.g. wildfires)
- Emissions from anthropogenic sources (i.e. from incomplete combustion, from evaporation of naphthalene-containing materials and products, and from production processes).

From an emission inventory perspective, releases of naphthalene to the environment are often classified as (Jia and Batterman, 2010):
- Industrial
  - E.g. production processes when used as an intermediate,
  - Evaporation or sublimation of naphthalene-containing materials such as coal tar, crude oil, petroleum products
  - Power plants, industrial power plants etc.
- Mobile
  - Vehicle exhausts
- Agricultural
  - Controlled burning of agricultural fields
- Natural
  - E.g. wildfires
- Domestic
  - E.g. cigarette smoke,
  - Evaporation or sublimation of naphthalene from consumer products
  - Incineration (woodburning stoves etc.)

According to the ECB (2003), the main source of release of naphthalene to the environment is from indirect sources, particularly **combustion processes – in particular from vehicle exhausts** generating naphthalene as well as other PAHs. Jia and Batterman (2010) give an example from California: In this American state it is estimated that the following sources contribute with the listed percentages to the state-wide total emissions (reference from 2005, data older than 2005, but not specified):
- Gasoline engines 40% of total estimated emissions of naphthalene in California
- Diesel engines 9%
- Slow cure asphalt 13%
- Consumer products 15%
- Industrial sources 19%

This Californian data supports the fact that the main source of release of naphthalene to the environment is vehicle exhausts.

Naphthalene is also released during the treatment of wood with preservatives and from treated wood. Other releases are from industrial processes where naphthalene is released due to its natural occurrence in some of the materials used, e.g. production of aluminium (volatising from the electrodes used), oil refineries, offshore drilling activities. The indirect release of naphthalene from some exemplary products and activities is summarised in the next paragraphs, including some of the products mentioned in section 3.3.2. All the information below is based on ECB (2003).

Release from products containing naphthalene
The fact that naphthalene is present in these products is not intended, but rather a consequence from adding some materials to the products where naphthalene is naturally occurring. Some examples are:

- Release from treating processes where creosote is added
- Release from the industrial and domestic use of creosote
- Release from the use of treated wood products
- Release from tar and bitumen industrial processes
- Release from the use of paints, waterproof membranes and bituminous materials

Release from the production of other sources
PAHs including naphthalene are released during the production of some chemicals and materials where, again, raw materials or ancillary products are used which naturally contain naphthalene. Some examples are:

- Production of phenol, where the processing of cumene releases naphthalene
- Production of propylene oxide production, where naphthalene is released by the chlorohydrin process
- Production of aluminum, where PAHs can be released from the electrode paste used during the electrolysis process

Release from oil production
Naphthalene is a component of formation water (used for offshore drilling), which is discharged from production operations. Naphthalene is also emitted from the oil industries and refineries as fugitive emissions.

Release from traffic
As naphthalene is a component of fuels and oils, it is emitted from the combustion of gasoline and lubricants by use of transport vehicles. Different measurements were carried out to identify naphthalene concentrations in different fuels such as gasoline, kerosene, and fuel oil. Naphthalene emissions have been identified from the following different types of vehicles:

- Diesel trucks
- Gasoline powered vehicles
- Diesel powered vehicles
- Motor boats, where naphthalene has been found in the water-soluble fractions of new and used motor oils

Release from coal combustion
Different monitoring studies carried out on coal combustion plants have shown that naphthalene is also released to air by use of different combustion technologies (the type of coal also plays a role).

Release from coal carbonization and gasification processes
Naphthalene may be formed from a wide variety of coal carbonization and gasification processes. Both involve heating coal to high temperatures in order to produce other products. Carbonization processes are used to convert coal to coke, tars, chemicals and industrial gases whereas gasification processes are designed to produce a gaseous product for use in the heating and chemical industry. A couple of examples are coke production and coal gasification.

5.3.1.1 Origin of sources to PAHs

As described in chapter 1 naphthalene is considered to be a PAH (the most simple and most volatile PAH). For this reason the origin of sources to PAHs is also described in more details here.

PAHs are natural constituents of mineral oil (petrogenic PAHs) or are generated during combustion (pyrogenic PAHs). More or less the same PAHs will be present whether the source is pyrogenic or petrogenic, but the relative composition of the mixture of PAHs is different depending on the source (Lassen et al., 2011). Sources of PAHs can be both natural and anthropogenic:

Natural sources include[49]:

- Forest and grass fires
- Oil seeps
- Volcanoes
- Chlorophyllous plants, fungi, and bacteria

Anthropogenic sources of PAHs include[50]:

- Petroleum
- Electric power generation
- Refuse incineration
- Home heating
- Production of coke, carbon black, coal tar, and asphalt
- Internal combustion engines

Controlled combustion is a major source for PAH emission, though the concentration is rather small, when combustion is efficient[51]. Normally the concentration of naphthalene in emissions from combustion processes is higher than the sum of the concentrations of the other 15 PAHs (US EPA – 16 PAH). This is illustrated and described in chapter 1.

5.3.1.2 Calculated main sources of release in the EU

In the risk assessment report on naphthalene (ECB, 2003), the release of naphthalene has been calculated for the continental environment for the EU. The calculations/estimations in this risk assessment were carried out in the period from 1996 to 2001, which means that the data used probably is from the 1990es. The calculations are made by use of emission factors for the specific areas combined with knowledge of the yearly production for the specific areas and are calculated as worst-case releases. The calculations are presented in Image 7 below and illustrate that naphthalene mainly is released to the air and only to minor extent to water and soil. Furthermore, the calculations illustrate that **combustion of gasoline and diesel by vehicles is by far the most significant release of naphthalene to air** (about 86% of the total releases to air). However, it is emphasised in the ECB (2003) that the calculated figures for combustion of gasoline and diesel by vehicles may be an overestimate as the influence of catalytic converters has not been considered. In the ECB (2003) the emission factor used for gasoline vehicles was 8.6 mg/km and 7.4 mg/km for diesel trucks. In comparison Jia and Batterman (2010) present an emission factor for catalyst-equipped gasoline-powered vehicle of 1 mg/km and emission factors for heavy-duty diesel vehicles between 0.01 and 0.5 mg/mile (corresponding to 0.006 to 0.3 mg/km). This illustrates that the calculated figures for releases of naphthalene will be much lower today compared to the calculated release in the ECB (2003) – however, transportation (calculated in kilometres per year) with both gasoline and diesel vehicles may in contrast have increased considerably the last years.

In Image 7 release of naphthalene from mothballs is also a high contributor to the total emissions. However, the use of naphthalene in mothballs in the EU is no longer supported since the making of the risk assessment report of naphthalene and this release of naphthalene will therefore no longer exist in Europe today.

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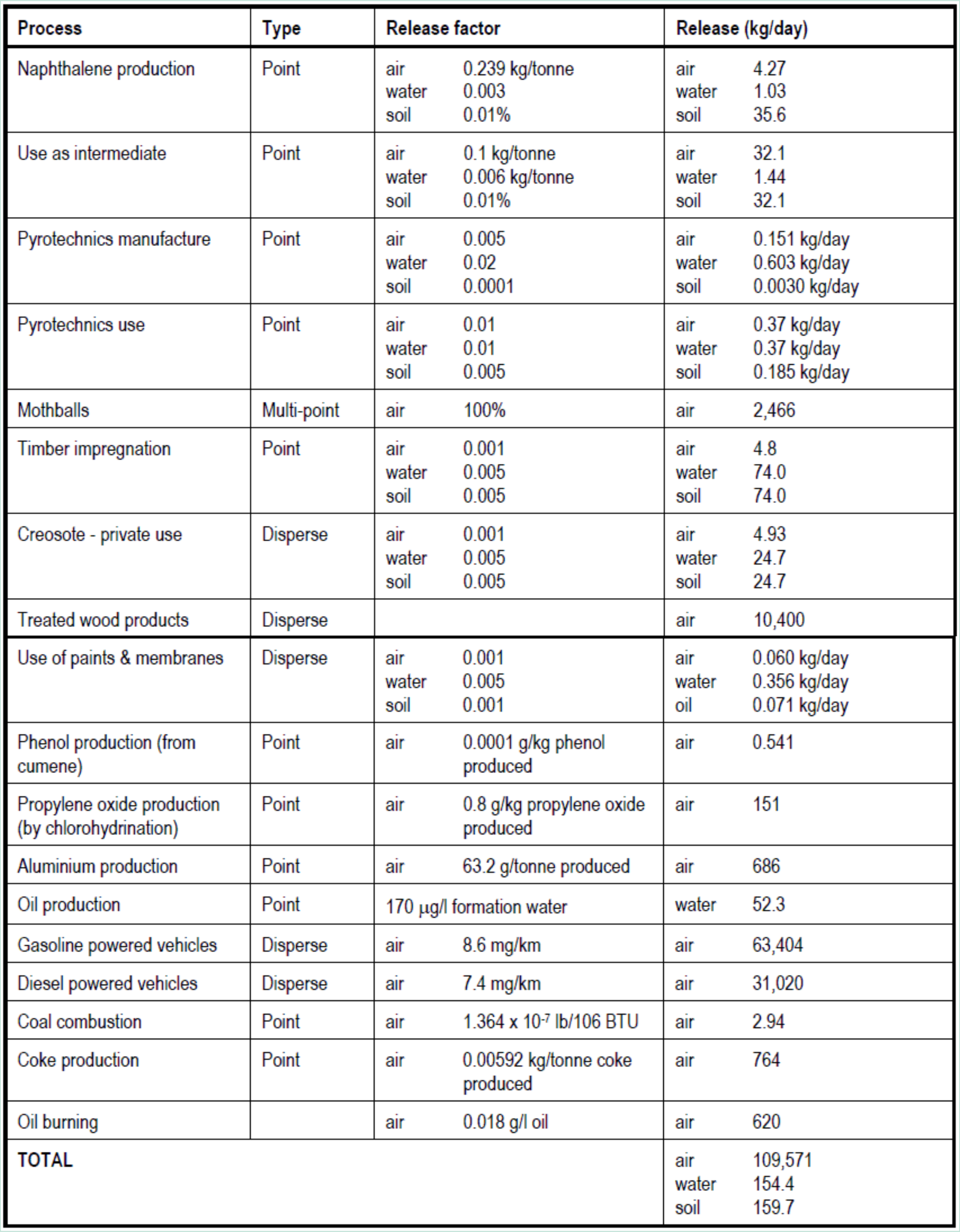
[49] http://www.toxipedia.org/display/toxipedia/Polycyclic+Aromatic+Hydrocarbons+(PAHs)+-+Abridged

[50] http://www.toxipedia.org/display/toxipedia/Polycyclic+Aromatic+Hydrocarbons+(PAHs)+-+Abridged

[51] Information from Ole Schleicher, Department of Air and Environmental Technique, FORCE Technology

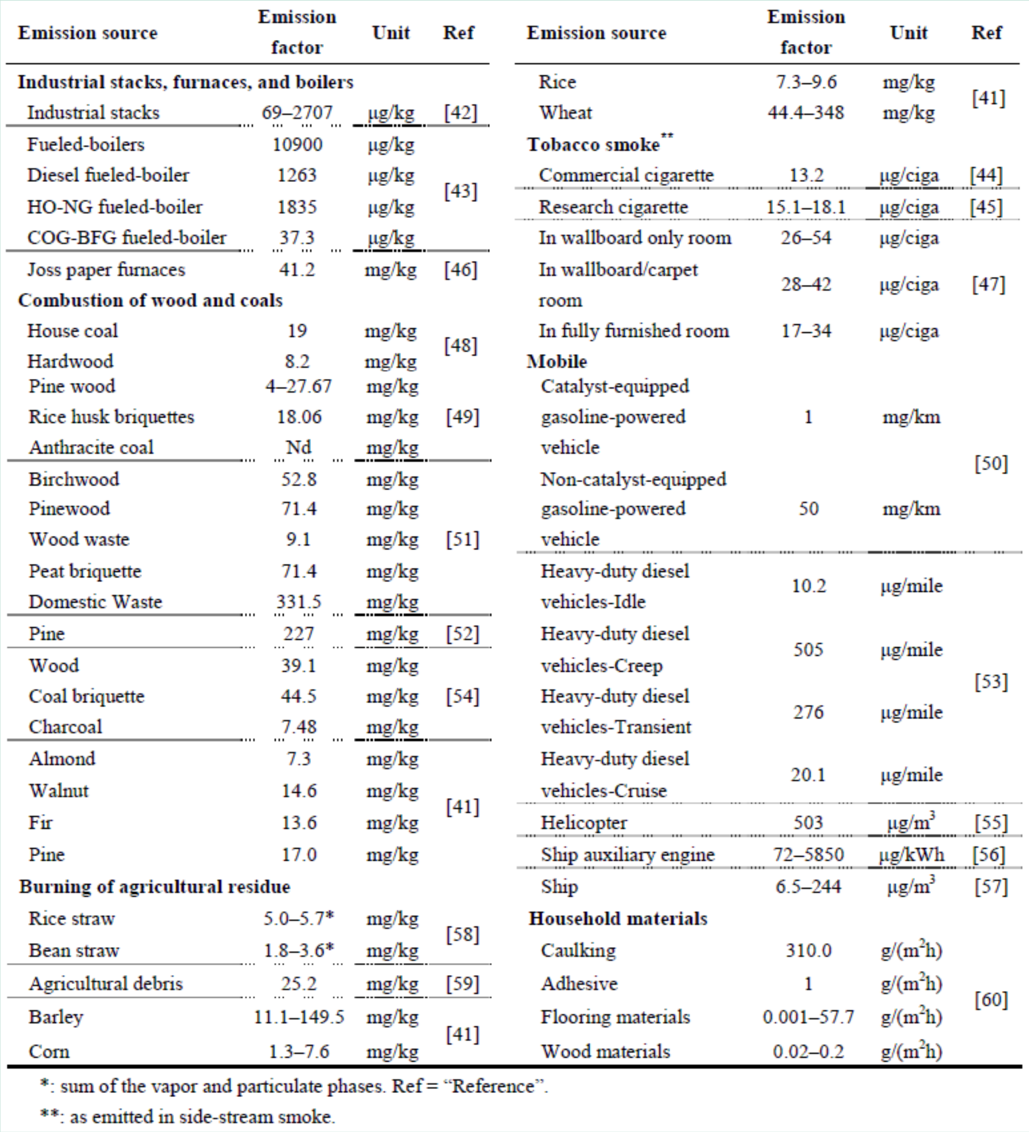


Process	Type	Release factor	Release (kg/day)
Naphthalene production	Point	air 0.239 kg/tonne water 0.003 soil 0.01%	air 4.27 water 1.03 soil 35.6
Use as intermediate	Point	air 0.1 kg/tonne water 0.006 kg/tonne soil 0.01%	air 32.1 water 1.44 soil 32.1
Pyrotechnics manufacture	Point	air 0.005 water 0.02 soil 0.0001	air 0.151 kg/day water 0.603 kg/day soil 0.0030 kg/day
Pyrotechnics use	Point	air 0.01 water 0.01 soil 0.005	air 0.37 kg/day water 0.37 kg/day soil 0.185 kg/day
Mothballs	Multi-point	air 100%	air 2,466
Timber impregnation	Point	air 0.001 water 0.005 soil 0.005	air 4.8 water 74.0 soil 74.0
Creosote - private use	Disperse	air 0.001 water 0.005 soil 0.005	air 4.93 water 24.7 soil 24.7
Treated wood products	Disperse		air 10,400
Use of paints & membranes	Disperse	air 0.001 water 0.005 soil 0.001	air 0.060 kg/day water 0.356 kg/day oil 0.071 kg/day
Phenol production (from cumene)	Point	air 0.0001 g/kg phenol produced	air 0.541
Propylene oxide production (by chlorohydrination)	Point	air 0.8 g/kg propylene oxide produced	air 151
Aluminium production	Point	air 63.2 g/tonne produced	air 686
Oil production	Point	170 µg/l formation water	water 52.3
Gasoline powered vehicles	Disperse	air 8.6 mg/km	air 63,404
Diesel powered vehicles	Disperse	air 7.4 mg/km	air 31,020
Coal combustion	Point	air 1.364 x 10^{-7} lb/106 BTU	air 2.94
Coke production	Point	air 0.00592 kg/tonne coke produced	air 764
Oil burning		air 0.018 g/l oil	air 620
TOTAL			air 109,571 water 154.4 soil 159.7

IMAGE 7
CONTINENTAL ENVIRONMENTAL RELEASE OF NAPHTHALENE FOR THE EU, PROBABLY BASED ON FIGURES FROM THE 1990ES (SOURCE: ECB, 2003)

5.3.1.3 Calculation of main sources of releases in Denmark

In the risk assessment report of naphthalene (ECB, 2003) emission factors for naphthalene are presented for selected sources. Jia and Batterman (2010) have also prepared a list of emission factors for naphthalene for selected sources and as their work is based on newer sources (from 1996 to 2009) their emission factors for naphthalene are presented below in Image 8.



Emission source	Emission factor	Unit	Ref
Industrial stacks, furnaces, and boilers			
Industrial stacks	69–2707	μg/kg	[42]
Fueled-boilers	10900	μg/kg	[43]
Diesel fueled-boiler	1263	μg/kg	
HO-NG fueled-boiler	1835	μg/kg	
COG-BFG fueled-boiler	37.3	μg/kg	
Joss paper furnaces	41.2	mg/kg	[46]
Combustion of wood and coals			
House coal	19	mg/kg	[48]
Hardwood	8.2	mg/kg	
Pine wood	4–27.67	mg/kg	[49]
Rice husk briquettes	18.06	mg/kg	
Anthracite coal	Nd	mg/kg	
Birchwood	52.8	mg/kg	[51]
Pinewood	71.4	mg/kg	
Wood waste	9.1	mg/kg	
Peat briquette	71.4	mg/kg	
Domestic Waste	331.5	mg/kg	
Pine	227	mg/kg	[52]
Wood	39.1	mg/kg	[54]
Coal briquette	44.5	mg/kg	
Charcoal	7.48	mg/kg	
Almond	7.3	mg/kg	[41]
Walnut	14.6	mg/kg	
Fir	13.6	mg/kg	
Pine	17.0	mg/kg	
Burning of agricultural residue			
Rice straw	5.0–5.7*	mg/kg	[58]
Bean straw	1.8–3.6*	mg/kg	
Agricultural debris	25.2	mg/kg	[59]
Barley	11.1–149.5	mg/kg	[41]
Corn	1.3–7.6	mg/kg	
Rice	7.3–9.6	mg/kg	[41]
Wheat	44.4–348	mg/kg	
Tobacco smoke[**]			
Commercial cigarette	13.2	μg/ciga	[44]
Research cigarette	15.1–18.1	μg/ciga	[45]
In wallboard only room	26–54	μg/ciga	[47]
In wallboard/carpet room	28–42	μg/ciga	
In fully furnished room	17–34	μg/ciga	
Mobile			
Catalyst-equipped gasoline-powered vehicle	1	mg/km	[50]
Non-catalyst-equipped gasoline-powered vehicle	50	mg/km	
Heavy-duty diesel vehicles-Idle	10.2	μg/mile	[53]
Heavy-duty diesel vehicles-Creep	505	μg/mile	
Heavy-duty diesel vehicles-Transient	276	μg/mile	
Heavy-duty diesel vehicles-Cruise	20.1	μg/mile	
Helicopter	503	μg/m^3	[55]
Ship auxiliary engine	72–5850	μg/kWh	[56]
Ship	6.5–244	μg/m^3	[57]
Household materials			
Caulking	310.0	g/(m^{2}h)	[60]
Adhesive	1	g/(m^{2}h)	
Flooring materials	0.001–57.7	g/(m^{2}h)	
Wood materials	0.02–0.2	g/(m^{2}h)	

*: sum of the vapor and particulate phases. Ref = "Reference".

