Danish Ministry of the Environment
Environmental Protection Agency

Survey of selected phthalates

Part of the LOUS-review

Environmental Project No. 1541, 2014

Title:
Survey of selected phthalates

Authors and contributors:
Sonja Hagen Mikkelsen
Jakob Maag
Jesper Kjølholt
Carsten Lassen
Christian Nyander Jeppesen
Anna Juliane Clausen

COWI A/S, Denmark

Published by:

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

Year:

2014

ISBN no.

978-87-93026-95-7

Disclaimer:

When the occasion arises, the Danish Environmental Protection Agency will publish reports and papers concerning research and development projects within the environmental sector, financed by study grants provided by the Danish Environmental Protection Agency. It should be noted that such publications do not necessarily reflect the position or opinion of the Danish Environmental Protection Agency.
However, publication does indicate that, in the opinion of the Danish Environmental Protection Agency, the content represents an important contribution to the debate surrounding Danish environmental policy.
While the information provided in this report is believed to be accurate, the Danish Environmental Protection Agency disclaims any responsibility for possible inaccuracies or omissions and consequences that may flow from them. Neither the Danish Environmental Protection Agency nor COWI or any individual involved in the preparation of this publication shall be liable for any injury, loss, damage or prejudice of any kind that may be caused by persons who have acted based on their understanding of the information contained in this publication.

Contents

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 selected phthalates which both attracts attention as alternatives to already regulated phthalates such as DEHP, DBP and BBP (especially DINP, DIDP and DPHP) and are used for other purposes (these include DEP). Certain phthalates were included in the first list in 1998 and have remained on the list since that time.

Of the selected phthalates for the survey only DMEP is included in LOUS 2009.

The entry, "Certain phthalates" in LOUS includes DMEP, DEHP, DBP, BBP and DBP. The function of the substances is described as plasticisers in several products, primarily PVC. Of these phthalates only DMEP is selected for the survey. Other substances included in LOUS 2009, DEHP, DBP, BBP and DBP, are already covered by a national ban in consumer products and they are therefore not included in the survey. Instead DEP, DIPP, DPHP, DINP and DIDP have been selected based on either reproductive toxicity, suspected endocrine disruptive effects, or use in large tonnages.

The main reason for the inclusion of DMEP in LOUS is the classification of the substance as a reproductive toxicant.

DEP is listed in Annex B of LOUS 2009 as part of the EU 'Priority list of substances for further evaluation and their role in endocrine disruption'. However, because the registered use in Denmark has been below 100 tonnes per year since 2001 (SPIN database) the substance is not included in LOUS 2009.

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

The process

The survey has been undertaken by COWI A/S (Denmark) in cooperation xx from March to October 2012. The work has been followed by an advisory group consisting of:

- Shima Dobel, Danish EPA
- Frank Jensen, Danish EPA
- Thilde Fruergaard Astrup, Danish EPA
- Bente Fabech, Danish Veterinary and Food Administration
- Ulrik Heimann, The Danish Society for Nature Conservation
- Hilde Balling, Danish Health and Medicines Authority
- Ole Grøndahl Hansen, PVC Information Council Denmark
- Jakob Zeuten, Danish Chamber of Commerce
- Lone Mikkelsen, Ecological Council, Denmark
- Inge Werther, DAKOFA
- Cathrine Berliner Boteju, The Association of Danish Cosmetics, Toiletries, Soap and Detergent Industries
- Sonja Hagen Mikkelsen, COWI

Data collection

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

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

- Legislation in force from Retsinformation (Danish legal information database) and EUR-Lex (EU legislation database);
- Ongoing regulatory activities under REACH and intentions listed on ECHA's website (incl. Registry of Intentions and Community Rolling Action Plan);
- Relevant documents regarding International agreements from HELCOM, OSPAR, the Stockholm Convention, the PIC Convention, and the Basel Convention.
- Data on 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).
- 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);
- Date 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,

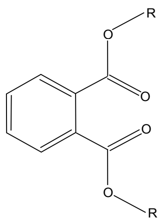
RIVM), Austria (UBA). Information from other EU Member States was retrieved if quoted in identified literature.
  - US EPA, Agency for Toxic Substances and Disease Registry (USA) and Environment Canada.
- PubMed and Toxnet databases for identification of relevant scientific literature.

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

Conclusion and summary

Over the period 2012-2015, all 40 substances and substance groups on the Danish Environmental Protection Agency's List of Undesirable Substances (LOUS) will be subject to survey and review. On the basis of the results, the Danish EPA will assess the need for any further regulation: substitution/phase out, classification and labelling, improved waste management or increased dissemination of information.

The selected phthalates
This survey concerns certain phthalates. The term "phthalate" is generally used to identify diesters of *ortho*-phthalic acid which is an aromatic dicarboxylic acid in which the two carboxylic acid groups are located in the *ortho* position in the benzene ring. The general chemical structure is shown below where the ester side chains (R), commonly ranging from C_4 to C_{13}, may be linear, branched or a combination of linear, branched, and ringed.



Generally both side chains are structurally identical as it is the case for the phthalates included in the present survey, but they may differ in other phthalates. The specific characteristics affect the physico/chemical and toxicological properties of the phthalate.

This review includes a survey of the following six *ortho*-phthalates:

Abbre-viation	Substance name	EC No	CAS No
DEP	Diethyl phthalate	201-550-6	84-66-2
DIPP	Diisopentyl phthalate	210-088-4	605-50-5
DPHP	Bis(2-propylheptyl) phthalate	258-469-4	53306-54-0
DMEP	Bis(2-methoxyethyl) phthalate	204-212-6	117-82-8
DINP *1	1,2-Benzenedicarboxylic acid, di-C8-10-branched alkyl esters, C9-rich Di-"isononyl" phthalate	271-090-9 249-079-5	68515-48-0 28553-12-0
DIDP *1	1,2-Benzenedicarboxylic acid, di-C9-11-branched alkyl esters, C10-rich Di-"isodecyl" phthalate	271-091-4 247-977-1	68515-49-1 26761-40-0

Note: *1 For DINP and DIDP two CAS numbers are listed, as the "substance", or rather mix of substances, differ slightly depending on production process used; both numbers are addressed in much of the available literature.

Regulatory framework

Harmonised classification - DIPP and DMEP are subject to harmonised CLP classification and are classified for reproductive toxicity in category 1B. In addition DIPP is classified as acute toxic 1 in aquatic environments. Besides the harmonised classification for DIPP and DMEP, few notifiers have self-classified DEP, DINP, and DIDP. The majority do not suggest a classification and have indicated "data lacking" and "conclusive but not sufficient for classification".

Other EU legislation - EU legislation restricts the use of DINP and DIDP in toys and childcare articles which can be placed in the mouth by children and prohibits the use of DMEP and DIPP in cosmetic products. Specific EU labelling requirements apply to certain medical devices containing phthalates classified as reproductive toxicants in category 1 and 2. A ban on CMR substances in concentration above the classification limits in toys also apply to DMEP and DIPP. EU also restricts the use of DINP and DIDP in plastic materials intended to come into contact with food.

DIPP and DMEP are included in the Candidate List under the REACH Regulation and thus in the line for being subject to the authorisation process.

Danish and other Member State legislation - Denmark has issued a national ban on the import, sale and use of phthalates in toys and childcare articles for children aged 0-3 years if the products contain more than 0.05 per cent by weight of phthalates. Other national legislation addresses the maximum concentration of phthalates in water leaving the water works and in consumer tap water. In addition DEP has a defined occupational exposure limit. The Danish regulation of waste sets limits for the contents of substances with classification as reprotoxic (includes DIPP and DMEP). If the limits are exceeded the waste shall be considered as hazardous waste and be treated as such. Denmark has specific environmental taxes on PVC plasticised with phthalates.

The Swedish Chemicals Agency plans to investigate the need for national restriction on phthalates toxic to reproduction or endocrine-disrupting.

International agreements - Phthalates are generally not addressed directly in international agreements. However, hazardous wastes from production, formulation and use of plasticisers, falls under the provisions of the Basel Convention.

Ecolabelling schemes - Phthalates are addressed by EU and Nordic eco-labelling schemes, in numerous product types either directly ("phthalates", DINP, DIDP) or by means of their classification (DIPP, DMEP and in some cases DEP).

Manufacture and use of the general plasticisers DINP, DIDP and DPHP

Manufacture - DINP is produced by four companies within the EU in Germany, Belgium and Italy, DIDP is produced by two companies within the EU in Belgium and Italy, and DPHP is produced in Germany and Sweden. All three substances are registered in the 100,000-1,000,000 tonnes/y band. Phthalates are not produced in Denmark.

The breakdown of the plasticiser market in Western Europe, USA and Asia is estimated as follows: DINP/DIDP represented 63% of the plasticiser market in Western Europe in 2010, whereas it only represented 33% of the market in the USA and 21% of the market in Asia. The total global market for plasticisers was estimated at 6 million tonnes. Of the global plasticiser market, all phthalates represented 84%. The on-going substitution of the traditional main general plasticiser DEHP has not reached the same level in Asia as in Europe and the USA. Also, non-phthalate plasticiser and "linears/other phthalates" are used to a higher extent in the USA than in Europe. According to the European trade organisation ECPI, DINP/DIDP now (2013) represents 83% of the plasticiser market in the EU.

The total plasticiser content of both imported and exported articles into and out of the EU has been estimated at about 170,000 t/y. The import of the general plasticisers DINP/DIDP (should likely be considered as including the third key general plasticiser DPHP) in articles was estimated at approximately 50,000 tonnes, and the export at 125,000 tonnes. Of the import into the EU, 51% of the tonnage of the articles originates from China, whereas only 9% of the imported DINP/DIDP (on their own) is estimated to originate from China. An overview of the extra-EU import/export by article type is given in the report.

Application and consumption in the EU – A total breakdown of the consumption by application in the EU of the three phthalates is not available. COWI *et al.* (2012) produced a best available scenario for the breakdown of the consumption by 2015 based on the available data from industry. The major article types were wires and cables, film and sheet, flooring, and various other coated products.

DINP, DIDP and DPHP are typically used as primary plasticisers in PVC, sometimes in combination with other plasticisers. The actual concentrations are quite variable and depend on the desired properties of the final PVC. Actual analyses of plasticisers in different products demonstrate that, for the same product, often different combinations of plasticisers are found. The combination of plasticisers in a PVC material is partly governed by the desired performance characteristics of the plasticised material and partly by the desired process parameters in the manufacturing of the PVC materials. Typical concentrations of DIDP in flexible PVC applications are reported to be around 25-50%, and the same seems to be the case for DINP.

DINP is a general plasticiser, which is applied in many products as the direct alternative for DEHP, the formerly major general PVC plasticiser. As such DINP has a high consumption and is probably the plasticiser which can be found in most flexible PVC products from the EU today. DINP has a wide range of indoor and outdoor applications. DINP is a commonly used plasticiser, 95% of which is used for flexible PVC used for construction and industrial applications, and durable goods (wire and cable, film and sheet, flooring, hoses and tubing, footwear, toys, etc.). More than half of the DINP used in non-PVC applications involves polymer-related uses (e.g. certain rubbers). The remaining DINP is used in inks and pigments, certain adhesives and sealants, paints and lacquers (where it also acts as a plasticiser) and lubricants.

DIDP is a common phthalate plasticiser, used primarily to soften PVC. DIDP has properties of volatility resistance, heat stability and electric insulation and is typically used as a plasticiser for heat-resistant electrical cords, leather for car interiors, and PVC flooring. Non-PVC applications are relatively small, but include use in anti-corrosion and anti-fouling paints, sealing compounds and textile inks.

DPHP is often used as an alternative to DIDP because only minor compound changes are needed to adapt wire formulations for example to DPHP. It is used for automotive and outdoor applications (roofing, geo-membranes, tarpaulins, etc.). Almost all DPHP is used as a plasticiser to make PVC soft and flexible.

Application and consumption in Denmark in 2012 of phthalates on their own was still dominated by DEHP (C8; net import around 800-1000 tonnes/y), but with the general C9-C10 plasticisers types including DINP and DIDP/DPHP (net imports around 600-800 tonnes/y) as a major follow-up.

The latest available aggregate survey of annual general phthalate consumption by application for Denmark covers 2005-2007 and is based on the revenues from the Danish environmental tax on PVC plasticised with phthalates, in combination with other data on the application of phthalates.

The major article groups as regards phthalate consumption were wires and cables (1.900 tonnes/y), tubes and hoses (630 t/y), and gloves and rainwear (540 t/y).

According to the Danish Product Register DINP is clearly the major registered phthalate in professional products marketed in Denmark, while the registered consumption of DIDP is moderate and the consumption of the other phthalates covered is minimal, as expected. DIPP is not registered in the Product Register. The Product Register only covers professional uses within certain criteria and it cannot be considered to fully cover the consumption pattern in Denmark. Among others, it does not include non-chemical articles such as wire and cable, shoe-soles, clothing, toys, etc., which constitute major parts of the Danish consumption of phthalates. Major registered uses which can be mentioned with respect for confidentiality are adhesives and binding agents, fillers (likely to be understood as including sealants), paints, lacquers and varnishes. Some other dominant applications across most substances cannot be mentioned due to confidentiality.

Manufacture and use of DIPP, DEP and DMEP

The aggregated information available on the use of DEP, DIPP and DMEP is scarce compared to DINP and DIDP, and the few reviews available are mostly relatively old and with little information about use and alternatives.

DIPP is registered by one company in the 100-1000 tonnes/y band (a producer of explosives importing DIPP), and is not produced in the EU anymore. According to the registration of the substance, DIPP is registered by a company which produces explosives as well as charges - so-called propellants - for ammunition. DIPP may also be used as plasticiser for PVC products and other polymers due to their similar structure and physicochemical properties, but this use is not registered.

DEP is registered by 5 companies in the 1000-10,000 tonnes/y band; among the companies is one of the major manufacturers of phthalates. DEP is a specialty polymer plasticiser and a solvent for cosmetics and personal care products, among others. DEP is reported to be have been used as a plasticizer in consumer products, including plastic packaging films, cosmetic formulations, and toiletries, and in medical treatment tubing. Examples of uses in cosmetics and personal care products include hair sprays, nail polishes, and perfumes, primarily as a solvent and vehicle for fragrances and other cosmetic ingredients and as an alcohol denaturant. DEP is however not mentioned as an accepted denaturant in EU and Danish rules from 2013 on tax exemption for denatured alcohol. Other applications include as a camphor substitute, plasticizer in solid rocket propellants, wetting agent, dye application agent, diluent in polysulfide dental impression, and surface lubricant in food and pharmaceutical packaging, in preparation of pesticides. Polynt, one of the registrants, markets DEP for the following uses: Cellulose, flavours & fragrances, cosmetics, pharma. An anonymous source indicates current DEP use as plasticiser in EU. ECPI does not have information of its use as a plasticiser.

DMEP is not registered under REACH and is reported not to be produced in Europe anymore. DMEP is a specialty plasticiser which can be used in a number of polymers. The general global applications of DMEP have included its use as a plasticiser in the production of nitrocellulose, acetyl cellulose, PVA, PVC and polyvinylidene chloride intended for contact with food or drink. DMEP is giving these polymeric materials good light resistance. Further, it is used as a solvent. Only limited information regarding DMEP in consumer products in the European marketplace has been identified. There is no information whether the substance is still in use in articles on the EU market.

Application and consumption in Denmark - Danish net imports of DEP, DIPP and DMEP is recorded along with other phthalates in the trade statistics and the group is traded in much lower quantities than the general plasticisers DINP and DIDP (net import of the whole group is around 90 tonnes/y).

Waste management
The quantities of waste generated from the use of the covered phthalates as plasticisers in production processes (formulation and conversion) are not well described. Releases to waste are expected to occur with disposal of emptied packaging, from handling of raw materials and intermediates, and as cut-offs in the conversion process, where the final products (articles) are produced. For sealants, paints and non-polymer uses, the "conversion" situation includes application on construction sites, etc. and here, a higher fraction of the material may be disposed as waste due to the less well defined conditions.

The amounts of flexible PVC in articles subject to the Danish tax on flexible PVC with phthalates are roughly estimated at 18,000 tonnes/year. Not all product groups containing flexible PVC are covered, but the figure is deemed to include most of the flexible PVC consumption which is plasticised with phthalates. The phthalates-containing waste fractions with biggest phthalates contents are cable and wire, tube and hoses, gloves and rainwear, roof plates; film, sheets and tape. The non-PVC uses of the phthalates represent much smaller phthalate amounts and at lower phthalate concentrations.

Ranges and averages of concentrations of the general plasticisers DINP and DIDP in articles are summarised in the report.

There are no known recycling schemes for flexible PVC in Denmark and according to the Danish waste order, non-recycled PVC should be collected separately and be deposited. Consumers however generally have difficulties in separating specific waste fractions, as flexible PVC is part of many ordinary consumer products such as rainwear, boots, and packaging, for which the content of PVC is not obvious to the consumer. Consequently much consumer waste with flexible PVC is deemed disposed of to municipal waste to be incinerated.

Environmental effects and exposure
None of the substances are considered to meet the criteria for classification as PBT or vPvB.

DIDP and DINP - A number of notifiers have provided self-classifications of DINP and DIDP. About half of the notifiers have classified DINP Aquatic Acute 1 + Aquatic Chronic 1 while the other half have classified it as Aquatic Chronic 4. DIDP has been classified Aquatic Acute 1 or Aquatic Acute 1 + Aquatic Chronic 1 by approx. half of the notifiers and Aquatic Chronic 2 by the other half. DIDP and DINP resemble each other much with regard to chemical structure and relevant physical-chemical properties such as water solubility, Log Kow and sorption constants, and therefore also with regard to effect properties and fate in the environment. As the water solubility of both substances is very low (sub-ppb) it has only been possible to conduct tests at higher concentrations (sub-ppm) using emulsions.

No significant acute or chronic toxic effects were observed in any tests on either of the two substances except for a "slight but statistically significant increase in egg viability in the DINP treated group when compared to the no treatment control" in a two-generation feeding study with medaka (*Oryzias latipes*). This observation did not affect the overall conclusion by EC (2003a and b) that DINP and DIDP are not considered to have adverse effects on the organisms (aquatic and terrestrial) studied. With regard to possible endocrine disruption properties it was concluded that "there is apparently no impact on any population parameter from chronic exposure to DIDP on fish".

The total release of DINP from wastewater treatment plants to the marine areas surrounding Denmark was estimated at around 135 kg/year.

DIPP is the only one of the phthalates in this study that has an EU harmonised environmental classification, namely Aquatic Acute 1 (H400).

DMEP is much more water soluble and a lowest experimental acute LC50 = 56 mg/l was determined for *Daphnia magna*. QSAR modelling results indicate acute LC50 for fish in the range 4.3 – 452 mg/l and a lowest chronic NOEC = 14 mg/l.

Only few environmental effect data are available on the remaining substances. However, the available data do not indicate that any of them are very toxic to aquatic organisms.

All the phthalates appear to be readily biodegradable (with DMEP as a possible exception) while abiotic processes such as hydrolysis and photolysis do not appear to be of any significance. A BCF (bioconcentration factor) <14.4 for DIDP in fish has been determined experimentally but is considered to be too low. Instead the BCF = 860 for DEHP is recommended by EC (2003a and b) for use in risk assessment.

Human health hazards and exposure

The main reason for concern in relation to phthalates and health hazards are adverse effects on the reproductive system of in particular male animals and endocrine disruption.

DIPP and DMEP are subject to harmonised health classification and both substances are classified for reproductive toxicity in Category 1 B. The four other phthalates selected for the study are self-classified by industry. No classification is suggested for DPHP and only few of the notifiers have self-classified DEP, DINP, and DIDP based on a number of adverse effects. The reason for not classifying the substances is typically lack of sufficient data.

The six phthalates are generally of low acute toxicity via all routes and with low skin and eye irritation potential. There are case reports referring to skin sensitisation to plastic articles in patients with dermatitis, e.g. in relation to DEP, but in general phthalates are not considered sensitising. Of the selected phthalates, DEP has been evaluated against the proposed Danish criteria for endocrine disrupters as a suspected endocrine disrupter in category 2a. The Danish EPA has suggested that also DINP be evaluated against agreed criteria for endocrine disruption.

No significant exposure to DMEP is expected as the substance is not registered for use in the EU. DEP has not been identified as an ingredient in cosmetic and personal care products in Denmark but may be imported from other countries and an exposure of DEP could therefore happen.

Occupational exposure is primarily expected via dermal contact in relation to handling of flexible PVC products, formulation and use of sealants and paints, and contact with cosmetics and personal care products. Direct consumer exposure is expected from dermal contact with various flexible PVC products, wires and cables and in particular imported cosmetics and personal care products. Indirect exposure of consumers occurs in relation to the indoor climate via dust and air.

In a newly published study with results from human biomonitoring on a European scale, all 17 participating countries analysed among others metabolites of some phthalates including DEP, DINP, and DIDP, in urine. Samples were taken from children aged 6-11 years and their mothers aged 45 years and under. The results showed higher levels in children compared to mothers, with the exception of MEP which is not regulated and is mainly used in cosmetics. A possible explanation is children's relatively higher exposure: they are more exposed to dust, playing nearer the ground, and have more frequent hand-to-mouth contact; and they eat more than adults in relation to their weight. Consumption of convenience food, use of personal care products and indoor exposure to vinyl floors and wallpaper have all been linked to higher phthalate levels in urine.

DINP and DIDP have been reviewed by ECHA in relation to the ban of these two phthalates in toys and childcare articles (entry 52 in Annex XVII to REACH). It was concluded that a risk from the mouthing of toys and childcare articles with DINP and DIDP cannot be excluded if the existing restriction were lifted. No further risks were identified. These conclusions were supported by ECHA's Committee for Risk Assessment.

The ECHA review also addressed the need for considering combined effects of phthalates and other substances with same mode of action in the risk assessment of the substances, e.g. in relation to antiandrogenic properties.

Alternatives

When considering the possibilities for substitution of specific plasticisers, it is important to note that a vast number of organic substances can act as plasticisers in polymers. Contrary to many other substitution efforts, plasticising is not dependent on highly specific chemical bonding, but rather on a series of characteristics which the plasticiser must have to meet functional demands. Finding the good plasticiser is therefore not a distinct theoretical science, but rather an empiric process supported by a large number of measuring methods designed for this purpose.

Many families of plasticisers are available. Most of them have however certain chemical functionalities in common with the phthalates family. They are typically branched, quite "voluminous" molecules, with many oxygen bonds (= carbonyl groups). Many have benzyl rings or the hydrogenated counterpart, cyclohexane.

DINP, DIDP and DPHP - Most available information on alternatives to primary plasticisers like DINP, DIDP and DPHP has been reviewed as part of the search for substitutes for the classic general plasticiser DEHP (to which DINP and to as lesser extend DIDP and DPHP are the key alternatives today). Several alternatives are however available, both *ortho*-phthalates (with basic structure similar to DINP, DIDP and DPHP), *tere*-phthalates and non-phthalate plasticisers. The one non-*ortho*-phthalate with the widest coverage for traditional DEHP applications is likely its terephthalate counterpart DEHT, which has the same chemical composition, but a different form, and therefore different environmental characteristics. No single non-*ortho*phthalate plasticiser seems to be identified which covers all traditional applications of DEHP (and thus DINP, its main alternative). Together, however, the reviewed non-*ortho*phthalates cover most or all the key applications. The non-*ortho*phthalate alternatives best described include: DINCH, ASE, DGD, DEGD (in mixtures), COMGHA, DINA, ATBC and GTA. While most of these have their own environmental issues, many of them are deemed to have overall better environmental performance than DEHP based on the available information. A direct environment and health comparison of DINP, DIDP and DPHP and their alternatives has not been found.

DEP, DIPP and DMEP - A wide search of alternatives to the phthalates DEP, DIPP and DMEP has not been possible within this project. For DEP's use as a denaturant, many alternatives exist, and DEP is not a part of the 2013 list of denaturants accepted for attaining exemptions from alcohol tax in EU Member States (including Denmark). Based on a 2010 review of alternatives to DEHP, DBP and BBP, there are clear indications that non-*ortho*phthalate alternatives to key applications of DEP, DIPP and DMEP are available. Examples include GTA, ATBC, COMGHA, DINCH, DINA, DGD, ASE and a mix with DEGD as a major component.

Alternative materials - Focusing on alternative materials with characteristics similar to the characteristics of flexible PVC, the following flexible polymers are among the principal alternatives to flexible PVC (Maag *et al.*, 2010): Ethylene vinyl acetate (EVA), Low density polyethylene (LDPE), poly olefin elastomers, polyurethanes (may in some cases be plasticised with phthalates), isobutyl rubber, EPDM rubber (may in some cases be plasticised with phthalates) and silicone rubber.

Data gaps

In summary, the use of the general plasticisers DINP and DIDP is well described, even an actual distribution on end-products is not available for Denmark. DPHP is less well described, but has functional characteristics similar to DIDP and can be used as an alternative to DIDP. As regards DEP, the registered tonnages and other information indicate that it still has a significant use in the EU, but more details about the use are needed. DIPP seem to have a very narrow application range in the EU, and it is questionable if much more information can be found. DMEP is still not registered, indicating that its future use in the EU may be very limited or absent.

In conclusion, the following major data gaps are identified:

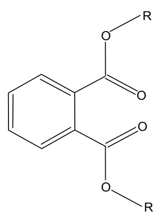
- More specific information on the consumption of DINP, DIDP, DPHP and DEP by application with special focus on DINP and DEP due to their human health characteristics.
- Investigation of the fate of plasticised PVC waste in Denmark, including collection rates, for both consumer waste and waste from professionals.
- Information on direct alternatives to DEP by major applications, in view of its significant production range and related exposure potential.
- Direct comparisons of DINP, DIDP and DPHP with available alternatives for relevant applications.
- Identification of the most important metabolites to be used as a biomarker for human exposures.
- Limited information on endocrine specific end-points for some phthalates
- Further documentation of the effects of cumulative exposure to e.g. antiandrogenic and estrogenic substances at different levels.