**: as emitted in side-stream smoke.

IMAGE 8
EMISSION FACTORS OF NAPHTHALENE FOR SELECTED SOURCES (SOURCE: JIA AND BATTERMAN, 2010. THE REFERENCE NUMBERS [41] TO [60] REFER TO REFERENCES SITED IN JIA AND BATTERMAN, 2010)

These emission factors can be used to calculate releases of naphthalene in Denmark. This has been carried out for combustion of gasoline and diesel by vehicles only, as these releases are regarded as the major contributor to naphthalene emissions in Denmark.

Calculation of release from gasoline and diesel vehicles in Denmark

According to the Danish Road Directorate the transport covered 46,047 million vehicle*km in 2012. Of this, 22,794 million were done in gasoline-powered vehicles and 23,252 million in diesel-powered vehicles[52].

It is assumed in the calculations that all gasoline-powered vehicles are equipped with a catalyst and therefore have an emission of 1 mg naphthalene per km (as listed in Image 8 above). It is also assumed that diesel-powered vehicles emit 0.15 mg/km, reflecting a driving pattern with 50%

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[52] Excel spreadsheet "Trafikarbejdet 2000-2012 fordelt på køretøjstyper". Downloaded from www.vejdirektoratet.dk/DA/viden_og_data/statistik/trafikken%20i%20tal/hvor_meget_korer_vi/Sider/Trafikarbejde.aspx July 9, 2014

transient and 50% cruising (i.e. an average of the emission figures listed in Image 8 above and calculated to per kilometre instead of per mile).

Based on these assumptions, the annual emissions from road traffic are estimated to be 24,934 kg naphthalene or close to **25 tonnes naphthalene** (see Table 10).

	Transport work (mill. vehicle*km)	Emission factor (mg/km)	Emission (kg/year)
Gasoline-powered vehicles	22,794	1	22,794
Diesel-powered vehicles	23,252	0.092	2,140
Total			24,934

TABLE 10
ESTIMATION OF NAPHTHALENE RELEASES FROM VEHICLES IN DENMARK IN 2012

Calculation of release from cigarette smoke in Denmark

According to Statistics Denmark[53] the following numbers could be found for 2013:

- Total number of cigarettes sold in Denmark were 6,852 million

By multiplying the number of cigarettes sold in Denmark in 2013 by the emission factor for cigarettes found in Jia and Batterman (2010) of 13.2 µg/cigarette, the total emission of naphthalene in Denmark in 2013 due to cigarette smoke was:

- In total = 13.2 µg/cigarette x 6 852 million cigarettes = **90.4 kg naphthalene**

5.3.2 Main source of industrial releases in the EU and Denmark

According to Regulation No 166/2006 concerning the establishment of a European Pollutant Release and Transfer Register (E-PRTR) as described in chapter 2, certain facilities/activities with releases to air, water and land of naphthalene above the applicable capacity threshold values specified for naphthalene must report their releases to the environment to the authorities and the E-PRTR database[54].

The criteria for facilities reporting to the E-PRTR database are[55]:

- The facility falls under at least one of the 65 E-PRTR economic activities as listed in Annex I of Regulation 106/2006.
    - Manufacture, process or use threshold: 10,000 kg/year
- The facility transfers waste off-site which exceeds the specific thresholds set out in Article 5 of Regulation 106/2006.
    - Threshold for off-site transfer of pollutants: 100 kg/year
- The facility releases pollutants which exceed specific thresholds specified for each media – air, water and land in Annex II of the Regulation 106/2006:
    - Threshold for release to air: 100 kg/year
    - Threshold for release to water: 10 kg/year
    - Threshold for release to land: 10 kg/year

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[53] http://statistikbanken.dk
[54] http://prtr.ec.europa.eu/PollutantReleases.aspx
[55] http://prtr.ec.europa.eu/pgAbout.aspx

This means that several facilities are obliged to report on their naphthalene emissions to the environment, but of course facilities not reporting or facilities not fulfilling the reporting criteria will not be included in the data presented below for Denmark and the EU respectively.

The EU

In the E-PRTR database several releases of naphthalene have been reported on EU level. The data presented below represents the yearly releases of naphthalene for EU-27.

Year	Number of facilities	Release to air (tonnes)	Release to water (tonnes)	Release to soil (tonnes)
2007	153	186	76.0	0
2008	156	195	190	0
2009	147	945	124	0.0149
2010	138	133	156	0
2011	134	125	82.4	0
2012	148	87.4	94.0	0

TABLE 11
YEARLY RELEASES OF NAPHTHALENE TO AIR, WATER AND SOIL FOR THE YEARS 2007 TO 2012 FOR FACILITIES IN EU-27 WHICH ACCORDING TO REGULATION 166/2006 HAVE TO REPORT TO THE E-PRTR DATABASE (SOURCE: E-PRTR DATABASE[56])

Accidental releases are also reported. The following accidental releases are found in the E-PRTR database:

- 2007: 1 accidental release of a total of 1.67 tonnes
- 2008: 2 accidental releases of a total of 1.67 tonnes
- 2009: 2 accidental releases of a total of 1.40 tonne.
- 2010: 1 accidental release of a total of 140 grams
- 2011: 1 accidental release of a total of 20 grams

From Table 11 it can be concluded that even though the number of facilities reporting on environmental releases of naphthalene has been rather constant for the last six reporting years the releases to air of naphthalene seem to decline with the lowest yearly release in 2012 of 87.4 tonnes in total for EU-27. However, releases to water seem rather constant over the last six reporting years with a total release for EU-27 in 2012 of 94 tonnes. In general releases to soil are non-existing.

Image 9 below illustrates where in EU-27 the 148 facilities reporting of naphthalene releases to the environment (air and water) in 2012 are situated. 73 facilities have reported on release of naphthalene **to water**. Of these 73 facilities, 59 facilities are situated in the North Sea and have reported a total release to water of 99.6 tonnes in 2012. This amount corresponds to 99% of the release to water in 2012 and is caused by facilities carrying out extraction of crude petroleum.

Most of the environmental releases of naphthalene **to air** from the 79 facilities reporting of releases to air in 2012 are situated in the following countries:

- Belgium – 5 facilities releasing a total of 33.0 tonnes naphthalene to air (38%)
- France – 17 facilities releasing a total of 14.7 tonnes naphthalene to air (17%)

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[56] http://prtr.ec.europa.eu/PollutantReleases.aspx

- UK – 28 facilities releasing a total of 12.0 tonnes naphthalene to air (14%)
- Italy– 1 facility releasing a total of 8.8 tonnes naphthalene to air (10%)
- Slovakia – 1 facility releasing a total of 7.1 tonnes naphthalene to air (8%)
- Holland – 4 facilities releasing a total of 4.0 tonnes naphthalene to air (5%)

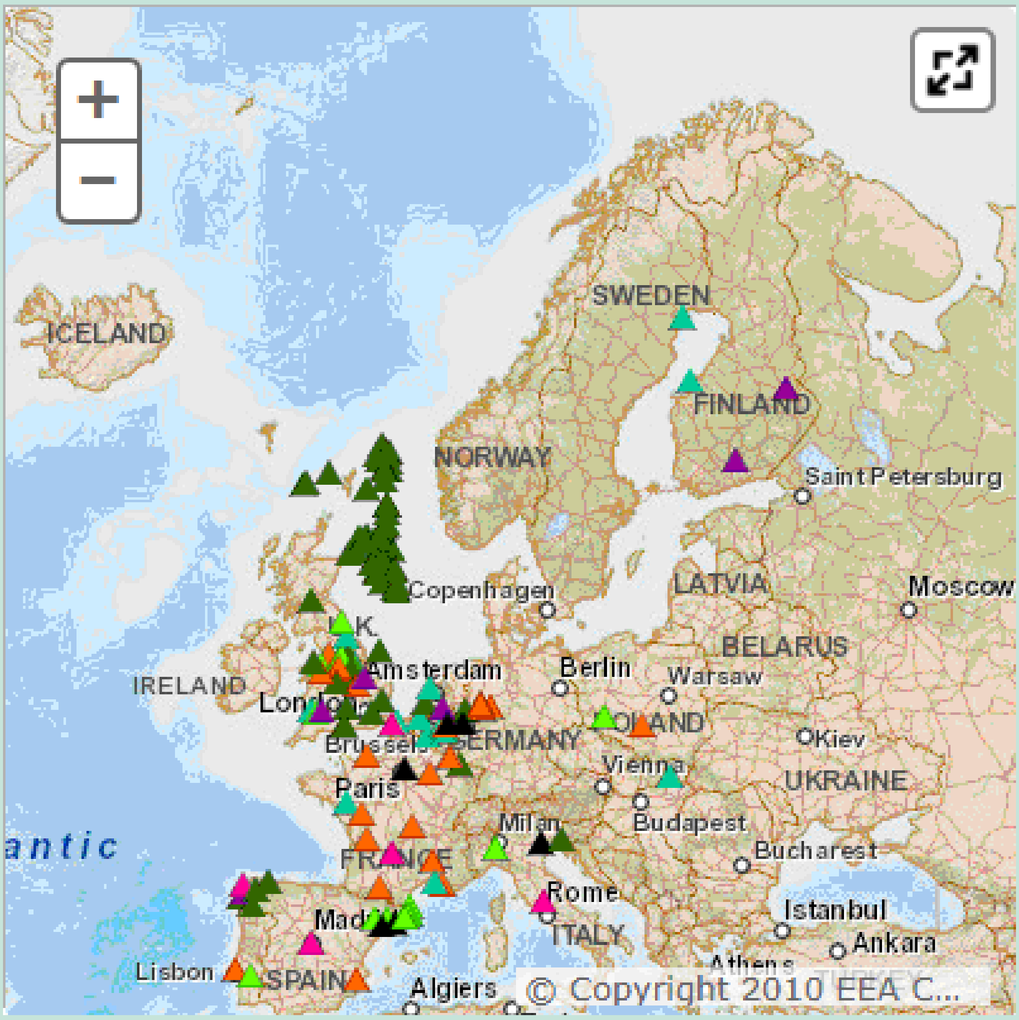
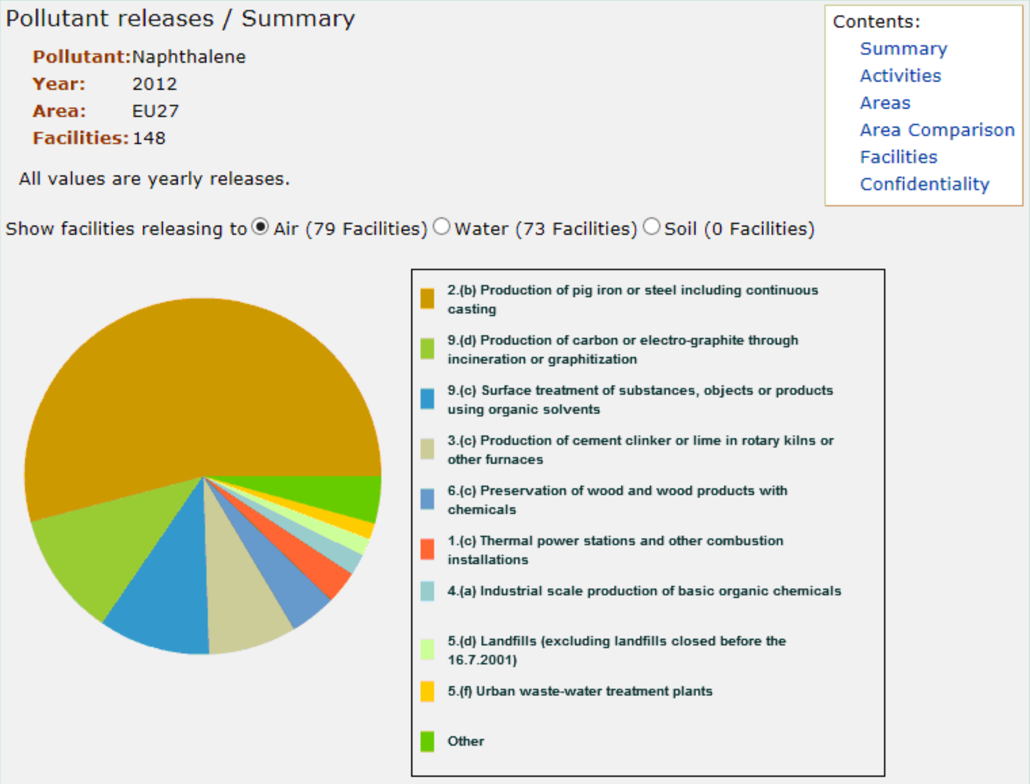


IMAGE 9
SITUATION OF FACILITES REPORTING OF NAPHTHALENE EMISSIONS IN 2012 IN EU-27 (SOURCE: E-PRTR DATABASE – A SEARCH ON NAPHTHALENE FOR EU-27 IN 2012)

Image 10 and Image 11 illustrate the distribution in percentage of the releases of naphthalene between different activities. Image 10 illustrates the distribution of releases of naphthalene to air and Image 11 the releases of naphthalene to water. Both images show the distribution for the activities for the year 2012 for EU-27.

Image 10 illustrates that the largest contributors to releases of naphthalene to air come from the following sources:
- Production of pig iron or steel including continuous casting (54.1% or 47.3 tonnes)
- Production of carbon or electro-graphite through incineration or graphitization (11.3% or 9.9 tonnes)
- Surface treatment of substances, objects or products using organic solvents (10.1% or 8.8 tonnes)



Pollutant releases / Summary

Pollutant: Naphthalene
Year: 2012
Area: EU27
Facilities: 148

All values are yearly releases.

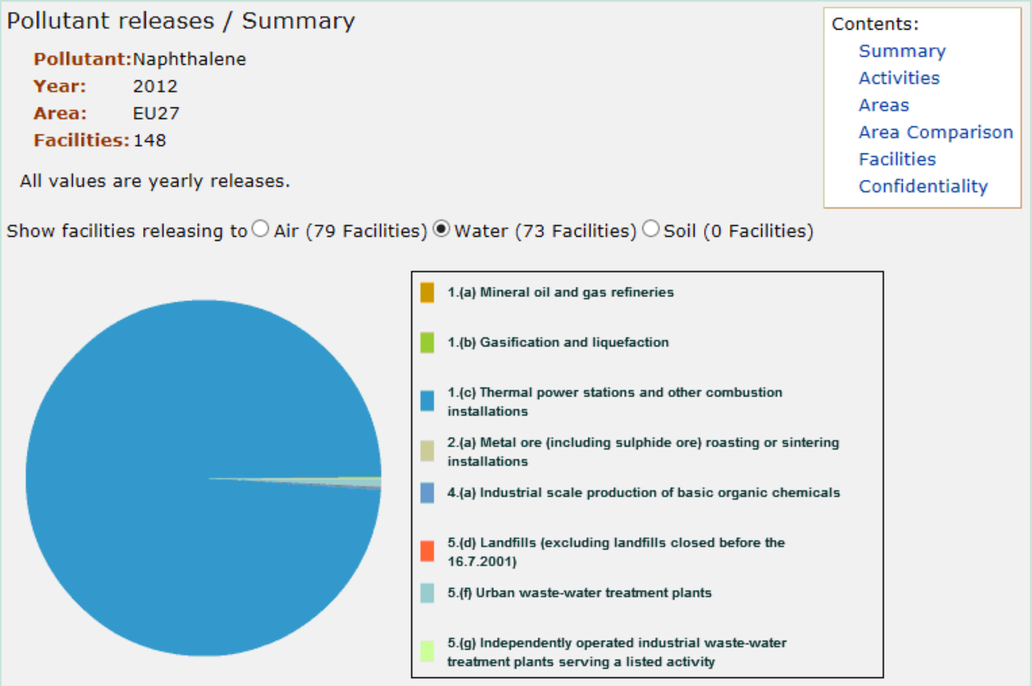
Show facilities releasing to ● Air (79 Facilities) ○ Water (73 Facilities) ○ Soil (0 Facilities)

- 🟧 2.(b) Production of pig iron or steel including continuous casting
- 🟩 9.(d) Production of carbon or electro-graphite through incineration or graphitization
- 🟦 9.(c) Surface treatment of substances, objects or products using organic solvents
- 🟫 3.(c) Production of cement clinker or lime in rotary kilns or other furnaces
- 🟦 6.(c) Preservation of wood and wood products with chemicals
- 🟥 1.(c) Thermal power stations and other combustion installations
- 🟦 4.(a) Industrial scale production of basic organic chemicals
- 🟩 5.(d) Landfills (excluding landfills closed before the 16.7.2001)
- 🟨 5.(f) Urban waste-water treatment plants
- 🟩 Other

IMAGE 10
PERCENTAGE DISTRIBUTION OF RELEASES OF NAPHTHALENE TO AIR FROM DIFFERENT FACILITIES IN EU-27 IN 2012 (SOURCE: E-PRTR DATABASE – A SEARCH ON NAPHTHALENE FOR EU-27 AND 2012)

Image 11 illustrates that the largest contributor to releases of naphthalene to water comes from the following source:

- Thermal power stations and other combustion installations (98.8% or 92.9 tonnes)
- Urban waste-water treatment plants (0.7% or 0.7 tonnes)


Pollutant releases / Summary

Pollutant: Naphthalene
Year: 2012
Area: EU27
Facilities: 148

All values are yearly releases.

Show facilities releasing to ○ Air (79 Facilities) ● Water (73 Facilities) ○ Soil (0 Facilities)

IMAGE 11
PERCENTAGE DISTRIBUTION OF RELEASES OF NAPHTHALENE TO WATER FROM DIFFERENT FACILITIES IN EU-27 IN 2012 (SOURCE: E-PRTR DATABASE – A SEARCH ON NAPHTHALENE FOR EU-27 AND 2012)

Denmark

According to the E-PRTR there are no facilities reporting on releases of naphthalene for the years 2007 to 2012 in Denmark. However, this is not the same as stating that there is no environmental release of naphthalene from industrial sources in Denmark. More likely it is due to the fact that the facilities in Denmark are not fulfilling the criteria which require the facilities to report to the E-PRTR database. Mainly large facilities with large environmental emissions to the environment have to report to the E-PRTR database.

An emission inventory is reported for Denmark for selected pollutants including PAHs. However, naphthalene is not included in the emission inventory as a PAH. Therefore, the Danish emission inventory provides no data on naphthalene releases[57].

As Koppers Denmark produces naphthalene in Denmark, a small release of naphthalene to the environment may also be expected. According to Schleicher et al. (2009), Koppers Denmark reported that their yearly release of naphthalene to the environment was 7 tonnes (in 2006 with a yearly production of 21,500 tonnes). It is expected that this emission of naphthalene will be around the same amount today or perhaps 40% higher, if it is assumed that the emission will follow the increased production (40% higher equal to 30,000 tonnes in 2013) which Koppers Denmark has today (2013). A 40% higher emission would correspond to a yearly emission of around 10 tonnes.

5.3.3 Monitoring data

In the following sections monitoring data in air, water and soil is presented. For monitoring data in air a review carried out by Jia and Batterman (2010) has been used as the main source as this review summarises several relevant monitoring studies. For the water and soil compartment the risk assessment report (ECB, 2003) and ATSDR (2005) have been used as the main sources.

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[57] http://envs.au.dk/videnudveksling/luft/emissioner/emissioninventory/

Monitoring data from the Danish NOVANA (National Action Plan for the Aquatic Environment) programme has been listed as well. Monitoring of naphthalene in stream, lakes, waste water, sludge and sediment has been part of the NOVANA programme for several years (DMU, 2006), and monitoring data for waste water and sludge has been reported.

5.3.3.1 Monitoring data for air

Monitoring data exists for naphthalene for various countries worldwide. However, according to Jia and Batterman (2010), who have carried out a critical review of naphthalene sources and exposures relevant to outdoor air, naphthalene has often been excluded in both VOC and PAH studies, as naphthalene is a borderline substance both with respect to VOC (least volatile VOC) and PAH (most volatile PAH). In the following sections the monitoring data presented for naphthalene by Jia and Batterman (2010) is described, as their review is the most comprehensive and recent reporting of monitoring data on naphthalene.