Dansk resumé

I perioden 2012-2015 vil alle 40 stoffer og stofgrupper på Miljøstyrelsens liste over uønskede stoffer (LOUS) blive kortlagt, og Miljøstyrelsen vil på grundlag af resultaterne vurdere behovet for yderligere regulering, substitution/udfasning, klassificering og mærkning, forbedret affaldshåndtering eller øget udbredelse af information.

De udvalgte ftalater

Denne undersøgelse vedrører udvalgte ftalater. Ordet ftalat bruges i almindelighed om diestre af *ortho*-ftalsyre, som er en aromatisk dicarboxylsyre hvori de to carboxylsyregrupper sidder i *ortho* positionen på benzenringen, dvs. lige ved siden af hinanden. Den generelle struktur for *ortho*-ftalater er vist nedenfor, hvor ester sidegrenene (R) – normalt C4-C13 – kan være lineære eller forgrenede, evt. også med yderligere ringstrukturer.



I de fleste tilfælde er sidegrenene identiske, hvilket er tilfældet for ftalaterne omfattet af dette studie, men de kan være forskellige. Den specifikke sammensætning af stoffet påvirker dets fysisk-kemiske og toksikologiske egenskaber.

Denne kortlægning omhandler følgende seks *ortho*-ftalater:

Forkortelse	Stofnavn	EC Nr	CAS Nr
DEP	Diethylftalat	201-550-6	84-66-2
DIPP	Diisopentylftalat	210-088-4	605-50-5
DPHP	Bis(2-propylheptyl)ftalat	258-469-4	53306-54-0
DMEP	Bis(2-methoxyethyl)ftalat	204-212-6	117-82-8
DINP *1	1,2-Benzendicarboxylsyre, di-C8-10-forgrenede alkyl estre, C9-rige Di-"isononyl" ftalat	271-090-9 249-079-5	68515-48-0 28553-12-0
DIDP *1	1,2-Benzendicarboxylsyre, di-C9-11-forgrenede alkyl estre, C10-rige Di-"isodecyl" ftalat	271-091-4 247-977-1	68515-49-1 26761-40-0

Note: *1 DINP og DIDP har hver to CAS numre, da “stoffet”, eller rettere stofbladingen er lidt forskellig afhængig af hvilken proces, der er brugt ved dets produktion. Begge numre er brugt i megen af den tilgængelige litteratur.

Regulering
Der er vedtaget harmoniserede klassifikationer for DIPP (Reprotoxic 1B; H360FD and Aquatic Acute; H400) og DMEP (Reprotoxic 1B; H360Df).

Foruden den harmoniserede klassificeringer af DIPP og DMEP er der udført selv-klassificering for en række effekter for DEP, DINP og DIDP af et mindretal af anmelderne. Mange anmeldere har angivet, at data ikke er tilstrækkelige til en klassificering, som årsag til at stofferne er notificeret uden klassificering.

Ifølge EU lovgivningen er anvendelsen af DINP og DIDP i legetøj og artikler til børnepleje, der kan tages i munden, samt i plastik anvendt til fødevarekontakt begrænset og DMEP og DIPP er forbudt i kosmetiske produkter. Der er særlige mærkningskrav for visse typer medicinsk udstyr, som indeholder ftalater, der er klassificerede som toksiske for reproduktionen i kategori 1 og 2, dvs. DMEP og DIPP. Et forbud mod CMR-stoffer i legetøj i koncentrationer over klassificeringsgrænsen omfatter også DMEP og DIPP.

I Danmark er der forbud mod import, salg og anvendelse af legetøj og børneartikler, som indeholder mere end 0,05 vægt-% ftalater, til børn under 3 år. Anden regulering sætter grænser for afløbsvand fra spildevandsrensningsanlæg og drikkevand. For DEP, DINP og DIDP er der etableret grænseværdier for arbejdsmiljøet. Affaldsbekendtgørelsen sætter grænser for indhold af stoffer, der er klassificeret som skadelige for reproduktionen (det gælder her DMEP og DIPP). Affald med højere indhold er defineret som farligt affald og skal behandles derefter. Danmark har særlige afgifter på PVC blødgjort med ftalater.

DIPP og DMEP anses som særlig problematiske stoffer (SVHC) og er optaget på Kandidatlisten under REACH reguleringen.

Den svenske Kemikalieinspektion har planer om at undersøge behovet for national regulering af ftalater, der er toksiske for reproduktionen eller har hormon-forstyrrende effekter.

Internationale aftaler - Ftalater er generelt ikke nævnt direkte i internationale miljøaftaler. Farligt affald fra produktion, formulering og anvendelse af plastik er dog omfattet at Basel konventionen.

Miljømærkning - Brug af ftalater, eller enkeltstoffer herunder, er ikke tilladt i en lang række produkttyper omfattet af det nordiske Svanemærke og EU Blomsten. Ftalater (som stofgruppe), DINP og DIDP er direkte nævnt i mærkningskriterierne for mange af disse produkttyper, mens DIPP, DMEP og i visse tilfælde DEP er omfattet via deres klassificering.

Fremstilling og anvendelse
Der produceres ikke ftalater i Danmark, men EU som helhed er en stor eksportør af (*ortho*-) ftalater.

Fremstilling og anvendelse af de generelle blødgørere DINP, DIDP og DPHP
DINP producers af 4 virksomheder i EU i Tyskland, Belgien og Italien, **DIDP** producers af 2 virksomheder i EU i Belgien og Italien, mens **DPHP** fremstilles i Tyskland og i Sverige. Alle 3 stoffer er registreret i 100.000-1.000.000 tons/år intervallet.

Fordelingen af blødgører-markedet i Vesteuropa, USA og Asien er anslået som følger af en af kilderne på området: DINP/DIDP repræsenterede i 2010 63% af blødgører-markedet i Vesteuropa, mens det kun udgjorde 33% i USA og 21% i Asien. The globale blødgører-marked udgjorde i alt ca. 6 millioner tons, hvoraf ftalater udgjorde 84%. Den igangværende substitution af DEHP har ikke nået samme niveau i Asien som i Europa og USA. Desuden anvendes ikke-ftalat blødgørere samt "lineære/andre ftalater" i højere grad i USA end i Europa. Det skal bemærkes, at ifølge ECPI repræsenterer DINP/DIDP nu 83% af markedet i EU.

Dansk netto-import i 2012 af ftalater (stofferne alene) var fortsat domineret af DEHP (C8, netto-import 800-1000 t/år), men med C9-C10 blødgørerne (DINP-DIDP/DPHP) på en andenplads (600-800 t/år).

Det totale blødgører-indhold i henholdsvis importerede og eksporterede artikler ind og ud af EU er anslået til omkring 170.000 t/år. Importen af de generelle blødgørere DINP/DIDP (skal i dag nok opfattes som inkluderende DPHP) i artikler er blevet anslået til omkring 50.000 t/år, mens eksporten var ca. 125.000 t/år. Af importen ind i EU kom 51% af vare-tonnagen fra Kina, mens kun 9% af importen af DINP/DIDP (som stofferne) kom fra Kina. En oversigt over EU import og eksport per artiketype er vist i rapporten.

DINP, DIDP og DPHP anvendes typisk som primære blødgørere i PVC, somme tider i kombination med andre blødgørere. De konkrete koncentrationer varierer en del og afhænger af hvilke egenskaber, der ønskes for den færdige PVC blanding. Kemiske analyser viser, at selv for den samme produkttype kan der findes forskellige kombinationer af blødgørere. Typiske DIDP koncentrationer angives at være 25-50 vægt-%, og det samme synes at være tilfældet for DINP.

DINP er en generel blødgører, der anvendes i mange produkter, som det direkte alternativ til DEHP, der tidligere var den dominerende blødgører. Der er således et stort forbrug af DINP og denne blødgører er nok den, der kan findes i de fleste PVC-produkter produceret i EU i dag. DINP anvendes således i en lang række sammenhænge både indendørs og udendørs. 95% af forbruget anvendes til blødgøring i byggeri og industri, herunder varer som kabler og ledninger, film og ark, gulvbelægning, rør og slanger, fodtøj, legetøj med mere. Mere end halvdelen af den DINP, der ikke anvendes til blød PVC, bliver brugt til andre polymerer (for eksempel visse gummityper). Resten anvendes i blæk, pigmenter, visse lime og fugemasser, maling og lak (hvor den også fungerer som blødgører) og i smøremidler.

DIDP er en almindelig blødgører, der hovedsageligt anvendes til PVC. DIDP er modstandsdygtig overfor fordampning og varme og den anvendes typisk som blødgører i el-ledninger, betræk i biler samt PVC-gulvbelægning. Andre anvendelser end til PVC er relativt begrænsede, men omfatter anti-korrosions- og antifouling maling, fugemasser og blæk til tekstiler.

DPHP anvendes ofte som alternativ til DIDP, fordi kun mindre ændringer i PVC-formuleringerne er nødvendige, for eksempel til el-ledninger. DPHP bruges til biler og udendørsanvendelser (tagmembraner, geo-membraner, presenninger mv.). Næsten al DPHP anvendes til blød PVC.

Et fuldt overblik over **forbruget af disse tre ftalater** opdelt efter anvendelse findes ikke. COWI *et al.* (2012) udarbejdede dog et overslags-scenarie for forbrugsfordelingen baseret på tilgængelige data fra industrien. De væsentligste artikel-typer var el ledninger og kabler, film og ark, gulvbelægninger samt en række andre coatede produkter.

Den seneste tilgængelige oversigt over det generelle årlige ftalatforbrug fordelt på anvendelser i Danmark er fra 2005-2007 og er baseret på den indkomne miljøafgift på ftalatholdige PVC produkter, i kombination med andre data om anvendelsen af ftalater. De største artikelgrupper hvad angår ftalatforbrug var el-ledninger og kabler (1.900 t ftalater/år), rør og slanger (630 t/år) og handsker og regntøj (540 t/år).

Ifølge det danske Produktregister er DINP er helt klart den væsentligste ftalat i professionelle produkter, der markedsføres i Danmark, mens det registrerede forbrug af DIDP er moderat, og forbruget af de andre udvalgte ftalater som forventet er minimalt. DIPP er ikke registreret i

Produktregistret. Produktregistret dækker kun erhvervsmæssig brug inden for visse kriterier, og det kan ikke anses for fuldt ud at dække forbruget i Danmark. Blandt andet omfatter det ikke artikler såsom ledninger og kabler, skosåler, tøj, legetøj osv., der udgør væsentlige dele af det danske forbrug af ftalater. Større registrerede anvendelser, der kan nævnes uden at krænke fortroligheden, er lim og bindemidler, fyldstoffer (formentlig omfattende fugemasser), maling, lak og fernis. Andre vigtige anvendelser kan ikke nævnes på grund af fortrolighed.

Fremstilling og anvendelse af DEP, DIPP og DMEP
DIPP er registret af én virksomhed i 100-1.000 t/år intervallet (en producent af sprængstoffer, der importerer DIPP), og produceres ikke i EU mere. DEP er registreret af fem virksomheder i 1.000-10.000 t/år intervallet. Blandt virksomhederne er en af de større producenter af ftalater. DMEP er ikke registreret og det angives at den ikke producers mere i EU.

Dansk netto-import af DEP, DIPP og DMEP er opgjort sammen med andre ftalater i udenrigsstatistikken og den gruppe handles i meget lavere mængder end de generelle blødgørere DINP/DIDP (netto-importen af hele stofgruppen er ca. 90 t/år).

Den eksisterende sammenfattede information om anvendelsen af DEP, DIPP og DMEP er sparsom sammenlignet med DINP og DIDP, og de få eksisterende sammenfatninger er for det meste relativt gamle og kun med lidt information om anvendelser og alternativer.

DEP er en specialblødgører til polymerer og et opløsningsmiddel til kosmetik og produkter til personlig pleje. DEP er tidligere anvendt som blødgører i forbrugerprodukter såsom pakkefilm af plast, kosmetikblandinger, toiletartikler og i medicinske slanger. Eksempler på kosmetik og personlige plejeprodukter er hårspray, neglelak og parfumer, hvor det kan være anvendt som opløsningsmiddel, som bærer af duftstoffer og til denaturering af alkohol. DEP er imidlertid ikke nævnt blandt de stoffer, der i EU og Danmark fra 2013 er accepteret som denatureringsmidler, der giver fritagelse for nationale alkoholafgifter. En anonym kilde indikerer, at DEP aktuelt anvendes som blødgører i EU. ECPI har ikke kendskab til en anvendelse af DEP som blødgører. Andre nævnte anvendelser er som alternativ til kamfer, som blødgører i ladninger i ammunition, slipmiddel, hjælpestof til indfarvning, opløsningsmiddel i tandaftryk af polysulfider, overflademiddel til pakninger af fødevarer og farmakologiske produkter, samt til fremstilling af pesticider. Polynt, en af registranterne, markedsfører DEP til følgende anvendelser: Cellulose, smags- og duftstoffer, kosmetik og farmakologi.

DIPP er registreret af en producent af sprængstoffer og ladninger – såkaldte drivmidler ("propellants") – til ammunition. DIPP kan muligvis også anvendes som blødgører i PVC og andre polymerer i kraft af dets lighed i struktur og fysisk-kemiske egenskaber, men denne anvendelse er ikke registret.

DMEP er en specialblødgører, som kan anvendes i en række polymerer. DMEP har globalt set blandt andet været brugt som blødgører i produktion af nitrocellulose, acetyl cellulose, PVA, PVC og polyvinylidenklorid til fødevarekontakt og drikkevarer. DMEP giver disse polymermaterialer god lysresistens. Det er desuden anvendt som opløsningsmiddel. Kun meget begrænset information om DMEP i forbrugerprodukter på det europæiske marked er fundet. Der er ingen information om, hvorvidt dette stof stadig anvendes på det europæiske marked.

Ifølge det Danske Produktregister er **DINP** klart den mest anvendte ftalat i produkter til professionelle på det danske marked, mens det registrerede forbrug af **DIDP** er moderat og forbruget af de **andre omfattede ftalater** er marginalt, som forventet. DIPP er ikke registreret i Produktregisteret. Produktregisteret dækker kun professionelle anvendelser indenfor visse kriterier, og det kan ikke anses som dækkende for det danske forbrugsmønster. Blandt andet er sådanne ikke-kemiske artikler som ledninger og kabler, skosåler, tøj, legetøj, osv., som udgør store dele af det danske forbrug af ftalater, ikke dækket. Væsentlige registrerede, ikke-fortrolige anvendelser er lime og bindemidler, spartelmasser (sandsynligvis skal det opfattes som også omfattende fugemasser), maling og lak. Visse større anvendelser på tværs af de fleste af stofferne kan ikke nævnes på grund af krav om fortrolighed.

Affaldshåndtering

Mængderne af affald, der frembringes fra brug af stofferne som blødgørere i produktionsprocesser (formulering og konvertering), er ikke velbeskrevet. Affald forventes at frembringes ved bortskaffelse af tømt emballage, fra håndtering af råmaterialer og intermediære forbindelser og som afskær i konverteringsprocessen, hvor slutprodukterne fremstilles. For fugemasser, maling og visse ikke-polymere anvendelser sker "konverteringen" på byggepladser med videre, og her kan større andele af materialet gå tabt som affald på grund af de mindre veldefinerede forhold.

Mængden af blød PVC i artikler som er underlagt dansk afgift på ftalater i blød PVC er groft anslået til 18.000 t/år. Ikke alle varegrupper med indhold af blød PVC er dækket af opgørelsen, men denne mængde anses for at dække størstedelen af forbruget af PVC blødgjort med ftalater. De ftalatholdige affaldsfraktioner, der repræsenterede de største ftalatindhold, var ledninger og kabler, rør og slanger, handsker og regntøj, tagplader, film og ark samt tape. Andre anvendelser af ftalaterne end PVC udgjorde langt mindre mængder ftalater og i lavere ftalatkoncentrationer. Intervaller og gennemsnit for koncentrationer af de generelle blødgørere DINP og DIDP i artikler er opsummeret i rapporten.

Der findes ikke genanvendelsesordninger for blød PVC i Danmark og ifølge Affaldsbekendtgørelsen skal PVC, der ikke genanvendes, indsamles separat og deponeres. Forbrugerne har imidlertid generelt svært ved at separere specifikke affaldsfraktioner da blød PVC er en del af mange almindelige forbrugerprodukter som regntøj, støvler, indpakning, osv., hvori indholdet af PVC ikke indlysende. Det vurderes derfor, at meget affald med blød PVC går til affaldsforbrænding.

Miljøeffekter og eksponering

DIPP er den eneste ftalat i dette studie, der har en harmoniseret miljøklassifikation, nemlig Aquatic Acute 1 (H400). En række anmeldere har angivet selvklassifikation for **DINP og DIDP**. DINP er af ca. halvdelen af anmelderne klassificeret som Aquatic Acute 1 plus Aquatic Cronic 1, mens den anden halvdel har klassificeret den som Aquatic Cronic 4. DIDP er klassificeret Akvatisk Akut 1 eller Akvatisk Akut 1 + Akvatisk Kronisk 1 af ca. halvdelen af anmelderne og Akvatisk Kronisk 2 af den anden halvdel.

DIDP og DINP ligner hinanden meget hvad angår kemisk struktur og relevante fysisk-kemiske egenskaber såsom vandopløselighed, Log Kow og adsorptionskonstanter, og derfor også hvad angår effekter og skæbne i miljøet. Da vandoplyseligheden af begge stoffer er meget lav (under pbb-niveau) har det kun været muligt at teste højere koncentrationer (under ppm niveau) ved hjælp af emulsioner.

Ingen signifikante akutte eller kroniske effekter blev observeret i nogen tests af de to stoffer, undtagen en "lille men statistisk signifikant stigning i ægs overlevelsesevne i den DINP-behandlede gruppe ved sammenligning med kontrolgruppen" i et to-generations madningsforsøg med medaka (*Oryzias latipes;* japansk risfisk). Denne observation påvirkede ikke hovedkonklusionen i EU's risikovurdering af stofferne (EC, 2003a og b) at DINP og DIDP ikke anses for at have negative effekter på de studerede organismer (akvatiske og terrestriske). Med hensyn til hormonlignende egenskaber blev det konkluderet, at "der er tilsyneladende ingen påvirkning af populationsparametre ved kronisk eksponering af fisk med DIDP".

Det totale udslip af DINP fra spildevandrensningsanlæg til havområderne der omgiver Danmark er anslået til omkring 135 kg/år.

DMEP er meget mere vandoplyselig og en lavest eksperimentel akut LC50 for fisk på 56 mg/l blev fundet for *Daphnia magna*. QSAR model resultater indikerer en akut LC50 for fisk i intervallet 4.3 – 452 mg/l og en laveste kronisk NOEC på 14 mg/l.

Kun få miljøeffektdata er tilgængelige for de øvrige stoffer. De tilgængelige data indikerer dog ikke at nogen af dem er meget giftige for vandlevende organismer.

Alle de omfattede ftalater lader til at være let bionedbrydelige (med DMEP som en mulig undtagelse) mens abiotiske processer såsom hydrolyse og fotolyse tilsyneladende ikke har nogen videre betydning. En BCF på <14,4 for DIDP in fisk er blevet fastlagt eksperimentelt, men anses som værende for lav. I stedet er BCF'en = 860 for DEHP anbefalet af EC (2003a and b) til brug i risikovurderinger.

Ingen af de omfattede stoffer anses for at opfylde kriterierne for klassifikation som PBT eller vPvB.

Humantoksiske effekter
Den væsentligste årsag til bekymring i forhold til ftalater er stoffernes påvirkning af reproduktionen hos især hanner og mistanke om hormonforstyrrende effekter.

DIPP og DMEP har begge en harmoniseret klassificering for reproduktionstoksicitet i kategori 1B. De fire andre ftalater udvalgt til undersøgelsen er selvklassificeret af industrien. Der er ikke foreslået nogen klassificering af DPHP og kun få af anmeldere har selvklassificeret DEP, DINP og DIDP. Årsagen er angivet som mangel på tilstrækkelige data.

De seks ftalater har generelt lav akut toksicitet via alle eksponeringsveje og begrænset potentiale for hud-og øjenirritation. Der findes case-rapporter, der viser hudsensibilisering over for plastartikler hos patienter med dermatitis, fx i forhold til DEP, men generelt ftalater anses ikke sensibiliserende. Af de udvalgte ftalater er DEP blevet evalueret i forhold til de foreslåede danske kriterier for hormonforstyrrende effekter, som mistænkt hormonforstyrrende i kategori 2a. Den danske Miljøstyrelse har foreslået, at også DINP blive evalueret i forhold til vedtagne kriterier for hormonforstyrrende effekter.

Der forventes ikke nogen væsentlig eksponering for DMEP, da stoffet ikke er registreret til brug i EU. DEP er ikke blevet identificeret som en ingrediens i kosmetiske produkter i Danmark, men eksponering kan forekomme i forbindelse med importerede produkter.

Erhvervsmæssig eksponering forventes primært via hudkontakt i relation til håndtering af produkter af blød PVC, formulering og anvendelse af fugemasse og maling, og kontakt med kosmetik og produkter til personlig pleje. Direkte forbrugereksponering forventes fra hudkontakt med forskellige fleksible PVC-produkter, ledninger og kabler og især importeret kosmetik og produkter til personlig pleje. Indirekte eksponering af forbrugerne sker i forhold til indeklimaet via støv og luft.

I en nyligt offentliggjort undersøgelse med resultater fra human biomonitering på europæisk plan, analyserede alle 17 deltagerlande blandt andet metabolitter af visse ftalater i urin, herunder DEP, DINP og DIDP. Prøverne blev taget fra børn i alderen 6-11 år og deres mødre i alderen 45 år og derunder. Resultaterne viste højere niveauer i børn i forhold til deres mødre, med undtagelse af MEP, metabolit af DEP, som ikke er reguleret, og hovedsagelig anvendes i kosmetik. En mulig forklaring er børns relativt højere eksponering: de er mere udsat for støv, leger tæt ved jorden, og har hyppigere hånd-til-mund-kontakt, og de spiser mere end voksne i forhold til deres vægt. Indtag af føde, brug af produkter til personlig pleje og indendørs eksponering for vinylgulve og tapet er alle blevet forbundet med højere ftalat-niveauer i urinen.

DINP og DIDP er blevet vurderet af ECHA i forbindelse med forbud mod disse to phthalater i legetøj og småbørnsartikler (artikel 52 i bilag XVII til REACH). Det blev konkluderet, at en risiko forbundet med at sutte på legetøj og småbørnsartikler med DINP og DIDP ikke kan udelukkes, hvis den eksisterende begrænsning blev ophævet. Ingen yderligere risici blev identificeret. Disse konklusioner blev støttet af ECHAs udvalg for risikovurdering.

Behovet for at overveje kombinationseffekter af phthalater og andre stoffer med samme virkningsmekanisme i risikovurderingen af stofferne, fx i forhold til antiandrogene egenskaber, blev også fremhævet.

Alternativer

Ved vurdering af mulighederne for substitution af specifikke blødgørere, er det vigtigt at notere sig, at et stort antal organiske stoffer kan fungere som blødgørere i polymerer. I modsætning til mange andre forsøg på substituering er blødgøring ikke afhængig af helt specifikke kemiske bindinger, men snarere af en række karakteristika som blødgøreren må have, for at opnå de krævede egenskaber. At finde den rette blødgører er således ikke en distinkt teoretisk videnskab, men snarere en empirisk proces støttet af et stort antal målemetoder, der er designet til formålet.

Mange mulige familier af blødgørere er til rådighed. De fleste af dem har imidlertid visse kemiske funktionaliteter til fælles med ftalatfamilien. De er typisk forgrenede, ret "voluminøse" molekyler med mange iltbindinger (= carbonylgrupper). Mange indeholder benzylringe eller deres hydrogenerede sidestykke, cyclohexan.

De fleste af de tilgængelige oplysninger om alternativer til primære blødgørere som **DINP, DIDP og DPHP** er blevet gennemgået som led i søgen efter alternativer til den klassiske generelle blødgører DEHP (for hvilken DINP og i mindre grad DIDP og DPHP er hovedalternativerne i dag). Adskillige alternativer er imidlertid til rådighed, både *ortho*-ftalater (med samme grundlæggende struktur som DINP, DIDP og DPHP), *tere*-ftalater og andre stoffer end ftalater. Af stoffer der ikke er *ortho*-ftalater dækker DEHP's *tere*-ftaliske sidestykke DEHT den største del af de traditionelle DEHP-anvendelser. DEHT har den samme kemiske sammensætning som DEHP, men en anden form og derfor andre miljøegenskaber. Derudover synes der ikke at være identificeret nogen enkelt ikke-ftalat, der dækker alle traditionelle anvendelser af DEHP (og dermed DINP, dens hovedalternativ). Tilsammen dækker de gennemgåede ikke-*ortho*-ftalater dog de fleste eller alle hovedanvendelser. De bedst beskrevne ikke-*ortho*-ftalat alternativer er, foruden DEHT, DINCH, ASE, DGD, DEGD (i blandinger), COMGHA, DINA, ATBC og GTA. De fleste af disse har deres egne miljøproblemer, men mange af dem anses overordnet set som havende bedre miljøegenskaber end DEHP baseret på den tilgængelige information. En direkte sammenligning mellem DINP, DIDP og DPHP med deres alternativer er ikke fundet.

En bred søgning af alternativer til ftalaterne **DEP, DIPP og DMEP** har ikke været mulig i dette projekt. Hvad angår DEPs anvendelse som denatureringsmiddel findes der dog mange alternativer og DEP er ikke på 2013 listen over denatureringsmidler, der kan give afgiftsfritagelse for national alkoholafgift i EU lande, herunder Danmark. Vurderet ud fra en review fra 2010 af alternativer til DEHP, DBP og BBP er der klare indikationer af at der er ikke-*ortho*-ftalat alternativer til rådighed, der dækker hovedanvendelserne af DEP, DIPP og DMEP. Eksempler er GTA, ATBC, COMGHA, DINCH, DINA, DGD, ASE og en blanding med DEGD som hovedkomponent.

Hvad angår **alternative materialer** med egenskaber som ligner blød PVCs er de følgende bløde polymerer blandt hovedalternativerne: Ethylene vinyl acetate (EVA), Low density polyethylene (LDPE), polyolefin elastomerer, polyurethaner (kan i visse tilfælde være blødgjort med ftalater), isobutyl gummi, EPDM (kan i visse tilfælde være blødgjort med ftalater) og silikone gummi.

Manglende oplysninger
Sammenfattende må anvendelsen af de generelle blødgørere DINP og DIDP anses som velbeskrevet, selvom en reel fordeling af deres anvendelse på slutprodukter ikke findes for Danmark. DPHP er mindre velbeskrevet, men har funktionelle egenskaber svarende til DIDP og kan anvendes som alternativ til denne. Hvad angår DEP, så antyder den registrerede mængde, samt andre oplysninger, at den stadig har en betydelig anvendelse i EU, men flere detaljer om dens anvendelse er nødvendige. DIPP ser ud til at have en meget afgrænset anvendelse i EU og det er spørgsmålet om der kan findes mere relevant information om den. DMEP er forstsat ikke registreret og det kan antyde at dens fremtidige anvendelse i EU er meget begrænset eller helt fraværende.

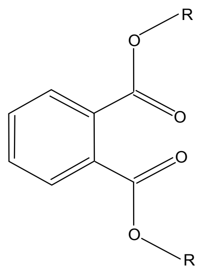
De følgende større databehov er således identificeret:

- Mere specifik information om brugen af DINP, DIDP, DPHP og DEP med særlig fokus på DINP og DEP på grund af stoffernes toksikologiske egenskaber..
- Undersøgelse af blød PVCs skæbne i affaldshåndteringen i Danmark, herunder indsamlingsrater, for både husholdningsaffald og erhvervsaffald.
- Information om direkte alternativer til DEP i væsentlige anvendelsesområder på baggrund af produktionsmængder og deraf følgende mulig eksponering..
- Direkte sammenligninger mellem DINP, DIDP og DPHP og deres (respektive) tilgængelige alternativer for relevante anvendelser.
- Identifikation af de vigtigste metabolitter, som kan anvendes som en biomarkører for humane eksponeringer
- Begrænset information om hormonforstyrrende virkning for nogle ftalater
- Yderligere dokumentation for virkningerne af kumulativ eksponering for fx anti-androgene og østrogene stoffer på forskellige niveauer

1. Introduction to the substance group

1.1 Definition of the substances

The term "phthalate" is generally used to identify diesters of *ortho*phthalic acid which is an aromatic dicarboxylic acid in which the two carboxylic acid groups are located in the *ortho* position in the benzene ring. The general chemical structure is shown below where the ester side chains (R), commonly ranging from C_4 to C_{13}, may be linear, branched or a combination of linear, branched, and ringed.

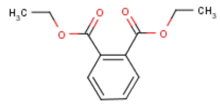
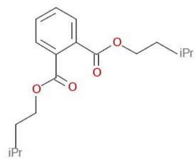
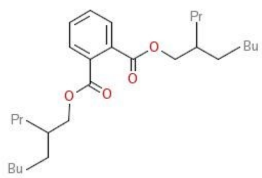
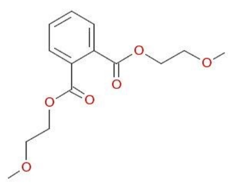
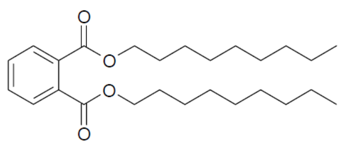
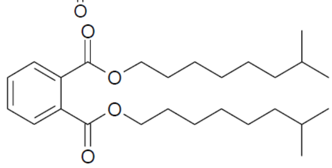


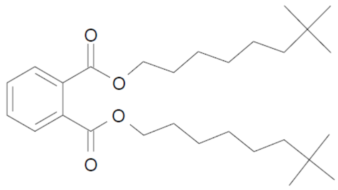
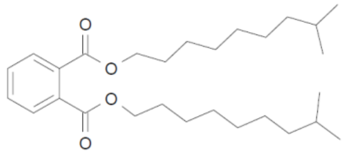
Generally both side chains are structurally identical as it is the case for the phthalates included in the present survey, but they may differ in other phthalates. The specific characteristics affect the physicochemical and toxicological properties of the phthalate.

Phthalates are divided into low-molecular phthalates and high-molecular phthalates based on the number of carbon atoms in the chains. Low Molecular Weight (LMW) phthalates, include those with 3-6 carbon atoms in their chemical backbone and 3-8 total carbons in the alkyl side chains. High Molecular Weight (HMW) phthalates, include those with 7-13 carbon atoms in their chemical backbone and 3-8 total carbons in the alkyl side chains (ECPI, 2013f).

The group of selected phthalates includes the substances shown in Table 1. The status of the substances as low or high molecular weight substances is also indicated.

TABLE 1
OVERVIEW OF SUBSTANCES COVERED BY THE SURVEY

Abbreviation	Substance name	EC No	CAS No	Structure *1
DEP	Diethyl phthalate	201-550-6	84-66-2	 LMW
DIPP	Diisopentyl phthalate	210-088-4	605-50-5	 LMW
DPHP	Bis(2-propylheptyl) phthalate	258-469-4	53306-54-0	 HMW
DMEP	Bis(2-methoxyethyl) phthalate	204-212-6	117-82-8	 LMW
DINP *2	1,2-Benzenedicarboxylic acid, di-C8-10-branched alkyl esters, C9-rich Di-"isononyl" phthalate	271-090-9 249-079-5	68515-48-0 28553-12-0	  HMW

Abbre-viation	Substance name	EC No	CAS No	Structure *1
DIDP *2	1,2-Benzenedicarboxylic acid, di-C9-11-branched alkyl esters, C10-rich	271-091-4	68515-49-1	
	Di-"isodecyl" phthalate	247-977-1	26761-40-0	 HMW

*1 Source: ECHA registrations (DEP, DIPP, DPHP, DMEP); EU RAR: DINP, DIDP. Note that the structures shown for DINP and DIDP are examples, as each of these "substances" actually is a mix of substances with an average stoichiometric composition of di-nonyl phthalate and di-decyl phthalate, respectively.

*2 For DINP and DIDP two CAS numbers are listed because the substance composition varies slightly with the production process used and because both numbers are addressed in much of the available literature.

DINP and DIDP constitute mixtures of substances which are further described in ECHAs Evaluation of New Scientific Evidence Concerning DINP and DIDP in Relation to Entry 52 of Annex XVII to Regulation (EC) No 1907/2006 (REACH) (ECHA, 2013) and cited under the substance headings below.

DINP

Two different types of DINP are currently on the market:

- DINP-1 (CAS No 68515-48-0) is manufactured by the "Polygas" process.
- DINP-2 (CAS No 28553-12-0) is n-butene based. (EC 2003a)

The production of a third form DINP-3 (also CAS 28553-12-0) has reportedly been discontinued (EC 2003a).

According to the trade organisation European Council of Plasticisers and Intermediates, ECPI (ECPI, 2011d), DINP is composed of different alcohol chains depending on the production method. It is a manufactured substance made by esterifying phthalic anhydride and isononanol. Isononanol is composed of different branched C9 alcohol isomers. The two branches on the molecule R1 and R2 are not necessary identical, and are either mainly C_8H_{17} to $C_{10}H_{21}$ (DINP-1) or C_9H_{19} isomers (DINP-2).

DINP-1 (CAS No 68515-48-0) contains alcohol groups made from octane, by the "polygas" process (EC 2003a). At least 95 percent of these alcohol groups comprise roughly equal amounts of 3,4-, 3,5-, 3,6-, 4,5-, 4,6-, and 5,6-dimethyl heptan-1-ol (Hellwig *et al.* 1997 as cited in Babich and Osterhout 2010). DINP-1 is also known by the trade name JayflexR.

DINP-2 (CAS No 28553-12-0) contains alcohol groups made from n-butene, which results mainly in methyl octanols and dimethyl heptanols. DINP-2 is also known by the trade names Palatinol NR and Palatinol DNR (NLM 2009a). DINP-3 (also CAS No 28553-12-0) contains alcohol groups made from n-butene and i-butene, resulting in 60 percent methylethyl hexanols. DINPs generally contain 70% or more nonyl alcohol moieties, with the remainder being octyl or decyl (Madison *et al.* 2000 as cited in Babich and Osterhout 2010).

Although their isomeric composition differs, the different types of DINP are considered to be commercially interchangeable. (Babich and Osterhout 2010).

The percent composition of the different chain structures of the two forms of DINP is shown in Table 10.

TABLE 2
BEST ESTIMATE OF CONTENT (%) OF THE DIFFERENT CHAIN STRUCTURES OF THE DINP'S (EC, 2003A)

Substance name	DINP-1	DINP-2
Methylethyl hexanols	5-10	5-10
Dimethyl heptanols	45-55	40-45
Methyl octanols	5-20	35-40
n-Nonanol	0-1	0-10
Isodecanol	15-25	--

DIDP
Two different types of DIDP are currently on the market:

- DIDP-1 (CAS No 26761-40-0)
- DIDP-2 (CAS No 68515-48-0)

DIDP is a complex mixture containing mainly C10-branched isomers (EC 2003b). DIDP is marketed under two CAS numbers. No data on the differences between the types of DIDP has been identified and the EU Risk Assessment (EC 2003b) does not distinguish between the different forms (unlike the Risk Assessment for DINP).

The correct structures can only be estimated. Based on nonene (CAS No 97593-01-6) isomer distribution analysis and 1H-NMR analysis of isodecyl alcohol, the EU Risk Assessment provides an estimation of key isomeric structures of isodecyl alcohol and hence of DIDP, as shown in Table 2. The lower ranges do not add up to 100% indicating that the substance may include other chain lengths.

TABLE 3
BEST ESTIMATE OF CONTENT (%) OF THE DIFFERENT CHAIN STRUCTURES OF THE DIDP (EC, 2003B)

Longest chain (estimate)	DIDP (CAS 68515-49-1 & CAS 26761-40-0)	Best estimated content (%)
C7	tri-methyl heptanols	0-10
C8	di-methyl octanols	70-80
C9	methyl nonanols	0-10
C10	n-decanol	

1.2 Physical and chemical properties

The physico-chemical properties of the selected phthalates presented in the tables below are where available referred from the REACH registration dossiers on the home page of the European Chemicals Agency (ECHA).

TABLE 4
NAME AND OTHER IDENTIFIERS OF DIETHYLPHTHALATE (DEP)

	Diethyl phthalate (DEP)	Reference
Synonyms	Diethyl benzene-1,2-dicarboxylate, 1,2-Benzenedicarboxylic acid, diethyl ester	
Molecular formula	$C_{12}H_{14}O_4$	Registration at ECHAs website
Molecular weight range	222.24	National Toxicology Programme
Physical state	Liquid (25 °C)	Registration at ECHAs website
Melting/freezing point	-60 °C	Registration at ECHAs website
Boiling point	297.3 °C (101.3 kPa)	Registration at ECHAs website
Relative density	1118.1 kg/m³ (20 °C)	Registration at ECHAs website
Vapour pressure	< 28 mBar (25 °C)	Registration at ECHAs website
Surface tension	37.5 dynes/cm (20 °C)	National Toxicology Programme
Water solubility (mg/L)	932 mg/L (20 °C)	Registration at ECHAs website
Log P (octanol/water)	2.47	National Toxicology Programme

TABLE 5
NAME AND OTHER IDENTIFIERS OF DIISOPENTYL PHTHALATE (DIPP)

	Diisopentyl phthalate (DIPP)	Reference
Synonyms	Bis(3-methylbutyl) phthalate; diisoamyl phthalate	Registration at ECHAs website
Molecular formula	$C_{18}H_{26}O_4$	Registration at ECHAs website
Molecular weight range	306.41	
Physical state	Liquid (20 °C, 1013 hPa)	Registration at ECHAs website
Melting/freezing point	< -25 °C	Registration at ECHAs website
Boiling point	339 °C (1016 mBar)	Registration at ECHAs website
Relative density	1.02 (20 °C)	Registration at ECHAs website
Vapour pressure	0.025 Pa (25 °C)	Registration at ECHAs website

	Diisopentyl phthalate (DIPP)	Reference
Surface tension	58 mN/m (20 °C)	Registration at ECHAs website
Water solubility (mg/L)	1.1 mg/L (20 °C)	Registration at ECHAs website
Log P (octanol/water)	5.45 (KowWin)	Registration at ECHAs website

TABLE 6
NAME AND OTHER IDENTIFIERS OF BIS(2-PROPYLHEPTYL) PHTHALATE (DPHP)

	Bis(2-propylheptyl) phthalate (DPHP)	Reference
Synonyms	1,2-benzenedicarboxylic acid, di-2-propylheptyl ester	Registration at ECHAs website
Molecular formula	$C_{28}H_{46}O_4$	Registration at ECHAs website
Molecular weight range	446,7	Registration at ECHAs website
Physical state	Liquid (20 °C, 1013 hPa)	Registration at ECHAs website
Melting/freezing point	-48 °C (pour point)	Registration at ECHAs website
Boiling point	252.5 – 253.4 °C (7 hPa)	Registration at ECHAs website
Relative density	0.96 (20 °C)	NICNAS, 2003
Vapour pressure	0.000000037 hPa (20 °C)	Registration at ECHAs website
Surface tension	35.1 dyne/m (20 °C)	http://www.lookchem.com/Bis-2-propylheptyl-phthalate/
Water solubility (mg/L)	< 0,0001 mg/L (25 °C)	Registration at ECHAs website
Log P (octanol/water)	1: > 6 (25 °C; pH 5,77) 2: 10.36 (25 °C) (QSAR)	Registration at ECHAs website

*) http://www.cpsc.gov//PageFiles/125788/dphp.

TABLE 7
NAME AND OTHER IDENTIFIERS OF BIS(2-METHOXYETHYL) PHTHALATE (DMEP)

	Bis(2-methoxyethyl) phthalate (DMEP)	Reference
Synonyms	1,2-Benzenedicarboxylic acid, bis(2-methoxyethyl) ester	NICNAS, 2008
Molecular formula	$C_{14}H_{18}O_6$	
Molecular weight range	282.3	NICNAS, 2008
Physical state	Liquid	NICNAS, 2008
Melting/freezing point	-40 °C	NICNAS, 2008
Boiling point	340 °C	NICNAS, 2008
(Relative) density	1.170 g/cm³	NICNAS, 2008
Vapour pressure	< 0.013 kPa (20 °C)	NICNAS, 2008
Surface tension	40.5 dyne/m	http://www.chemspider.com/Chemical-Structure.8041.html
Water solubility (mg/L)	0.9 g/L (20 °C)	NICNAS, 2008
Log P (octanol/water)	2.9	NICNAS, 2008

TABLE 8
NAME AND OTHER IDENTIFIERS OF 1,2-BENZENEDICARBOXYLIC ACID, DI-C8-10-BRANCHED ALKYL ESTERS, C9-RICH (DINP)

	1,2-Benzenedicarboxylic acid, di-C8-10-branched alkyl esters, C9-rich (DINP)	Reference
Synonyms	Di-iso-nonyl phthalate; 1,2-benzenedicarboxylic acid, di-isononyl ester	
Molecular formula	$C_{26}H_{42}O_4$	
Molecular weight range	420.6	ECB, 2003a
Physical state	Liquid (20 °C, 1013 hPa)	Registration at ECHAs website
Melting/freezing point	< -50 °C (pour point: -54 °C)	Registration at ECHAs website
Boiling point	> 400 °C (1 atm) (calc) 331 °C (96.47 kPa) (exp)	Registration at ECHAs website

(Relative) density	0.97 g/cm3 (20 °C)	Registration at ECHAs website
Vapour pressure	0.00006 Pa (20 °C)	Registration at ECHAs website
Surface tension	30.7 mN/m (20 °C)	Registration at ECHAs website
Water solubility (mg/L)	0.6 µg/L (21 °C, pH 7)	Registration at ECHAs website
Log P (octanol/water)	8.8 (25 °C, pH 7)	Registration at ECHAs website

TABLE 9
NAME AND OTHER IDENTIFIERS OF 1,2-BENZENEDICARBOXYLIC ACID, DI-C9-11-BRANCHED ALKYL ESTERS, C10-RICH (DIDP)

	1,2-Benzenedicarboxylic acid, di-C9-11-branched alkyl esters, C10-rich (DIDP)	**Reference**
Synonyms	Di-isodecyl phthalate; 1,2-benzenedicarboxylic acid, di-isodecyl ester	
Molecular formula	$C_{28}H_{46}O_4$	
Molecular weight range	447	Registration at ECHAs website
Physical state	Liquid (20 °C, 1013 hPa)	Registration at ECHAs website
Melting/freezing point	- 45 °C (101325 Pa)	Registration at ECHAs website
Boiling point	463 °C (1013 hPa)	Registration at ECHAs website
(Relative) density	0.97 g/cm3 (20 °C)	Registration at ECHAs website
Vapour pressure	0.000051 Pa (25 °C)	Registration at ECHAs website
Surface tension	30.9 mN/m (20 °C)	Registration at ECHAs website
Water solubility (mg/L)	0.0381 µg/L (25 °C, pH 7)	Registration at ECHAs website
Log P (octanol/water)	9.46 (25 °C, pH 7)	Registration at ECHAs website

* http://echa.europa.eu/web/guest/information-on-chemicals/registered-substances.

1.3 Function of the substances for the main application areas

Phthalates are primarily used to soften and make PVC flexible. They are however also found in other product types where they e.g. are added to avoid stiffness and cracking of surface films or because of their adhesive properties.

Phthalates belong to the group of general purpose (GP) plasticisers which provide the desired flexibility to PVC along with an overall balance of optimum properties at the lowest cost (Wilkes *et al.*, 2005). Phthalates are external plasticisers which mean that they are not firmly chemically bound to the plastic but are only dispersed in it. As a result, these plasticisers may degas or migrate from the plastic under certain conditions, and they can be released in relatively large proportions, e.g. when in contact with lipophilic media (such as oil or grease).

An effective plasticiser in PVC, must contain two types of structural components, polar and apolar. The polar portion of the molecule must be able to bind reversibly with the PVC polymer, thus softening the PVC, while the non-polar portion of the molecule allows the PVC interaction to be controlled so it is not so powerful a solvent as to destroy the PVC crystallinity. Examples of polar components would be the carbonyl group of carboxylic ester functionality; the non-polar portion could be the aliphatic side chain of an ester. The balance between the polar and non-polar portions of the molecule is critical to control its solubilising effect. If a plasticizer is too polar, it can destroy PVC crystallites; if it is too non-polar, compatibility problems can arise (Wilkes *et al.*, 2005).

Several theories are developed to account for the observed characteristics of the plasticisation process, e.g. the theory of *free volume*. Free volume is a measure of the internal space available within a polymer. As free volume is increased, more space or free volume is provided for molecular or polymer chain movement. A polymer in the glassy state has its molecules packed closely but is not perfectly packed. The free volume is low and the molecules cannot move past each other very easily. This makes the polymer rigid and hard. When the polymer is heated to above the glass transition temperature, Tg, the thermal energy and molecular vibrations create additional free volume which allows the polymer molecules to move past each other rapidly. This has the effect of making the polymer system more flexible and rubbery. Free volume can be increased through modifying the polymer backbone, such as by adding more side chains or end groups. When small molecules such as plasticisers are added, this also lowers the Tg by separating the PVC molecules, adding free volume and making the PVC soft and rubbery. Molecules of PVC can then rapidly move past each other.

Glass transition temperature is the temperature at which a polymer changes from a glassy brittle state to a fluid flexible state. PVC has a glass transition temperature of about 80 degrees centigrade, well above room temperature and it is therefore brittle at room temperature. Low density polyethylene (LDPE) on the other hand has a glass transition temperature below 0 degrees. Therefore it is flexible and not brittle at normal room temperatures, and would not be expected to require a plasticizer to keep it flexible (http://www.consultingchemist.com/Phthalates.pdf)

DINP
DINP is a general plasticiser, which is applied in many products as the direct alternative for DEHP, the formerly major general PVC plasticiser in the EU. As such DINP has a high consumption and is probably the plasticiser which can be found in most flexible PVC products produced in the EU today.

DIDP
DIDP has slightly higher weight and lower solubility than DINP and is thus mainly used in applications where continued product quality is needed under more demanding conditions, such as elevated temperatures, for example in electric cables. A major DIDP use is consequently as plasticiser in PVC insulation on cable and wiring. Other uses include car interiors and PVC flooring.

DPHP
According to ECPI's DPHP site (2013), almost all DPHP is used as a plasticiser to make PVC soft and flexible. Owing to its low volatility and weathering resistance, DPHP is suitable for high temperature applications such as wire and cable and automotive interior trim and outdoor applications such as roofing membranes and tarpaulins.

DEP

DEP is a specialty polymer plasticiser and a solvent for cosmetics and personal care products, among others. It is a low-weight phthalate; these generally have higher volatility and mobility in the polymer when used as plasticisers. Plasticiser uses include cellulose polymers, nail polishes, etc. An example of a solvent application is as a bearer of fragrances, and a delayer of release of the fragrance, in cosmetics and personal care products. It has also been used as a denaturant in alcohol for cosmetics and personal care products (and possibly in other applications).

DIPP

DIPP has been registered for its use in the manufacture of propellants (explosives in ammunition). As other low molecular weight phthalates DIPP may also be used as plasticiser for PVC products and other polymers. However there is currently no registration for that use. According to ECPI (2013e), DIPP is not produced in Europe anymore.

DMEP

DMEP is a specialty plasticiser which can be used in a number of polymers. According to BAuA (2011), only limited information regarding DMEP in consumer products in the European marketplace has been identified. The Australian NICNAS (2008) has reported about the import of DMEP in balls for playing and exercise, hoppers and children's toys (e.g. as inflatable water products). CPSC (2011) reports its use as a plasticiser (in the USA), but it is not mentioned if these are current observations.

According to ECPI (2013e), DMEP is not used as a plasticiser and the only European producer stopped making this substance a few years ago. As of June 2013, DMEP has not been registered under REACH.

2. Regulatory framework

This chapter gives an overview of how the selected phthalates are addressed in existing and upcoming EU and Danish legislation, international agreements and also by eco-label criteria.

In Appendix 1: a brief overview of legal instruments in the EU and DK and how they are related is presented. The appendix also gives a brief introduction to the chemicals legislation, it explains the lists referred to in section 2.1.3, and it provides a brief introduction to international agreements and selected eco-label schemes.

2.1 Legislation

This section will first list existing legislation addressing the selected phthalates and then give an overview of on-going activities, focusing on which substances are in the pipeline in relation to various REACH provisions.

2.1.1 Existing legislation

Table 10 provides an overview of existing legislation addressing the selected phthalates. For each area of legislation, the table first lists the EU legislation (if applicable) and then the transposition of this into Danish law and/or other national rules where this is required. National rules will only be elaborated upon in case the Danish rules differ from EU rules. For each legislative area the name of the Competent authority is mentioned in the heading.

In addition to the legislation concerning named substances the phthalates will of course also be covered by criteria-based legislation where relevant, e.g. bans and restrictions covering substances classified as toxic for reproduction which would concern DIPP and DMEP. This includes as an example the new rules for toys which prohibit CMR-classified substances in concentrations above the specific classification limit in all accessible components of toys.

TABLE 10
EU AND DANISH LEGISLATION ADDRESSING SELECTED PHTHALATES (AS OF JULY 2013)

Legal instrument *1	EU/DK	Substances	Requirements
Legislation addressing products (Danish EPA)			
Regulation No 1907/2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)	EU	Included in Annex XVII, no. 52: (a) Di-'isononyl' phthalate (DINP) CAS No 28553-12-0 and 68515-48-0; EC No 249-079-5 and 271-090-9 (b) Di-'isodecyl' phthalate (DIDP) CAS No 26761-40-0 and 68515-49-1 EC No 247-977-1 and 271-091-4	The listed phthalates:: (1) Shall not be used as substances or in mixtures, in concentrations greater than 0.1 % by weight of the plasticised material, in toys and childcare articles which can be placed in the mouth by children. (2) Such toys and childcare articles containing these phthalates in a concentration greater than 0.1 % by weight of the plasticised material shall not be placed on the market. (3) The Commission shall re-evaluate, by 16 January 2010, the measures provided for in relation to this entry in the light of new scientific information on such substances and their substitutes, and if justified, these measures shall be modified accordingly. (4) For the purpose of this entry 'childcare article' shall mean any product intended to facilitate sleep, relaxation, hygiene, the feeding of children or sucking on the part of children.
Statutory Order on the ban on phthalates in toys and childcare articles (Bekendtgørelse om forbud mod ftalater i legetøj og småbørnsartikler til børn i alderen 0-3 år, BEK Nr. 855 af 5 September 2009)	DK	All phthalates except DEHP, DBP, BBP, **DINP, DIDP** and DNOP (Covered by Regulation No. 1907/2006/EC)	Ban on the import, sale and use of phthalates in toys and childcare articles for children aged 0-3 years if the products contain more than 0.05 per cent by weight of phthalates.
DIRECTIVE 2009/48/EC of 18 June 2009 on the safety of toys **Statutory Order on the safety of toys (Bekendtgørelse om sikkerhedskrav til legetøjsprodukter, BEK nr 13 af 10/01/2011)**	EU DK	CMR substances (including DMEP and DIPP)	CMR substances are as of 20 July 2013 banned in all accessible components of toys in concentrations above the specific classification limit.