Naphthalene concentrations in indoor air may be higher than outdoors (ATSDR, 2005; Jia and Batterman, 2010). However, in this chapter only monitoring data for outdoor air is presented; for indoor air se chapter 6 ”Human health effects”.

Jia and Batterman (2010) describe that they have reviewed 24 studies which have reported on outdoor concentrations of naphthalene. The studies report on outdoor naphthalene concentrations in the US, Canada, UK, Germany, Finland, Australia, India, Korea, China and Taiwan. The average outdoor concentrations of naphthalene are below 1.0 µg/m^3 and medians below 0.5 µg/m^3. Maximum outdoor concentration ranges from 0.01 to 4.7 µg/m^3. Jia and Bitterman (2010) concluded that a concentration of 5 µg/m^3 might be used as a conservative exposure scenario for “general” urban air. Levels may be elevated near industrial and waste disposal sites containing strong sources, e.g. naphthalene levels averaged 11 µg/m^3 at a landfill site in summer in China.

Jia and Batterman (2010) conclude that the median outdoor concentrations of naphthalene in urban areas ranked by region generally follow the following trend: U.S.A. > Europe > Canada. Median concentrations measured elsewhere (i.e. Korea, China, India and Taiwan) fall within the bounds of these studies. It is not feasible to compare ambient concentrations measured in rural or remote areas due to the very low concentrations seen and the small number of studies.

Like many other pollutants, naphthalene concentrations in outdoor air undergo daily variation. Concentrations tend to peak at night and in the morning and are lowest at mid-day. Levels decrease during midday due to enhanced dispersion, lower traffic and reduced emissions. Outdoor concentrations also show seasonal variations, and higher levels are seen in winter as compared to summer (Jia and Batterman, 2010).

Unsurprisingly, outdoor concentrations are lower in rural areas that have little traffic and fewer if any industrial facilities. Based on measurements in the US and rural Western Canada, rural concentrations typically fall below 0.1 µg m^3 and below detection limit of 0.01 µg/m^3 in remote locations. Occasionally, rural areas experience locally elevated concentrations due to open burning of crop residues and possibly other materials, as shown in an agricultural county in Taiwan where naphthalene levels increased by 1.3 to 2.6 times to 0.38 to 0.44 µg m^3 during the burning period (Jia and Batterman, 2010).

Jia and Batterman (2010) describe that although naphthalene is a known constituent of vehicle exhaust, few studies have examined the effect of traffic on naphthalene concentrations. Naphthalene has been rarely reported in tunnel studies, a common way to characterize traffic emissions. One study in two highway tunnels in Chicago (USA) reported a concentration of 8.0 µg m^3. Proximity to industrial facilities can increase naphthalene concentrations. In Canada, a clear concentration gradient was seen around a large cluster of industrial and chemical facilities, and as mentioned earlier quite high concentrations (11 µg m3) were noted at a landfill site in China in summer.

5.3.3.2 Monitoring data for water

There are a large number of reported levels for water – the data is, however, mainly older data from the 1980es or 1990es. Only the Danish NOVANA monitoring data is newer (1998-2003). Levels of naphthalene in unpolluted surface waters range up to 5 ng/l and in other areas levels up to a few µg/l have been found. In one heavily contaminated area (the site of extreme contamination by creosote following a fire at a wood treatment plant), naphthalene levels up to 14.1 mg/l have been found (ECB, 2003). ATSDR (2005) reports of naphthalene concentrations on the µg/l level in urban runoff samples. Naphthalene was detected in 11% of the samples in concentrations ranging from 0.8 to 2.3 µ/l and was found in even higher concentrations (33 mg/l) downstream of potential pollutant sources in Florida.

Levels of naphthalene in uncontaminated groundwater range up to 0.03 µg/l. Many measurements are available for contaminated sites where levels ranged up to 15.3 mg/l (ECB, 2003).

Naphthalene levels in precipitation and drinking water range up to 370 ng/l although elevated levels have been found in drinking water samples from wells near a chemical waste dump in the US (ECB, 2003). ATSDR (2005) reports that naphthalene is rarely detected in drinking water, but has been measured at levels up to 1.4 µg/l.

Some measurements of naphthalene in marine waters are available and the highest value found was 300 ng/l (ECB, 2003). Mean concentration measured in seawater in the south Atlantic Ocean was 6.3 ng/l (ATSDR, 2005).

In Denmark monitoring of naphthalene in water has been part of the NOVANA programme (National Action Plan for the Aquatic Environment) for several years. The report from DMU (2006) that summarises on the NOVANA programme for the years 1998-2003, shows the following monitoring data for naphthalene in water:

- Naphthalene was found in **ground water** in 2.7% of the analysed samples. In all cases the levels found was below the limit value for drinking water of 2 µg/l.
- Naphthalene was found in water at the **point of discharge from sewage treatment plants** in average concentrations of 0.02 µg/l (95% percentile value was 0.06 µg/l). For comparison the limit value for surface waters is 1 µg/l. 26% of the 184 measurements had values above the detection limit.
- Naphthalene was found in **sludge** in average concentrations of 298 µg/kg dry matter (95% percentile value was 1045 µg/kg dry matter). 93% of the 58 measurements had values above the detection limit.
- **The total emission of naphthalene to water** at the point of discharge from sewage treatment plant was estimated to be 12 kg/year in the years from 1998-2003, and the total industrial emissions of naphthalene was estimated to be 0.12 kg/year in the years from 2001-2003.

5.3.3.3 Monitoring data for soil and sediment

Measured levels of naphthalene in sediments are available from a wide range of locations, but are also mainly older data from the 1980es or 1990es.

Naphthalene was widely detected in surface water sediments with maximum levels exceeding 100 µg/kg in many of these studies. Levels in sediments from estuarine and coastal sites were generally lower although peak values again exceeded 100 µg/kg. There are no widespread uses of naphthalene to account for its widespread occurrence and the high values were not associated with sites where naphthalene itself is produced or used (ECB, 2003). The same levels are reported in ATSDR (2005) for mean concentrations of urban soil in the US. The levels of naphthalene in untreated agricultural soil ranges from 0 to 3 µg/kg (ATSDR, 2005).

Naphthalene is also found in the sediment from motorway run-offs and near sites of boating activity as a result of the combustion processes in car and boat engines (ECB, 2003). ATSDR (2005) reports of median concentration in sediment below 500 µg/kg.

The highest value reported for urban areas is 1.47 mg/kg for suspended matter at a site near a sewage treatment plant. Other values for urban areas ranged up to 720 µg/kg and are likely to arise from combustion processes. Values of up to 520 µg/kg have been reported for motorway run-offs (ECB, 2003).

Very high levels of naphthalene in soil (up to 7,720 mg/kg) have been found, but these levels are related to contamination, for example by creosote, where naphthalene is a component in the mixture (ECB, 2003). However, creosote treated wood is restricted in Denmark today.

5.4 Environmental impact

Naphthalene is mainly used as an intermediate chemical for manufacturing of other chemicals, but being a PAH (the simplest and most volatile PAH) naphthalene is also found in products containing mineral oil (such as asphalt, rubber and plastic products, etc.) and will be emitted from all combustion processes where the combustion is incomplete.

Naphthalene is characterised as a semi-volatile organic compound, but is considered to be the most volatile PAH. Therefore, naphthalene will primarily be emitted to air, but also to some extent to soil and water. Monitoring data illustrates that naphthalene is found in concentrations up to a few µg/m^3 **in air** ("general urban air"). For point source emissions of naphthalene the concentrations may of course be higher. Monitoring data for **water** illustrates that naphthalene is found in concentrations ranging from a few ng/l (unpolluted areas) to a few µg/l. For heavily polluted areas concentrations in the range of a few mg/l have been observed. Monitoring data for **soil** illustrates that naphthalene is found in untreated soil in concentrations up to 3 µg/kg. However, very high concentrations of naphthalene up to 7 g/kg have been found in creosote contaminated soils. Naphthalene concentrations in the range of 100- 500 µg/kg have been found.

Naphthalene is regarded as persistent. Naphthalene may be readily biodegradable under aerobic conditions, but only in oil-polluted waters. Under normal conditions and under anaerobic conditions, biodegradation does not seem to occur. Biodegradation of naphthalene seems to occur slowly (half-lives up to 1700 days) in unpolluted water, but much more rapidly in oil-polluted water (half-life about 7 days). Naphthalene seems to be persistent in sediment and soil, but not in the aqueous environment under aerobic conditions.

If naphthalene is released into air, water, or soil, it will reside predominantly in the compartment to which it is released. The atmospheric half-life of naphthalene is less than 1 day, whereas the half-life in surface water is estimated to be about 71 hours, but the half-life in deeper water (5 m) is much longer and estimated to be 550 hours. Half-lives in sediment and soils have been reported from a couple of days to a couple of months, which seems to be dependent on the presence of oxygen. The degradation is much quicker under aerobic conditions.

Naphthalene has a low bioconcentration potential and overall, naphthalene cannot be considered as a PBT substance (P, but not B and T).

In the risk assessment report (ECB, 2003), **PEC/PNEC** ratios have been calculated in order to assess the effects on the environment. Predicted environmental concentrations to **water** are calculated on a local, regional and continental scale ranging between 0.0025 to 0.31 µg/l[58], however, with a much higher PEC of 2.35 µg/l compared to the other values for pyrotechnics manufacture. It is noted in the ECB (2003) that the predicted environmental concentration for production of pyrotechnics is based on an absolutely worst-case scenario. Comparing these PEC values with the calculated predicted no effect concentration PNEC for water of 2.4 µg/l, it is concluded in the ECB (2003) that the release of naphthalene to water is unlikely to cause adverse effects on the aquatic environment. Comparing the PNEC value for water with the monitoring data illustrates that for very polluting point sources environmental effects on the aquatic environment could occur.

Predicted environmental concentrations to **sediment** are calculated on a local, regional and continental scale ranging between 0.07 to 8.7 µg/kg[59]; however, with a much higher PEC of 66 µg/kg compared to the other values for pyrotechnics manufacture. In the ECB (2003) it is noted that the predicted environmental concentration for production of pyrotechnics is based on an absolutely worst-case scenario. Comparing these PEC values with the calculated predicted no effect concentration PNEC for sediment of 67.2 µg/kg, it is concluded in the ECB (2003) that the release of naphthalene to sediment is unlikely to cause adverse effects on the aquatic environment.

Predicted environmental concentrations to **soil** are calculated on a local, regional and continental scale ranging between 0.023 to 1.7 µg/kg[60]; however, with a much higher PEC of 36 µg/kg compared to the other values for pyrotechnics manufacture and 50 µg/kg for use as intermediate. In the ECB (2003), it is noted that the predicted environmental concentration is based on absolutely worst-case scenarios. Comparing these PEC values with the calculated predicted no effect concentration PNEC of 53.3 µg/l, it is concluded in the ECB (2003) that the release of naphthalene to soil is unlikely to cause adverse effects in the terrestrial environment. Comparing the PNEC value for soil with the monitoring data illustrates that for very polluting point sources (such as creosote contaminated soil) environmental effects on the terrestrial environment could occur.

The predicted environmental no effect concentration could not be calculated for the **atmosphere**.

Environment Canada (2008) comes to the overall conclusion that naphthalene is not considered to cause ecological harm.

The ECB (2003) has predicted that combustion processes are responsible for 88% of the environmental releases of naphthalene on a regional scale. This figure is based on older emission factor values for gasoline and diesel driven non-catalytic vehicles and will therefore probably be an overestimation with respect to the naphthalene release today in spite of a higher transportation figures today. The calculated examples in section 5.3 “Environmental exposure” illustrate that estimated release of naphthalene from diesel and gasoline driven vehicles in Denmark in 2013 is around 25 tonnes per year, whereas the rough estimation of the naphthalene emission from production of naphthalene in Denmark at Koppers Denmark ApS is around 10 tonnes per year. Naphthalene emissions from vehicles are diffuse emissions from many sources whereas the emission from Koppers Denmark is one single point source. To these emissions should be added all other sources of releases of naphthalene from especially incomplete combustion processes like combustion of wood and coals, and industrial furnaces/boilers. In comparison the yearly industrial

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[58] It should be noted that in the EU RAR the production of grinding wheels originally had a much higher calculated PEC. However, a new assessment has been carried out for production of grinding wheels in EU RAR Addendum (2007) resulting in a much lower PEC for production of grinding wheels, below the PNEC value.

[59] It should be noted that in the EU RAR the production of grinding wheels originally had a much higher calculated PEC. However, a new assessment has been carried out for production of grinding wheels in EU RAR Addendum (2007) resulting in a much lower PEC for production of grinding wheels, below the PNEC value.

[60] It should be noted that in the EU RAR the production of grinding wheels originally had a much higher calculated PEC. However, a new assessment has been carried out for production of grinding wheels in EU RAR Addendum (2007) resulting in a much lower PEC for production of grinding wheels, below the PNEC value.

emission to air of naphthalene in 2012 according to the E-PRTR database was 87.4 tonnes in total for EU-27.

5.5 Summary and conclusions

Naphthalene has a harmonised classification for environmental effects of:

- Aquatic Acute 1 H400: Very toxic to aquatic life
- Aquatic Chronic 1 H410: Very toxic to aquatic life with long lasting effects

Naphthalene is regarded as persistent. Naphthalene may be readily biodegradable under aerobic conditions, but only in oil-polluted waters. Under normal conditions and under anaerobic conditions biodegradation does not seem to occur. Naphthalene seems to be persistent in sediment and soil, but not in the aqueous environment under aerobic conditions. Naphthalene has a low bioconcentration potential and overall the substance cannot be considered a PBT substance (P, but not B and T) even though naphthalene is 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". This is due to the differences in the effect levels for criteria for the PBT assessment and the classification criteria.

As naphthalene is a PAH, the largest environmental releases (estimated to be 88% of the environmental releases by the European Chemicals Bureau (ECB, 2003)) are due to incomplete combustion of organic material. For this reason naphthalene may also be present in small amount (impurity levels) in consumer products made of plastics or rubber where softeners or carbon black is used. Release to the environment of naphthalene may also occur from production sites or from industrial use of naphthalene as an intermediate chemical. However, it is the formation of naphthalene from indirect emissions, especially incomplete combustion that seems to be the major source of naphthalene in the environment. Examples of indirect emissions of naphthalene are:

- Release from the use of products which naturally contain naphthalene
- Release from the production of substances using raw materials or ancillaries which naturally contain naphthalene
- Release from oil production
- Release from use of transport vehicles
- Release from coal combustion
- Release from coal carbonisation and gasification

Based on the available monitoring data on naphthalene, it is not expected that naphthalene in general will cause adverse effects in the aquatic or terrestrial environment. However, point source pollution has shown concentrations that are much higher than the calculated predicted no effect concentrations (PNEC), which means that there may be situations that may have an environmental effect, e.g. point releases to the environment or contaminated soil due to release of naphthalene from creosote treated wood[61]. Predicted environmental effect concentrations (PNEC) could not be calculated for the atmosphere. Therefore an assessment of the environmental effects of naphthalene to air has not been made (in spite of the fact that most naphthalene is released to air). However, the atmospheric half-life of naphthalene is less than one day, and when released to the air about 90% of this naphthalene will remain in the air. In the air naphthalene will be transformed to 1-naphtol[62], 2-naphtol[63] and 2-nitronaphthalene[64] as the major constituents by photochemical reaction. Two of these reaction products are also classified as toxic to the environment, but with a less toxic classification compared to the environmental classification of naphthalene.

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[61] The production of creosote treated wood is no longer allowed in Denmark, but creosote treated wood may still be in use in Denmark.

[62] Harmonised classification as Acute Tox. 4, H302, H312; Skin Irrit. 2, H315; Eye Dam. 1, H318; STOT SE 3, H335.

[63] Harmonised classification as Acute Tox. 4, H302, H332; Aquatic Acute 1, H400.

[64] Harmonised classification as Carc. 1B, H350; Aquatic Chronic 2, H411.

6. Human health effects

Humans are mainly exposed to naphthalene if working with naphthalene (occupational exposure) or by indirect exposure from combustion of fossil fuels (e.g. combustion of gasoline and diesel by vehicles) and the off-gassing of naphthalene-containing products. However, as naphthalene is classified as being carcinogenic, certain precautionary measures are dictated by law in the EU and Denmark, when working with naphthalene in order to minimise the exposure of naphthalene. Furthermore, the use of the naphthalene-containing moth repellents is no longer supported and thereby minimising the direct consumer exposure of naphthalene.

The majority of the data presented in this chapter is based on information from the European Risk Assessment Report on naphthalene (ECB, 2003). However, information from the ATSDR (2005) and Environment Canada (2008b) reports has been used as well. Finally, the Registered Substances database of ECHA (ECHA RSD, 2014) has also been used.

6.1 Human health hazard

6.1.1 Classification

The harmonised classification of naphthalene according to CLP is (as also presented in Table 5):

- Acute Tox. 4, H302 “Harmful if swallowed”
- Carc. 2, H351 “Suspected of causing cancer”

Naphthalene is also classified with hazard classes for the environment, which are not mentioned here. See Table 5 and chapter 5 “Environmental effects and fate” for details.

6.1.2 Toxicokinetics, absorption, distribution, metabolism and excretion

Exposure to naphthalene may occur through inhalation, ingestion or dermal contact. The toxicokinetics (in vivo) studies listed in the ECHA RSD (2014) are from the 1980es and are the same studies as listed in the EU RAR on naphthalene (ECB, 2003). Here the conclusion is that limited information is available on humans, but the information indicates that:

- Naphthalene is readily absorbed by all routes of exposure:
  - Inhalation: In vivo studies with rats suggest extensive uptake via the lungs.
  - Oral: In vivo studies with rats show rapid and complete absorption of naphthalene from the gastro-intestinal tract.
  - Dermal: Limited information is available; however the high lipid soluble nature of naphthalene suggests that dermal absorption is likely. A single in vivo study with rats suggests that dermally applied naphthalene is absorbed relatively quickly into plasma.
- Animal data shows that almost complete and rapid absorption occurs following ingestion.
- The urine is the main route of rapid excretion in humans and in animals. Extensive metabolism occurs and elimination is rapid.

In humans, naphthalene is metabolised to 1-naphtol, 2-napthol and 1,2- and 1,4-naphthoquinone. In vitro studies in human liver microsomes and human lung preparations indicate that epoxide hydrolase is involved in the metabolic pathway by which naphthalene is metabolised to naphthalene 1,2-dihydrodiol (ECB, 2003). However, more recent studies from 2012 (listed in ECHA RSD (2014), conclude that the metabolic route described and found in rodents does not apply for humans or is only slowly generated in human tissue, i.e. the mode of action in rodents is very unlikely to be operative in humans (ECHA RSD (2014) – Other WoE Basic Toxicokinetics.006).

6.1.3 Acute toxicity

The lowest lethal doses/lethal concentrations (acute toxicity studies in animals) found in ECHA RSD (2014) are listed below. The levels are identical to the acute toxicity levels listed in (ECB, 2003):

- Oral: LD_{50} (mouse, male) = 533 mg/kg bw (Shopp et al. (1984) in ECHA RSD)
- Inhalation LC_{50} (rat, 4h) = > 0.4 mg/L (> 400 mg/m^3) (unknown author (1985) in ECHA RSD)
- Dermal: LD_{50} (rat) = > 2500 mg/kg bw (Gaines (1969) in ECHA RSD). Another study (unknown author (1980) in ECHA RSD refers to LD_{50} (rats) of > 16 000 mg/kg bw.

There is no information on the effects of naphthalene following acute inhalation or dermal exposure in humans. However, acute oral exposure to naphthalene causes haemolytic anaemia (abnormal breakdown of red blood cells) which may be fatal. Twelve cases of oral ingestion by young children of naphthalene-containing mothballs have been reported. The first signs of toxicity were usually seen within hours to up to 2 days after exposure. Haemolytic anaemia was diagnosed in all cases, no deaths occurred. However, the amount of naphthalene ingested or whether the incidences were a one-time exposure or repeated exposure was not known (ECB, 2003).