Legal instrument *1	EU/DK	Substances	Requirements
Legislation addressing cosmetics (Danish EPA)			
REGULATION (EC) No 1223/2009 of 30 November 2009 on cosmetic products	EU	bis(2-Methoxyethyl) phthalate (DMEP) (CAS no. 117-82-8) and Diisopentylphthalate (DIPP) (CAS no. 605-50-5)	Included in Annex II (LIST OF SUBSTANCES PROHIBITED IN COSMETIC PRODUCTS)
Legislation addressing medical devices (Ministry of Health and Prevention)			
DIRECTIVE 2007/47/EC of 5 September 2007 amending Council Directive 90/385/EEC on the approximation of the laws of the Member States relating to active implantable medical devices, Council Directive 93/42/EEC concerning medical devices and Directive 98/8/EC concerning the placing of biocidal products on the market. **Statutory Order concerning medical devices (Bekendtgørelse om medicinsk udstyr nr.1263 af 15/12/2008)**	EU DK	Phthalates classified as reproductive toxicants in category 1 or 2 (DIPP and DMEP)	Labelling requirement for certain medical devices containing the phthalates and requirements for information about risks.
Legislation addressing emissions (Danish EPA)			
Statutory Order on water quality and monitoring of water supply system (Bekendtgørelse om vandkvalitet og tilsyn med vandforsyningsanlæg, BEK nr 1024 af 31/10/2011)	DK	Phthalates other than DEHP (DEHP is specifically mentioned)	The sum of phthalates other than DEHP must not exceed 1 µg/L in water leaving the waterworks and at the point of entering consumer properties. The value at the consumers tap must not exceed 5 µg/L water. (All values are 1 µg/L for DEPH)

Legal instrument *1	EU/DK	Substances	Requirements
Statutory Order on quality requirement to environmental analyses (Bekendtgørelse om kvalitetskrav til miljømålinger, BEK no 900 af 17/08/2011	DK	Plasticisers including the sum of diisononylphthalates (DINP)	Sets requirements concerning quality control of chemical analyses of environmental and product samples and requirements concerning standard deviation on the measurements. Concerns analyses prepared as part of the authorities' enforcement of the Danish Environmental Protection Act, the Chemical Substances and Products Act and other legal instruments in the field of the environment and analysis prepared as part of environmental monitoring programmes.
Legislation addressing occupational health and safety (Ministry of Employment)			
Statutory Order on occupational limit values for substances and materials (Bekendtgørelse om grænseværdier for stoffer og materialer, BEK nr 507 af 17/05/2011 – with later amendments)	DK	Diethyl phthalate (DEP) (CAS no. 84-66-2)	A limit value of 3 mg/m^3 is established for DEP (gasses, vapours and particulates) in workplace air.
Council Directive 98/24/EC of 7 April 1998 on protection of the health and safety of workers from the risks related to chemical agents at work. **Statutory order nr. 292 of 26 April 2001 on working with substances and materials (chemical agents) – with later amendments.**	EU DK	Classified phthalates	

Legal instrument *1	EU/DK	Substances	Requirements
Legislation addressing food contact materials (Ministry of Food, Agriculture and Fisheries)			
REGULATION (EU) No 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food	EU	Included in Annex I, FCM subst. no. 728 and 729: (a) Di-'isononyl' phthalate (DINP) CAS No 28553-12-0 and 68515-48-0; EC No 249-079-5 and 271-090-9 (b) Di-'isodecyl' phthalate (DIDP) CAS No 26761-40-0 and 68515-49-1 EC No 247-977-1 and 271-091-4	Manufacture and marketing of plastic materials and articles: DINP and DIDP in plastic materials and articles: (a) intended to come into contact with food; or (b) already in contact with food; or (c) which can reasonably be expected to come into contact with food; must only be used as: (a) plasticiser in repeated use materials and articles; (b) plasticiser in single-use materials and articles contacting non-fatty foods except for infant formulae and follow-on formulae as defined by Directive 2006/141/EC or processed cereal-based foods and baby foods for infants and young children as defined by Directive 2006/125/EC; (c) technical support agent in concentrations up to 0,1 % in the final product.
Legislation addressing tariffs (Ministry of Taxation)			
Law on the taxation of polyvinylchloride and phthalates (Danish PVC Tax Act) (Bekendtgørelse af lov om afgift af polyvinylklorid og ftalater (PVC-afgiftsloven), LBK nr 253 af 19/03/2007)	DK	Flexible (and hard) PVC with content of *ortho*-phthalate esters	Goods made of PVC or PVC with phthalates for the most important applications are subject to tax based on the type and weight of the PVC goods marketed in Denmark. Rates are set for each article/material category; flexible PVC documented to be without phthalate contents have substantially lower tax rates. The Act covers a large number of goods categories containing PVC or PVC and phthalates.
Legislation addressing waste			
Directive 2008/98/EC of 19 November 2008 on waste and repealing certain Directives – The Waste Directive	EU	(In this context:) Classified substances, that is DIPP and DMEP	Sets out criteria for waste definitions and handling, including defining waste as hazardous waste if it exhibits specified toxic properties.
Statutory Order on waste (Affaldsbekendtgørelsen) - BEK 1309 af 18. dec. 2012	DK	=	Implements the Waste Directive in DK. Specifies threshold concentrations for waste including substances with specified classifications, including Repr. 1 substances (DIPP and DMEP), for which the concentration threshold is 0.5%. Waste above this limit is to be considered hazardous waste and be treated as such.

Legal instrument *1	EU/DK	Substances	Requirements
Directive 94/62/EC of 20 December 1994 on packaging and packaging waste (as later amended) – the Packaging Directive	EU	Hazardous substances in general	Does not explicitly mention phthalates, but states that "Packaging shall be so manufactured that the presence of noxious and other hazardous substances and materials as constituents of the packaging material or of any of the packaging components is minimized with regard to their presence in emissions, ash or leachate when packaging or residues from management operations or packaging waste are incinerated or landfilled."
Statutory Order on packaging (Emballagebekendtgørelsen; BEK 1049 af 10/11/2011)	DK	=	Implements the Packaging Directive in DK.
Statutory Order on sewage sludge (Slambekendtgørelsen - BEK nr. 1650 af 13. dec. 2006).	DK		Does not specifically mention the substances included in this review, but sets a threshold value for the concentration of the phthalate DEHP in sewage sludge used for agricultural purposes: 50 mg/kg dry matter.
Regulation EC 1013/2006 of 14 June 2006 on shipments of waste	EU	Waste	Does not specifically mention the substances included in this review. Regulates trans-boundary transport of waste (implements the Basel Convention in the EU).

*1 Un-official translation of name of Danish legal instruments.

As illustrated by the table, Denmark has national rules banning the use of phthalates in toys and childcare articles intended for children under 3 years. These rules exclude DINP and DIDP, which however are covered by the EU ban for toys and childcare articles intended to be placed in the mouth.

2.1.2 Classification and labelling

Harmonised classification in the EU

Table 11 lists the two phthalates (DIPP and DMEP) for which a harmonised CLP classification has been agreed upon. It shows that both substances are classified for reproductive toxicity in category 1B and that DIPP is classified as acute toxic 1 in aquatic environments.

Industry classifications for substances without a harmonised classification and labelling agreement are summarised in Table 12 and will be taken into account in Chapters 5 and 6 on environment and human health assessments.

TABLE 11
HARMONISED CLASSIFICATION ACCORDING TO ANNEX VI OF REGULATION (EC) NO 1272/2008 (CLP REGULATION)

Index No	International Chemical Identification	CAS No	Classification	
			Hazard Class and Category Code(s)	Hazard statement Code(s)
607-426-00-1	Diisopentylphthalate (DIPP)	605-50-5	Repr. 1B Aquatic Acute 1	H360FD H400
607-228-00-5	Bis(2-methoxyethyl) phthalate (DMEP)	117-82-8	Repr. 1B	H360Df

Self-classification in the EU
The Classification & Labelling (C&L) Inventory database at the website of the European Chemicals Agency (ECHA) contains classification and labelling information on notified and registered substances submitted by manufacturers and importers. The database includes as well the harmonised classification. Companies have provided this information in their C&L notifications or registration dossiers (ECHA, 2013d). ECHA maintains the Inventory, but does not verify the accuracy of the information.

Classifications of DEP, DPHP, DINP and DIDP listed in the database are shown in the table below. Substances with a harmonised classification are not indicated, reference is made to the table above.

In the table the total number of notifiers is indicated first followed by the number of notifiers that have classified the substance in each individual hazard class, e.g. Acute tox 1. The full classification submitted by the notifiers can be seen in the overview on ECHAs homepage.

TABLE 12
CLASSIFICATION INFORMATION OM NOTIFIED AND REGISTERED SUBSTANCES RECEIVED FROM MANUFACTURERS AND IMPORTERS (C&L INVENTORY)

CAS No	Substance name	Hazard Class and Category Code(s)	Hazard Statement Codes	Number of notifiers
84-66-2	Diethyl phthalate (DEP)	**Total** Acute Tox. 1 Acute Tox. 1 Skin Irrit. 2 Skin Sens. 1 Eye Irrit. 2 Acute Tox. 3 Acute Tox. 4 STOT SE 3 Repr. 2 STOT RE 2	 H302 H312 H315 H317 H319 H331 H332 H335 H361 H373	**70** 1 1 11 1 15 16 4 9 2 10
53306-54-0	Bis(2-propylheptyl) phthalate (DPHP)	**Total** Not classified		**126** 126

CAS No	Substance name	Hazard Class and Category Code(s)	Hazard Statement Codes	Number of notifiers
68515-48-0	1,2-Benzenedicarboxylic acid, di-C8-10-branched alkyl esters, C9-rich (DINP)	**Total** Not classified Skin Irrit. 2 Eye Irrit. 2 Repr. 2 Aquatic Acute 1	 H315 H319 H361 H400	**269** 240 1 1 3 24
28553-12-0	Di-"isononyl" phthalate (DINP)	**Total** Not classified Acute Tox. 4 Aquatic Acute 1 Aquatic Chronic 1 Aquatic Chronic 4	 H332 H400 H410 H413	**857** 781 1 24 23 28
68515-49-1	1,2-Benzenedicarboxylic acid, di-C9-11-branched alkyl esters, C10-rich (DIDP)	**Total** Not classified Skin Irrit. 2 Eye Irrit. 2	 H315 H319	**410** 353 25 32
26761-40-0	Di-"isodecyl" phthalate (DIDP)	**Total** Not classified Skin Irrit. 2 Eye Irrit. 2 Aquatic Acute 1 Aquatic Chronic 1 Aquatic Chronic 2	 H315 H319 H400 H410 H413	**182** 97 1 1 41 23 43

2.1.3 REACH

Candidate list

As of August 2013, two of the selected phthalates have been included in the candidate list as substances meeting the criteria for classification in the hazard class reproductive toxicity category 1B.

TABLE 13
SELECTED PHTHALATES ON THE CANDIDATE LIST (ECHA, 2013B; LAST UPDATED: 20/06/2013)

CAS No	EC No	Substance Name	Date of inclusion	Reason for inclusion	Decision number
605-50-5	210-088-4	Diisopentyl phthalate (DIPP)	2012/12/19	Toxic for reproduction (Article 57 c)	ED/169/2012
117-82-8	204-212-6	Bis(2-methoxyethyl) phthalate (DMEP)	2011/12/19	Toxic for reproduction (Article 57 c)	ED/77/2011

Authorisation List / REACH Annex XIV

As of March 2013, none of the selected phthalates are included in REACH annex XIV which is a list of substances that require authorisation for continued use in the EU.

Community rolling action plan

Table 14 shows the grounds for concern in relation to the planned REACH substance evaluation of DEP that may lead to further community action in the form of e.g. a restriction or authorisation.

TABLE 14
SUBSTANCES IN THE DRAFT COMMUNITY ROLLING ACTION PLAN, 2013-2015 UPDATE (ECHA, 2012A)

CAS No	EC No	Substance Name	Year	Member State	Initial grounds for concern
84-66-2	201-550-6	Diethyl phthalate	2014	Germany/Portugal*	Suspected Endocrine Disruptor; Exposure/Wide dispersive use, consumer use, high aggregated tonnage

* Where two Members States are indicated, this is a joint evaluation. The first Member State mentioned leads the Evaluation and is the responsible competent authority in the meaning of Article 45(2) of REACH.

Registry of Intentions

Table 15 includes entries from Registry of Intentions by ECHA and Member States' authorities for restriction proposals, proposals for harmonised classifications and labelling and proposals for identifying Substances of Very High Concern (SVHC). For further description of the Registry of Intentions and other background information on the legislative framework, see Appendix 1.

According to the information on the ECHA homepage, Annex XV dossiers are submitted for DIPP and DMEP and both substances are included in the Candidate list.

TABLE 15
SELECTED PHTHALATES IN REGISTRY OF (SVHC) INTENTIONS AS OF AUGUST 2013)

Registry of:	CAS No	Substances	SVHC Scope	Dossier intended by:	Date of submission:
SVHC intentions					
Annex XV dossiers submitted	**605-50-5**	Diisopentyl phthalate (DIPP)	CMR (Repr. 1B)	Austria	Submitted: 06/08/2012
	117-82-8	Bis(2-methoxyethyl) phthalate (DMEP)	CMR (Repr. 1B)	Germany	Submitted: 01/08/2011

Annex XIV recommendations

None of the selected phthalates have been recommended for Annex XIV inclusion (only relevant for those already included in the candidate list) in the latest lists of Annex XIV recommendations of 17 January 2013.

2.1.4 Other legislation/initiatives

Denmark

The Ministry of Environment in Denmark has after a finalised consultation period published a strategy for phthalates in June 2013. The strategy was developed in collaboration with the Ministry of Health, which has contributed with knowledge about phthalates in medical devices. The strategy identifies areas where more information is needed and areas where initiatives are required on a short term basis and in the long term in order to achieve sufficient protection of man and environment. Areas where sufficient information is available for further risk management are also identified.

In November 2012 Denmark issued a statutory order, BEK nr 1113, on the ban of certain phthalates in indoor articles. The order bans the phthalates DEHP, DBP, BBP and DIBP in indoor articles and articles with direct contact with the skin or mucous membranes. The ban is postponed until 2015 to allow industry time for the phase-out. The phthalates in question have been associated with endocrine related endpoints.

According to the Phthalate Strategy, in 2013 the Danish EPA will initiate a screening of information available on the endocrine disrupting effects of phthalates which have been registered, with the exception of phthalates which have already been classified as toxic to reproduction, as these are expected to meet the future EU criteria for identification as endocrine disruptors. Consequently, a screening will be carried out for 20 phthalates, as six of the registered or pre-registered phthalates have been classified as toxic to reproduction. The onward process will then be decided, as substances may be nominated for substance evaluation under the REACH Regulation in order to procure further documentation, or a proposal for EU legislation (harmonised classification (in case the evaluation concludes the effects meet the classification criteria for e.g. reprotoxicity), inclusion in the Candidate List, restrictions) may be prepared (Danish EPA, 2013).

Sweden

The Swedish Chemicals Agency (KEMI) informs on their website, that the Swedish government has assigned KEMI to conduct a survey of the use of phthalates suspected to be toxic to reproduction or endocrine-disrupting and the availability of alternative materials. On the basis of the survey, KEMI will be working, for instance through industry dialogues, for companies voluntarily to replace these phthalates with less hazardous substances or materials.

The mandate includes investigating the need and prerequisites for Sweden to impose national restrictions on the use of phthalates suspected to be toxic to reproduction or endocrine-disrupting. Possible ways to act at the EU level should be investigated. The work should take into account initiatives within the EU to classify, restrict or establish an authorisation process for phthalates. Any legislative proposals should include an impact assessment and an analysis of the impact on trade with other countries, as well as a risk assessment.

KEMI is to present its report to the Government Offices (Ministry of the Environment) no later than 30 November 2014 (KemI, 2013).

2.2 International agreements

Table 16 shows that none of the selected phthalates are covered by the listed international agreements.

TABLE 16
INTERNATIONAL AGREEMENTS ADDRESSING PHTHALATES

Agreement	Substances	How the selected phthalates are addressed
OSPAR Convention	None of the selected phthalates are covered.	Other phthalate esters are included in the list of Substances of Possible concern, Section B (Substances which are of concern for OSPAR but which are adequately addressed by EC initiatives or other international forums)
HELCOM (Helsinki Convention)	Same as above	
Rotterdam Convention (PIC Convention)	Same as above	

Agreement	Substances	How the selected phthalates are addressed
Stockholm Convention	Same as above	
Basel Convention	Wastes from production, formulation and use of resins, latex, plasticisers, glues/adhesives	These wastes are considered hazardous waste under the provisions of the Basel Convention unless they do not possess any of the characteristics contained in Annex III of this Convention.
Convention on Long-range Transboundary Air Pollution (CLRTAP)	Not relevant	

2.3 Eco-labels

Table 17 gives an overview of how selected phthalates are addressed by the EU and Nordic eco-labelling schemes.

Under the Nordic Swan product criteria, many of the criteria mentioning phthalates exclude the use of phthalates as a substance group; whereas for some product types hazardous substances with classification relevant to DIPP, DMEP and in some DEP are not permitted. For the EU flower, criteria targeting phthalates do generally and explicitly not permit the use of DINP and DIDP, whereas DIPP and DMEP are not mentioned explicitly but are not permitted due to their classification.

TABLE 17
ECO-LABELS TARGETING SELECTED PHTHALATES

Eco-label	Articles	Criteria relevant for phthalates	Document title
Nordic Swan	Dishwasher detergents	General restriction or ban regarding CMR classified substances. This requirement includes phthalates classified as Repr. 1B (**DIPP and DMEP**).	Nordic Ecolabelling of Dishwasher detergents, Version 5.3 • 15 December 2009 – 30 June 2015
	De-icers	Same as above	Nordic Ecolabelling of De-icers, Version 2.3 • 18 March 2004 – 31 December 2014
	Cleaning agents for use in the food industry	Same as above	Nordic Ecolabelling of Cleaning agents for use in the food industry, Version 1.6 • 13 October 2005 – 31 March 2016
	Hand Dishwashing Detergent	General restriction or ban regarding content of CMR classified substances or endocrine disruptors in category I or II. This requirement includes phthalates classified as Repr. 1B (**DIPP and DMEP**) and **DEP** included in the EU list of endocrine disruptors, category I. General CMR	Nordic Ecolabelling of Hand Dishwashing Detergents, Version 5.1 • 21 March 2012 – 31 March 2016
	Cosmetic products	Same as above	Nordic Ecolabelling of Cosmetics, Version 2.6 • 12 October 2010 – 31 December 2014
	Cleaning products	Same as above	Nordic Ecolabelling of Cleaning products, Version 5.0 • 13 March 2013 – 31 March 2017
	Laundry detergents and stain removers	Same as above	Nordic Ecolabelling of Laundry detergents and stain removers, Version 7.3 • 15 December 2011 – 31 December 2015
	Toner cartridges	Same as above	Nordic Ecolabelling of Remanufactured OEM Toner cartridges, Version 5.1 • 15 June 2012 – 30 June 2016
	Photographic developments services	Same as above	Nordic Ecolabelling of digital Photographic developments services, Version 2.4 • 19 October 2007 – 31 December 2014
	Printing Companies	Same as above	Nordic Ecolabelling of Printing companies, printed matter, envelopes and other converted paper products,

Eco-label	Articles	Criteria relevant for phthalates	Document title
			Version 5.1 • 15 December 2011 – 31 December 2017
	Car and boat care products	Same as above	Nordic Ecolabelling of Car and boat care products, Version 5.1 • 21 March 2012 – 31 March 2016
	Laundries/Textile Services	Same as above	Nordic Ecolabelling of Laundries/Textile Services, Version 3.0 • 12 December 2012 – 31 December 2016
	Dishwasher detergents for professional use	Same as above	Nordic Ecolabelling of Dishwasher detergents for professional use, Version 5.3 • 15 December 2009 – 30 June 2015
	Laundry detergents for professional use	Same as above	Nordic Ecolabelling of Laundry detergents for professional use, Version 2.2 • 15 December 2009 – 31 December 2014
	Chemical building products	Phtalates must not form part of the product.	Nordic Ecolabelling of Chemical building products, Version 1.6 • 29 May 2008 – 31 October 2014
	Indoor paints and varnishes	Ingredients classified as acutely toxic in category I, II and II, as resp. sensitisers, as CMR in category I or II or as STOT, category I and II shall not be used. Only phthalates that are risk assessed. Additionally DNOP (di-n-octyl phthalate), **DINP** (di-isononyl phthalate), **DIDP** (di-isodecyl phthalate) are not permitted in the product.	Nordic Ecolabelling of Indoor paints and varnishes, Version 2.3 • 4 November 2008 – 31 March 2015
	Machines for parks and gardens	Certain phthalates must (with a few exceptions) not be added to plastic or rubber materials. Phthalates include: **DINP, DIDP, DEP, DMEP, and DIPP.**	Nordic Ecolabelling of Machines for parks and garden, Version 5.0 • 13 March 2013 – 31 March 2017
	Floor coverings	Phthalates must not be actively added to the floor covering.	Nordic Ecolabelling of Floor coverings, Version 5.1 • 12 October 2010 – 31 December 2014
	Industrial cleaning and degreasing agents	Phthalates must not be present in the product.	Nordic Ecolabelling of Industrial cleaning and degreasing agents, Version 2.5 • 13 October 2005 – 31 March 2016
	Panels for the	Phthalates must not be added to chemical	Nordic Ecolabelling of Panels

Eco-label	Articles	Criteria relevant for phthalates	Document title
	building, decorating and furniture industry	products and materials including surface treatments. In addition the total amount of added chemical substances classified by suppliers as environmentally hazardous, e.g. Aquatic Acute 1 (H400), Aquatic Chronic 1 (H410), , must be <0.5 g/kg of the panel's constituent material (Concerns **DIPP**, **DINP**, **DIDP**).	for the building, decorating and furniture industry,
	Furniture and fitments	Phthalates must not be present in/added to the chemical product or material.	Nordic Ecolabelling of Furniture and fitments, Version 4.4 • 17 March 2011 – 30 June 2015
	Textiles, skins and leather	Plastic parts must not contain phthalates. Phthalates and REACH candidate substances are also forbidden in chemicals in textile processes following the production of the fibre, such as spinning, weaving, wet processes (washing, bleaching and dyeing) and chemicals for coating, membranes and laminates	Nordic Ecolabelling of Textiles, skins and leather, Version 4.0 • 12 December 2012 – 31 December 2016
	Outdoor furniture and playground equipment	No outdoor furniture or playground equipment or raw materials may contain phthalates.	Nordic Ecolabelling of Outdoor furniture and playground equipment, Background for version 3.
	Fabric cleaning products containing microfibres	Phthalates are prohibited from use in chemical products and additives used for the pre-treatment and surface treatment of metals and plastics (e.g. coatings) as well as adhesives.	Nordic Ecolabelling of Fabric cleaning products containing microfibers, Version 2.1 • 12 October 2010 – 31 March 2016
	Toys	Phthalates shall not be actively added to plastic/plastic parts and rubber, be contained in surface treatment of plastic/plastic parts, rubber or metal, or be added to the chemical products used in wood-based materials including surface treatment, or added to glue.	Nordic Ecolabelling of toys, Version 2.0 • 21 March 2012 – 31 March 2016
	Sanitary products	Polymers or adhesives must not contain halogenated organic compounds or phthalates, except pollutants.	Nordic Ecolabelling of Sanitary products, Version 5.4 • 5 March 2008 – 31 October 2015
	Disposable bags, tubes and accessories for health care	No plasticisers or other additives added to the plastic or substances used in adhesives may have properties categorised in REACH (Registration, Evaluation and Authorisation of Chemicals) as substances of very high concern (SVHC) and similar substances, e.g. EU-listed endocrine disruptors such as **DEP**. The phthalates DEHP, BBP, DBP, **DINP**, DNOP and **DIDP** may not be used as plasticisers or other additives, nor may they be used in adhesives.	Nordic Ecolabelling of Disposable bags, tubes and accessories for health care, Version 1.4 • 13 December 2007 – 31 December 2015

Eco-label	Articles	Criteria relevant for phthalates	Document title
	Compost bins	Additives based on phthalate, may not be present in the plastic material	Nordic Ecolabelling of Compost bins, Version 2.9 • 7 June 1996 – 30 June 2014
	Closed Toilet System	Same as above	Nordic Ecolabelling of Closed Toilet System, Version 2.8 • 9 April 1997 – 30 June 2015
	Heat pumps	Phthalates must (with a few exceptions) not be added to chemical products (e.g. cleaning products, colours, lacquers, adhesives and sealants) and rubber and plastic products. Phthalates include: **DINP, DIDP, DEP, DMEP, and DIPP.**	Nordic Ecolabelling of Heat pumps, Version 3.0 • 13 March 2013 – 31 March 2017
	Stoves	Phthalates must not be actively added to chemical products such as adhesives, sealants, cleaning agents, paints and lacquers that are used during the manufacture and surface treatment of the stove.	Nordic Ecolabelling of Stoves, Version 3.1 • 12 October 2010 – 31 October 2014
	Candles	Candles must not contain phthalates.	Nordic Ecolabelling of Candles, Version 1.3 • 13 December 2007 – 30 June 2015
EU Flower	Footwear	Phthalates: Only phthalates that at the time of application have been risk assessed and have not been classified with the phrases (or combinations thereof): R60, R61, R62, R50, R51, R52, R53, R50/53, R51/53, R52/53 (aquatic toxicity and toxicity to reproduction, among others, i.e. (**DIPP and DMEP**) may be used in the product (if applicable). Additionally DNOP (di-n-octyl phthalate), **DINP** (di-isononyl phthalate), **DIDP** (di-isodecyl phthalate) are not permitted in the product.	COMMISSION DECISION of 9 July 2009 on establishing the ecological criteria for the award of the Community eco-label for footwear
	Indoor paints and varnishes	Phthalates: Only phthalates that at the time of application have been risk assessed and have not been classified with the phrases (or combinations thereof): R60, R61, R62, R50, R51, R52, R53, R50/53, R51/53, R52/53 (aquatic toxicity and toxicity to reproduction, among others, i.e. **DIPP and DMEP**) may be used in the product before or during tinting (if applicable). Additionally DNOP (di-n-octyl phthalate), **DINP** (di-isononyl phthalate), **DIDP** (di-isodecyl phthalate) are not permitted in the product.	COMMISSION DECISION of 13 August 2008 establishing the ecological criteria for the award of the Community eco-label to indoor paints and varnishes
	Outdoor paints and varnishes	Phthalates: Only phthalates that at the time of application have been risk assessed and have not been classified with the phrases (or combinations thereof): R60, R61, R62, R50, R51,	COMMISSION DECISION of 13 August 2008 establishing the ecological criteria for the award of the

Eco-label	Articles	Criteria relevant for phthalates	Document title
		R52, R53, R50/53, R51/53, R52/53 (aquatic toxicity and toxicity to reproduction, among others, i.e. **DIPP and DMEP**) may be used in the product before or during tinting (if applicable). Additionally DNOP (di-n-octyl phthalate), **DINP** (di-isononyl phthalate), **DIDP** (di-isodecyl phthalate) are not permitted in the product.	Community eco-label to outdoor paints and varnishes
	Personal computers	If any plasticiser substance in the manufacturing process is applied, it must comply with the requirements on hazardous substances set out in criteria 5 and 6 (aquatic toxicity and toxicity to reproduction, among others, i.e. **DIPP and DMEP**). Additionally DNOP (di-n-octyl phthalate), **DINP** (di-isononyl phthalate), **DIDP** (di-isodecyl phthalate) shall not intentionally be added to the product.	COMMISSION DECISION of 9 June 2011 on establishing the ecological criteria for the award of the EU Ecolabel for personal computers
	Notebook computers	Same as above	COMMISSION DECISION of 6 June 2011 on establishing the ecological criteria for the award of the EU Ecolabel for notebook computers
	Wooden floor coverings	The requirements of part 2.1 on dangerous substances for the raw wood and plant treatments shall also apply for any phthalates used in the manufacturing process (aquatic toxicity and toxicity to reproduction, among others, i.e. **DIPP and DMEP**). Additionally DNOP (di-n-octyl phthalate), **DINP** (di-isononyl phthalate), **DIDP** (di-isodecyl phthalate) are not permitted in the product.	COMMISSION DECISION of 26 November 2009 on establishing the ecological criteria for the award of the Community Ecolabel for wooden floor coverings.
	Textile floor coverings	If any plasticizer substance in the manufacturing process is applied, only phthalates that at the time of application have been risk assessed and have not been classified with the phrases (or combinations thereof) may be used: R50 (very toxic to aquatic organisms), R51 (toxic to aquatic organisms), R52 (harmful to aquatic organisms), R53 (may cause long-term adverse effects in the aquatic environment), R60 (may impair fertility), R61 (may cause harm to the unborn child), R62 (possible risk of impaired fertility). Alternatively, classification may be considered according to Regulation (EC) No 1272/2008. In this case no substances or preparations may be added to the raw materials that are assigned, or may be assigned at the time of application, with and of the following hazard statements (or	COMMISSION DECISION of 30 November 2009 on establishing the ecological criteria for the award of the Community Ecolabel for textile floor coverings

Eco-label	Articles	Criteria relevant for phthalates	Document title
		combinations thereof): H400, H410, H411, H412, H413, H360F, H360D, H361f, H361d H360FD, H361fd, H360Fd, H360Df. Additionally DNOP (di-n-octyl phthalate), **DINP** (di-isononyl phthalate), **DIDP** (di-isodecyl phthalate) are not permitted in the product	
	Wooden furniture	If any plasticizer substance in the manufacturing process is applied, phthalates must comply with the requirements on hazardous substances set out in section 2 (aquatic toxicity and toxicity to reproduction, among others, i.e. **DIPP and DMEP**). Additionally DNOP (di-n-octyl phthalate), **DINP** (di-isononyl phthalate), **DIDP** (di-isodecyl phthalate) are not permitted in the product.	COMMISSION DECISION of 30 November 2009 on establishing the ecological criteria for the award of the Community eco-label for wooden furniture.
	Light bulbs	If any plasticizer substance in the manufacturing process is applied, it must comply with the requirements on hazardous substances set out in Criteria 5 and 6 (aquatic toxicity and toxicity to reproduction, among others, i.e. **DIPP and DMEP**). Additionally, DNOP (di-n-octyl phthalate), **DINP** (di-isononyl phthalate) and **DIDP** (di-isodecyl phthalate) shall not intentionally be added to the product.	COMMISSION DECISION of 6 June 2011 on establishing the ecological criteria for the award of the EU Ecolabel for light source
	Printed paper	The following substances or preparations shall not be added to inks, dyes, toners, adhesives, or washing agents or other cleaning chemicals used for the printing of the printed paper product: — Phthalates that at the time of application are classified with risk phrases H360F, H360D, H361f (toxic to fertility; i.e. **DIPP and DMEP**) in accordance with Regulation (EC) No 1272/2008	COMMISSION DECISION of 16 August 2012 establishing the ecological criteria for the award of the EU Ecolabel for printed paper

2.4 Summary and conclusions

DIPP and DMEP are subject to harmonised CLP classification and are classified for reproductive toxicity in category 1 B. In addition, DIPP is classified as acute toxic 1 in aquatic environments.

The majority of industry notifiers do not suggest a classification for the selected phthalates without a harmonised classification due to lack of sufficient data. Besides classification proposals for acute toxicity, skin and eye irritation, and acute aquatic toxicity for some of the substances the most serious classification proposals suggested include classification for reproductive toxicity in category 2 for DEP suggested by 2 notifiers out of 70 and for DINP (CAS no. 68515-48-0) suggested by 3 notifiers out of 269. Specific target organ toxicity – single and repeated exposure is suggested for DEP by 9 and 10 out of 70 notifiers. One has suggested a classification as a skin irritant. Chronic aquatic toxicity in category 4 is suggested for DINP (CAS no. 28553-12-0) by 28 out of 857 notifiers and chronic aquatic toxicity in category 1 and 2 is suggested for DIDP (CAS no. 26761-40-0) by 23 and 43 notifiers respectively.

EU legislation restricts the use of DINP and DIDP in toys and childcare articles which can be placed in the mouth by children and prohibits the use of DMEP and DIPP in cosmetic products. Specific EU labelling requirements apply to certain medical devices containing phthalates classified as reproductive toxicants in category 1 and 2. A ban on CMR substances in a concentration above the classification limits in toys also apply to DMEP and DIPP as well as requirements for labelling for certain medical devices. EU also restricts the use of DINP and DIPD in plastic materials intended to come into contact with food.

Denmark has issued a national ban on the import, sale and use of phthalates in toys and childcare articles for children aged 0-3 years if the products contain more than 0.05 per cent by weight of phthalates. Other national legislation addresses the maximum concentration of phthalates in water leaving the water works and in consumer tap water. In addition, DEP has a defined occupational exposure limit.

DIPP and DMEP are included in the Candidate List under the REACH Regulation and thus in the line for being subject to the authorisation process.

The Swedish Chemicals Agency plans to investigate the need for national restrictions on phthalates toxic to reproduction or endocrine-disrupting.

Phthalates are generally not addressed directly in international agreements. However, hazardous wastes from production, formulation and use of plasticisers, falls under the provisions of the Basel Convention.

Phthalates are addressed by EU and Nordic eco-labelling schemes, in numerous product types either directly ("phthalates", DINP, DIDP) or by means of their classification (DEP, DIPP and DMEP).

3. Manufacture and uses

3.1 Manufacturing

Manufacturers of phthalates and other plasticisers in the EU are organised in the European Council for Plasticisers and Intermediates (ECPI). The organisation has a membership of eight companies involved in the production of plasticisers. Some of the manufacturers of phthalates in the EU are not members of the organisation. ECPI provides some overall information on the use of the phthalates on the website "Plasticisers and flexible PVC information centre" (ECPI, 2013a). The organisation has been contacted in order to obtain updated information on the manufactured volumes and use of the six phthalates. ECPI (2013e) has responded that they cannot give production volumes and have given information on the status of the phthalates in question in the EU (see descriptions in relevant sections below).

Manufacturing processes

According to ECPI (2013a) DIDP, DINP and DPHP are produced by esterification of "oxo" alcohols averaging a carbon chain length of nine or ten. The "oxo" route differs from the 2-ethylhexanol route in that the alcohol for subsequent esterification is produced through the hydroformylation of an alkene (olefin; rather than the dimerisation of butyraldehyde). The hydroformylation process adds one carbon unit to an alkene chain by reaction with carbon monoxide and hydrogen under specific temperature and pressure conditions and with the help of a catalyst. In this way a C8 olefin (alkene) is carbonylated to yield a C9 alcohol; a C9 alkene is carbonylated to produce a C10 alcohol.

Due to the distribution of the C=C double bonds in the olefin and differences in catalysts selectivity, the position of the added carbon atom can vary, as is the case for DINP and DIDP. In such a reaction, an isomer distribution is generally created (e.ei. with varying physical and chemical structure), with the precise nature of this distribution being dependent upon the precise reaction conditions. Consequently, these alcohols are termed iso-alcohols and subsequently iso-phthalates. (ECPI, 2013a).

DINP - Isononyl alcohol, used in the synthesis of DINP, is produced via either the dimerization of butene or the oligomerization of propylene/butene. DINP is produced by esterification of phthalic anhydride with isononyl alcohol in a closed system. The reaction rate is accelerated by elevated temperatures (140-250 °C) and a catalyst. Following virtually complete esterification, excess alcohol is removed under reduced pressure and the product is then typically neutralised, water washed and filtered (ECPI, 2013b).

DIDP - DIDP is according to the EU Risk Assessment prepared from propylene and butenes through an oligomerisation process forming hydrocarbons with 8 to 15 carbon atoms (EC, 2003a). After distillation (in view of obtaining nonene), oxonation forms aldehydes with one more carbon atom ("isodecanal"). The latter are hydrogenated and distilled to form monohydric alcohols (mainly C10). These are reacted with phthalic anhydride (PA). The first reaction step, alcoholysis of PA to give the monoester, is rapid and goes to completion. By charging in excess alcohol and by removing the water which is formed, the equilibrium can be shifted almost completely towards the products side. The reaction rate is accelerated by using a catalyst and high temperature. Depending on the used catalyst the temperature range is in between 140°C and 250°C. For an acid catalyst, neutralisation with aqueous caustic soda or sodium carbonate is necessary. However, traces of alkali remain in the organic phase, and therefore a washing step is included. After distillation of remaining water and alcohol the catalyst is removed by filtration.

Information on the manufacture of the other phthalates has not been identified.

Manufacturing sites
Specific information on manufacturing sites in the EU has not been searched for.

DINP is produced by four companies within the EU: BASF AG (Germany), Evonik Oxeno GmbH (Germany), ExxonMobil Chemical (Belgium), Polynt (Italy) (ECPI, 2013b).

DIDP is produced by two companies within the EU: ExxonMobil Chemical (Belgium) and Polynt (Italy) (ECPI, 2013c) while DPHP is produced by BASF (Germany) and Perstorp Oxo AB (Sweden) (ECPI, 2013b).

DIPP is registered by one company only, Eurencu Bofors AB (likely an importer; the company produces explosives), but may be imported or manufactured by other companies in smaller quantities.

DEP is registered by 5 companies, among these one of the major manufacturers of phthalates: Polynt (Italy) and Proviron (Belgium).

DMEP is not registered under REACH.

3.1.1 Manufacturing volumes

All six selected phthalates are pre-registered substances under REACH and listed in Table 18 with an indication of registered tonnage bands and names of companies which have registered the substances (manufacturers or importers).

Substances registered with ECHA: The database on registered substances includes as of June 2013:

- substances manufactured or imported at 100 tonnes or more per year (deadline 31st May 2013),
- substances which are carcinogenic, mutagenic or toxic to reproduction with manufacture or import above 1 tonne per year (Deadline for registration was 30 November 2010)"

Three of the substances DINP, DIDP and DPHP are manufactured or imported in the 100,000-1,000,000 t/y tonnage band; DEP in the 1,000-10,000 t/y tonnage; DIPP in 10-100 t/y. DMEP is not registered indicating that the manufactured and imported volume is less than 1 t/y or that there is no intention to market the substance in Denmark.

TABLE 18
REGISTERED TONNAGE OF THE SIX PHTHALATES AS OF 20 JUNE 2013

CAS No	EC No	Substance name	Abbreviation	Registered, tonnage band, t/y *1	Registrants
84-66-2	201-550-6	Diethyl phthalate	DEP	Full: 1,000-10,000 Intermediate Use Only	COIM SpA, IT Lapiz Europe Limited, UK POLYNT S.p.A. Proviron Basic Chemicals nv Sustainability Support Services (Europe) AB GRACE Catalyst AB, SE GRACE GmbH & Co. KG, DE
605-50-5	210-088-4	Diisopentyl phthalate	DIPP	10-100	EURENCO Bofors AB, SE
53306-54-0	258-469-4	Bis(2-propylheptyl) phthalate	DPHP	100,000-1,000,000	ARKEMA FRANCE, FR BASF SE, DE DEZA a.s., CZ Grupa Azoty Zakłady, PO Perstorp Oxo, SE POLYNT S.p.A., IT
117-82-8	204-212-6	Bis(2-methoxyethyl) phthalate	DMEP	Not registered	
68515-48-0 **28553-12-0**	271-090-9 249-079-5	1,2-Benzenedicarboxylic acid, di-C8-10-branched alkyl esters, C9-rich Di-"isononyl" phthalate	DINP-1 DINP-2	100,000-1,000,000 100,000-1,000,000	ExxonMobil Chemical, NL BASF SE, DE DEZA a.s., CZ DOW BENELUX B.V.,NL Evonik Industries AG, DE Evonik Oxeno GmbH, DE Instituto Suizo para el Fomento de la Seguridad-Swissi España S.L.U., ES KTR Europe GmbH, DE POLYNT S.p.A., IT REACH GLOBAL SERVICES S.A., BE
68515-49-1 **26761-40-0**	271-091-4 247-977-1	1,2-Benzenedicarboxylic acid, di-C9-11-branched alkyl esters, C10-rich Di-"isodecyl" phthalate	DIDP-1 DIDP-2	100,000-1,000,000 Not registered	ExxonMobil Chemical,NL Infineum UK Ltd, UK

*1 As indicated in the lists of pre-registered and registered substances at ECHA's website.

In the production statistics of Eurostat all phthalates, apart from dibutyl (mainly DBP) and dioctyl (mainly DEHP), are included in one group with a total production in 2011 of approximately 780,000 t/y whereas the average for the period 2006-2010 was approximately 870,000 t/y (Table 19).

TABLE 19

EU27 PRODUCTION OF SELECTED PHTHALATES (EUROSTAT, 2012A)

Product code	Text	Production, t/y	
		Average 2006-2010	2011
20143410	Dibutyl and dioctyl *ortho*phthalates	278,416	146,333
20143420	Other esters of *ortho*phthalic acid	865,573	782,533

According to ECPI, the consumption of DINP, DIDP and DPHP (di-2-propylheptyl phthalate), has increased from representing about 50% of total phthalate sales in Europe in 2001 to approximately 83% of the total sales in 2010 (COWI *et al.*, 2012). In Europe, about one million tonnes of phthalates were manufactured in 2010 (COWI *et al.*, 2012).

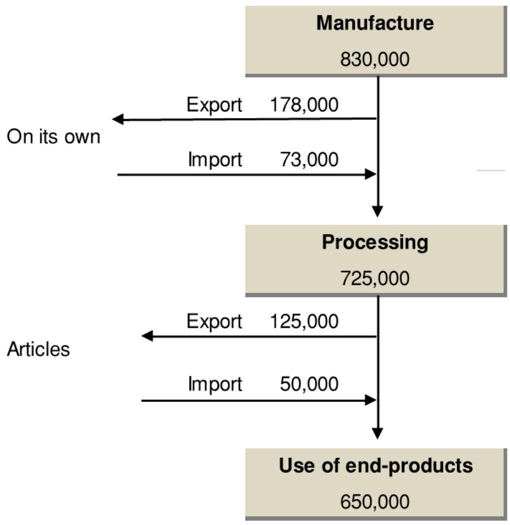
DINP and DIDP

As background for an assessment of DINP and DIDP prepared by ECHA in 2011, a report on the volumes of DINP and DIDP was prepared which presents the most current overview of publicly available information on the manufacture and use of DINP and DIDP (COWI *et al.*, 2012). The overall flow of the sum of DINP, DIDP and DPHP is shown in Figure 1. As shown, the EU is a net exporter of these substances DINP and DIDP, both as regards the substances as such and in articles.

These data are further discussed in the next section.

FIGURE 1

SCHEMATIC VIEW OF THE APPROXIMATE FLOW OF DINP, DIDP AND DPHP IN EU IN 2010 (BASED ON COWI *ET AL.*, 2012)



Global manufacture of the substances

DINP, DIDP and DPHP account for a major part of the plasticiser market in Europe than in other parts of the world, which influence to what extent the substances are imported in articles from countries outside the EU.

The most recent available estimate of the use of plasticisers by region, presented at the 22nd Annual Vinyl Compounding Conference in July 2001, concerns 2010 (Calvin, 2011). The breakdown of the plasticiser market in Western Europe, USA and Asia is shown in Table 20. According to this presentation, DINP/DIDP represented 63% of the plasticiser market in Western Europe in 2010, whereas it only represented 33% of the market in the USA and 21% of the market in Asia. The total

global market for plasticisers was estimated at 6 million tonnes, with 1.4 million tonnes in Europe, the Middle East and Africa, 1.1 million tonnes in the Americas and 3.5 million tonnes in Asia (Calvin, 2011). Of the global plasticiser market, phthalates represented 84% (Calvin, 2011).
As shown in the table, the on-going substitution of the traditional main general plasticiser DEHP has not reached the same level in Asia as in Europe and the USA. Also, non-phthalate plasticiser and "linears/other phthalates" are used to a higher extent in the USA than in Europe. This may, at least partly, be because non-*ortho*-phthalates like terephthalates (for example DEHT) were traditionally produced and used to a higher extend in North America.

TABLE 20
WORLD PLASTICISER MARKET 2010 (CALVIN, 2011)

Plasticiser	Percentage of total plasticiser market *1		
	Western Europe	USA	Asia
DEHP	16	19	60
C9/C10 phthalates *2	63	33	21
Linears/other phthalates *3	6	19	9
Non phthalates	16	38	10
Total	100	100	100

*1 The data are indicated to be based on two market reports (SRI, CMAI) and BASF estimates.
*2 Note of the authors of this survey: Mainly DINP (C9) and DIDP/DPHP (C10).
*3 Note of the authors of this survey: The three other phthalates subject of this survey will be included in this group.

3.2 Import and export

3.2.1 Import and export of selected phthalates in Denmark

The import of all phthalates as retrieved from Statistics Denmark is shown in the table below. In Denmark, the production statistics uses the same CN8 nomenclature as used for the import/export statistics. The table includes import, export and production statistics for all phthalates. Phthalates are however not produced in Denmark.

As the registered trade seems to have an inconsequent use of commodity codes, data for all codes relevant to phthalates (on their own) are presented in the table. DINP, DIDP and DPHP would be expected to be included in the commodity group "Diisooctyl, diisononyl and diisodecyl *ortho*phthalates". The imported quantities, indicate however that the substances are more likely included in the group "Dinonyl or didecyl *ortho*phthalates". The dinonyl *ortho*phthlates (C9) includes DINP and this substance accounts for the main part of the C9 phthalates. Other phthalates that might be included under this CN8 code is 911P (linear nine-eleven phthalate, slightly branched) and 79P (linear seven-nine phthalate (highly branched)) (COWI *et al.*, 2012). The didecyl *ortho*phthlates (C10) may include DIDP and this substance accounts for a major part of the C10 phthalates. Other phthalates that might be included under this CN8 code are DPHP, 1012P (linear ten-twelve phthalate) and 610P (linear six-ten phthalate).

The other three selected phthalates are expected to be included in an aggregated commodity groups "Esters of *ortho*phthalic acid (excl. dibutyl, dioctyl, dinonyl or didecyl *ortho*phthalates)".

TABLE 21
DANISH PRODUCTION, IMPORT AND EXPORT OF ALL PHTHALATES (IMPORT/EXPORT FROM EUROSTAT, 2012A; PRODUCTION STATISTICS FROM STATISITICS DENMARK, 2012)

CN8 code	Text	Import, t/y		Export, t/y		Production, t/y	
		Average 2007-2011	2012	Average 2007-2011	2012	Average 2007-2011	2012
29173100	Dibutyl *ortho*phthalates	0	0	0	0	0	0
29173200	Dioctyl *ortho*phthalates	1,239	889	226	59	0	0
29173300	Dinonyl or didecyl *ortho*phthalates	1,573	1,355	823	710	0	0
29173400	Esters of *ortho*phthalic acid (excl. Dibutyl, dioctyl, dinonyl or didecyl *ortho*phthalates)	0	102	0	12	0	0
29173410	Diisooctyl, diisononyl and diisodecyl *ortho*phthalates	8	0	13	0	0	0

3.2.2 Import and export of the selected phthalates in EU

Statistics on manufacture and import/export of selected phthalates on their own
EU external trade in tonnes of all phthalates on their own is shown in the Table 22. As indicated above for import to Denmark, DINP, DIDP and DPHP are most probably included in the group of "Dinonyl or didecyl *ortho*phthalates", with a total export of 260,000 t/y (from EU) in 2011 while the import was approximately 20,000 t/y in 2011 i.e. the net export was approximately 240,000 t/y. DINP, DIDP and DPHP are expected to account for nearly 100% of the reported import and export, with DINP likely representing the majority.

The three other phthalates are included in an aggregated commodity group ("Esters of *ortho*phthalic acid (excl. cibutyl, dioctyl, dinonyl or didecyl *ortho*phthalates") and the import export data cannot be extracted from the statistics. As expected, the import and export numbers for this aggregate group are however smaller than the imports and exports of DIDP/DINP/DPHP (" Dinonyl or didecyl *ortho*phthalates"), which are today the key general plasticisers as described above. Again there is however a net export, signalling the EU's position as a key producer of phthalates globally.

TABLE 22
EU27 EXTERNAL IMPORT AND EXPORT OF ALL PHTHALATES (EUROSTAT, 2012A)

CN code	Text	Import, t/y		Export, t/y	
		Average 2006-2010 *1	2011*	Average 2006-2010 *1	2011*
2917.3100	Dibutyl *ortho*phthalates	298	:	4,864	:
2917.3200	Dioctyl *ortho*phthalates	5,218	4,716	53,002	31,872
2917.3300	Dinonyl or didecyl *ortho*phthalates	17,471	19,838	151,188	260,506
2917.3400	Esters of *ortho*phthalic acid (excl. cibutyl, dioctyl, dinonyl or didecyl *ortho*phthalates)	3,129 *1	-	71,181 *1	-
2917.3410	Diisooctyl, diisononyl and diisodecyl *ortho*phthalates	739	1,201	7,301	864

*1 Average for those years where data are reported.

As part of background document for ECHA's DINP/DIDP assessment, an estimate of the import/export of DIDP and DINP with **articles** was performed. The methodology applied was based on a methodology developed for the Danish EPA (Skårup and Skytte, 2003). The results are shown in Table 23.

The **total plasticiser content** of both imported and exported products (articles) was estimated at about 170,000 t/y. For the estimate of import/export of DINP/DIDP in articles it was be assumed that DINP/DIDP accounted for the following percentages of the total plasticiser consumption by region: EU, Switzerland, Norway, Iceland: 63%; the Americas: 33%; Asia and rest of the world: 21%.

Assuming **DINP/DIDP** accounted for the percentages indicated above of the total plasticiser content, the import and export is estimated at 45,000 tonnes and 105,000 tonnes respectively, and the export corresponds to about 15% of the total use of DINP/DIDP for manufacturing of products with plasticisers in the EU.

Of the import into the EU, 51% of the tonnage of the articles originates from China, whereas only 9% of the imported DINP/DIDP (on their own) is estimated to originate from China.

It should be noted that some import/export may take place with articles not covered by the assessment (e.g. vehicles and electrical and electronic equipment), and the total tonnage imported in these articles are considered to add some 10-30% to the totals, as the major application areas are covered by the statistics.

As a best estimate, adding 20% to the numbers in Table 23, the import of DINP/DIDP (should likely be considered as including the third key general plasticiser DPHP) in articles was be estimated at approximately 50,000 tonnes and the export at 125,000 tonnes.