Naphthalene is of low toxicity in rats, with mice being more sensitive. However, studies in animal models (mainly rats, mice and rabbits) have indicated that the toxic effects of naphthalene seen in these species are different from those in humans (haemolytic anaemia is not observed in these animal species). Based on this fact, it is concluded in the EU RAR of naphthalene that rodents are not suitable animal models for the acute toxic human health effects of naphthalene in relation to haemolytic anaemia. Thus, while the LD_{50} values from studies with rats suggest relatively low acute toxicity in this species, the available information in humans indicates significant toxicity. One case of very severe haemolytic anaemia has been reported to occur (a 16 year old female). She ingested an estimated single oral dose of approximately 6 grams naphthalene. It is possible that this represents a human lethal dose given that a number of blood transfusions were required (ECB, 2003).

6.1.4 Skin and eye irritation

Two studies of the **skin irritation** of naphthalene on rabbits are reported. In both studies 0.5 gram of naphthalene was dermally administered to the skin of six rabbits for 4 hours and 24 hours exposure time respectively. In the first study very slight redness of the skin was observed in 3 of the animals and was visible from 30 minutes to 5 days after administration. However by day 6, irritation was no longer visible. In the second study similar very slight redness of the skin was observed and was diminished after 48 hours of removal of the patch, but not completely gone. However, it was concluded in this latter study that the irritation effects would have disappeared after a regular 2 weeks observation period.

In humans there are only a very few incidences reported on skin irritation for naphthalene. Most of these are more than 60 years old. Overall, it is therefore concluded in the EU risk assessment report of naphthalene that it is difficult to draw any conclusions on the irritancy of naphthalene in humans (ECB, 2003).

Only one study on **eye irritation** of naphthalene is reported. An unspecified amount of naphthalene was applied to the eyes of 6 rabbits. Eye irritations were minor and could only be noted at day 1 and 2 of the observation period (7 days). Effects had disappeared at day 3. Naphthalene was described as being non-irritating (ECB, 2003; ECHA RSD, 2014).

The conclusion in the EU risk assessment of naphthalene is that no conclusions can be drawn regarding the irritant properties of naphthalene from studies in humans. However, data from animal studies indicated that it is only a slight skin and eye irritant – insufficient to warrant classification (ECB, 2003).

6.1.5 Sensitisation

Only two skin sensitisation studies are reported (ECB, 2003; ECHA RSD, 2014). One study flawed, but is even though considered to have shown a negative result. In the other skin sensitisation study 24 guinea pigs were applied with a 0.1% and 1% concentration of naphthalene in acetone. No signs of skin sensitisation were observed. However, 2-naphthol was also tested and was positive in all 16 animals tested. 2-naphthol is one of the major reaction products when naphthalene is being photochemically degraded in the atmosphere (see chapter 5).

There is no information available on the potential of naphthalene to produce respiratory sensitisation in animals, and there is no information available on skin or respiratory sensitisation in humans. However, it is concluded in the EU risk assessment report that since naphthalene has been in the public and commercial domain for many years and its use has involved dermal contact, the absence of case reports in humans indicates that naphthalene is not a skin or respiratory sensitizer (ECB, 2003).

6.1.6 Repeated dose toxicity

There are no epidemiological studies on the human health effects of naphthalene. The only human information available is derived from a limited number of early case-reports which provide no quantitative data on the levels or duration of exposure. A human health effect could be haemolytic anaemia (abnormal breakdown of red blood cells), which may be fatal, as in some cases this has been reported in humans exposed by inhalation to naphthalene vapour and by ingestion to solid naphthalene (mothballs). Dermal exposure to the solid and vapour could also be likely in these cases (ECB, 2003).

Animal studies reveal species differences in response to naphthalene. A short description of repeated dose toxicity animal studies is given in Table 15 in Appendix 5. Haemolytic anaemia was noted in a dog following oral dosing of 220 mg/kg bw/day for 7 days, but not in rodents even with higher and prolonged exposure. Cataract formation was the principal effect seen in rats and rabbits following oral exposure (700 to 1000 mg/kg bw/day), but this effect on the eyes was not seen in mice with similar exposures. The lack of reliable reports of cataract in humans despite the widespread use of naphthalene and high dose accidental exposure suggests that cataract formation is unlikely to be a significant health effect in humans (ECB, 2003).

Limited signs of nasal inflammation were reported in a 4-weeks rat inhalation study at 5 mg/m^3. The nasal effects became more marked with increasing level of naphthalene exposure. No exact NOAEL was identified and no evidence of systemic toxicity was found in the inhalation studies, but a **LOAEL of 5 mg/m^3** could be set for **repeated inhalation toxicity** (ECB, 2003).

General signs of toxicity, including deaths, were reported in rats and rabbits orally dosed with 700 and 1000 mg/kg bw/day respectively. Mice seem to be more susceptible to naphthalene than rats or rabbits (with 100% mortality at 500 mg/kg bw/day). **For systemic effects a NOAEL of 133 mg/kg bw/day** was identified in a 13-week oral mouse study. By the dermal route a NOAEL for systemic toxicity of 1,000 mg/kg bw/day (the highest dose) was identified in a 13-week rat study.

A derived no effect level – **DNEL of 25 mg/m^3 for workers via the inhalation route** has been set for naphthalene in the ECHA database of registered substances (ECHA RSD, 2014). It is stated that this DNEL value is derived by using the national occupational exposure level (EU and USA) of 50 mg/m^3 based on human experience and an assessment factor of 2. This value is transferred to a

DNEL for systemic effects of 3.57 mg/kg bw/day by assuming an inhalation of 10 m^3/day and 70 kg bodyweight. No DNEL values are derived for the general population in the ECHA RSD (2014) as the hazard is regarded to be low.

6.1.7 Chronic toxicity and carcinogenicity

Data is limited on the chronic toxicity and carcinogenicity in humans. The EU risk assessment report mentions a few cases from the 1970es of laryngeal (throat) cancer in workers working with purification of naphthalene. However, all workers were smokers and exposed to coal tar volatiles as well. Therefore no conclusions can be drawn from the reports regarding the role of naphthalene in the production of cancer. However, the carcinogenic potential of naphthalene has been well investigated in animals (ECB, 2003).

In an inhalation study with rats groups of 49 male and female rats were exposed to naphthalene at concentrations of 0, 10, 30 and 60 ppm (approximately equivalent to 0, 50, 150 and 300 mg/m^3) for 6 hours per day, 5 days per week for 105 weeks. This study gave clear evidence of carcinogenic activity of naphthalene based on increased incidences of respiratory epithelial adenoma and olfactory epithelial neuroblastoma of the nose (a very rare tumour type) even with the lowest exposure concentration of 10 ppm, approximately equivalent to 50 mg/m^3 (NTP (2000) in ECHA RSD (2014). In another similar study with male and female mice there was no evidence of carcinogenic toxicity in male mice, but some evidence of carcinogenic toxicity in female mice based on increased incidences of a benign lung tumour (pulmonary alveolar/bronchiolar adenomas) (unknown author (1992) in ECHA RSD (2014)). In view of the negative results obtained in the *in vivo* genotoxicity studies (see section 6.1.9 “Genotoxicity” below), naphthalene is considered to be non-genotoxic. This means that the tumours in the animal studies are considered to arise via a non-genotoxic mechanism (ECB, 2003).

In the EU risk assessment of naphthalene it is concluded that it is not possible to determine whether or not the effect seen in the rat (nasal tumours) is relevant for humans. Anatomical differences in the nasal passages between rats and humans exist as well as differences in breathing patterns. Thus, there is some uncertainty concerning the relevance of the rat nasal effects to human health. However, overall, it is not possible to dismiss the rat nasal data as being of relevance for humans. In contrast it is concluded that the naphthalene-induced lung tumours in mice are unlikely to be of relevance to human health due to differences in the lung metabolism (naphthalene is metabolised at substantially greater rates (up to 100-fold) in mice compared to hamster, rat or monkey). In addition, no lung tumours have been observed in rats. Therefore, the mouse seems to be more susceptible to lung toxicity than other species (ECB, 2003).

Based on the above NTP (2000) study with increased incidence of tumours in the respiratory tract even at the lowest administered concentration of 50 mg/m^3, naphthalene is classified with the harmonised classification of Carc. 2, H351 “Suspected of causing cancer” – a classification also given by IARC (2002).

The above NTP (2000) study on rats lead (according to Preuss et al. (2003)) to the conclusion that naphthalene contributes considerably to human cancer risk. Therefore, it has been discussed intensely whether the occupational threshold limit value of 50 mg/m^3 should be lowered as the NTP (2000) study on rats lead to increased tumour incidences at this concentration (Preuss et al., 2003). However, the occupational threshold limit value for naphthalene has not been lowered yet. Preuss et al. (2003) suggests lowering the occupational threshold limit value to 1.5 mg/m^3 based on the measurement results at international workplaces.

6.1.8 Reproductive and developmental toxicity

No information in relation to fertility is available in humans and there are no animal studies specifically investigating these effects (other than a few studies showing e.g. no testes changes following inhalation of naphthalene for 90 days), (ECB, 2003).

Regarding developmental toxicity in animals, fetotoxicity has been observed in rats (but no malformations) at doses causing significant maternal toxicity (450 and mg/kg bw/day); however maternal toxicity has also been noted at lower doses (150 mg/kg bw/day) without fetotoxicity. In mice fetotoxicity has been observed at doses causing significant maternal toxicity (300 and mg/kg bw/day). In rabbits, no developmental effects have been observed in studies causing mild or close to producing maternal toxicity (400 mg/kg bw/day), (ECB, 2003; ECHA RSD, 2014).

The only information available concerning developmental toxicity in humans comes from cases of haemolytic anaemia (abnormal breakdown of red blood cells) in infants born to mothers also suffering from haemolytic anaemia, following ingestion of unquantified doses of naphthalene during their pregnancy (by sucking on moth balls), (ECB, 2003).

Overall, the studies on reproductive and developmental toxicity suggest that naphthalene is not fetotoxic – only at the doses that are also maternally toxic; and in general the studies show no effect in any reproductive organ examined (uterus, ovary, prostate and testes), (ECB, 2003; ECHA RSD, 2014).

6.1.9 Genotoxicity

It is concluded in the risk assessment report of naphthalene that overall, the different tests indicate that naphthalene is not genotoxic (ECB, 2003).

In vitro naphthalene has given reproducible negative results in bacterial mutation assays and was also negative in an unscheduled DNA synthesis. In most studies, naphthalene was tested up to cytotoxic (cell toxic) concentrations. Naphthalene was, however, reported to be clastogenic (i.e. capable of causing breakage of chromosomes) in Chinese hamster ovary cells, but only in the presence of Aroclor-induced rat liver S9 (Aroclor is a commercial PCB mixture[65]) (ECB, 2003).

Naphthalene was found to be negative in *in vivo* bone-marrow micronucleus tests and *in vivo* rat liver unscheduled DNA synthesis (ECB, 2003).

The few newer studies reported in ECHA RSD (2014) support the conclusion of naphthalene not being genotoxic as these studies also are negative. In fact a newer study from 2010 concludes that mode of action for naphthalene for causing cancer *is not* caused by a genotoxic event, as naphthalene is not genotoxic (Rhomberg et al. in ECHA RSD (2014)).

6.1.10 Neurotoxicity

No information has been found regarding the neurotoxic effects of naphthalene. Neurotoxic effects of naphthalene are not mentioned in the EU risk assessment report or in ECHA RSD (2014).

6.1.11 Immunotoxicity

Very limited information exists on the immunotoxic effects of naphthalene. In the EU risk assessment report on naphthalene it is mentioned in an oral repeated dose toxicity study on mice that immunological naphthalene treatment had no effect on the responses otherwise observed in this study. No other information regarding the immunotoxicity of naphthalene has been identified.

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[65] http://www.greenfacts.org/glossary/abc/aroclor-1254.htm

6.1.12 Endocrine disruption

No information has been found regarding the endocrine disrupting effects of naphthalene. Naphthalene is not on the EU list of potential endocrine disruptors. However, the above studies on reproductive and developmental effects illustrate that naphthalene has no effects on any reproductive organs and that naphthalene only is fetotoxic in concentrations that are also maternally toxic. This suggests that naphthalene may not be an endocrine disrupting chemical.

6.1.13 Combination effects

No data regarding combinations effects of naphthalene has been found.

6.2 Human exposure

Exposure to naphthalene may occur through air, water, soil, food and consumer products. In this chapter the data found for naphthalene regarding human exposure is presented. The direct exposure from e.g. use of consumer products (such as tar paints and waterproof membranes containing naphthalene) and occupational exposure is addressed as well as the indirect exposure from air, soil, drinking water, food and the indoor climate.

6.2.1 Direct exposure

Environment Canada (2008b) has prepared a screening assessment report concerning the exposure of the Canadian people to naphthalene. According to this report the direct exposure to naphthalene is considered to be higher than the indirect exposure, but more infrequently of course depending on especially the occupational working environment.

Humans can be exposed directly from the use of products containing naphthalene or when working with naphthalene. The EU risk assessment of naphthalene concludes that it is the occupational exposure which is the largest and most significant exposure to humans. Concerning consumers, the do-it-your-self consumers will have the highest exposure, but it will not be as high as the level observed in occupational settings (ECB, 2003).

6.2.1.1 Consumers

As described in section 3.3.2 "Products containing naphthalene", the following type of products contains naphthalene in large or smaller amounts or contains e.g. coal tar which contains naphthalene:

- Creosote treated wood (contains 5-25% naphthalene)
- Tar paints/specialist paints (contains about 1-2% naphthalene)
- Waterproof membranes for floors and walls (contains about 1% naphthalene)
- Asphalt
- PAH containing products such as extender oils and carbon black which are both found in rubber and plastic products

In general the exposure from these products is expected to be low and some of the exposures insignificant. The EU risk assessment of naphthalene concludes that it will only be the do-it-yourself consumers that will have the highest exposure of all consumers, but it will not be as high as the level observed in occupational settings (ECB, 2003). Do-it-your-self consumers are only expected to be exposed to higher naphthalene concentrations in the few and infrequent situations they are actually using naphthalene containing products (waterproof membranes).

Creosote treated wood

Creosote treated wood is no longer used for treatment of wood in Denmark (it has been restricted since 1997). However, creosote treated wood may still be in use for some purposes (mainly railway sleepers). Private use of creosote treated wood is, however, also restricted in order to avoid exposure[66]. It is therefore expected that the direct exposure to consumers from creosote treated wood is insignificant.

Tar paints/specialist paints

In the early 2000s, the European market moved away from the use of tar paints. Furthermore, the content of naphthalene in these products is low (1-2%). It is therefore expected that exposure from these types of products will be minor, insignificant or even non-existent today.

Waterproof membranes

Waterproof membranes are generally used in the building industry to waterproof floors and walls. Consumer exposure from these products will therefore be more indirectly through indoor climate and is expected to be minor if proper ventilation and airing is used. Of course if consumers are the do-it-yourself-type the exposure may be significant when actually laying the waterproof membrane themselves. However, in the EU risk assessment of naphthalene it is emphasised that in the post laying period of the waterproof membrane the exposure of naphthalene may be elevated and that there may be a need for limiting the risks. A calculated inhalation exposure level has been modelled for a single event of laying and post laying of waterproof membranes for consumers to be 76 mg/m^3 naphthalene – the exposure time is not given. This should be compared with the 8-hour average threshold limit value of naphthalene of 50 mg/m^3 (ECB, 2003). Of course it is not expected that the stay in such a room will be 8 hours or longer – even when including the laying period.

Asphalt

The consumer exposure of naphthalene evaporating from asphalt is expected to be minor and insignificant and more of an environmental issue (outdoor) than a direct human exposure. The naphthalene content in asphalt will hence contribute to the indirect exposure from the air.

PAH containing products

Naphthalene is often considered to be a PAH and therefore it can be expected to be present in PAH containing consumer products such as rubber and plastic products. Table 6 shows that naphthalene has been found in several rubber and plastic products at a ppm level (between 0.04 and 110 ppm (mg/kg)). Lassen et al. (2011) concludes in a survey on the content of PAH in toys (however the naphthalene content was *not investigated*) that PAHs are common in toys and childcare articles in Denmark, but that the concentration levels of PAHs are low.

From the examples listed in Table 6 it is expected that the highest consumer exposure will be from the naphthalene content in gags (sex toy) for adults and from bibs for babies. If as an absolute worst case it is assumed that both gags and pacifiers are used on a daily basis and that *all* of the amount in the product will migrate and orally will be ingested *each day*, the daily exposure to naphthalene can be calculated as:

- Gag: 110 µg/g · 200 g (gag weight) / 60 kg (adult weight) = 366 µg/kg bw/day
- Pacifier: 0.1 µg/g · 50 g (weight of pacifier) / 5 kg (baby weight) = 1 µg/kg bw/day

The German Federal Institute for Occupational Safety and Health (BAuA) has proposed a restriction of 8 PAHs in consumer products. This restriction proposal was adopted in December 2013 (Regulation 1272/2013) and is a restriction on 8 specific PAHs (*but not naphthalene*) in rubber and plastic products that come into direct contact (long-term and short-term repetitive

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[66] http://mst.dk/virksomhed-myndighed/kemikalier/regulering-og-regler/faktaark-om-kemikaliereglerne/creosot/

contact) with the human skin. The restriction will enter into force by December 2015. This restriction could influence on the level of naphthalene impurities in consumer products as well.

6.2.1.2 Occupational exposure

Occupational exposure of workers to naphthalene may occur:

- In workplaces where naphthalene is manufactured
- In workplaces where naphthalene is used as an intermediate chemical to produce other chemicals

Occupational exposure at production site can be expected at operations such as drum and tank filling operations, preparation and packaging operations etc. The major route of exposure is inhalation, but dermal exposure can be expected as well if protective gloves are not worn. Ingestion of naphthalene is considered to be very unlikely.

The threshold limit value for naphthalene in the working environment in Denmark and the EU is 10 ppm or 50 mg/m^3.

Inhalation exposure

In the EU Risk assessment report of naphthalene a range of measured inhalation exposure levels is given for occupational exposure. Preuss et al. (2003) has also listed the most relevant studies of naphthalene exposure at different workplaces for the period 1978 – 2002. This means that only some data from Preuss et al. (2003) is not presented in the EU risk assessment.

Most values range between 0.02 to 6 mg/m^3, whereas values as high as 10, 20, 21, 41 and 51 mg/m^3 have been measured for manufacture of moth-balls (preparation), manufacture of grinding wheels (without local exhaust ventilation), manufacture of mothballs, manufacture of creosote (cleaning of chamber) and use of creosote (impregnation plants) respectively. The highest value of 51 mg/m^3 was measured for an operator cleaning out a bulk impregnation chamber and was measured as a total of naphthalene, indene and methyl naphthalene. Information received from the plant suggests that this working process and high value are rare and always are carried out wearing respiratory protective equipment (ECB, 2003; Preuss et al., 2003). As the use of naphthalene in mothballs is no longer supported in the EU today this occupational exposure to naphthalene is considered to be irrelevant in the EU.

Preuss et al. (2003) also reports on a Germany PAH study where personal air samples were measured for 220 workers in seven different main branches of industry. The median naphthalene concentration was measured to be 4.37 µg/m^3, i.e. a factor 10,000 below the occupational limit value for the working environment. The 90th percentile for all 220 personal air samples was 100.77 µg/m^3, i.e. 90% of all measurements were below this value. The highest concentration found was in the installation of fire proof materials where the 90th percentile was measured to be 1 136 µg/m^3 – still well below the occupational limit value.

All in all the occupation exposure is in general judged to be well below the occupational limit value for naphthalene in the working environment of 50 mg/m^3. However, this occupational threshold limit value has been discussed and has been suggested to be lowered to 1.5 mg/m^3 based on measurements from workplaces (is realistic to obtain) and based on a study with rats showing increased nasal tumours at this concentration (50 mg/m^3), (NTP, 2000).

The animal data presented earlier (LOAEL of 5 mg/m^3) suggests that the acute toxicity of naphthalene may be limited under ‘normal’ occupational exposure levels, whereas repeated dose toxicity could present a human risk. However, it is stated in the EU risk assessment of naphthalene that the effects seen in rodents do not seem to be relevant for humans. A lack of human toxicity reports may support this. However, Preuss et al. (2003) calls for more examination on this area and a lowering of the occupation threshold limit value until this effect of naphthalene has been investigated further – still, it is not known how naphthalene initiates cancer. A theory which has been stated is that naphthalene inactivates enzymes that are responsible for normal cell "suicide"[67].

Dermal exposure

Dermal exposure to naphthalene is likely to be most prominent during manufacture of mothballs and during the use of creosote according to the EU risk assessment of naphthalene (ECB, 2003). As both these uses are no longer supported in the EU (creosote restricted in some European countries including Denmark), the dermal occupational exposure is judged to be minor.

Oral exposure

Ingestion of naphthalene is considered to be very unlikely. The oral route of exposure is, however, the only route of exposure where human toxic effects (haemolytic anaemia (abnormal breakdown of red blood cells)) have been reported – and this effect has been caused by people sucking on mothballs, which use is now restricted in the EU.

6.2.2 Indirect exposure

The human indirect exposure of naphthalene from air, soil, drinking water, food and the indoor climate is described in more details below. According to ATSDR (2005), exposure to naphthalene from ingestion of drinking water and/or food is expected to be much less than inhalation exposures for the general population. This is also stated by Environment Canada (2008b) which has estimated the daily intake of naphthalene for the general population in Canada. The values are presented in the table below and illustrate that indoor air is responsible for about 96 to 98% of the total human indirect exposures to naphthalene dependant on the age group.

Route of exposure	Estimated intake (µg/kg bw/day) for various age groups			
	Babies (0-6 months)	Children (0.5-4 years)	Children (5-11 years)	Adults (20-59 years)
Ambient air	0.52 (1.3%)	1.11 (1.3%)	0.87 (1.3%)	0.42 (1.3%)
Indoor air	38.71 (96.0%)	82.95 (97.4%)	64.67 (97.4%)	31.59 (97.3%)
Drinking water	0.05	0.06	0.05	0.03
Food and beverages	1.05 (2.6%)	1.01 (1.2%)	0.79 (1.2%)	0.42 (1.3%)
Soil	0.0093	0.031	0.020	0.0093
Total intake	40.33	85.13	66.37	32.46

TABLE 12
ESTIMATES OF DAILY INTAKE OF NAPHTHALENE FOR THE GENERAL POPULATION IN CANADA – VALUES ARE UPPER-BOUNDING ESTIMATES (ENVIRONMENT CANADA, 2008B)

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[67] http://phys.org/news70042017.html

6.2.2.1 Air

As described in section 5.3.3.1 "Monitoring data for air" Jia and Batterman (2010) has reviewed several studies which have reported on outdoor concentrations of naphthalene. The studies report on outdoor naphthalene concentrations in the US, Canada, UK, Germany, Finland, Australia, India, Korea, China and Taiwan. The average outdoor concentrations of naphthalene are below 1.0 µg/m^3 and medians below 0.5 µg/m^3. Maximum outdoor concentration ranged from 0.01 to 4.7 µg/m^3. Jia and Bitterman (2010) concluded that a concentration of 5 µg/m^3 might be used as a conservative exposure scenario for "general" urban air even though naphthalene levels may be elevated near industrial and waste disposal sites.

Preuss et al. (2003) reports on the estimated average naphthalene concentration from air to be 5.19 µg/m^3. Based on this figure a daily intake from air has been calculated by the US EPA to be 1.127 µg/kg bw/day for adults and 4.515 µg/kg bw/day for children respectively. The figure for adults is about a factor of 40 higher than the figure listed below in the EU risk assessment of naphthalene. The reason for this large difference has not been investigated further.

The EU risk assessment of naphthalene has calculated the daily regional exposure to naphthalene from air to be 0.029 µg/kg bw/day or about 48.3% of the total daily calculated human exposure (not including indoor air). This calculation is based on predictions performed in the EUSES programme (ECB, 2003). This daily calculated exposure from air only covers outdoor air and not indoor air.

Environment Canada (2008b) estimates the daily intake of naphthalene from ambient air for the Canadian population to be 0.42 µg/kg bw/day for adults and 0.52 µg/kg bw/day for children (see Table 12). For both adults and children these figures represent 1.3% of the total indirect exposure to naphthalene for the Canadian population.

6.2.2.2 Soil

As described in section 5.3.3.3 "Monitoring data for soil and sediment", most data on the levels of naphthalene in soil is of older date (1980es or 1990es). Levels of naphthalene in untreated agricultural soil range from 0 to 3 µ/kg (ATSDR, 2005) whereas levels at urban areas are much higher. The highest value reported for urban areas is 1.47 mg/kg for suspended matter at a site near a sewage treatment plant. Other values for urban areas ranged up to 720 µg/kg and are likely to arise from combustion processes. Values of up to 520 µg/kg have been reported for motorway run-offs (ECB, 2003).

Very high levels of naphthalene in soil (up to 7,720 mg/kg) have been found, but these levels are related to contamination, for example by creosote, where naphthalene is a component in the mixture (ECB, 2003). However, creosote treated wood is restricted in Denmark today.

Preuss et al. (2003) reports on the estimated average naphthalene concentration from soil and dust to be 330 µg/kg for adults and children. Based on this figure a daily intake from soil/dust has been calculated by the US EPA to be 0.235 µg/kg bw/day for adults and 3.3 µg/kg bw/day for children respectively.

Environment Canada (2008b) estimates the daily intake of naphthalene from soil for the Canadian population to be 0.0093 µg/kg bw/day for adults and 0.031 µg/kg bw/day for children (see Table 12). For both adults and children these figures represent 0.03% of the total indirect exposure to naphthalene for the Canadian population.

6.2.2.3 Drinking water

According to section 5.3.3.2 “Monitoring data for water”, naphthalene levels in drinking water range up to 370 ng/l although elevated levels have been found in drinking water samples from wells near a chemical waste dump in the US (ECB, 2003). ATSDR (2005) reports that naphthalene is rarely detected in drinking water, but has been measured at levels up to 1.4 µg/l. In comparison the limit value for drinking water for naphthalene in Denmark is 2 µg/l according to Danish Statutory Order No. 292 (2014).

The EU risk assessment of naphthalene has calculated the daily exposure from drinking water to naphthalene to be 0.00085 µg/kg bw/day or about 1.4% of the total daily calculated human exposure (not including indoor air). This calculation is based on predictions performed in the EUSES programme (ECB, 2003).

Environment Canada (2008b) estimates the daily intake of naphthalene from drinking water for the Canadian population to be 0.03 µg/kg bw/day for adults and 0.06 µg/kg bw/day for children (see Table 12). For adults and children these figures represent 0.09 and 0.07% respectively of the total indirect exposure to naphthalene for the Canadian population.

6.2.2.4 Food

The information about the content of naphthalene in food is limited, whereas the information on PAHs in general in food is described in more details – especially in an opinion of the health risks to humans of PAHs in food (SCF, 2002). However, in this opinion the health risks of naphthalene are described, but no data on the concentration of naphthalene in food is given. The focus is on the 15 PAHs considered to be carcinogenic (Carc 1A or 1B).

Food can be contaminated by environmental PAHs that are present in air (by deposition), soil (by transfer) or water (by deposition and transfer), or during processing and cooking. In food, PAHs may be formed during processing and domestic food preparation, such as smoking, drying, roasting, baking, frying or grilling. Cooking of foods at high temperatures is major sources of PAHs. Levels as high as 200 µg/kg in food have been found for individual PAHs in smoked fish and meat. In barbecued meat, 130 µg/kg has been reported whereas the average background values are usually in the range of 0.01-1 µg/kg in uncooked foods. Contamination of vegetable oils (including olive residue oils) with PAHs usually occurs during technological processes like direct fire drying, where combustion products may come into contact with the oil seeds or oil (SCF, 2002).

The contamination of food with PAHs in the environment depends on a number of physical and chemical properties of the PAHs such as their relative solubility in water and organic solvents, volatility, chemical reactivity, and biotic and abiotic degradability. In general PAHs have low water solubility, however, naphthalene is the most simple PAH and is therefore the PAH with the highest aqueous solubility (slightly soluble in water). Furthermore, naphthalene has the highest vapour pressure and is the PAH, which is most likely to oxidise in chemical reactions.

PAHs will generally not accumulate in plant tissues with high water content, because of the low water solubility (SCF, 2002). A slightly higher naphthalene accumulation compared to other PAHs may occur, because of naphthalene being slightly soluble in water, but no data exists to verify this theory.

Transfer from contaminated soil to root vegetables will be limited, because adsorption of PAHs to the organic fraction of soil is strong. This will also be valid for naphthalene. Thus, the concentrations of PAHs are generally greater on plant surface (peel, outer leaves) than on internal tissue. Consequently, washing or peeling may remove a significant proportion of the total PAHs (SCF, 2002).

In areas remote from urban or industrial activities, the levels of PAHs found in unprocessed foods reflect the background contamination which originates from long distance airborne transportation of contaminated particles and natural emissions from e.g. volcanoes and forest fires. In the neighbourhood of industrial areas or along highways, the contamination of vegetation can be ten-fold higher than in rural areas (SCF, 2002).

Preuss et al. (2003) reports on the estimated average naphthalene concentration from food to be 3.75 µg/kg for the food adults eat and 4.08 µg/kg for the food children eat. Based on these figures a daily intake from food has been calculated by the US EPA to be 0.041 – 0.237 µg/kg bw/day for adults and 0.204 – 0.940 µg/kg bw/day for children respectively. The figure for adults is about a factor of 1.3 to 7 higher than the figures listed below in the EU risk assessment of naphthalene, but the maximum values are a little lower or about the same level as listed in the Canadian study below (Environment Canada, 2008b).

The EU risk assessment of naphthalene has calculated the daily exposure to naphthalene from food to be as listed below, i.e. a total of 0.03076 µg/kg bw/day or about 51.3% of the total daily calculated human exposure (not including indoor air). These calculations are based on predictions performed in the EUSES programme (ECB, 2003):

- Fish: 0.021 µg/kg bw/day
- Leaves of plants: 0.0059 µg/kg bw/day
- Root of plants: 0.0035 µg/kg bw/day
- Meat: 0.000023 µg/kg bw/day
- Milk: 0.000013 µg/kg bw/day

Environment Canada (2008b) estimates the daily intake of naphthalene from food and beverages for the Canadian population to be 0.42 µg/kg bw/day for adults and 1.01 µg/kg bw/day for children (see Table 12). For both adults and children these figures represent about 1.2% of the total indirect exposure to naphthalene for the Canadian population.

6.2.2.5 Indoor climate

Jia and Batterman (2010) has summarised 21 studies (in US, Canada, UK, Germany, Finland, Australia and China) that have measured indoor concentrations of naphthalene from 1986 to 2006. They conclude that the measured concentrations in these studies are highly skewed, both within and between studies as shown by the study averages (0.8 to 9.5 µg/m^3) greatly exceeding the medians (0.17 to 4.1 µg/m^3), and by high peak concentrations (up to 144 µg/m^3). Two of the studies showed strikingly high concentrations – one of them being a 150-home study in the state New York (US) in which over 80% of the homes had one or more tobacco smokers indoor. After excluding these studies, median concentrations ranged from 0.18 to 1.7 µg/m^3 in non-smoking residences, which by Jia and Batterman (2010) was considered to be a representative range for non-smoking residences.

Maximum concentrations in the 21 studies vary considerably – from 1.24 to 144.44 µg/m^3. Two of the 21 studies showed maximum concentrations above 50 µg/m^3 (values of 92 and 144 µg/m^3 respectively). Otherwise all maximum concentrations were below 50 µg/m^3 which has also been stated by Preuss et al. (2003). In comparison the threshold limit value for naphthalene in the working environment is 50 mg/m^3.

Very elevated concentrations of naphthalene (e.g. 28.7 µg/m^3 in Africa) have been reported in rural homes in developing countries such as China and African countries, where coal, wood and crop residues are widely used in simple and unvented cook stoves (Jia and Batterman, 2010).

The 21 studies summarised by Jia and Batterman (2010) show that naphthalene concentrations in US and Canadian residences are similar and these levels generally exceed the levels in the European studies, where the median naphthalene concentrations indoor were below 0.6 µg/m^3.

The indoor concentrations of naphthalene did not show consistent seasonal patterns. Higher concentrations were expected in winter due to lower air exchange rates and increased emissions from wood-burning fireplaces. However, the opposite trend may occur due to higher emissions rates from materials and outdoor barbecuing in summer (Jia and Battermand, 2010).

Jia and Batterman (2010) conclude from their review that several emission sources influence indoor concentrations:

- Indoor tobacco smoking
- Use of moth repellents (no longer relevant in the EU)
- The presence of an attached garage (garages containing vehicles or gasoline are known sources of PAHs and naphthalene, i.e. garages attached to residences can significantly elevate indoor concentrations)
- Domestic wood burning for heating

Furthermore, the following additional factors are affecting the indoor concentrations:

- Season
- Building characteristics (location, house age, type of heating system)
- Furniture
- Ventilation conditions

Kang et al. (2012) has calculated that the highest naphthalene indoor concentrations are due to the following household materials:

- Vinyl furniture
- Painted walls and ceilings

In a newer study Kang et al. (2012) has analysed different household materials for emission of naphthalene and based on analysed emission factors they have calculated (predicted) the indoor concentrations of naphthalene. The predicted indoor concentrations of naphthalene range from 4.9 to 187.5 µg/m^3 by use of minimum and maximum emission factors for the different household materials. This maximum calculated indoor concentration is on the same level as the maximum actual measured indoor concentration as listed by Jia and Battermand (2010). These calculated emission figures do not include emission of naphthalene as moth repellents used in mothball or toilet deodorant blocks. If these are included another 25.6 to 32.2 µg/m^3 should be added to the predicted indoor concentration. However, the use as naphthalene in moth repellent is not relevant for the EU as this use is no longer supported.

Jia and Batterman (2010) also reports on a few European studies (three) on personal exposure measurements of naphthalene. The average concentrations range from 0.78 to 2.3 µg/m^3, but a maximum concentration of 12.7 µg/m^3 was measured. In these measurements the air surrounding the persons is measured throughout the entire measuring period (time not stated).

The EU risk assessment for naphthalene does not estimate the daily intake of naphthalene for the indoor environment. Environment Canada (2008b) estimates the daily intake of naphthalene from indoor air for the Canadian population to be 31.59 µg/kg bw/day for adults and 82.95 µg/kg bw/day for children. For both adults and children these figures represent 97% of the total indirect exposure to naphthalene for the Canadian population.

Cigarette smoke
As presented by Image 8 cigarette smoke is one of the main sources of naphthalene release in the indoor environment and is among the largest contributor to personal exposure of naphthalene. Emissions factors for cigarettes are found to be between 12 and 54 µg per cigarette. Emission factors of naphthalene in the side-stream smoke measured in the laboratory range from 12-15 µg/cigarette. Under realistic conditions, emission factors of naphthalene have been reported between 17 and 54 µg/cigarette and will depend on air exchange rates, furnishing level and smoking conditions. All or most of these emissions are due to the side stream smoke. Jia and Batterman states that the emission factors for cigarettes across different studies are reasonably consistent.

Jia and Batterman (2010) states that the effect of tobacco smoking is not always consistent, when looking at the 21 studies of naphthalene measurements in the indoor environment. However, an average representative range of naphthalene concentrations 1.8 to 9.5 µg/m^3 in residences with smokers is considerably higher than the concentration range of 0.18 to 1.7 µg/m^3 for smoke-free residences (even though this range is median values).

Emissions from CFL light bulbs
As described in chapter 3 the German laboratory ALAB tested in 2011 14 different CFL light bulbs and found that naphthalene was emitted from 12 of the 14 tested CFL light bulbs in concentrations between 0.1 and 18.8 µg/m^3. Most measured emissions (for 11 of the CFL light bulbs) were in the range of 0.1-0.7 µg/m^3. The emission rate was measured to be between 0.001 – 0.205 µg per light bulb per hour (and mostly in the range of 0.001 – 0.008 µg per light bulb per hour), (ALAB, 2011).

Therefore, naphthalene emissions from CFL light bulbs may contribute to the naphthalene concentration in the indoor climate. However, there is no doubt that smoking is the largest contributor to the indoor concentration of naphthalene.

6.3 Bio-monitoring data

The urine is the main route of rapid excretion of naphthalene in humans and in animals. Extensive metabolism occurs and the elimination is rapid (ECB, 2003). As naphthalene is rapidly excreted in urine and does not accumulate in the body bio-monitoring data in humans would only express the exposure a short time before the measurement.

One bio-monitoring study of naphthalene has been identified. In this study (Kamal et al., 2011) the blood naphthalene concentration was measured as a marker for occupational exposures to PAHs for 20 workers in automobile workshops, for 20 car-spray painters and for 20 controls (un-exposed workers). The survey was conducted in Pakistan and it is stated that most workers were working in poor working conditions (poor mechanical exhaust system, poor workplace ventilation and poor overall workplace hygiene). The blood naphthalene concentration measured was 54.1 to 892.9 µg/L for painters (median = 131.8 µg/L), 53.7 to 1980.6 µg/L for mechanics (median = 333.0 µg/L) and 56.0 to 632.4 µg/L for the un-exposed control group (median = 114.1 µg/L). It is concluded from the study that mechanics are more exposed to naphthalene compared to the painters, and that workplace hygiene and improper ventilation are among key factors accounting for potential risks. However, the blood levels of naphthalene were also directly associated with smoking as the smokers in all three groups had higher blood naphthalene concentrations compared to non-smokers. The median blood naphthalene concentration in un-exposed non-smokers was 17.7 µg/L and 109.5 µg/L for un-exposed smokers (Kamal et al., 2011).

There is no indication of the naphthalene concentration level in the working environment resulting in the listed blood concentration levels. However, it is expected that the naphthalene concentrations in the working environment are high as the working conditions in general are described to be poor.

6.4 Human health impact

In this section the human health impact for the different exposures to naphthalene is discussed.

6.4.1 Consumers

Acute effect – haemolytic anaemia

The acute effect of naphthalene in humans is haemolytic anaemia. However, no NOEAL or dose-response characteristics can be derived from the available data for humans. Haemolytic anaemia is not an effect seen in rodents, but has been noted in a dog following oral dosing of 220 mg/kg bw/day for 7 days. This could suggest that an oral dose in the mg/kg range could produce the acute effect haemolytic anaemia in humans. It is therefore concluded in the EU risk assessment of naphthalene that any significant body burden is considered to give rise to concern for human health and that there is a need for limiting the risk (ECB, 2003). However, it should be noted that since the preparation of the EU risk assessment of naphthalene, the main consumer exposures to naphthalene, i.e. mothballs, creosote and tar paints are no longer in use or in the latter case been reduced drastically. Therefore, these consumer exposures are not considered to be relevant today. On the other hand, it may still be possible to be exposed to naphthalene in the event of laying and post laying of waterproof membranes, and in this case there may be a need for limiting the risk for human health for the do-it-your-self consumers, especially if carried out in unventilated rooms.

It is not expected that naphthalene contained in rubber and plastic products in small quantities will give any rise to concern regarding haemolytic anaemia.

Systemic effects, chronic effects/carcinogenicity

The long term effects/repeated dose toxicity of naphthalene is considered to be carcinogenicity. In the EU risk assessment report on naphthalene it is again the use of moth repellents (not relevant today) and post laying of waterproof membranes that are listed as exposures given rise to concern for the human health. There may therefore be a need for limiting the risk for human health for the do-it-your-self consumers using waterproof membranes (ECB, 2003) – especially if carried out in unventilated rooms. However, it is not expected that do-it-your-self consumers will be exposed to naphthalene on long term basis.