TABLE 23
ESTIMATED DINP/DIDP CONTENT OF EU27-EXTRA TRADED ARTICLES. AVERAGE OF THE YEARS 2008-2010 (COWI ET AL, 2012)

Product group	Tonnage products t/y		Tonnage plasticiser t/y		Tonnage DINP/DIDP t/y	
	Import	Export	Import	Export	Import	Export
Hoses and profiles	21,572	38,727	3,515	7,501	1,263	4,437
Flooring and wall covering	127,187	231,592	10,569	29,830	2,396	18,993
Film/sheets and coated products	1,164,779	922,288	75,201	68,578	21,505	42,706
Coated fabric and other products from plastisol	283,151	695,235	3,426	5,986	927	3,749
Wires and cables	117,036	153,675	8,183	9,695	2,336	5,780
Moulded products and other	449,756	475,303	63,448	47,006	15,058	29,364
Total	2,163,482	2,516,820	164,342	168,597	43,485	105,029

Similar numbers for the other phthalates assessed here; DEP, DIPP, DMEP have not been found.

3.3 Use

3.3.1 Use in the EU

DINP, DIDP and DPHP
DINP, DIDP and DPHP (with DINP as the major) have over the last decade taken over as primary plasticiser for a major part of the former applications of DEHP. As a consequence of the different properties of the three substances, some differences in the use by application are seen.

DINP – DINP is a general plasticiser, which is applied in many products as the direct alternative for DEHP, the formerly major general PVC plasticiser. As such DINP has a high consumption and is probably the plasticiser which can be found in most flexible PVC products today. DINP has a wide range of indoor and outdoor applications. DINP is a commonly used plasticiser, 95% of which is used for flexible PVC used for construction and industrial applications, and durable goods (wire and cable, film and sheet, flooring, industrial hoses and tubing, footwear, toys, food contact plastics). More than half of the DINP used in non-PVC applications involves polymer-related uses (e.g. rubbers). The remaining DINP is used in inks and pigments, adhesives, sealants, paints and lacquers (where it also acts as a plasticiser) and lubricants (ECPI, 2013b).

DIDP - DIDP is a common phthalate plasticiser, used primarily to soften PVC. DIDP has properties of volatility resistance, heat stability and electric insulation and is typically used as a plasticiser for heat-resistant electrical cords, leather for car interiors, and PVC flooring. (ECPI, 2013c). Non-PVC applications are relatively small, but include use in anti-corrosion and anti-fouling paints, sealing compounds and textile inks.

DPHP - DPHP is often used as an alternative (to DIDP) because only minor compound changes are needed to adapt wire formulations for example to DPHP (ECPI, 2013d). It similarly matches DIDP performance in automotive applications. Its weather resistance makes it a strong candidate for outdoor applications (ECPI, 2013d). DPHP boasts better UV stability than most general-purpose plasticisers, making it especially suitable for applications like roofing, geomembranes, or tarpaulins. Almost all DPHP is used as a plasticiser to make PVC soft and flexible.

A total breakdown of the consumption by application in the EU of the three phthalates is not available. COWI *et al.* (2012) produced a best available scenario for the breakdown of the consumption by 2015 based on the available data from industry. According to the data source, it was however not possible to evaluate how well these estimates reflect the actual situation in Europe, but no objections to the breakdown from industry were provided.

TABLE 24
SCENARIO FOR THE BREAKDOWN OF THE CONSUMPTION OF DINP AND DIDP BY APPLICATION AREA IN 2015 (ECHA, 2012)

Process	Application area	DINP + DIDP		DINP		DIDP	
		Percentage of total	Consumption, tonnes	Percentage of total	Consumption, tonnes	Percentage of total	Consumption, tonnes
Calendering	Film, sheet and coated products	14.9	109,178	11.5	57,018	22.0	52,140
	Flooring, roofing, wall covering	3.3	24,339	1.6	7,739	7.0	16,590
Extrusion	Hose and profile	5.0	36,856	5.1	25,006	5.0	11,850
	Wire and cable	27.3	199,580	17.3	85,761	48.0	113,760
	Clear, medical, film	6.7	49,373	8.1	39,901	4.0	9,480
Injection moulding	Footwear and miscellaneous	7.9	57,718	9.7	48,249	4.0	9,480
Plastisol spread coating	Flooring	10.0	73,017	13.8	68,299	2.0	4,740
	General (coated fabric, wall covering, etc.)	10.8	79,276	15.5	76,933	1.0	2,370
Other plastisol applications	Car undercoating and sealants	7.2	52,850	10.2	50,498	1.0	2,370
	Slush/rotational moulding etc.	1.8	13,213	2.2	10,845	1.0	2,370
Mixture formulation	Non-PVC applications	5.0	36,600	5.0	24,750	5.0	11,850
Total		100.0	732,000	100	495,000	100	237,000

Note: The values above have been calculated without rounding. The fact that the figures are calculated to the nearest tonne does not mean that they should be interpreted as precise to the nearest tonne.

DINP, DIDP and DPHP are typically used as primary plasticisers in PVC, sometimes in combination with other plasticisers. The actual concentrations are quite variable and depend on the desired properties of the final PVC. Actual analyses of plasticisers in different products demonstrate that, for the same product, often different combinations of plasticisers are found. The combination of plasticisers in a PVC material is partly governed by the desired performance characteristics of the plasticised material and partly by the desired process parameters in the manufacturing of the PVC materials.

Examples of actual measurement of DINP and DIDP from surveys of the substances in products are listed in Table 25 based on COWI *et al.* (2012).

Several of the surveys have been undertaken as part of the Danish EPA's programme on consumer products (Tønning *et al.*, 2009; Müller *et al.*, 2006; Nilsson *et al.*, 2006; Pors and Fuhlendorf, 2001; Poulsen and Schmidt, 2007, Svendsen *et al.*, 2007). A number of other surveys of the programme published in 2010 address phthalates in different product groups, but these surveys have not included DINP and DIDP or other of the phthalates subject to the present survey. DIPP, DPHP and DMEP have not been included in any of the surveys of the programme on consumer products, while a few surveys have included DEP as mentioned below.

The EU risk assessment for DINP does not indicate the typical content of DINP in flexible PVC. The substance is typically used as a 1:1 substitute for DEHP. According to the EU Risk Assessment for DEHP, the typical concentration of DEHP varies, but is often around 30% (w/w).

According to information from ECPI (2013c) the typical content of DIDP in flexible PVC products is between 25 and 50% (w/w).

The background data report for an Annex XV restriction dossier for DEHP, BBP, DBP and DIBP provides the following data specifically on the use of DINP and DIDP as collected from manufacturers of different articles (Højbye *et al.*, 2011). The information from this report, supplemented by information provided by ECPI for the study of COWI *et al.* (2012) leads to the following conclusions to be made (cited from COWI *et al.*, 2012):

- *"DINP is the major plasticiser for plastisol applications, in particular for the production of flooring products. Plasticiser concentrations vary quite extensively depending on flooring type. 10-20% plasticiser content, depending on product type, has been reported for products for the professional market, while higher concentrations (25-30%) are reported for low-price cushioned PVC flooring for the private market. It is not specifically indicated whether the lower plasticiser content in the products for the professional market is correlated with a lower flexible PVC content of the flooring.*
- *German investigations performed in 2003 (Stiftung Warentest, 2003 as cited by Høibye et al., 2011) revealed a rather complex picture regarding plasticiser usage in flooring. PVC flooring marketed in Germany contained one or more of the following phthalates: DIBP, DBP, BBP, DEHP, DINP, DIDP, DIHP and DIOP. DINP and DIDP were found in significant concentrations. A total of 25 different products were analysed. The total concentration of phthalates registered in the products was in the range of 6.3% to 36.5%. According to ECPI, vinyl floors produced nowadays are based on DINP as the general purpose plasticizer and use a secondary fast fusing plasticizer, often esters of benzoic acid. DEHP, DIBP, DBP, DIHP and BBP have been phased out by European flooring manufacturers in the last 3 to 5 years. They may still be detected in vinyl floorings including a high level of recycled content or in some flooring produced outside the EU.*
- *DINP is the main plasticiser used in wallpaper/wall covering. According to major producers of PVC wallpaper, typical plasticiser concentrations are 25-30%.*
- *One producer has reported DINP concentrations in air mattresses of 20-30%.*
- *Typically, swimming pool liners made of flexible PVC contain 20-30% DINP and pool covers contain 25-30% DEHP.*
- *DEHP is the preferred plasticiser in bathing equipment with concentrations in the range 20-40%. Alternatively 20-30% DINP is used.*
- *DIDP and DEHP are likely the main plasticisers used for cables in the EU. According to one manufacturer, DIDP constitutes about 80% of the current plasticiser consumption for cables in the EU. Typical plasticiser concentrations in the PVC insulation are reported at 20-30%. (According to information provided by ECPI for this study [*COWI *et al.*, 2012*], DINP is rarely used for cables*)"

TABLE 25
EXAMPLES OF ACTUAL MEASUREMENT OF DINP AND DIDP IN PRODUCTS (COWI *ET AL.*, 2012)

Product group	n *1	Number of samples with substance > 1% *2		DINP content % (w/w)		DIDP content % (w/w)		Year	Organisation	Source (please find full reference in COWI *et al.*, 2012)
		DINP	DIDP	Range	Average	Range	Average			
Packaging for shampoo and bath soap	10	4	n.a.	1-31	22	n.a.	n.a.	2006	Danish EPA	Poulsen and Schmidt, 2007
Erasers	26 (10) *3	3	n.a.	37-70	47	n.a.	n.a.	2006	Danish EPA	Svendsen et. al. 2007
Sex toys	15	2	n.a.	>50-60	55	n.a.	n.a.	2005	Danish EPA	Nilsson *et al.*, 2006
Sex toys	71	18	8	6-77	39	10-55	27	2009	The Netherlands Food and Consumer Product Safety Authority	VWA, 2009
Toys for animals	13	10	n.a.	7-54	28	n.a.	n.a.	2005	Danish EPA	Müller *et al.*, 2006
Toys and baby articles	252	23	4	0.7-41	29	9-32	24	2007	*8	Biedermann-Brem *et al.*, 2008
Toys*6	205	45	12	1-75	41	1-11	3	2008	*7	FCPSA, 2009
Childcare articles *6	25	2	1	4-28	16	25	25	2008	*7	- " -
Toys *6	258	36	31	1-58	28	2-38	8	2009	*7	FCPSA, 2010
Childcare articles *6	13	2	0	37-56	47	-	-	2009	*7	- " -
Mitten labels	2	2	n.a.	8-9	8	n.a.	n.a.	2008	Danish EPA	Tønning *et al.*, 2009
Shower mat	7	1	n.a.	14	14	n.a.	n.a.	- " -	- " -	- " -
Soap packaging	6	1	n.a.	9	9	n.a.	n.a.	- " -	- " -	- " -
Plastic shoes	27	1	1	3	3	1	1	2009	Swedish Society for Nature Conservation	SSNC, 2009
Conveyer belts	12	1	0	2.5	2.5	0	0	2008/ 2009	Danish Veterinary and Food Administration	DVFA, 2010
Flooring	5	2	*4	5-31	18	*4	*4	2000	Danish EPA	Pors and Fuhlendorf, 2001
PVC gloves	4	1	*4	59	59	*4	*4	- " -	- " -	- " -

Product group	n *1	Number of samples with substance > 1% *2		DINP content % (w/w)		DIDP content % (w/w)		Year	Organisation	Source (please find full reference in COWI *et al.*, 2012)
		DINP	DIDP	Range	Average	Range	Average			
Vinyl wallpaper	4	2	*4	23-26	25	*4	*4	- " -	- " -	- " -
Carpet tiles	2	1	*4	27	27	*4	*4	- " -	- " -	- " -
Shoulder bags, (transparent plastic, cloth like, artificial leather)	3	1	*4	11	11	*4	*4	- " -	- " -	- " -
PVC gloves	n.i	n.i	n.i	32	32			2000	*9	Sauvegrain and Guinard, 2001
Gloves	n.i.	n.i.	n.i.	41-43	42	16-17	17	n.i.	Institute for Chemical and Bioengineering	Wormuth *et al.*, 2006
Paints	n.i.	n.i.	n.i.	0.05-0.5	0.3	0.03-0.3	0.2	n.i.	- " -	- " -
Adhesives	n.i.	n.i.	n.i.	3-6 *5	4	0.5-6	2	n.i.	- " -	- " -

*1 Number of samples

*2 Number of samples with concentration above a certain level defined in the studies (typically 1 % w/w)

*3 10 out of 26 erasers were made of PVC; of these 3 contained DEHP.

*4 The data indicated for DINP is the sum of DINP and DIDP

*5 The paper indicates the min at the same magnitude as the max – here the min is adjusted on the basis of the indicated mean and max.

*6 Number of samples indicate materials with more than 0.1% of the substances.

*7 The Food and Consumer Product Safety Authority, the Dutch Ministry of Agriculture, Nature and Food Quality.

*8 Official Food Control Authority of the Canton of Zurich, Chemical and Veterinarian State Laboratory of Baden-Württemberg, Institute for Food Investigation of the State Vorarlberg, State Laboratory of Basel-City, Kantonales Amt für Lebensmittelkontrolle, St Gallen.

*9 Laboratoire National d'Essais Centre Logistique et Emballage at the request of Ansell Healthcare Europe N.V

n.a. Not analysed

n.i. Not indicated by the data source

DEP, DIPP and DMEP

The aggregated information available on the use of DEP, DIPP and DMEP is scarce compared to DINP and DIDP, and the few reviews available mostly cite relatively old information and with little information about use and alternatives. The information given here is therefore not restricted to the EU.

ECPI has been asked for information on uses, consumption and alternatives in the European context, but apart from the information cited below, it was not possible for ECPI to supply information on these substances ECPI (2013e).

DEP

DEP is a specialty polymer plasticiser and a solvent for cosmetics and personal care products, among others.

According to (NIEHS, 2006, USA): *"DEP is used as a plasticizer in consumer products, including plastic packaging films, cosmetic formulations, and toiletries, and in medical treatment tubing (IPCS, 2003). It is used in various cosmetic and personal care products (e.g., hair sprays, nail polishes, and perfumes), primarily as a solvent and vehicle for fragrances and other cosmetic ingredients and as an alcohol denaturant (Labunska and Santillo, 2004). Other applications include as a camphor substitute, plasticizer in solid rocket propellants, wetting agent, dye application agent, diluent in polysulfide dental impression, and surface lubricant in food and pharmaceutical packaging (ATSDR, 1995)."*

FDA (2013, USA) states that: "*The principal phthalates used in cosmetic products are dibutylphthalate (DBP), dimethylphthalate (DMP), and diethylphthalate (DEP). They are used primarily at concentrations of less than 10% as plasticizers in products such as nail polishes (to reduce cracking by making them less brittle) and hair sprays (to help avoid stiffness by allowing them to form a flexible film on the hair) and as solvents and perfume fixatives in various other products.* "

DEP has been marketed by BASF (2008), as Palatinol® A (R), an additive with low odour for the fragrances and cosmetic industries. According to BASF, DEP is soluble in the usual organic solvents and is miscible and compatible with all of the monomeric plasticizers commonly used in PVC. DEP was registered at ECHA under the commercial name Palatinol® A (R). This name was however not found at BASF's current product sites, and BASF is not among the registering companies, so they may have abandoned the product by now, or transferred it to others. Polynt (2010), one of the registrants, markets DEP for the following uses: Cellulose, flavours & fragrances, cosmetics, pharma.

An anonymous source indicates current DEP use as plasticiser in EU. ECPI (2013e) does not have information of its use as a plasticiser.

The German Bayrishes Landesamt für Gesundheit und Lebensmittelsicherheit (the Bavarian Health and Food Authority; 2012) stated that DEP was allowed for denaturing of alcohol in Germany, and they found DEP in most of the analysed products in a survey of aftershaves, perfumes and eau de toilette. These products were selected as having most relevance due to their high alcohol contents, yet the survey does describe that DEP in cosmetics and personal care products can be used as a fragrance carrier and plasticiser also. Their results are shown in Table 26.

As described further in Section 3.3.2, DEP is as of 1 July 2013 not anymore among the accepted substances for denaturing of alcohol in the EU (substances that are required in alcohol in order to get exemption from alcohol tax).

TABLE 26
DEP CONCENTRATIONS FOUND IN TWO SURVEYS OF AFTERSHAVES, PERFUMES AND EAU DE TOILETTE ON THE GERMAN MARKET (BAYRISHES LANDESAMT FÜR GESUNDHEIT UND LEBENSMITTELSICHERHEIT, 2012).

DEP concentration range (%)	Test series in 2003; number of samples (% of samples)	Test series in 2006; number of samples (% of samples)
0 – 0,1	3 (=12)	6 (=23)
0,1 – 0,5	13 (=52)	14 (=54)
0,5 – 1,0	8 (=32)	4 (=15)
1,0 – 5,0	1 (=4)	2 (=8)
> 5,0	0 (=0)	0 (=0)

As regards nail polishes, DEP acts as a plasticiser to reduce cracking of the polish and as a film aid, probably by keeping the polish floating until a clear film has been established and thereafter partially evaporating from the surface (a principle used in PVC flooring with a resilient surface film, not with DEP however). DBP seems to have been the most used plasticiser for nail polishes, but DEP has been observed in some cases (US FDA, 2013). On the other hand, a survey of 23 nail polishes/lacquers marketed in California in 2012 (focusing on DBP, toluene and formaldehyde), found no DEP with the analysis methods used, but found DBP in 9 products (of which 7 with other plasticisers as well) and no DBP but other plasticisers in other 9 products. In 5 products, no plasticisers were observed with the used analytical methods. The other plasticisers observed were camphor (mentioned as a secondary plasticiser as well as a fragrance), dioctyl adipate, tributyl phosphate, butyl citrate, triphenyl phosphate, N-ethyl-o-toluene sulfonamide, N-ethyl-p-toluene sulphonamide, P-toluene sulphonamide (tosylamide). Several of the product samples claimed to be without DBP, but newer the less contained DBP in substantial concentrations (California EPA, 2012).

Similar information has not been found for the EU.

DIPP
According to the DIPP SVHC dossier (Environment Agency Austria, no year): "*DIPP has been registered for its use in the manufacture of propellants. As other low molecular weight phthalates of carbon backbone lengths of C4 – C6 DIPP may also be used as plasticiser for PVC products and other polymers due to their similar structure and physicochemical properties. Di-n-butyl phthalate (DBP) and diisobutyl phthalate (DIBP) (linear and branched C4 esters) are used in many PVC formulations, principally for ease of gelation. Owing to their relatively high volatility, in comparison with other phthalates, they are often used in conjunction with higher molecular mass esters. Diisopentyl phthalate (DIPP) is generally used in a similar manner (Ullmann, 2012). However there is currently no registration for that use.*"

According to the REACH registration of the substance, it is registered by EURENCO Bofors AB, SE, a company which produces explosives as well as charges - so-called propellants - for ammunition (http://www.eurenco.com/en/propellants/index.html).

According to ECPI (2013e), DIPP is not produced in Europe anymore.

DMEP
DMEP is a specialty plasticiser which can be used in a number of polymers. According to BAuA (2011): "*The general global applications of DMEP have included its use as a plasticiser in the production of nitrocellulose, acetyl cellulose, polyvinyl acetate* (PVA, eds.)*, polyvinyl chloride*

(PVC, eds.) *and polyvinylidene chloride intended for contact with food or drink. DMEP is giving these polymeric materials good light resistance. Further, it is used as a solvent. DMEP can improve the durability and toughness of cellulose acetate (e.g. in laminated documents (Ormsby, 2005)) and can be used in "enamelled wire, film, high-strength varnish and adhesive. It can also be used in pesticide products internationally" (Canadian Screening Assessment, 2009).*

Only limited information regarding DMEP in consumer products in the European marketplace has been identified. The Danish Product Register records DMEP as a plasticiser in the concentration range 0.1–1% in a material used to cover floors. The Swiss Product Register records five consumer products with 1–5% DMEP. One consumer product is a leather care product e.g. for shoes, the other four consumer products are categorised as "paints, lacquers and varnishes". The information comes from older records and there are no current registrations of DMEP used in consumer products (personal communication). Baumann et al. (1999) described the application of DMEP as an additive for printer inks ("Kodaflex DMEP"). Cellulose acetate lamination films typically contain 20–30% plasticisers by weight. DMEP and other phthalates are commonly found in laminated documents (Ormsby, 2005). The Australian NICNAS (2008) has reported about the import of DMEP in balls for playing and exercise, hoppers and children's toys (e.g. as inflatable water products) (Australian NICNAS, 2008).

There is no information whether the substance is still in use in articles on the EU market."

According to CPSC (2011): "*DMEP is used as a plasticizer for cellulosic resins, some vinyl ester resins, PVC, and as a solvent, a molding component, and in adhesives, laminating cements, and flash bulb lacquers. In Italy, dimethoxyethyl phthalate is permitted for use with food. U. S. production of DMEP was estimated to be greater than 5000 pounds in 1977 and 1979 (HSDB 2010). The U.S. EPA's Inventory Update Report (IUR) lists U.S. production/importation volume of DMEP to be between 500,000 and 1,000,000 pounds in 1986, and 10,000 to 500,000 pounds in the surveys conducted every four years from 1990–1998 (U.S. EPA 2002). After 1998, DMEP production was no longer tracked by IUR.*"

According to ECPI (2013), DMEP is not used as a plasticiser and the only European producer stopped making this substance a few years ago.

3.3.2 Use in Denmark

The latest available aggregate survey of annual phthalate consumption in Denmark covers 2005-2007 and is based on the revenues from the Danish environmental tax on phthalates (Brandt and Hansen, 2009), in combination with other data on the application of phthalates. The situation may likely be the same today, except that the assessment of which phthalates are used may be slightly different today, as DINP is expected to be the main general plasticiser, while DIDP and DPHP are primarily expected to be used in applications where resistance to heat or sunlight is prioritised (wire and cable, roofing, tarps, etc.). DEHP may however still be present in a number of articles, especially in import from Asia.

TABLE 27
ESTIMATED ANNUAL PHTHALATE CONSUMPTION IN 2005-2007 BASED ON THE REVENUES FROM THE DANISH ENVIRONMENTAL TAX ON PHTHALATES (BRANDT AND HANSEN, 2009)

Product group	Used phthalates (assessment by Brandt and Hansen, 2009)	Consumption of phthalates, t/y		New remarks
		Calculated from income from tax on phthalates in 2005-2007	Estimates share of DEHP, DBP and BBP	
Wire and cable	DIDP, DINP, DEHP	1900	300-1200	DIDP likely dominate today; DINP, DPHP, DEHP and PVC-and-phthalate-free insulation also used
Tube and hoses	DINP, DEHP	630	70-140	
Gloves, rainwear, etc.	DINP, DIDP, DEHP	540	270-430	
Roof plates	DINP/DIDP, DEHP	160	<16	
Film, sheets, tape	DEHP, DINP	120	60-100	
Ring binders and document pockets ("stationary")	DINP, DEHP	85	<17	PVC-free binders and pockets dominate the market today
Tarpaulins	DINP, DIDP, DIOP (DEHP)	28	<3	DEHP may have higher share in this product category
Table cloths, curtains, etc.	DEHP (DINP)	9	5-7	
Coated steel gutters	DINP, DIDP, DEHP?	2	0,2-1	
Totals		3844	705-2014	

Data from the Danish Product Register

Data on selected phthalates registered in the Danish Product Register were retrieved in June 2013 on the basis of the list of selected phthalates. The Danish Product Register includes substances and mixtures for professional use which contain at least one substance classified as dangerous in a concentration of at least 0.1% to 1% (depending on the classification of the substance). Of the selected phthalates, only DIPP and DMEP are classified as dangerous. For the other non-classified substances, the registration will only occur if they are constituents of mixtures which are classified and labelled as dangerous due to the presence of other constituents. The data consequently do not provide a complete picture of the presence of the substances in mixtures placed on the Danish market. On the other hand, for substances included in mixtures used for formulation of other mixtures in Denmark (e.g. those included in raw materials used for production of paint), the quantities may be double-counted as both the raw material and the final mixture in the register. As stated above, the amounts registered are for occupational use only, but for substances used for the manufacture of mixtures in Denmark the data may still indicate the quantities of the substances in the finished products placed on the market both for professional and consumer applications.

As shown in Table 28, DINP is clearly the major phthalate in professional products marketed in Denmark, while the registered consumption of DIDP is moderate and the consumption of the other phthalates is minimal, as expected. DIPP is not registered in the Product Register. It is expected that most of this import is used in Danish production, of which some is marketed domestically and some is exported. DEP is seen to be used in 113 products across 49 companies, with non-agricultural pesticides and preservatives as the major citable use (larger uses exist but may not be cited). DMEP is only registered by a few companies.

The Product Register does not include non-chemical articles such as wire and cable, shoe-soles, clothing, toys, etc., which likely constitute major parts of the Danish consumption of phthalates.

As shown in

Table 29, the major registered uses which can be mentioned with respect for confidentiality are adhesives and binding agents, fillers, paints, lacquers and varnishes. As noted, some other major applications across most substances cannot be mentioned due to confidentiality.

TABLE 28
SELECTED PHTHALATES – PURE AND IN MIXTURES PLACED ON THE DANISH MARKET IN 2011 AS REGISTERED IN THE DANISH PRODUCT REGISTER

CAS No	Short name	Chemical name	Prod/Com *2	Registered tonnage, t/y		
				Import*1	Export	Consumption
84-66-2	DEP	Diethyl phthalate	113/49	13	2,2	11
117-82-8	DMEP	Bis(2-methoxyethyl) phthalate	3/3	0-82	0-12	0-70
53306-54-0	DPHP	Bis(2-propylheptyl) phthalate	18/5	1	0	1
26761-40-0	DIDP-1	1,2-Benzenedicarboxylic acid, di-C9-11-	14/11	8	1	7
68515-49-1	DIDP-2	branched alkyl esters, C10-rich Di-"isodecyl" phthalate	44/15	423	375	48
	DIDP total		58/26	431	376	55
28553-12-0	DINP-2	1,2-Benzenedicarboxylic acid, di-C8-10-	68/34	682	378	304
68515-48-0	DINP-1	branched alkyl esters, C9-rich Di-"isononyl" phthalate	25/8	76	2	74
	DINP total		93/42	758	380	378

*1: There is no phthalates production in Denmark.