Of other relevant consumer products are all rubber and plastic products that may contain small quantities of naphthalene. Of the examples listed in Table 6 it is expected that the highest consumer exposure will be from the naphthalene content in gags (sex toy) for adults and from bibs for babies. The absolute worst case exposure, where 100% of the amount of naphthalene is assumed to migrate from the product and be ingested each day, is calculated to be 366 and 1 μg/kg bw/day respectively for the two examples. These values are well below the DNEL value of 3.57 mg/kg bw/day listed by ECHA RSD (2014) – even when it is taken into consideration that this DNEL value may be derived from an occupational exposure limit value that has been criticised for being too high.

Nevertheless, the exposure to carcinogenic substances should in general be lowered as much as possible, especially in products for children. It is, however, expected that the adopted restriction on 8 specific PAHs (even though naphthalene is not included) in rubber and plastic products that come into direct contact (long-term and short-term repetitive contact) with the human skin will have an influence on the level of naphthalene impurities in consumer products as well. The restriction will enter into force by December 2015.

6.4.2 Workers

As described above in section 6.2.1.2 “Occupational exposure”, inhalation is the route of exposure that is most relevant for naphthalene. For this reason only the inhalation route is addressed in the following, as the risk from dermal and oral exposure is considered to be minor and/or irrelevant.

As described most measured values for occupational exposure range between 0.02 to 6 mg/m³, whereas values as high as 10 to 51 mg/m³ have been measured in special situations (e.g. cleaning, preparation) and mostly for working situations no longer relevant in the EU (mothball manufacture and creosote impregnation plants). In the newest study reported (a German study from 2003) the 90th percentile for all 220 personal samples was 1.14 mg/m³ (Preuss et al., 2003); no maximum levels were reported.

Comparison of these levels to the existing occupational exposure limit (OEL) value of 50 mg/m³ illustrates that most exposure levels measured are well below the OEL. The DNEL value of 25 mg/m³ derived also illustrates that most exposure levels measured are well below this value. However, this OEL value has been discussed and has been suggested to be lowered to 1.5 mg/m³ by Preuss et al. (2003) based on measurements from workplaces (it is realistic to obtain) and based on a study with rats showing increased nasal tumours at the existing OEL (50 mg/m³), (NTP, 2000). Furthermore, the EU risk assessment on naphthalene states that some levels in the working environment are found to be higher than the LOAEL value of 5 mg/m³ for repeated inhalation toxicity and therefore concludes in general for occupational exposure to naphthalene that "there is a need for limiting the risk; risk reduction measures which are already being applied should be taken into account".

It should, however, be taken into consideration that the effects seen in rodents for naphthalene do not seem to be relevant for humans. A lack of human toxicity reports may support this. However, Preuss et al. (2003) calls for more examination on this area and a lowering of the occupation threshold limit value until this effect of naphthalene has been investigated further – it is still not known exactly how naphthalene initiates cancer (theories have been presented, but not verified).

6.4.3 Indirect exposure

As described earlier the main source of indirect naphthalene exposure is indoor air which accounts for about 97% of the total indirect human exposure to naphthalene (Environment Canada, 2008b). When looking at the exposure from the indoor environment, cigarette smoke is one of the main sources of naphthalene release in the indoor environment and is among the largest contributor to personal exposure of naphthalene. However, mothballs may also be a contributor to the calculated indoor air exposure, as the calculations are performed based on older data, where mothballs containing naphthalene were more widespread in its use. The indirect exposure from indoor air may therefore be even lower today.

When using the total indirect human exposure figures from the Canadian study, which are the highest values reported, it can be concluded that estimated daily intakes of 85.13 and 32.46 µg/kg bw/day for children and adults respectively, are well below the DNEL value 3.57 mg/kg bw/day listed by ECHA RSD (2014) – even when it is taken into consideration that this DNEL value may be derived from an occupational exposure limit value that has been criticised for being too high. It is therefore not expected that the indirect exposure of naphthalene will cause concerns regarding human impacts.

6.4.4 Combined exposure

When adding the total exposure from indirect exposure (air and food), consumer products and occupational exposure, it is not expected that the total exposure from indirect exposure and consumer products in general will cause concerns regarding human impacts.

However, in the following situations humans may be exposed to higher naphthalene concentrations that may be of concern:

- All occupational exposure/workers working with naphthalene
- Do-it-yourself consumers using waterproof membrane products containing naphthalene – both laying and post laying may be of concern

In general the observed concentrations in air if found to be below the LOAEL value of 5 mg/m^3. However, as concentrations above this LOAEL value has been observed in the working environment and that calculations illustrate that laying of waterproof membranes containing naphthalene may result in indoor concentrations above the LOAEL value, it is concluded in the EU risk assessment that there is a need for limiting the risk for the above listed situations (ECB, 2003).

6.5 Summary and conclusions

Toxicokinetics, absorption, distribution, metabolism and excretion
Exposure to naphthalene may occur through inhalation, ingestion or dermal contact. The information available on the toxicokinetics of naphthalene in humans is limited. However, the information available indicates that naphthalene is readily absorbed by all routes of exposure and that almost complete and rapid absorption occurs following ingestion. The urine is the main route of rapid excretion in humans and in animals. Extensive metabolism occurs and elimination from the body is rapid (ECB, 2003; ECHA RSD, 2014).

Human health hazard
Naphthalene has a moderate oral acute toxicity (Acute Tox. 4, H302 “Harmful if swallowed”). There is no information on the effects of naphthalene following acute inhalation or dermal exposure in humans. However, acute oral exposure to naphthalene causes haemolytic anaemia (abnormal breakdown of red blood cells), which may be fatal.

No conclusions can be drawn regarding the irritant properties of naphthalene from studies in humans. However, data from animal studies indicates that naphthalene is only a slight skin and eye irritant – insufficient to warrant classification. Absence of case reports on sensitisation in humans suggests that naphthalene is not a skin or respiratory sensitizer.

Animal studies on repeated dose toxicity reveal species differences in response to naphthalene. The effects seen in rodents do not seem to be relevant for humans and the effect seen in humans (and dogs) - haemolytic anaemia - has not been observed in rodents. In general there are no epidemiological studies on the human health effects of naphthalene except for a limited number of case reports on haemolytic anaemia.

Limited signs of nasal inflammation were reported in a 4-weeks rat inhalation study at 5 mg/m^3. No exact NOAEL was identified and no evidence of systemic toxicity was found in the inhalation studies, but a LOAEL of 5 mg/m^3 could be set for repeated inhalation toxicity.

Naphthalene is suspected of being carcinogenic and is classified as Carc. 2, H351 “Suspected of causing cancer”. This classification is based on clear evidence of nasal tumours found in rats (at 50 mg/m^3) and clear evidence of lung tumours found in mice. However, the naphthalene-induced lung tumours in mice are unlikely to be of relevance for humans, whereas the relevance for humans of the rat nasal tumours is unclear. It has been discussed intensely whether the occupational threshold limit value of 50 mg/m^3 should be lowered, as the nasal tumour study on rats lead to increased tumour incidences at this concentration. Preuss et al. (2003) suggests lowering the occupational threshold limit value to 1.5 mg/m^3 based on the measurement results at international workplaces. However, the occupational threshold limit value for naphthalene has not been lowered yet.

Naphthalene is not genotoxic, i.e. the mode of action for naphthalene for causing cancer is not caused by a genotoxic event, but by another unknown mode of action. Naphthalene has not been found to be fetotoxic nor an endocrine disruptor.

Exposure sources
Inhalation is the route of exposure that is most relevant for naphthalene. The major direct exposure sources to naphthalene are for workers occupational exposure when working with naphthalene and for consumers (primarily the do-it-your-self consumers) exposure to waterproof membranes containing naphthalene used for floors and walls. Occupational exposure is the largest and most significant exposure to humans. The general population is indirectly exposed to naphthalene primarily via indoor air where cigarette smoke is the largest contributor to indirect naphthalene exposure.

Human health impact
Historically the main health impact being reported for humans is the acute effect haemolytic anaemia as a result of exposure to (sucking on) mothballs. However, this exposure is no longer relevant as the use of naphthalene in mothballs is no longer supported in the EU. The inhalation route of exposure is therefore considered to be most relevant for naphthalene today.

The acute effect haemolytic anaemia may still be of concern for both workers and consumers, as no NOAEL or dose-response characteristics can be derived from the available data for humans. Animal data (in dogs) suggests that an oral dose in the mg/kg range could produce the acute effect haemolytic anaemia in humans. Based on this data, the only consumer exposure that possibly could be of concern is in the situation of laying and post laying of waterproof membranes for do-it-your-self consumers, especially if carried out in unventilated rooms, but a further investigation about the actual exposure and effect in these situations as well as the frequency of use of naphthalene in waterproof membranes may be needed. It is not expected that do-it-your-self consumers will be exposed to naphthalene on a long term basis.

The presented monitoring data for the working environment suggests that most exposure levels are well below the occupational exposure limit (OEL) value of 50 mg/m^3. However, a LOAEL value of 5 mg/m^3 for repeated inhalation toxicity has started a debate about whether the OEL value should be lowered. Preuss et al. (2003) calls for more examination on this area and a lowering of the occupational threshold limit value to 1.5 mg/m^3.

The human health impact from naphthalene residues in rubber and plastic articles is regarded as being insignificant. Nevertheless, the exposure to carcinogenic substances should in general be lowered as much as possible, especially in products for children. However, it is expected that the adopted restriction on 8 specific PAHs (even though naphthalene is not included) in rubber and plastic products that come into direct contact (long-term and short-term repetitive contact) with the human skin will have an influence on the level of naphthalene impurities in consumer products as well. The restriction will enter into force by December 2015.

The major indirect exposure to naphthalene is due to indoor air and primarily cigarette smoke. However, when adding the total exposure from indirect exposure (air and food), consumer products and occupational exposure, it is not expected that the total exposure from indirect exposure and consumer products will in general cause concerns regarding human impacts. In the following situations humans may be exposed to higher naphthalene concentrations that may be of concern:

- All occupational exposure/workers working with naphthalene
- Do-it-yourself consumers using waterproof membrane products containing naphthalene – both laying and post laying may be of concern

Data gaps
The following data gaps have been identified:

- It is still not known how naphthalene initiates cancer, and the true cancer risk due to naphthalene exposure remains controversial, i.e. IARC (2002) judges that epidemiological data is inadequate for determining human carcinogenicity.

- More in depth discussion about the occupational exposure limit value – should it be lowered? This will depend on the interpretation of the animal data – the debate is ongoing whether the effects seen in rodents apply for humans.
- For do-it-your-self consumers using waterproof membrane products containing naphthalene – both laying and post laying may be of concern regarding the acute effects of naphthalene. There may be a need for limiting the risk for human health – especially if carried out in unventilated rooms. This should be investigated further.

7. Information on alternatives

Previously in this study, the primary use of naphthalene has been identified as an intermediate in the manufacturing of other chemicals, including the production of dyes and colorants, pesticides and chemical rubbers (Schleicher et al., 2009). The use of naphthalene is also seen included in final products, although this application in general is decreasing due to the use of naphthalene no longer is supported in certain consumer products (mothballs). In order to identify alternatives for the use of naphthalene, it is, however, necessary to investigate both uses (as intermediate and in final products) and their respective possibilities for substitution.

7.1 Identification of possible alternatives

7.1.1 Alternatives for use as an intermediate for manufacturing of chemicals

The following uses of naphthalene, where naphthalene is used as an intermediate to produce other chemicals, are described further:

- Naphthalene sulphonic acids
- Phthalic anhydride
- Alkylated naphthalene solvents
- Azo dyes

7.1.1.1 Naphthalene sulphonic acids

Naphthalene sulphonate formaldehyde condensate (NSF) is used as plasticiser in construction materials such as concrete. Furthermore, NSF is used as plasticiser in rubber, in dyes and as tanning to produce leather (ECB, 2003).

The chemical mechanism of NSF creates a dispersion of the cement particles through an electrostatic repulsion hereby generating the plasticity effect acting as water-reducing agents in the concrete mixture (Lin Gao et al., 2011). An alternative to create a similar effect in cement has been investigated in a comparative study between the use of NSF and polycarboxylate (PC) (Lin Gao et al., 2011). The study showed better performance in concrete with PC both in terms of water-reduction and strength capability. In contrast to NSF, the PC plasticizer disperses the cement through steric stabilization which in various studies has proved to add more strength and flexibility in the work with the cement (Fiat et al., 2012; Lin Gao et al., 2011; Plank et al., 2009).

Besides the before mentioned qualities, PC based plasticizer has also been found to reduce the amount of water needed in cement production to up to 40 % (Fiat et al., 2012) and is increasingly gaining acceptance in the industry as an overall better investment (Daczko, 2008; Mullin, 2004). PC is accessible on the market[68] and represents a better structurally performing alternative to naphthalene based plasticisers in cement.

No specific CAS No. is listed for the alternative polycarboxylate (PC). According to ECHAs Classification & Labelling Database, polycarboxylate sodium salt is, however, self-classified as either Skin. Irrit. 2, H315 “Causes skin irritation” or not classified.

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[68] http://www.chinachemnet.com/

7.1.1.2 Phthalic anhydride

The main application of phthalic anhydride is to produce plasticisers to plastic products through an oxidation reaction of naphthalene. The most commonly used phthalate plasticisers are applied in growing industries such as construction, automotive, electrical & electronics and paints & coatings (Research and Markets, 2014).

Phthalic anhydride can be produced either by use of naphthalene or by use of o-xylene (Mendes & Seita, 2009). This means that o-xylene in practise could replace the use of naphthalene entirely. The harmonised classification of o-xylene is Flam. Lig. 3 (H226: Flammable liquid and vapour), Acute Tox. 4 (H312: Harmful in contact with skin, H332: Harmful if inhaled), Skin. Irrit. 2 (H315: Causes skin irritation) and thereby it presents a somewhat better alternative compared to the classification of naphthalene.

Due to increasing focus on environmental issues and occupational safety, the use of phthalic anhydride in products is subject to increasingly restrictions or even banning in certain end-use products (Research and Markets, 2014). For this reason, chemical companies are looking to find alternative substitutions for phthalic anhydride (Research and Markets, 2014). A desktop research showed bio-based replacement as an alternative method in production processes such as succinate acids (Zhang et al, 2004). Chemical company Myriant claims same structural and chemical performance as phthalic anhydride[69].

Reports from the Danish EPA (Herget, 2014; Høibye et al., 2011) conclude that it is technically possible to substitute certain phthalates, or to use other plastics without plasticisers for the same purpose. However, it is considered unrealistic for a Danish importer to require changes in composition from an international supplier (Herget, 2014) and requires further regulations to change applications (Høibye et al., 2011).

7.1.1.3 Alkylated naphthalene solvents

Regarding alternatives to alkylated naphthalene solvents, one study was identified to investigate the use of fluid carbon dioxide as a potential replacement solvent in chemical reactions (Marathe et al., 2004). However, it has not been possible to find sufficient literature and documentation of the effects of the use of fluid carbon dioxide or potential substitutions to suggest a better alternative to alkylated naphthalene solvents.

7.1.1.4 Azo dyes

Azo dyes (dyestuff) are commonly used in textiles and leather products. Azo dyes known to release certain aromatic amines[70] are prohibited in textiles and leather products in Europe[71]. Alternative dyes to azo dyes for disperse textile colourings do exist. However, the different dyes have different properties regarding how efficiently each dye binds to different textile fibres (Bryld et al, 2014). Azo dyes are commonly applied to cotton and cellulose fibres. Other types of dyes (such as direct, vat, sulphur and reactive dyes) are also commonly applied to cotton and cellulose fibres (Bryld et al, 2014). The use of these alternative dyes compared to azo dyes has not been investigated further in this report. However, it should be noted that azo dyes that by reductive cleavage may release one or more of 22 specified aromatic amines are restricted by Annex XVII of REACH in textiles and leather articles (Regulation No. 1907/2006). Therefore, the use of azo dyes may be limited at least in textiles and leather.

7.1.2 Alternatives for use in final product

The following uses of naphthalene, where naphthalene is a part of the final product, are described further:

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[69] http://www.myriant.com/pdf/succinate-based-plasticizers.pdf
[70] http://www.cbi.eu/system/files/marketintel/2012_eu_legislation_azo_dyes_2_ta_adb_0.pdf
[71] http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CONSLEG:2006R1907:20120605:EN:PDF

- Grinding wheels as an artificial pore former
- Explosives in pyrotechnics
- Mothballs

7.1.2.1 Grinding wheels as an artificial pore former

Naphthalene is used to manufacture grinding wheels, an inorganic-bonded abrasive. Naphthalene acts as an artificial pore forming agent in the wheel when burned at high temperatures. Previously, other pore forming agents commonly used were sawdust or crushed nut shells (Marinescu et al., 2007). A recent study investigated the use of granulated sugar (Mao et al., 2014). However due to the fixed size of granulated sugar, it cannot be considered to be a better overall replacement for naphthalene. To find a better alternative, further investigation is required.

Para-dichlorobenzene (CAS No. 106-46-7) is another alternative to naphthalene in grinding wheels which is commonly applied. A desktop research showed that several studies mention para-dichlorobenzene and naphthalene equally frequent, but in some cases with para-dichlorobenzene described as "less toxic" and therefore may represent a better alternative (Winkler, 1985). However, para-dichlorobenzene has a harmonised classification of Aquatic Acute 1 H400, Aquatic Chronic 1 H410 and Carc 2. H351 similar to naphthalene, but not a classification as acutely toxic as naphthalene (it is classified as Eye Irrit. 2 H319 instead). Therefore, it is only with regard to the acute toxicity that para-dichlorobenzene is "less toxic" compared to naphthalene.

7.1.2.2 Explosives in pyrotechnics

Naphthalene is used in pyrotechnics to create smoke explosives. It has not been possible to find information about alternatives to the use of naphthalene in pyrotechnics.

7.1.2.3 Mothballs

The use of naphthalene in mothballs has not been supported in the EU since 2008. In Jia and Batterman (2010), it is mentioned that naphthalene has been replaced to some degree by para-dichlorobenzene as moth repellents. As described above para-dichlorobenzene has a harmonised classification similar to naphthalene, but is not classified as acutely toxic as naphthalene (it is classified as Eye Irrit. 2 H319 instead). Therefore, it is only with regard to the acute toxicity that para-dichlorobenzene is "less toxic" compared to naphthalene.

7.2 Historical and future trends

Generally, the use of naphthalene for the manufacturing of intermediates presents volumes a few orders of magnitude higher than its use for the manufacturing of products. However, some figures are outdated (from 1986), when the use of naphthalene in the EU was 20% higher, according to the ECB (2003). Anyhow, this decrease still holds the higher use of naphthalene as intermediate.

IHS Chemical (2013) has identified the manufacture of NSF as the largest use of naphthalene globally, which accounts for half of the total consumption globally (2011). This is due to the vast production of NSF used as plasticiser in construction materials such as concrete. This also represents the primary use of naphthalene in Denmark (SPIN).

It is estimated that the global use of phthalic anhydride will continue to increase over the next five years due to the growing economies in the Pacific Asia regions, which accounts for more than three fifth of global demand. However, estimations also show that the demand will continue in a slower pace in the European and North American regions due to restrictions (Research and Markets, 2014).

Not only does the demand of the applications influence the consumption of naphthalene. Alternatives substances such as o-xylene and p-dichlorobenzene and their relative prices compared to that of naphthalene also influence the usage of naphthalene. However, due a high diversification of its application, the overall demand may remain around the same level of magnitude whilst the relative applications may shift from one usage to another.

IHS Chemical (2013) predicts an overall global naphthalene consumption increase of 2% annually during 2011-2017. This forecast is based on the fact that an increased environmental pressure placed on naphthalene use in pesticides, dyestuff intermediates and solvent applications has contributed to demand declines in most industrialized regions. The United States, Japan and Western Europe are forecasted to experience less than 2% average annual growth through 2017, while developing regions (China, Central and Eastern Europe, and the Middle East) will continue to exhibit the fastest demand growth, ranging between 2% and 4% annually.

7.3 Summary and conclusions

Naphthalene is used both as an intermediate in the production of other chemicals as well as in end-use products. Alternatives for both uses have been considered.

Alternatives to naphthalene were found in some uses and to a varying extent. The naphthalene based plasticiser NSF to concrete mixtures, representing the largest use of naphthalene globally, seems to have been subject to most considerations with regard to alternatives with polycarboxylate increasingly gaining more acceptances in the market. Polycarboxylate is accessible on the market and represents a better structurally performing alternative to naphthalene based plasticisers in cement. Furthermore, polycarboxylate has a better health and environmental classification compared to naphthalene.
Phthalic anhydride is also produced today by use of o-xylene and could therefore potentially substitute the use of naphthalene for this purpose entirely. The classification of o-xylene is to some degree better than the classification of naphthalene and could thereby present a somewhat better alternative compared to naphthalene.

Alternatives to phthalic anhydride have not been found to be in the commercial production in spite of the known hazard to health of phthalic anhydride and its representation in major growing industries such as construction, automotive, electrical & electronics and paints & coatings. Phthalic anhydride has been prohibited in certain end-use products, which has created an incentive in the chemical industry to find future alternatives such as the bio-based replacements. Furthermore, the Danish EPA has concluded that alternatives exist technically, but with no realistic opportunities to influence current product compositions from international suppliers.

A desktop research showed that there is increasing public attention to the health risks related to azo dyes in clothing[72]. Furthermore, certain azo dyes are restricted in textile and leather articles according to REACH Annex XVII. Therefore, it could be assumed that the use of azo dyes globally will decline. Alternatives to azo dyes in textile fibres cotton and cellulose in form of other types of dyes do exist.

In some cases, the incentive to develop substitutions for naphthalene may be due to the increasing awareness of health and safety risks, in others due to environmental concerns, or both issues may play an equally important role. Globally, the use of naphthalene is predicted to continue to increase by 2 % annually, with expected growth between 2-4 % in growing economies in the Pacific Asia, whilst the use in the European and North American regions is predicted to increase in a slower rate than 2 % and gradually stagnating.

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[72] http://www.abc.net.au/news/2014-05-28/govt-considers-banning-carcinogenic-dyes-more-found-in-clothing/5482040

References

ALAB, 2011. “Div. Kompaktleuchtstofflampen”. Prüfbericht Nr. A61106003IR. Auftraggeber: Konsumenteninfo AG, Postfach 431, CH-8024 Zürich. Not public available.

ATSDR, 2005. “Toxicological profile for naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene”. US Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry. August 2005. Available at: http://www.atsdr.cdc.gov/toxprofiles/tp67.pdf

BAuA, 2010. Bundesanstalt für Arbeitsschutz und Arbeitsmedizin. ”Annex XV Restriction report - Proposal for a Restriction: Benzo(a)pyrene, Benzo(e)pyrene, Benzo(a)anthracene, Dibenzo(a,h)anthracene, Benzo(b)fluoranthene, Benzo(j)fluoranthene, Benzo(k)fluoranthene, Chrysene”. Version number 1, 31/05/2010. Available at: http://www.bfr.bund.de/cm/343/pak_annex_XV_restriction_report_proposal_for_a_restriction.pdf

Bryld et al., 2014. “Kortlægning af udvalgte allergene, disperse farvestoffer i tøj”. Kortlægning af kemiske stoffer i forbrugerprodukter nr. 129, 2014. Available at http://www2.mst.dk/Udgiv/publikationer/2014/04/978-87-93178-42-7.pdf

Chemical Book, 2014. Chemicals information database. Available at: http://www.chemicalbook.com/ProductIndex_EN.aspx

CoRAP, 2014. “Community rolling action plan (CoRAP) update covering years 2014, 2015 and 2016”. 26 March 2014. http://echa.europa.eu/documents/10162/13628/corap_list_2014-2016_en.pdf

Daczko, J., 2008. “The New Variety of Polycarboxylate Dispersants”. Concrete Constructions, published January 7, 2008. http://www.concreteconstruction.net/concrete-construction/the-new-variety-of-polycarboxylate-dispersants_2.aspx

Danish EPA, 2001. “Luftvejledningen. Begrænsning af luftforurening fra virksomheder”. Vejledning fra Miljøstyrelsen Nr. 2, 2001. Danish EPA. Available at: http://www2.mst.dk/udgiv/publikationer/2001/87-7944-625-6/pdf/87-7944-625-6.pdf

Danish EPA, 2014. The EU list of potential endocrine disruptors. http://eng.mst.dk/topics/chemicals/endocrine-disruptors/the-eu-list-of-potential-endocrine-disruptors/

Danish EPA Chemicals in consumer products Database, 2014. “Chemicals in consumer products – Database”. Available at: http://eng.mst.dk/topics/chemicals/consumers-consumer-products/database-of-chemicals-in-consumer-products/

Danish Ministry of Environment (2012). Statutory Order no. 1309, 18/12/2012 on Waste. Ministry of Environment of Denmark. Available at: https://www.retsinformation.dk/Forms/R0710.aspx?id=144826.

DeGraeve et al., 1982. “Effects of Naphthalene and Benzene on Fathead Minnows and Rainbow Trout”. DeGraeve G. M., Elder R. G., Woods D. C. and Bergman H. L. 1982. Arch. Environm. Contam. Toxicol. 11,487-490 (1982).

ECB, 2003. European Union Risk Assessment Report. CAS No. 91-20-3, naphthalene. Institute for Health and Consumer Protection. ECB. 1st Priority List. Volume 33. Available at: http://echa.europa.eu/documents/10162/4c955673-9744-4d1c-a812-2bf97863906a

ECB, 2008. European Union Risk Assessment Report. CAS No. 65996-93-2, Coal-Tar Pitch, High Temperature (CTPHT). ECB. Available at: http://esis.jrc.ec.europa.eu/doc/risk_assessment/REPORT/pitchcoaltarreport323.pdf

ECHA, 2014. C&L Inventory database. Available at: http://echa.europa.eu/web/guest/information-on-chemicals/cl-inventory-database

ECHA Guidance R.11, 2012. “Guidance on information requirements and chemical safety assessment. Chapter R.11: PBT Assessment”. November 2012. Version 1.1. Guidance for the implementation of REACH. http://echa.europa.eu/documents/10162/13632/information_requirements_r11_en.pdf

ECHA Registered Substance Database (ECHA RSD), 2014. ECHA RSD, 2014. Registered substances. Available at: http://echa.europa.eu/information-on-chemicals/registered-substances

Eggert and Hansen, 2004. “Survey and emission of chemical substances from incense”. Eggert T., Hansen O.C., Danish Technological Institute. Survey of chemical substances in consumer products No. 39, 2004. Available at: http://eng.mst.dk/media/mst/69122/39.pdf

Emergency Management Agency, 2013. Performance chart of Naphthalene for chemical accidents (in Danish). Available at: http://www.kemikalieberedskab.dk/upload/ik/1107.pdf

Environment Canada, 2008a. Proposed risk management approach for Naphthalene (CAS 90-20-3). Environment Canada, Health Canada. Available at: http://www.ec.gc.ca/ese-ees/default.asp?lang=En&n=B68532E6-1

Environment Canada, 2008b. Screening Assessment for Naphthalene (91-20-3). July, 2008. Environment Canada, Health Canada. Available at: http://www.ec.gc.ca/ese-ees/default.asp?lang=En&n=F212515C-1

EU RAR Addendum, 2007. Risk Assessment of Naphthalene. CAS no. 91-20-3. Environment Addendum of December 2007. Final approved version. Available at: http://echa.europa.eu/documents/10162/5f0beb6c-575f-4a1b-aff5-b37f06eb3852

EU Regulation No. 286, 2011. “Regulation (EC) No. 286/2011 of 10 March 2011 No 1272/2008 of the European Parliament and of the Council on classification, labelling and packaging of substances and mixtures”. http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CONSLEG:2011R0286:20130701:EN:PDF

European Commission, 2002. Opinion of the Scientific Committee on Food on the risks to human health of Polycyclic Aromatic Hydrocarbons in food. SCF/CS/CNTM/PAH/29/Final. Available at: http://ec.europa.eu/food/fs/sc/scf/out153_en.pdf

European Commission, 2010. Recommendation from the scientific committee on occupational exposure limits for naphthalene (SCOEL/SUM/90).

Fiat et al., 2012. “Superplasticizer Polyemeric Additives Used in Concrete”. Fiat, D., Lazar, M., Baciu, V. And Hubca, G. Materiale Plastice, vol. 49:1 (2012) pp 62-67. http://www.revmaterialeplastice.ro/pdf/FIAT%20D%201%2012.pdf

German Federal Institute for Risk Assessment, 2012. PAHs found in silicone pacifiers.

Guidechem, Chemical Trading Guide. Naphthalene (CAS No. 91-20-3). Accessed May 2014. Available at: http://www.guidechem.com/reference/dic-1129.html

Hansen and Steen, 2012. “Tjære-produkter i Danmark – forskellige sundhedsfarer.” Hansen M. K., Steen L., Arbejdsmiljøhuset. Kortlægning af kemiske stoffer i forbrugerprodukter nr. 119, Miljøstyrelsen, 2012. Tilgængelig på: http://www2.mst.dk/Udgiv/publikationer/2012/09/978-87-92903-50-1.pdf

Hansen et al., 2008. “Miljø- og samfundsøkonomisk analyse af indsamling og behandling imprægneret affaldstræ”. Hansen V., Cramer J., Hasler B., Larsen A., Poulsen P.B. akf, DMU, FORCE Technlogy. Environmental project No. 1208, 2008. Danish EPA. Available at: http://www2.mst.dk/udgiv/publikationer/2008/978-87-7052-654-8/pdf/978-87-7052-655-5.pdf

Hansen and Eggert, 2003. “Survey, emission and evaluation of volatile organic chemicals in printed Matter”. Hansen O.C., Eggert T., Danish Technological Institute. Survey of chemical compounds in consumer products No. 36, Danish EPA, 2003. Available at: http://eng.mst.dk/media/mst/69119/36.pdf

Herget, 2014. “Kortlægning af vanskeligheder ved at skaffe varer uden ftalaterne DEHP, BBP, DBP og DIBP”. Kortlægning af kemiske stoffer i forbrugerprodukter nr. 127, 2014. Available at http://www2.mst.dk/Udgiv/publikationer/2014/03/978-87-93178-23-6.pdf

Holcombe et al., 1984. “The Acute Toxicity of Selected Substituted Phenols, Benzenes and Benzoic Acid Esters to Fathead Minnows Pimephales promelas”. Holcombe Gary W., Phipps Gary L., Knuth Michael L. and Felhaber Taryl. Environmental Pollution (Series A) 35 (1984) 367-381.

HPA, 2007. “Naphthalene”. Health Protection Agency. Wakefield J.C., CHAPD HQ, HPA, 2007. Version 1. Available at: http://www.hpa.org.uk/webc/hpawebfile/hpaweb_c/1203084377836

Høibye et al., 2011. ”Background data for Annex XV dossier – DEHP, BBP, DBP and DIBP”. Miljøprojekt nr. 1362, 2011. Høibye, L., Maag, J. and Hansen, E. Available at http://www2.mst.dk/udgiv/publications/2011/04/978-87-92708-97-7.pdf ¨

IARC, 2002. “Monographs on the evaluation of carcinogenic risks to humans: some traditional herbal medicines, some mycotoxins, naphthalene and styrene”. Vol. 82, IARC (International Agency for Research on Cancer), 2002.

IHS Chemical, 2013. Naphthalene. Report from IHS Chemical on naphthalene, January 2013. Summary is available at: http://www.ihs.com/products/chemical/planning/ceh/naphthalene.aspx

IMDG Code, 2012. “International Maritime Dangerous Goods (IMDG) Code. Adoption of amendments to the IMDG Code (Ammendment 36-12)”. Resolution MSC.328(90). Annex 4. http://www.imo.org/KnowledgeCentre/IndexofIMOResolutions/Documents/MSC%20-%20Maritime%20Safety/328(90).pdf

Jacobsen et al., 2012. “Chemical substances in Tattoo Ink”. Jacobsen E., Tønning K., Bernth N., Danish Technological Institute.Serup J., Høgsberg T., Bispebjerg Hospital. Nielsen E., The National Food Institute of Denmark. Survey of chemical substances in consumer products No. 116, Danish EPA, 2012. Available at: http://www2.mst.dk/Udgiv/publications/2012/03/978-87-92779-87-8.pdf

Jensen & Blinksbjerg, 2000. “Baggrundsdokument for fastsættelse af emissionsgrænseværdi for PAH i luft”. Ref-Lab. dk-TEKNIK ENERGI & MILJØ, December 1999, corrected June 2000. Environmental Project. Available at: http://www.ref-lab.dk/ref-lab_docs/showdoc.asp?id=080505123900&type=doc&pdf=true

Jia and Batterman , 2010. A critical review of naphthalene sources and exposures relevant to indoor and outdoor air. International Journal of Environmental Research and Public Health ISSN 1660-4601. Jia C. and Batterman S. Available as open access at: http://www.ncbi.nlm.nih.gov/pubmed/20717549

Kamal et al., 2011. “Biological Monitoring of Blood Naphthalene Levels as a Marker of Occupational Exposure to PAHs among Auto-Mechanics and Spray Painters in Rawalpindi”. Kamal A., Qayyum M., Cheema I. U., Rashid A. BMC Public Health 2011, 11:467. Available at: http://www.biomedcentral.com/1471-2458/11/467/

Kang et al., 2012. “Household materials as emission sources of naphthalene in Canadian homes and their contribution to indoor air”. Kang D.H., Choi D. H., Won D., Yang W., Schleibinger H., David J. Atmospheric environment 50 (2012), 79-87. Available at: http://www.sciencedirect.com/science/article/pii/S1352231011013501

Lassen et al., 2011. “PAHs in toys and childcare products”. Lassen P., Hoffmann L., Thomsen M., National Environmental Research Institute, Aarhus University, Roskilde. Survey of chemical Substances in Consumer Products No. 114, 2011. Available at: http://www2.mst.dk/udgiv/publications/2012/01/978-87-92779-49-6.pdf

Laursen et al., 2003. “Survey of chemical compounds in textile fabrics”. Laursen S. P., Hansen J., Drøjdahl A., Danish Technological Institute, Clothing and Textile. Hansen O.C., Pommer K., Danish Technological Institute, Environmental and Waste Technology. Pedersen E., Bernth N., Danish Technological Institute, Chemical Technology. Survey of chemicals in consumer products No. 23, 2003. Available at: http://eng.mst.dk/media/mst/69105/23.pdf

Lin Gao et al., 2011. ”Comparative Study on the Application of Naphthalene Water-Reducing Agent and Polycarboxylate Water-Reducing Agent in High-Performance Concretre”. Gao Lin, Shi yan and Xu Guoqiang. Advanced Materials Research, vol. 217-218 (2011) pp 522-526. Abstract available at http://www.scientific.net/AMR.217-218.522

Mao et al, 2014. “Effect of granulated sugar as pore former on the microstructure and mechanical properties of the vitrified bond cubic boron nitride grinding wheels”. Mao, J.B., Zhang, F.L., Liao, G.C., Zhou, Y.M., Huang, H.P., Wang, C.Y. and Wu, S.H. Materials & Design, Vol. 60 (2014) pp 328-333. Abstract available at http://www.sciencedirect.com/science/article/pii/S026130691400274X

Marathe et al., 2004. “Alkylation of naphthalene with t-butanol: use of carbon dioxide as solvent”. Marathe, R.P., Mayadevi, S., Pardhy, S.A., Sabne, S.M. and Sivasanker, S. Journal of Molecular Catalysis A: Chemical, Vol. 181:1-2 (2004) pp 201-206. Abstract available at http://www.sciencedirect.com/science/article/pii/S1381116901003648

Marinescu et al., 2007. “Handbook of Machining with Grinding Wheels”. Marinescu, I.D.,Hitchiner, M., Uhlmann, E., Rowe, W.B. and Inasaki, I. CRC Press, Taylor & Francis Group, FL.

Mendes & Seita, 2009. “Design of Phthalic Anhydride Production Processes”. A. Mendes, A. R. Seita, Instituto Superior Técnico, Portugal. Available at: http://bari.upc.es/eurecha/docs/Solution_Student%20Problem_2009.pdf

Mikkelsen et al., 2004. “Survey and assessment of chemical substances in window colours”. Mikkelsen S.H., Havelund S., Skibsted A., COWI A/S. Survey of chemical substances in consumer products No. 48, 2004, Danish EPA. Available at: http://eng.mst.dk/media/mst/69128/48.pdf

Millemann et al., 1984. “Comparative Acute Toxicity to Aquatic Organisms of Components of Coal-Derived Synthetic Fuels”. Millemann Raymond E., Bridge Wesley J., Black Jeffrey A., Cushman Robert M., Daniels Karen L., Franco Paul J., Giddings Jeffrey M. , McCarthy John F. and Stewart Arthur J. Transactions of the American Fisheries Society 113:74-86, 1984

Moles et al., 1981. “Reduced Growth of Coho Salmon Fry Exposed to Two Petroleum Components, Toluene and Naphthalene, in Fresh Water”. Moles Adam, Bates Steve, Rice Stanley D. and Korn Sid, Trartsactions of the American Fisheries Society 110:430-436, 1981.

Mullin, R., 2004. “Synthetic Chemistry Moves Into Concrete: Polycarboxylate admixtures usher in a slew of performance improvements”. Chemical & Engineering News, Northeast News Bureau, vol. 82:41 (2004) pp 22-24. http://pubs.acs.org/cen/coverstory/8241/8241process2.html

Nilsson et al., 2006. ”Survey and health assessment of chemicals substances in sex toys” Nilsson N. H., Malmgren-Hansen B., Bernth N., Pedersen E., Pommer K., Danish Technological Institute. Survey of chemical substances in consumer products No. 77, Danish EPA, 2006. Available at: http://www2.mst.dk/udgiv/publications/2006/87-7052-227-8/pdf/87-7052-228-6.pdf

National Toxicology Program (NTP), 2000. U.S. Department of health and human services. NTP technical report on the toxicology and carcinogenesis studies of naphthalene in F344/N RATS (inhalation studies). Available at: http://ntp.niehs.nih.gov/ntp/htdocs/lt_rpts/tr500.pdf

Plank et al., 2009. “Effectiveness of Polycarboxylate Superplasticizers in Ultra-High Strenth Concrete: The Importance of PCE Compatability with Silica Fume”. Plank, J., Schroefl, C., Gruber, M., Lesti, M. and Sieber, R. Journal of Advanced Concrete Technology, vol. 7:1 (2009) pp 5-12. http://www.j-act.org/headers/7_5.pdf

Preuss, R., et al., 2003. “Naphthalene – an environmental and occupational toxicant (review)”. Int. Arch. Occup. Environ. Health. 76: 556-576. Abstract available at: http://link.springer.com/article/10.1007%2Fs00420-003-0458-1

Regeringen, 2003. “Affaldsstrategi 2003-2008”. Available at: http://www2.mst.dk/udgiv/Publikationer/2003/87-7972-971-1/pdf/87-7972-973-8.pdf

Regulation 1272/2013. “Commission Regulation (EU) No. 1271/2013 of 6 December 2013 amending Annex XVII to Regulation (EC) No. 1907/2006 of the European Parliament and of the Council on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) as regards polycyclic aromatic hydrocarbons. Available at: http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2013:328:0069:0071:EN:PDF

Research and Markets, 2014. “Phthalic Anhydride and Derivatives Market by Application & Geography – Trends & Forecast to 2018”. Summary available at http://www.researchandmarkets.com/research/qw3jwd/phthalic

Rice and Thomas, 1989. “Effect of the Pre-Treatment Exposures of Toluene or Naphthalene on the Tolerance of Pink Salmon (Oncorhynchus Gorbuscha) and Kelp Shrimp (Eualls Suckleyi)”. Rice Stanley D. and Thomas Robert E. Comp. Biochem. Phyiol., Vol 94C, No. I, pp. 289-293, 1989.