*2: Number of products/number of companies registered for substance.

TABLE 29
APPLICATION OF SELECTED PHTHALATES REGISTERED IN THE DANISH PRODUCT REGISTER, 2012

CAS No	Name	Function	Consumption (production + import – export)		
			Function code	Number of products	t/y
84-66-2	DEP*1	Absorbents and adsorbents	01	6	0.0046
		Cleaning/washing agents	09	35	0.0171
		Cosmetics	15	6	0.0041
		Impregnation materials	31	4	0.0001
		Odour agents	36	26	0.0096
		Non-agricultural pesticides and preservatives	39	12	0.4228
		Paints, lacquers and varnishes	59	4	0.0002
		Surface treatment	61	8	0.0002
117-82-8	DMEP *2	*2			
26761-40-0	DIDP-2	Fillers	20	4	5.9781
28553-12-0	DINP-2 *1	Adhesives, binding agents	02	20	5.5739
		Fillers	20	27	21.7020
		Paints, laquers and varnishes	59	9	0.0861
53306-54-0	DHPH *2	*2			
68515-48-0	DINP-1 *2	*2			
68515-49-1	DIDP-2	Adhesives, binding agents	02	21	8.6736
		Fillers	20	15	38.5337

*1 : The dominant uses cannot be reported due to confidentiality.

*2 : The uses cannot be reported due to confidentiality.

DEP in articles and mixtures

As regards cosmetics, personal care products and cleaning agents, The Danish Association of Danish Cosmetics, Toiletries, Soap and Detergent Industries (SPT, 2013), informed that DEP has three possible applications in their sector: Denaturing of alcohol used in articles and mixtures, as a component in some fragrances and as film-forming substance in polymers used in nail polish. They did not have specific information on whether there was any actual use in their sector for these purposes in Denmark.

As mentioned above, DEP has been reported used for denaturing of alcohol. The aim of denaturing is to make the alcohol unacceptable for consumption (alcohol for consumption is subject to national tax).For attaining tax exemption for "fully denatured" alcohol in Denmark, alcohol produced or used after 1 July 2013 shall be produced according to a specific formula containing 3 l isopropylalcohol (IPA), 3 l methylethylketon (MEK) and 1 gram denatoniumbenzorate per 100 litre absolute alcohol. Alcohol being denatured by the previously demanded formula and being bought before 1 July 2013 may be marketed until the end of 2013 (Skat, 2013); i.e. not any contents of DEP. Allowed denaturants for alcohol vary between EU countries, but according to the current rule, denaturants allowed in one EU country are accepted in imports to other EU countries (SPT, 2013).

As per EU Regulation 162/2013 of 21 February 2013[1], a unified rule (with exemptions) was made that the denaturing formula mentioned above should apply in EU countries for which nothing else is mentioned in the regulation. A number of specified Member States have exemptions to the rule, allowing other specified formulas for denaturing alcohols, but in none of the EU countries DEP is on the list of accepted denaturants according to the regulation. The regulation also includes a list of denaturing products accepted in the EU (across all Member States). The list does not include DEP. The regulation entered into force 1 July 2013. The previous regulation on the issue (Regulation (EC) No 3199/93) had a different scope but did also not mention DEP. Based on this information, it must be expected that any denatured alcohol produced in the EU and marketed on its own or in articles or mixtures after 1 January 2014 must be DEP-free. In other words, import of articles/mixtures to Denmark from EU countries must be expected to be DEP-free, at least as of 1 January 2014. It has not been investigated if DEP is currently accepted as a denaturing substance in non-EU countries, and DEP could perhaps thus be a component in extra-EU import of cosmetics, etc.

Jørgen Gade Hyldgaard (2013), who is a consultant for more than half of the Danish producers of cosmetics and personal care products on product safety issues, does not know of any Danish producers using DEP. Contact to a major Danish producer of cosmetics confirmed this statement as regards their own production. According to Hyldgaard, the function of DEP in fragrances is to delay the evaporation of the fragrance from the article/mixture.

While data on the consumption of DEP in articles have not been found, DEP has been included in a number of analyses of consumer products performed as part of the Danish EPA's surveys of chemicals in consumer products on the Danish market (as well as in other reports published by the Danish EPA).

DEP was found in one of 20 toothbrushes at a quantity of 3.1 µg/toothbrush (Svendsen *et al.*, 2004). Similarly, DEP was found in two out of 60 plastic sandals analysed by Tønning *et al.* (2010); foam clogs and flip-flops, no concentration data were given. Tønning *et al.* (2008) found DEP in a printed badge in a baby carrier at concentration of 60 and 350 µg/g, respectively, in two different samples from the same product. In total, 13 baby products in the following product types were analysed for phthalate content: Pillows for baby feeding, baby carriers, nursing pillows/ cushions with different covers and stuffing, baby mattresses with stuffing of foam for beds, aprons for perambulators, disposable foam wash cloths. Borling *et al.* (2006) found DEP at 1.5 mg/kg (or 1.5 µg/g) in an activity carpet and < 3 mg/kg in a ball; for the other 6 products analysed, the concentration was below <0.5 mg/kg. Nilsson *et al.* (2006) found DEP in the concentration 0.12 g/kg in one out of 15 sex toys analysed; a fetish glove of latex rubber. Tønning *et al.* (2009) found DEP in PVC soap packaging, but DEP concentrations were not measured.

Further, Larsen *et al.* (2000) reports that DEP was found in concentrations up to 2.3 mg/kg in textiles.

The relatively low concentrations indicate that DEP may either have been present as an impurity in the plasticiser used or as a specialty plasticiser, or an auxiliary process substance with another purpose, which function at low concentrations. While ECPI (2013e) has the understanding that DEP is not used as a plasticiser, an anonymous data source indicates that it is used as such.

Data request from Danish trade and industry associations

The following Danish trade and industry associations have been contacted for data on the phthalates covered in this survey:

- Fugebranchen (the sealants suppliers' and appliers' organisation)

[1] Regulation 162/2013 of 21 February 2013 amending the Annex to Regulation (EC) No 3199/93 on the mutual recognition of procedures for the complete denaturing of alcohol for the purposes of exemption from excise duty

- DFL (Danish paints and glues industry)
- The PVC Information Council Denmark
- The Danish Plastics Federation
- The Association of Danish Cosmetics, Toiletries, Soap and Detergent Industries

The Association of Danish Cosmetics, Toiletries, Soap and Detergent Industries provided general information about the use of DEP in their sector (as cited above) and forwarded the data request to their members, from which no replies were received as of the closure of the editing of this report . A few of their members were contacted directly by COWI. DFL (2013) has informed that members who responded to their inquiry in connection with this project did not use phthalates on the List of undesirable substances (LOUS). Some did however report use of DIDP, in antifouling paints in concentrations of 1-6 % and in a flexible adhesive, where it is part of an imported ingredient.

Fugebranchen (the sealants supplier and applier organisation) responded with specific information about Danish conditions (information about one Danish producer using some of these phthalates). The PVC Information Council Denmark (a part of The Danish Plastics Federation) kindly forwarded our request for data to ECPI, which provided remarks on their understanding of the use of the phthalates in question (as cited in relevant sections) and general data on consumption trends for primary plasticisers (DINP, DIDP and DPHP).

3.4 Historical trends in use

Overall data on the trend in the use of phthalates are available from the web site of ECPI. ECPI distinguishes between High Molecular Weight (HMW) phthalates with 7-13 carbon atoms in their chemical backbone (with an average of C9-C10) and Low Molecular Weight (LMW) phthalates (ECPI, 2013a) with less. According to ECPI, the most common types of HMW include DINP, DIDP, DPHP, DIUP, and DTDP. DINP, DIDP and DPHP account for nearly 100% of the HMW. As shown in the figure below, the consumption of the HMW (mainly DINP, DIDP and DPHP), has increased from representing less than 25% of total phthalate sales in Western Europe in 1982,via about 50% in 2001 to approximately 83% of the total sales in 2011 (ECPI, 2013a).

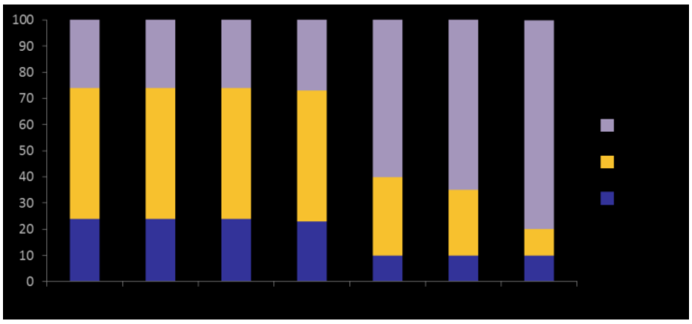


FIGURE 2
WESTERN EUROPE CONSUMPTION OF PHTHALATE PLASTICISERS (ECPI, 2013A)

It is not specifically indicated how much of the high molecular weight phthalates referred to in the figure above is represented by the different phthalates.

The total consumption of plasticisers, including phthalates, has been steady to slightly declining within the EU during the last 10 years, driven by the increasing manufacture of PVC articles outside the EU (as cited by COWI *et al.*, 2012). While on a global scale producers still foresee an increase in total manufacture and consumption of plasticisers, consumption within the EU is likely to continue to be steady to slightly declining

A survey of Brandt and Hansen (2009) of phthalates in articles placed on the market in Denmark in a historical perspective concludes in accordance with the general pattern in the EU that the classified phthalates DEHP, BBP and DBP to a large extent have been replaced by the non-classified phthalates such as DINP and DIDP.

DEP is reported to have been used in a large variety of consumer products. No information has however been found about quantities used by application.

3.5 Summary and conclusions

Phthalates are not produced in Denmark, but the EU is a major producer and exporter of (*ortho*-) phthalates.

DINP is produced by four companies within the EU in Germany, Belgium and Italy, and is registered in the 100,000-1,000,000 tonnes/y band. **DIDP** is produced by two companies within the EU in Belgium and Italy, and is registered in the 100,000-1,000,000 tonnes/y band. **DPHP DPHP** is produced in Germany and Sweden, and also registered in the 100,000-1,000,000 tonnes/y band.

DIPP is registered by one company in the 100-1000 tonnes/y band (a producer of explosives), and is not produced in the EU anymore. **DEP** is registered by 5 companies in the 1000-10,000 tonnes/y band; among the companies is one of the major manufacturers of phthalates. **DMEP** is not registered under REACH and is reported to not be produced in Europe anymore.

The **breakdown of the plasticiser market** in Western Europe, USA and Asia can be summarised as follows: DINP/DIDP represented 63% of the plasticiser market in Western Europe in 2010, whereas it only represented 33% of the market in the USA and 21% of the market in Asia. The total global market for plasticisers was estimated at 6 million tonnes, with 1.4 million tonnes in Europe, the Middle East and Africa, 1.1 million tonnes in the Americas and 3.5 million tonnes in Asia (Calvin, 2011). Of the global plasticiser market, phthalates represented 84% (Calvin, 2011). The on-going substitution of the traditional main general plasticiser DEHP has not reached the same level in Asia as in Europe and the USA. Also, non-phthlate plasticiser and "linears/other phthalates" are used to a higher extent in the USA than in Europe.

Danish net import in 2012 of phthalates on their own was still dominated by DEHP (C8; net import around 800-1000 tonnes /y), but with the general C9-C10 plasticisers types including DINP and DIDP/DPHP (net imports around 600-800 tonnes/y) as a major follow-up. The other three plasticisers covered in this study are recorded with other phthalates in the trade statistics and the group is traded in much lower numbers (net import around 90 tonnes/y).

The total plasticiser content of both **imported and exported articles** into and out of the EU has been estimated at about 170,000 t/y. For the estimate of import/export of DINP/DIDP in articles it was be assumed that DINP/DIDP accounted for the following percentages of the total plasticiser consumption by region: EU, Switzerland, Norway, Iceland: 63%; the Americas: 33%; Asia and rest of the world: 21%. Using these numbers, the import and export was estimated at 45,000 tonnes and 105,000 tonnes respectively, and the export corresponds to about 15% of the total use for manufacturing of products with plasticisers in the EU. Correcting for a few article types not covered in these estimates, the import of DINP/DIDP (should likely be considered as including the third key general plasticiser DPHP) in articles was be estimated at approximately 50,000 tonnes and the export at 125,000 tonnes. Of the import into the EU, 51% of the tonnage of the articles originates from China, whereas only 9% of the imported DINP/DIDP (as such) is estimated to originate from China. An overview of the extra-EU import/export by article type is shown in Table 23.

As regards the use in the EU, DINP, DIDP and DPHP have over the last decade taken over as primary plasticiser for a major part of the former applications of DEHP. As a consequence of the different properties of the three substances, some differences in the use by application are seen.

DINP, DIDP and DPHP are typically used as primary plasticisers in PVC, sometimes in combination with other plasticisers. The actual concentrations are quite variable and depend on the desired properties of the final PVC. Actual analyses of plasticisers in different products demonstrate that, for the same product, often different combinations of plasticisers are found. The combination of plasticisers in a PVC material is partly governed by the desired performance characteristics of the plasticised material and partly by the desired process parameters in the manufacturing of the PVC materials. Typical concentrations of DIDP in flexible PVC applications are reported to be around 25-50%, and the same seems to be the case for DINP.

DINP – DINP is a general plasticiser, which is applied in many products as the direct alternative for DEHP, the formerly major general PVC plasticiser. As such DINP has a high consumption and is probably the plasticiser which can be found in most flexible PVC products today. DINP has a wide range of indoor and outdoor applications. DINP is a commonly used plasticiser, 95% of which is used for flexible PVC used for construction and industrial applications, and durable goods (wire and cable, film and sheet, flooring, hoses and tubing, footwear, toys, etc.). More than half of the DINP used in non-PVC applications involves polymer-related uses (e.g. rubbers). The remaining DINP is used in inks and pigments, adhesives, sealants, paints and lacquers (where it also acts as a plasticiser) and lubricants (ECPI, 2013b).

DIDP - DIDP is a common phthalate plasticiser, used primarily to soften PVC. DIDP has properties of volatility resistance, heat stability and electric insulation and is typically used as a plasticiser for heat-resistant electrical cords, leather for car interiors, and PVC flooring. (ECPI, 2013c). Non-PVC applications are relatively small, but include use in anti-corrosion and anti-fouling paints, sealing compounds and textile inks.

DPHP - DPHP is often used as an alternative (to DIDP) because only minor compound changes are needed to adapt wire formulations for example to DPHP (ECPI, 2013d). It is used automotive and outdoor applications (roofing, geo-membranes, tarpaulins, etc). Almost all DPHP is used as a plasticiser to make PVC soft and flexible.

A total breakdown of the consumption by application in the EU of the three phthalates by is not available. COWI *et al.* (2012) produced a best available scenario for the breakdown of the consumption by 2015 based on the available data from industry. The major article types were wires and cables, film and sheet, flooring, and various other coated products.

DEP, DIPP and DMEP
The aggregated information available on the use of DEP, DIPP and DMEP is scarce compared to DINP and DIDP, and the few reviews available are mostly relatively old and with little information about use and alternatives.

DEP
DEP is a specialty polymer plasticiser and a solvent for cosmetics and personal care products, among others. DEP is reported to be have been used as a plasticizer in consumer products, including plastic packaging films, cosmetic formulations, and toiletries, and in medical treatment tubing. Also in various cosmetic and personal care products (e.g., hair sprays, nail polishes, and perfumes), primarily as a solvent and vehicle for fragrances and other cosmetic ingredients and as an alcohol denaturant. DEP is however not mentioned as an accepted denaturant in EU and Danish rules from 2013 on tax exemption for denatured alcohol (exemption requires use of specified denaturants). An anonymous source indicates current DEP use as plasticiser in EU. ECPI does not

have information of its use as a plasticiser. Other applications include as a camphor substitute, plasticizer in solid rocket propellants, wetting agent, dye application agent, diluent in polysulfide dental impression, and surface lubricant in food and pharmaceutical packaging, in preparation of pesticides. Polynt, one of the registrants, markets DEP for the following uses: Cellulose, flavours & fragrances, cosmetics, pharma.

DIPP

According to the registration of the substance, it is registered by EURENCO Bofors AB, SE, a company which produces explosives as well as charges - so-called propellants - for ammunition. DIPP may also be used as plasticiser for PVC products and other polymers due to their similar structure and physicochemical properties, but this use is not registered.

DMEP

DMEP is a specialty plasticiser which can be used in a number of polymers. The general global applications of DMEP have included its use as a plasticiser in the production of nitrocellulose, acetyl cellulose, PVA, PVC and polyvinylidene chloride intended for contact with food or drink. DMEP is giving these polymeric materials good light resistance. Further, it is used as a solvent. Only limited information regarding DMEP in consumer products in the European marketplace has been identified. There is no information whether the substance is still in use in articles on the EU market. As mentioned, DMEP is not registered under REACH.

The latest available aggregate **survey of annual phthalate consumption** for Denmark covers 2005-2007 and is based on the revenues from the Danish environmental tax on phthalates, in combination with other data on the application of phthalates. The major article groups as regards phthalate consumption were wires and cables (1900 tonnes/y), tubes and hoses (630 t/y), and gloves and rainwear (540 t/y). The situation depicted may likely be the same today, except that the assessment given of phthalates used may be slightly different today, as DINP is expected to be the main general plasticiser, while DIDP and DPHP are primarily expected to be used in applications where resistance to heat or sunlight is prioritised (wire and cable, roofing, tarps, etc.). DEHP is however likely still present in a number of articles.

Data on selected phthalates registered in the **Danish Product Register** were retrieved in June 2013 on the basis of the list of selected phthalates. The Danish Product Register includes substances and mixtures for professional use which contain at least one substance classified as dangerous in a concentration of at least 0.1% to 1% (depending on the classification of the substance). Of the selected phthalates, only DIPP and DMEP are classified as dangerous. DINP is clearly the major registered phthalate in professional products marketed in Denmark, while the registered consumption of DIDP is moderate and the consumption of the other phthalates is minimal, as expected. DIPP is not registered in the Product Register. The Product Register does not include non-chemical articles such as wire and cable, shoe-soles, clothing, toys, etc., which constitute major parts of the Danish consumption of phthalates. Major registered uses which can be mentioned with respect for confidentiality are adhesives and binding agents, fillers (likely to be understood as including sealants), paints, lacquers and varnishes. Some other dominant applications across most substances cannot be mentioned due to confidentiality.

Data gaps

More specific information on the consumption of DINP, DIDP, DPHP and DEP by application.

4. Waste management

4.1 Waste from manufacture and use of selected phthalates

For plasticiser uses of the covered phthalates, the releases to waste from production (formulation and conversion) are not well described according to COWI *et al.* (2009). Releases to waste are expected to occur with disposal of emptied packaging, from handling of raw materials and intermediates, and as cut-offs in the conversion process, where the final products (articles) are produced.

For paints and sealants, the "conversion" is defined as the occasion when the material is applied, typically at a construction site or in manufacturing of machines or other large articles. The use in construction sites is expected to potentially produce more waste as leftovers in sealants tubes, and in paint crates, because the need for materials is less well defined.

For all articles, the major release with waste is expected to take place with the end product at the stage of its disposal; this is dealt with below.

4.2 Waste products from the use of selected phthalates in mixtures and articles

Table 27 in Section 3.3.2 on use in Denmark gives the best available overview of the major waste fractions with contents of phthalates, as well as estimates of the amounts of phthalates in this waste. As shown there, the phthalates-containing waste fractions with the major phthalate contents are cable and wire, tube and hoses, gloves and rainwear, roof plates; film, sheets and tape.

The situation depicted is likely a good reflection of the current waste stream, and this picture is not expected to change quickly. Flexible PVC seems to be a material which will keep its prevalence on the market, and most manufacturers in the EU and globally still uses *ortho*-phthalates in the production. There are indications that the share of non-*ortho*-phthalates in the flexible PVC market has been rising gradually over the last decade or so, especially in sensitive applications such as toys, PVC for food contact and some medical applications. This trend is expected to continue, probably at a moderate pace, at least until the entering into force of the Danish general ban on certain phthalates (in 2014/2015).

The amounts of flexible PVC in each article group subject to the Danish PVC and phthalates tax, are roughly estimated in Table 30 based on the data presented by Brandt and Hansen (2009). Not all product groups containing flexible PVC are covered, but the study is deemed to include most of the flexible PVC consumption which is plasticised with phthalates. The uncertainty on the figures are mainly due to the fact that many of the article types are not reported in specific commodity groups in the trade statistics used, but rather in aggregated groups of different article types. The estimates are based on assumptions of the share of flexible PVC in each relevant commodity group of the statistics.

As regards non-PVC uses of the phthalates, they represent much smaller phthalate amounts and in most cases occur in lower concentrations (deemed from Danish Product Register data and knowledge about the use patterns.

TABLE 30
ROUGHLY ESTIMATED ANNUAL CONSUMPTION OF MAJOR ARTICLE GROPUS MADE WITH FLEXIBLE PVC IN 2005-2007. BASED ON DATA FROM (BRANDT AND HANSEN, 2009)

Product group	Consumption, t/y		Assumed share of flexible PVC in commodity code *1
	All materials in custom codes included*1	Flexible PVC with these articles	
Wire and cable	37,000	9,300	0.25
Tube and hoses	2,300	2,300	0.3
Gloves, rainwear, etc.	1,600	200	0.42
Flooring	4,100	4,100	0.25
Roof plates	900	900	NA
Film, sheets, tape	1,700	300	0.19
Ring binders and document pockets ("stationary")	5,300	300	0.3
Tarpaulins	400	100	0.42
Table cloths, curtains, etc.	160	30	0.42
Coated steel gutters	NA	NA	NA
Totals (rounded)	53,000	18,000	-

Note: *1: Many commodity codes in the trade statistics include several article types, also such which are not made with flexible PVC. Assumption was made on share of flexible PVC in articles reported under each code; see Brandt and Hansen (2009) and their sources.

Phthalate concentrations in articles
The total concentrations of plasticisers in polymer articles becoming waste vary depending on the flexibility of the article type; the more flexible, the higher plasticiser concentration (within each polymer type). This will particularly be reflected in the concentration of the main plasticiser in the article, typically DINP, DEHP, DIDP, DPHP or similar high molecular weight plasticiser. Ranges and averages of concentrations of the general plasticisers DINP and DIDP in articles are summarised from available studies in Table 25 in Section 3.3.1 on the use in EU. According to the Danish Waste Order (Affaldsbekendtgørelsen - BEK 1309 of 18. Dec. 2012), waste with more than 0.5% of substances which are classified as Repr. 1B (reprotoxic, such as DIPP and DMEP) is classified as hazardous waste

As for specialty plasticisers including DEP, DIPP and DMEP, if present, their concentration will more likely vary with the processing conditions prevailing in the manufacturing of the article (process temperature, speed, etc.), and as a consequence of price or other more incidental aspects (many different phthalates and non-phthalate plasticisers may be used for the same purposes). The few available examples of DEP concentrations in consumer products described in Section 3.3.2 are summarised in Table 31 below. Note that these results often each represent very broad articles groups, and that the rest of the articles analysed had DEP concentrations below the detection limits in the studies. The data shown in the table can thus not be considered as representative for the article type, but rather as an indication that DEP may occur in waste of these types. As shown, except for the sex toy sample, DEP was found in trace concentrations only, and for such low concentrations there is no certainty whether DEP has been added intentionally, or is a consequence of impurities in the plasticisers used.

TABLE 31
SUMMARY OF DEP CONCENTRATIONS FOUND IN SELECTED ARTICLE TYPES IN RECENT STUDIES

Article type	Number of samples	DEP concentration *1, mg/kg	Remarks
Baby carrier	13	60 and 350	In two parts of the same sample, a printed badge
Activity carpet for babies	8	1.5	in 1 sample
Ball for children	8	<3	Detection limit was 0.05
Sex toys; fetish glove	15	120	In 1 sample
Textiles	?	Up to 2.3 mg/kg	
Plastic sandals	60	?	DEP detected, but not measured, in 2 samples
PVC soap packaging	?	?	DEP detected, but not measured.

Note: *1: References for the data are shown in Section 3.3.2.

The Danish Waste Order (BEK nr 1309 of 18/12/2012) stipulates that PVC shall, to the extent possible, be sorted out from the waste and be collected for recycling. PVC waste for which no recycling schemes are available should be separated from waste intended for incineration and landfilled. In Denmark, recycling schemes exist for hard PVC only ("Wuppi" and others), meaning that flexible PVC shall be collected separately and deposited. Consumers generally have difficulties in separating specific waste fractions, and as flexible PVC is part of many ordinary consumer products like rainwear, boots, packaging, etc., for which the content of PVC is not obvious to the consumer, much consumer waste is deemed disposed to municipal waste to be incinerated. Phthalates are oil derivatives which will most likely be destroyed in controlled waste incineration plants under Danish conditions. The PVC polymer and other non-combustible additives however produce a high amount of solid residues per weight unit of PVC waste incinerated. During incineration PVC acts as a source of gaseous hydrochloric acid and may as such contribute to corrosion of the boiler. Because of this the incineration plants would like to avoid excessive amounts of PVC.

Industrial waste and other waste from professionals may likely have a higher separate collection rates for flexible PVC waste. No documentation for this was found however.