Rütgers Chemicals, 2008. “Coal Tar Pitch Markets in Europe & North America”, Power Point presentation by M. Sutton. VFT canadia Inc. Presented at 12th annual Met Coke World Summit, Chicago Illinois, October 22-24, 2008.

SCF, 2002. “Opinion of the Scientific Committee on Food on the risks to human health of Polycyclic Aromatic Hydrocarbons in food”. SCF/CS/CNTM/PAH/29 Final. 4 December 2002. Scientific Committee on Food, European Commission. Available at: http://ec.europa.eu/food/fs/sc/scf/out153_en.pdf

Schleicher et al., 2009. Revision of calculations of Danish VOC emissions from aromatic solvents and households (in Danish).

Saetre et al., 1984. “Toxicity and Chemical Reactivity of Naphthalene and Methylnaphthalenes”. Saethre L. J., Falk-Petersen I.-B., Sydnes L.K., Lonning S. and Naley A.M. Aquatic Toxicology, 5 (1984) 291-306.

SPIN database. Substances in Preparations in the Nordic countries. Searches performed April/May 2014. Available at: http://90.184.2.100/DotNetNuke/

Svendsen et al., 2004. “Survey of chemical substances in toothbrushes”. Svendsen N., Pedersen S.F., Hansen O.C., Mossing J.T., Bernth N., Danish Technological Institute. Survey of chemical substances in consumer products No. 42, 2004. Available at: http://eng.mst.dk/media/mst/69125/42.pdf

Takasuga et al., 2003. “Quantitative analysis of toxic compounds formed from combustion of some plastic materials and newspaper”. Takasuga T., Makino T., Umetsu N., Senthilkumar K. Shimadzu Techno-Research Inc., Japan. Organohalogen Compounds, Volume 60-65, Dioxin 2003, Boston MA. Available at: http://www.burnbarrel.org/Science/Dioxin2003_papers/TTakasuga424.pdf

US EPA, 1998. Toxicological review of Naphthalene. Summary available at: http://www.epa.gov/IRIS/subst/0436.htm

Wallen et al., 1957. “Toxicity to gambusia affinis of certain pure chemicals in turbid waters”. Wallen IE, Greer WC and Lasater R. Sewage Ind. Wastes 29, 695-711, 1957.

Winkler et al., 1985. ” Mothball differentiation: naphthalene from paradichlorobenzene”. Winkler, J.V., Kulig, K. and Rumack, B. H. Annals of emergency medicine, Vol. 1 (1985). Abstract available at http://www.ncbi.nlm.nih.gov/pubmed/3965000

Won et al., 2012. “Household materials as emission sources of naphthalene in Canadian homes and their contribution to indoor air”. Atmospheric environment 50, 79-87.

Zhang et al., 2004. “Synthesis of N-sugar-substituted phthalimides and their derivatives from sugar azides and phthalic anhydride”. Zhang, S., Li, Z. and Cai, M. Carbohydrate Research, Vol. 339:8

(2004) pp 1419-1420. Abstract available at DOI: 10.1016/j.carres.2004.03.032. http://www.sciencedirect.com/science/article/pii/S000862150400165X

Öko-Test 8, 2012. “Test Silikonschnuller. Wir müssen draussen blieben”. Öko-Test Kinder 8, 2012.

Appendix 1: Abbreviations and acronyms

BCF	Bioconcentration factor
CLP	Classification, Labelling and Packaging Regulation
DEFRA	Department for Environment, Food and Rural Affairs (UK)
EC_n	Effect concentration where n % of the species tested show the effect
ECB	European Chemicals Bureau
ECHA	European Chemicals Agency
EFSA	European Food Safety Authority
EPA	Environmental Protection Agency
E-PRTR	European Pollutant Release and Transfer Register
EU	European Union
HELCOM	The Baltic Marine Environment Protection Commission (Helsinki Commission)
Kow	Octanol/water partitioning coefficient
Koc	Organic carbon/water partitioning coefficient
Kp	Partial pressure equilibrium constant
LC	Lethal effect concentration
LOUS	List of Undesirable Substances (of the Danish EPA)
NOAEL	No observable adverse effect level
NOEC	No observable effect concentration
NOVANA	Danish national monitoring and assessment programme
OECD	Organisation for Economic Co-operation and Development
OSPAR	Convention for the Protection of the Marine Environment of the North-East Atlantic
PEC	Predicted environmental concentration
PNEC	Predicted no effect concentration
QSAR	Quantitative Structure and Activity Relationship
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
SIDS	Screening Information Data Sets
SPIN	Substances in Preparations in the Nordic countries
SVHC	Substance of Very High Concern
TDI	Tolerable daily intake
WE	Western Europe

Appendix 2: Background information on regulation

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

EU and Danish legislation

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

There are four main EU legal instruments:

- Regulations (DK: Forordninger) are binding in their entirety and directly applicable in all EU Member States.

- Directives (DK: Direktiver) are binding for the EU Member States as to the results to be achieved. Directives have to be transposed (DK: gennemført) into the national legal framework within a given timeframe. Directives leave 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).
- The European Commission has the right and the duty to suggest new legislation in the form of regulations and directives. New or recast directives and regulations often have transitional periods for the various provisions set-out in the legal text. In the following, we will generally list the latest piece of EU legal text, even if the provisions identified are not yet fully implemented. On the other hand, we will include currently valid Danish legislation, e.g. the implementation of the cosmetics directive) even if this will be replaced with the new Cosmetic Regulation.

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

- Recommendations and opinions are non-binding, declaratory instruments.

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

Chemicals legislation

REACH and CLP

The REACH Regulation[73] and the CLP Regulation[74] are the overarching pieces of EU chemicals legislation regulating industrial chemicals. The below will briefly summarise the REACH and CLP provisions and give an overview of 'pipeline' procedures, i.e. procedures which may (or may not) result in an eventual inclusion under one of the REACH procedures.

(Pre-)Registration

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

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

Evaluation

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

Authorisation

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

Restriction

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

Classification and Labelling

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

Two classification and labelling provisions are:

1. **Harmonised classification and labelling** for a number of chemical substances. These classifications are agreed at the EU level and can be found in CLP Annex VI. In addition to newly agreed harmonised classifications, the annex has taken over the harmonised

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

[74] Regulation (EC) No 1272/2008 on classification, labelling and packaging of substances and mixtures

classifications in Annex I of the previous Dangerous Substances Directive (67/548/EEC); classifications which have been 'translated' according to the new classification rules.

2. **Classification and labelling inventory**. All manufacturers and importers of chemicals substances are obliged to classify and label their substances. If no harmonised classification is available, a self-classification shall be done based on available information according to the classification criteria in the CLP regulation. As a new requirement, these self-classifications should be notified to ECHA, which in turn 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 web-site also provides the opportunity for searching for substances in the pipeline in relation to certain REACH and CLP provisions. These will be briefly summarised below:

Community Rolling Action Plan (CoRAP)
The EU member states have the right and duty to conduct REACH substance evaluations. In order to coordinate this work among Member States and inform the relevant stakeholders of upcoming substance evaluations, a Community Rolling Action Plan (CoRAP) is developed and published, indicating by who and when 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 being subject to Authorisation, it has to go through the following steps:

3. It has to be identified as a SVHC leading to inclusion in the candidate list[75]
4. It has to be prioritised and recommended for inclusion in ANNEX XIV (These can be found as Annex XIV recommendation lists on the ECHA web-site)
5. It has to be included in REACH Annex XIV following a comitology procedure decision (substances on Annex XIV appear on the Authorisation list on the ECHA web-site).

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

Registry of intentions
When EU Member States and ECHA (when required by the European Commission) prepare a proposal for:
- a harmonised classification and labelling,
- an identification of a substance as SVHC, or
- a restriction.

This is done as a REACH Annex XV proposal.

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

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[75] 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).

for the three types of Annex XV dossiers.

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 is works as:

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

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 built on the voluntary PIC procedure, initiated by UNEP and FAO in 1989 and ceased on 24 February 2006.

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

Basel Convention

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

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

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

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

Eco-labels

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

EU flower

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

Nordic Swan

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

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.

Appendix 3: Self classification

Classification		No. of notifiers (1665 notifiers in total)
Hazard Class and Category Codes	Hazard Statement Codes	
Flam. Sol. 2 **Acute Tox. 4** **Carc. 2** **Aquatic Acute 1** **Aquatic Chronic 1**	H228 **H302** **H351** **H400** **H410**	352+1 = 353 notifiers*
Acute Tox. 4 **Carc. 2** **Aquatic Acute 1** **Aquatic Chronic 1**	**H302** **H351** **H400** **H410**	343+286+118+ 66+48+29+28+20+ 18+16+16+7+6+4+ 4+2+2+1+1+1+1 = 1017 notifiers*
Acute Tox. 4 **Carc. 2** **Aquatic Acute 1** Aquatic Chronic 2	**H302** **H351** **H400** H411	93 notifiers
Reported as 'blank' **Acute Tox. 4** **Carc. 2** **Aquatic Acute 1** **Aquatic Chronic 1**	H411 **H302** **H351** **H400** **H410**	91 notifiers
Reported as 'blank' **Acute Tox. 4** **Carc. 2** **Aquatic Acute 1**	**H410** **H302** **H351** **H400**	32+10 = 42 notifiers*
Reported as 'blank' **Acute Tox. 4** **Carc. 2** **Aquatic Chronic 1**	**H400** **H302** **H351** **H410**	14+13+13 = 40 notifiers*

Classification		No. of notifiers (1665 notifiers in total)
Hazard Class and Category Codes	Hazard Statement Codes	
Reported as ‘blank’	H372	7 notifiers
Flam. Sol. 2	H228	
Acute Tox. 4	**H302**	
Carc. 2	**H351**	
STOT RE 1	H373	
Aquatic Acute 1	**H400**	
Aquatic Chronic 1	**H410**	
Acute Tox. 4	**H302**	5 notifiers
Carc. 2	**H351**	
Aquatic Chronic 1	**H410**	
Reported as ‘blank’	**H351**	4 notifiers
Flam. Sol. 2	H228	
Acute Tox. 4	**H302**	
Aquatic Acute 1	**H400**	
Aquatic Chronic 1	**H410**	
Reported as ‘blank’	**H410**	3 notifiers
Reported as ‘blank’	**H351**	
Reported as ‘blank’	**H302**	
Acute Tox. 4	**H302**	3 notifiers
Aquatic Acute 1	**H400**	
Aquatic Chronic 1	**H410**	
Not classified		1 notifier
Reported as ‘blank’	**H410**	1 notifier
Reported as ‘blank’	**H351**	
Reported as ‘blank’	**H302**	
Reported as ‘blank’	**H400**	
Reported as ‘blank’	H315	1 notifier
Reported as ‘blank’	**H410**	
Reported as ‘blank’	**H351**	
Reported as ‘blank’	**H302**	
Reported as ‘blank’	**H400**	

Classification		**No. of notifiers (1665 notifiers in total)**
Hazard Class and Category Codes	**Hazard Statement Codes**	
Reported as ‘blank’	H319	
Asp. Tox. 1 **Carc. 2** Aquatic Chronic 3	H304 **H351** H412	1 notifier
Flam. Sol. 2 **Acute Tox. 4** Acute Tox. 2 **Carc. 2** **Aquatic Acute 1** **Aquatic Chronic 1**	H228 **H302** H330 **H351** **H400** **H410**	1 notifier
Reported as ‘blank’ **Acute Tox. 4** **Carc. 2** **Aquatic Acute 1**	**H410** **H302** H350 **H400**	1 notifier
Reported as ‘blank’ **Acute Tox. 4** **Carc. 2** **Aquatic Acute 1** Aquatic Chronic 2	**H410** **H302** **H351** **H400** H411	1 notifier

H228: Flammable solid, H302: Harmful if swallowed, H304: May be fatal if swallowed and enters airways, H315: Causes skin irritation, H319: Causes serious eye irritation, H330: Fatal if inhaled, H350: May cause cancer, H351: Suspected of causing cancer, H372: Causes damage to organs, H373: May cause damage to organs through prolonged or repeated exposure, H400: Very toxic to aquatic life, H410: Very toxic to aquatic life with long lasting effects, H411: Toxic to aquatic life with long lasting effects, H412: Harmful to aquatic life with long lasting effects.
* Several identical classifications are for some reason listed separately in the C&L Database, but have in this table been joined (listed in the same row).

TABLE 13
NOTIFIED CLASSIFICATIONS FOR NAPHTHALENE – CAS 91-20-3 (FROM ECHA C&L DATABASE, MAY, 2014). CLASSIFICATIONS IDENTICAL TO THE HARMONISED CLASSIFICATION ARE MARKED IN BOLD.

Appendix 4: Use pattern of naphthalene in Denmark from 2000 to 2011

The use pattern of naphthalene in Denmark from 2000 to 2011 is listed below in Table 14. The data has been retrieved from the SPIN database (June 2014).

Year	Total tonnage (tonnes)	No. of products	Use
2000	5316.8	58	Anti-corrosion materials; Paint, lacquers and varnishes; Impregnation agents.
2001	34456.2	58	Underseal materials, incl. cavity seals; Paint, lacquers and varnishes; Anticorrosive paints.
2002	34458.1	72	Underseal materials, incl. cavity seals; Paint, lacquers and varnishes; Fuel additives; Anticorrosive paints.
2003	68786.3	86	Cleaning/washing agents; Corrosion inhibitors; Filling agents; Paint, lacquers and varnishes; Fuel additives - for adding to the fuel to improve yield.
2004	65247.6	92	Paint, lacquers and varnishes; Corrosion inhibitors; Fuel additives - for adding to the fuel to improve yield.
2005	65253.1	121	Filling agents; Lubricants; Paint, lacquers and varnishes; Corrosion inhibitors; Fuel additives - for adding to the fuel to improve yield; Solvents.
2006	53083.5	147	Filling agents; Lubricants; Paint, lacquers and varnishes; Biocides - pesticides for non agricultural uses; Corrosion inhibitors; Solvents; Fuels - for heating or as fuel for motorized vehicles including cars and boats; Fuel additives - for adding to the fuel to improve yield.
2007	53103.5	181	Filling agents; Lubricants; Paint, lacquers and varnishes; Cleaning/washing agents; Rust inhibitors; Solvents; Fuel additives - for adding to the fuel to improve yield; Fuels - for heating or as fuel for motorized vehicles including cars and boats.
2008	76591.7	170	Filling agents; Lubricants; Paint, lacquers and varnishes; Cleaning/washing agents; Rust inhibitors; Solvents; Fuels - for heating or as fuel for motorized vehicles including cars and boats; Fuel additives - for adding to the fuel to

Year	Total tonnage (tonnes)	No. of products	Use
			improve yield.
2009	62811.8	188	Filling agents; Plant protection - agricultural pesticides; Cleaning/washing agents; Lubricants; Paint, lacquers and varnishes; Rust inhibitors; Fuels - for heating or as fuel for motorized vehicles including cars and boats; Fuel additives - for adding to the fuel to improve yield.
2010	62768.9	191	Lubricants; Rust inhibitors; Cleaning/washing agents; Paint, lacquers and varnishes; Fuels - for heating or as fuel for motorized vehicles including cars and boats; Fuel additives - for adding to the fuel to improve yield.
2011	73739.1	192	Other cleaning/washing agents; Engine oils; Corrosion inhibitors; Other fuel additives.

TABLE 14
USE PATTERN OF NAPHTHALENE IN DENMARK FROM 2000 TO 2011 (SPIN DATABASE, 2014)

Appendix 5: Repeated dose toxicity animal studies

Test	Description	NOEL or LOEL value	Reference
Inhalation			
Rat, subchronic, inhalation	10 animals/sex/dose exposed to 11, 51 and 306 mg/m^3, 6 hours/day for 5 days/week for 13 weeks. Effects were reduced body weight and microscopic changes in the nasal epithelium.	LOAEC = 11 mg/m^3 air (2 ppm) No NOAEC could be established	Unknown author (1993) in ECHA RSD (2014)
Rat, subacute, inhalation	5 animals/sex/dose exposed to 5.2, 15.7, 52, 152 and 372 mg/m^3, 6 hours/day for 5 days/week for 4 weeks. Effects were reduced body weight and microscopic changes in the nasal epithelium.	NOAEC < 5.2 mg/m^3	Unknown author (1993) in ECHA RSD (2014)
Mice, chronic, inhalation	140 and 270 animals exposed to 50 and 150 mg/m^3/day for 6 hours/day 5 days/week for up to 104 weeks. Effects were minimal/mild inflammatory changes in the lungs and nasal passages. Increase in the incidence of benign alveolar/bronchiolar adenomas (high dose females), i.e. some evidence of carcinogenic activity of naphthalene in female mice.	No NOAEC or NOAEL identified	NTP (1992) in ECB (2003)
Oral			
Rat, subchronic, oral	10 animals/sex exposed to naphthalene by gavage at 25, 50, 100, 200 and 400 mg/kg bw /day for five days a week for 13 weeks Effect was clear signs of discomfort (e.g. diarrhoea) and increasing trend in organ damage (liver).	NOAEL = 200 mg/kg bw/day	Unknown author (1980) in ECHA RSD (2014)
Mice, subchronic, oral	10 animals/sex/dose exposed to 12.5, 25, 50, 100 and 200 mg/kg bw/day for five days a week for 13 weeks. Effect was clinical signs of toxicity (discomfort and physiological disorders) predominantly in male mice.	NOAEL = 100 mg/kg bw/day	Unknown author (1980) in ECHA RSD (2014)

Test	Description	NOEL or LOEL value	Reference
Rat, subacute, oral	6 animals/sex/dose exposed to 1 g/kg bw/day for 10 days Increase in liver weights was observed. No change in kidney weights. No mortality observed.	No NOAEL identified	Rao and Pandya (1981) in ECHA RSD (2014)
Mice, subchronic, oral	40 – 112 animals/sex/dose exposed to 5.3, 53 and 133 mg/kg bw/day for 90 days Effect was decrease in organ weights and increase in total serum protein levels (but considered to be of little toxicological significance).	NOAEL = 133 mg/kg bw/day	Shopp et al. (1984) in ECHA RSD (2014)
Mice, subacute, oral	40 – 112 animals/sex/dose exposed to 27, 53 and 267 mg/kg bw/day for 14 days Some mortality occurred at the highest dose. Effect was decrease in body weight and organ weight. Dose related changes were observed in the serum chemistry (i.e. decrease in blood urea nitrogen and increase in cholesterol).	NOAEL = 53 mg/kg bw/day	Shopp et al. (1984) in ECHA RSD (2014)
Rabbit, subacute, oral	31 animals/sex/dose exposed to 0 and 1000 mg/kg bw/day for 35 days No effect in 90% of the animals. 10% had effects on the eyes (cataract)	No NOAEL identified	Nicola et al. (1994) in ECHA RSD (2014)
Rat, subacute, oral	24 animals/sex/dose exposed to 100 mg/kg bw/day for the first 2 weeks, increased by 150 mg/kg bw/day from week 3 and 6 to a maximum of 750 mg/kg bw/day No mortality was observed. Effect was decrease in body weight and enhanced peroxidation in the liver only.	No NOAEL identified	Mark and Siraj (1988) in ECHA RSD (2014)
Dogs, subacute	1 animal was exposed to average dose of 220 mg/kg bw/day in 7 days. Effects beginning on the fifth day were lethargy, ataxia, diarrhoea and increase in white blood cell count. On the ninth day reduction in haemoglobin level, red blood cell count.	No NOAEL identified	Zuelzer and Apt (1949) in ECB (2003)

Test	Description	NOEL or LOEL value	Reference
Dermal			
Rat, subchronic, dermal	10 animals/sex/dose exposed to 100, 300 and 1000 mg/kg bw/day for 5 days/week for 13 weeks. No treatment-related effects observed. Testes weights in the highest dose group were slightly reduced.	NOAEL = at least 300 mg/kg bw/day (1000 mg/kg bw/day for systemic effects)	Unknown author (1986) in ECHA RSD (2014)

TABLE 15
SUMMARY OF THE RELEVANT REPEATED TOXICITY STUDIES ON NAPHTHALENE

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