4.3 Release of selected phthalates from waste disposal

In landfills, a part of the phthalates in polymers may slowly be washed out of the articles and will (in Denmark) be lead with the leachate to municipal wastewater treatment plants. In waste water treatment plants, much of the phthalate content will be adsorbed to particles and will be collected with the sludge and used as fertilizer on agricultural land if certain thresholds for phthalate concentrations and other specified environmental pollutants are met (see Section 2.1.1). If these thresholds are not met the sludge is incinerated or in rare cases landfilled (< 1 %).

In the case of DEP, which is to a higher degree used in applications where they may be washed of (cosmetics, personal care products, cleaning agents, etc.), a bigger part of the DEP present in the articles and mixtures may be lead to waste water treatment.

EC (2003b) refers a Danish study from 1999 where the content of DINP in sewage sludge from a few municipal WWTPs was measured and generally found to be in the range 1.5 – 6.7 mg/kg dw. Previously, DINP and DEP were determined routinely in sewage sludge from Danish municipal

WWTPs as part of the point source programme under the national Danish environmental monitoring programme, NOVANA. However, the newest NOVANA data that include sludge analyses are from 2004 (Danish EPA, 2005a) where the average concentration of DINP was found to be 16.8 mg/kg dw (a high concentration compared to e.g. 2003 where the average was 4.6 mg/kg dw (Danish EPA, 2005a)) while DEP was found at an average concentration of 0.15 mg/kg dw (0.03 mg/kg in 2003). None of the other selected phthalates were included in the study.

4.4 Summary and conclusions

For plasticiser uses of the covered phthalates, the releases to waste from production (formulation and conversion) are not well described according to COWI *et al.* (2009). Releases to waste are expected to occur with disposal of emptied packaging, from handling of raw materials and intermediates, and as cut-offs in the conversion process, where the final products (articles) are produced. For sealants, paints and non-polymer uses, the "conversion" situation includes application on construction sites, etc. and here, a higher fraction of the material may be disposed as waste due to the less well defined conditions

The amounts of flexible PVC in articles subject to the Danish PVC and phthalates tax, are roughly estimated at 18,000 tonnes/year. Not all product groups containing flexible PVC are covered, but the figure is deemed to include most of the flexible PVC consumption which is plasticised with phthalates. The phthalates-containing waste fractions with biggest phthalates contents are cable and wire, tube and hoses, gloves and rainwear, roof plates; film, sheets and tape. The situation depicted is likely a good reflection of the current waste stream, and this picture is not expected to change quickly, at least until a product life time after the entering into force of the Danish ban on certain phthalates (in 2014/2015). The non-PVC uses of the phthalates represent much smaller phthalate amounts and lower phthalate concentrations.

Ranges and averages of concentrations of the general plasticisers DINP and DIDP in articles are summarised from available studies in Table 25 in Section 3.3.1 on the phthalate use in EU.

As for specialty plasticisers including DEP, DIPP and DMEP, if present, their concentration will more likely vary with the processing conditions prevailing in the manufacturing of the article (process temperature, speed, etc.), and as a consequence of price or other more incidental aspects (many different phthalates and non-phthalate plasticisers may be used for the same purposes). Table 31 summarises the available measurements of DEP in consumer products; DEP has been observed in a few samples of children's articles, plastic sandals, PVC soap packaging and sex toys.

The Danish waste order stipulates that PVC shall, to the extent possible, be sorted out from the waste and be collected for recycling. PVC waste for which no recycling schemes are available should be separated from waste intended for incineration and deposited on controlled waste deposits. In Denmark, recycling schemes exist for hard PVC only ("Wuppi" and others), meaning that flexible PVC shall be collected separately and deposited. Consumers generally have difficulties in separating specific waste fractions, and as flexible PVC is part of many ordinary consumer products like rainwear, boots, packaging, etc., for which the content of PVC is not obvious to the consumer, much consumer waste is deemed disposed to municipal waste to be incinerated.

Data gaps

- Investigation of the fate of plasticised PVC waste in Denmark, including recycling rates, for both consumer waste and waste from professionals.

5. Environmental effects and exposure

Apart from the commercially most important phthalates, DEHP, DBP, BBP and DIBP, which have been studied extensively and for which e.g. Annex XV restriction dossiers have been prepared, the body of environmental information on most other phthalate esters is rather limited or even sparse. This also includes the phthalates selected for this review with the exception of DINP and DIDP, for which EU risk assessment reports have been prepared in 2003 (although not based on a very large amount of environmental data), and to some extent DMEP for which a screening assessment report has been prepared by Environment Canada (2009). This chapter is largely based on these reports and, for the remaining substances, on registration information published by ECHA.

5.1 Environmental hazard

5.1.1 Classification

Only two of the substances covered by this review have agreed harmonised CLP classifications; DIPP and DMEP (see section 2.1.2). Regarding environment only DIPP has an agreed classification, namely Aquatic Acute 1 with the Hazard Statement Code H400.

A number of notifiers of the remaining substances have provided self-classifications that are presented in full in section 2.1.2 and for which the proposed environmental classifications are summarised in Table 32 below. For substances not mentioned in the table, no environmental classification has been proposed. It should be noted that the vast majority of notifiers have not provided any self-classification of the notified substances (see section 2.1.2).

TABLE 32
ENVIRONMENTAL CLASSIFICATION INFORMATION ON NOTIFIED AND REGISTERED SUBSTANCES RECEIVED FROM MANUFACTURERS AND IMPORTERS (C&L INVENTORY)

CAS No	Substance name	Hazard Class and Category Code(s)	Hazard Statement Codes	Number of notifiers
68515-48-0	1,2-Benzenedicarboxylic acid, di-C8-10-branched alkyl esters, C9-rich	**Total** No. of environ. classifications Aquatic Acute 1	 H400	**269** 24 24
28553-12-0	Di-"isononyl" phthalate	**Total** No. of environ. classifications Aquatic Acute 1 Aquatic Acute 1 + Aquatic Chronic 1 Aquatic Chronic 4	 H400 H400 + H410 H413	**857** 52 1 23 28
26761-40-0	Di-"isodecyl" phthalate	**Total** No. of environ. classifications Aquatic Acute 1 Aquatic Acute 1 + Aquatic Chronic 1 Aquatic Chronic 2	 H400 H400 + H410 H413	**182** 84 18 23 43

It is assumed that some of the discrepancies in the above self-classifications are due to differences in the interpretation of toxicity results obtained at concentrations above the solubility limits of these poorly water soluble substances.

5.1.2 Environmental effects

DIDP

The risk assessment reports for DIDP (EC, 2003a) refers five acute studies on four species of fish (*Onchorhynchus mykiss, Pimephales promelas, Lepomis macrochirus, Cyprinodon variegatus*) for which no effects were observed at the maximum concentrations tested (0.47 to 1 mg/l). These concentrations are all significantly above the solubility limit of the substance in water (0.038 µg/l) and were therefore obtained by preparing emulsions of the test substance (some showing presence of undissolved particles). Reliable studies at concentrations below the solubility limit are not considered possible to carry out in practice. In the ECHA registration information, the study with *O. mykiss* (LC50 ≥0.62 mg/l) is considered to be the key study. No studies on chronic effects on fish exposed to DIDP via the water phase have been carried out and no significant effects were observed when medaka (*Oryzias latipes*) was exposed in a two-generation study to 20 mg DIDP/kg feed for 284 days (EC, 2003a).

Based on the results of chronic fish studies with a number of C6-C11 phthalates (e.g. DEHP, DOP and DINP), EC (2003a) concludes that "based on the available data, DIDP has no adverse effects upon fish" and "a NOEC cannot be determined".

Similarly, the acute toxicity studies with invertebrates performed with daphnids (*Daphnia magna, Mysidopsis bahia, Paratanytarsus parthenogenetica*) at max. concentrations above the solubility limit (0.15 to 500 mg/l) did not demonstrate any effects at the limit of solubility in water. A NOEC of 0.03 mg/l in a 21 day study with *D. magna* was considered to be due to physical entrapment of the test organisms rather than a toxic effect, and therefore EC (2003a) concludes that no chemical toxic effects could be observed and, consequently, no NOEC could be derived.

Neither could toxic effects on sediment dwellers, algae or microorganisms be observed in the tests performed (EC, 2003a).

Available data indicate no effects of DIDP on soil dwelling or other terrestrial organisms (EC, 2003a). A PNEC for soils was determined at 100,000 µg/kg soil.

The potential of DIDP to cause endocrine disruption in the environment is discussed by EC (2003a) based on the findings in the abovementioned feeding study with medaka (*Oryzias latipes*). As no parameters and endpoints indicated any effects on eggs, embryos or fish, EC (2003a) concludes that "there is apparently no impact on any population parameter from chronic exposure to DIDP on fish".

DINP
A risk assessment report very similar to the one for DIDP (and to a large extent based on the same studies and references) was prepared for DINP (EC, 2003b). Acute toxicity tests on fish were performed using the same four fish species as for DIDP (*Onchorhynchus mykiss, Pimephales promelas, Lepomis macrochirus, Cyprinodon variegatus*) and two more (*Brachydanio rerio, Leuciscus idus*) at concentrations ranging from 0.16 to 500 mg/l compared to a solubility limit in water of 0.6 µg/l. Based on the results obtained, EC (2003b) concludes that "no acute effects have been reported in fish with DINP at its limit of solubility and above in the test system".

In a chronic two-generation feeding study with medaka (*Oryzias latipes*) similar to the one described for DIDP, a "slight but statistically significant increase in egg viability in the DINP treated group when compared to the no treatment control" was observed, but no other effects. In total, based on this study and the results of chronic fish studies with a number of C6-C11 phthalates (e.g. DEHP, DOP and DINP), EC (2003b) concludes that "based on the available data, DINP has no adverse effects upon fish" and "a NOEC cannot be determined".

Similar to DIDP, no effects on invertebrates, sediment dwellers, algae and microorganisms were observed in the tests performed with DINP.

A PNEC for soils was determined at 30,000 µg/kg soil.

The potential of DINP to cause endocrine disruption in the environment is discussed by EC (2003b) based on the findings in the abovementioned feeding study with medaka (*Oryzias latipes*). EC (2003b) concludes that "there is apparently no impact on any population parameter from chronic exposure to DIDP on fish".

DMEP
DMEP is not registered by ECHA, which therefore has no data on the substance. However, a screening assessment was carried out in 2009 by Environment Canada, which is the main source of specific environmental information on this substance.

DMEP was tested experimentally for acute toxicity on 7 aquatic species representing three trophic levels: fish, invertebrates and molluscs. LC50 was higher than 117 mg/l (nominal) for all species except *Daphnia magna* (crustacean) for which an LC50 = 56 mg/l was determined.

Environment Canada (2009) also lists results of QSAR modelling by different models of acute and chronic toxicity of DMEP to fish, daphnia and algae of which the lowest acute LC50/EC50 value is

4.3 mg/l for fish (range of all acute toxicities is 4.3 – 452 mg/l) while the lowest chronic NOEC is 14 mg/l, also for fish.

It is mentioned by Environment Canada (2009) that there is uncertainty about the actual value of some central physical-chemical properties of DMEP such as Log Kow and water solubility and that the model results therefore are associated with some uncertainty (a water solubility of 8,500 mg/l and a Log Kow of 0.04 are used but there is also a reference to a reported water solubility of 900 mg/l and a Log Kow = 2.9).

DMEP was not toxic to ryegrass and lettuce at concentrations of 117 mg/l. No other effect data on terrestrial organisms are mentioned.

DEP
ECHA registration data for DEP comprises acute toxicity data on four species of fish of which the lowest value is 12 mg/l for rainbow trout (values for other fish species range from 17 to 29 mg/l). For daphnia the key study gives an EC50 = 90 mg/l while a supporting study gave an LC50 = 52 mg/l. The EC50 for algae was determined to be 23 mg/l in a 72 hour study.

The ECHA data do not comprise chronic data on fish or algae while the key study NOEC (21 days) for daphnia did not show any effects at the highest test concentration of 25 mg/l.

DIPP
The only information about DIPP at the ECHA site is a short statement for invertebrates and algae saying that DIPP is predicted not to be toxic to aquatic invertebrates or algae.

DPHP
For DPHP an 96 hour, static test LC50 >10,000 mg/l for zebra fish is reported by ECHA while there is data waiving for chronic data on fish. The acute (48 h) EC50 for daphnia is reported to be higher than 100 mg/l as is the 72 hour toxicity to green algae.

A chronic (21 days) reproduction study on daphnia did not result in observations of any adverse effects of DPHP at the highest test concentration of 1 mg/l.

5.2 Environmental fate
Environmentally relevant physic-chemical properties such as water solubility and Log Kow differ significantly between the phthalates selected for this study. Thus, the short-chain phthalates DEP and DMEP have water solubilities close to 1,000 mg/l whereas the solubilities of DPHP, DIDP and DINP are in the sub-µg/l range. Likewise, Log Kow's range from 2-3 for DEP and DMEP to 8-10 for DPHP, DIDP and DINP (see section 1.2).

However, according to the public registration data found on ECHA's web-site, all of the registered phthalates in this study appear to be classifiable as "readily biodegradable" and therefore it is considered likely that also the only non-registered substance, DMEP, is readily biodegradable although firm documentation of this is lacking. Experimental data indicate that also in aerobic sediment the biodegradation of DINP and DIDP takes place fast (DT50 values of 1 day or less) while for the other substances there is no information on degradation in natural water and sediment (data waiving). No data on degradation rates in soil are available.

Abiotic degradation/transformation in air takes place for DINP and DIDP with half-lives of about 5 hours, for DMEP with a half-life of 6.6 hours and for DPHP with a half-life of 14 hours (all results based on modelling). Only DEP appears to have a longer half-life in air; 111 hours (modelled). Photolysis and hydrolysis appear not to be processes of any relevance for the dissipation of phthalates in the environment.

Sorption to organic matter is strong for the long-chained phthalates, ECHA reports K_{OC} values for DIDP and DINP of 1,589,000 and 793,000-948,000, respectively, and >426,580 for DPHP. However, DEP has a K_{OC} in the range 150-500 (medium mobility in soil).

Regarding bioconcentration/bioaccumulation potential the EU risk assessment report for DIDP (EC, 2003a) mention an experimental BCF < 14.4 for the fish (*Cyprinus carpio*), which, however, the authors find is too low compared to other data e.g. on DEHP and therefore recommend the BCF = 860 established for DEHP in fish to be used for risk assessment. A BCF = 4,000 for DIDP in mussels is recommended for use in secondary poisoning risk assessment. For soil organisms a BCF = 1 is recommended as a reasonable worst-case BCF. The same BCF values are used/recommended for DINP (EC, 2003b).

None of the substances are considered to meet the criteria for being classified PBT or vPvB.

5.3 Environmental exposure

5.3.1 Sources of releases

None of the phthalates in this study are manufactured in Denmark and therefore such sources of release are not relevant for this country. There are downstream users of some of the phthalates, in particular DINP, for manufacturing of various polymers, which are considered point sources of release to the atmosphere and to some extent also to wastewater.

General sources of release are outlets from waste water treatment plants (WWTPs) and separate rain runoff systems as well as atmospheric deposition of substances emitted to air. A wet deposition rate for DINP of 17-33 µg/m²/year (1998) has been calculated for a background location in Denmark based on analytical measurements (EC, 2003b). No newer data on the issue has been identified.

As for DINP, measured data are not given by Boutrup and Svendsen (2012), but they refer to the so-called "key number" (Danish: Nøgletal; defined as the 75% percentile of measurements in the period 1998-2009, (Kjølholt *et al.*, 2011)) which is considered to be the best estimate of a national mean value for calculation of total releases from WWTPs. For DINP releases from municipal waste water plant outlets is 0,37 µg/l (interval 0.19-0.56). The similar key number for DEP is 0.33 µg/l (0.20-0.63).

TABLE 33
TRENDS IN CONCENTRATIONS OF SELECTED PHTHALATES IN OUTLETS FROM MWWTP 2000-2010 (BOUTRUP AND SVENDSEN, 2012)

Year	DEHP			DEP			DINP			DBP		
	Mean µg/L	95% ft µg/L	% above d.l.	Mean µg/L	95% ft µg/L	% above d.l.	Mean µg/L	95% ft µg/L	% above d.l.	Mean µg/L	95% ft µg/L	% above d.l.
2000	1,9	6	60	0,5	1	30	-	-	2	0,8	1,5	22
2001	2,8	11	68	0,8	2,2	37	0,3	0,4	5	0,9	1,8	28
2002	3	13	64	0,4	0,7	4	0,7	2,9	7	0,3	0,4	6
2003	1,8	6,1	27	0,2	0,6	15	-	-	0,5	0,1	0,4	7
2004	1,9	5,2	59	1,5	7,1	56	1,3	5,8	36	0,14	0,27	36
2010	0,5	-	65	-	-	9	0,6	-	17	NA	NA	NA

Boutrup and Svendsen (2012) also estimated the total release of certain plasticisers, including DINP and DEP, to Danish marine waters. The results are shown in Table 34, along with those for DEHP for comparison. No sums were calculated by the authors, but as shown, DEP releases were estimated as of the same order of magnitude as DINP from these numbers. Estimated releases of both DINP and DEP are considerably smaller than that for DEHP, which might reflect that the used concentration value for DINP may not adequately reflect the most recent consumption pattern, where DINP is the main general plasticizer and the DEHP consumption has declined.

TABLE 34
ESTIMATED TOTAL RELEASES OF DINP, DEP AND DEHP FROM MUNICIPAL WASTE WATER TREATMENT (BOUTRUP AND SVENDSEN, 2012).TERE

Year	DINP		DEP		DEHP	
Recipient	Input	Interval	Input	Interval	Input	Interval
1 Nordsøen	5,9	3,1-9	5,3	3,2-10	45	23-96
2 Skagerrak	1,4	0,7-2,1	1,2	0,8-2,4	11	5,3-23
3 Kattegat	30	16-46	27	16-51	226	114-490
4 N. Bælt	6,1	3,1-9	5,4	3,3-10	46	23-99
5 Lillebælt	18	9,4-28	16	9,9-31	139	70-298
6 Storebælt	14	7,3-22	13	7,7-24	108	54-231
7 Øresund	57	29-86	51	31-97	431	216-924
8 S. Bælthav	0,5	0,2-0,7	0,4	0,2-0,8	3,5	1,7-7,5
9 Østersøen	3,1	1,6-4,7	2,8	1,7-5,3	24	12-51

Boutrup and Svendsen (2012) has estimated a total release of DINP from WWTP's to the marine areas surrounding Denmark of around 135 kg/year.

5.3.2 Monitoring data

Boutrup and Svendsen (2012) summarised observed concentrations of selected plasticisers measured in municipal waste water treatment plant outlets. The data for DEHP and DINP as representatives of general plasticisers, and DEP and DBP as representatives of specialty plasticisers (and DEP as solvent) are presented in Table 33. The reference also gives data for BBP and the non-phthalate plasticiser DEHA (diethylhexyl adipate). The authors note that in general, the releases of the measured plasticisers were lower in 2010 than in earlier years; they however consider the data material to be too small to make clear statements as to whether this can be deemed as a decreasing trend.

Only two of the phthalates, DEP and DINP, are included in the national Danish environmental monitoring programme, NOVANA, and only for releases from point sources such as WWTPs and separate outlets for rain runoff. Data from NOVANA on these substances area summarised in Table 35 below.

TABLE 35
MONITORING DATA FOR SOME PHTHALATES IN OUTLETS FROM POINT SOURCES FROM THE NATIONAL DANISH MONITORING AND ASSESSMENT PROGRAMME (NOVANA).

Substance	Point source	Number of samples *1	Average µg/L	Median µg/L	Year	Source
DEP	WWTP	30 (10)	0.19	0.00	2011	Danish Nature Agency, 2012
DEP	WWTP	36 (20)	1.52	-	2004	Danish EPA, 2005b
DINP	WWTP	30 (10)	1.05	0.00	2011	Danish Nature Agency, 2012
DINP	WWTP	36 (13)	1.26	-	2004	Danish EPA, 2005b
DINP	Outlets for rain runoff	-	0.9	-	2007-2009	Boutrup and Svendsen, 2012

*1 Number of positive samples in brackets

EC (2003b) refers for DINP some earlier investigations carried out in Denmark by Vikelsoe *et al.* in 1999. In surface water (small rivers) the concentration of DINP was in all cases < 0.1 µg/l while in various soils (natural and cultivated), concentrations were in the range 1-32 µg/kg soil dw. However, in sludge amended soils the concentrations of DINP ranged from 63 to 910 µg/kg soil dw.

A joint Nordic study measured concentrations of different plasticisers (selected phthalates as well as others) in different aquatic media in each of the countries participating. In Denmark waste water treatment plant (WWTP) effluent and sludge were sampled at Esbjerg central WWTP and Ejby Mølle WWTP, Odense. Effluent was sampled at Råbylille strand WWTP, Vordingborg. Sediment samples were collected at Vedbæk, Øresund, from Kolding Fjord and from Limfjorden. Fish (Flounder) were sampled at Ho bugt (vicinity of Esbjerg), Hjelm bugt (vicinity of Vordingborg) and Agersö, Great Belt. The WWTPs in Esbjerg and Odense had in 2010 loads of 115,000 and 275,000 pe (person equivalents) respectively, while the load on Råbylille Strand was much smaller, 1,100 pe. Råby lille Strand only receives wastewater from households while the others receive from both household and industry. The results from the study are presented in Table 47 (Remberger *et al.*, 2013). Note that DINP and DIDP seem to have been concentrated in the sewage sludge samples measured.

TABLE 36
DINP AND DIDP CONCENTRATIONS IN SELECTED ENVIRONMENTAL MEDIA FROM LOCATIONS IN DENMARK, SAMPLED IN 2011 (FROM REMBERGER *ET AL.*, 2013).

Sample medium	Location	Unit	DINP	DIDP
WWTP effluent	Esbjerg	ng/l	160	<100
WWTP effluent	Odense	ng/l	<80	<100
WWTP effluent	Vordingborg	ng/l	<80	<100
WWTP sludge	Esbjerg	µg/kg dw	50,000	9,900
WWTP sludge	Odense	µg/kg dw	49,000	14,000
Sediment	Øresund	µg/kg dw	92	<20
Sediment	Kolding Fjord	µg/kg dw	490	63
Sediment	Limfjorden	µg/kg dw	59	<20
Fish	Ho bugt	µg/kg ww	<40	<40
Fish	Hjelm bugt	µg/kg ww	87	<40
Fish	Agersø	µg/kg ww	<40	<40

5.4 Environmental impact

In the EU risk assessment reports for DIDP and DINP (EC, 2003a and 2003b) no additional risk reduction measures for these two substances were found to be necessary. It should be noted however, that the consumption of these substances has increased significantly since then.

For DMEP, Environment Canada (2009) finds that this substance "does not persist in the environment and is not bioaccumulative". Further, Environment Canada (2009) considers that as "the substance is not highly hazardous to aquatic organisms and terrestrial plant and exposure potential is low, DMEP is unlikely to cause ecological harm in Canada".

For the other phthalates in this study no statements regarding environmental impact have been identified.

5.5 Summary and conclusions

DIPP is the only one of the phthalates in this study that has an EU harmonised environmental classification, namely Aquatic Acute 1 (H400). A number of notifiers have provided self-classifications of DINP and DIDP. Regarding DINP, about half of the notifiers have classified the substance Aquatic Acute 1 + Aquatic Chronic 1 while the other half have classified it as Aquatic Chronic 4. DIDP has been classified Aquatic Acute 1 or Aquatic Acute 1 + Aquatic Chronic 1 by approx. half of the notifiers and Aquatic Chronic 2 by the other half.

DIDP and DINP resemble each other much with regard to chemical structure and relevant physical-chemical properties such as water solubility, Log Kow and sorption constants, and therefore also with regard to environmental fate and effect properties. As the water solubility of both substances is very low (sub-pbb) it has only been possible to conduct tests at higher concentrations (sub-ppm) using emulsions.

No significant acute or chronic toxic effects were observed in any tests on either of the two substances except for a "slight but statistically significant increase in egg viability in the DINP treated group when compared to the no treatment control" in a two-generation feeding study with medaka (*Oryzias latipes*). This observation did not affect the overall conclusion by EC (2003a and b) that DINP and DIDP are not considered to have adverse effects on the organisms (aquatic and terrestrial) studied.

With regard to possible endocrine disruption properties it was concluded that "there is apparently no impact on any population parameter from chronic exposure to DIDP on fish".

DMEP is much more water soluble and a lowest experimental acute LC50 = 56 mg/l was determined for *Daphnia magna*. QSAR modelling results indicate acute LC50 for fish in the range 4.3 – 452 mg/l and a lowest chronic NOEC = 14 mg/l.

Only few environmental effect data are available on the remaining substances. However, the available data do not indicate that any of them are very toxic to aquatic organisms.

All the phthalates appear to be readily biodegradable (with DMEP as a possible exception) while abiotic processes such as hydrolysis and photolysis do not appear to be of any significance. A BCF <14.4 for DIDP in fish has been determined experimentally but is considered to be too low. Instead the BCF = 860 for DEHP is recommended by EC (2003a and b) for use in risk assessment.

None of the substances are considered to meet the criteria for classification as PBT or vPvB.

The total release of DINP from wastewater treatment plants to the marine areas surrounding Denmark was estimated at around 135 kg/year.

6. Human health effects

6.1 Human health hazard

Different phthalates have been shown to cause a variety of effects in laboratory animals. It is however the adverse effects on the development of the reproductive system in male animals of certain phthalates that have raised particular concern.

In this chapter the human health aspects of the selected phthalates are evaluated. The main focus is on the substances that are least well described in the current literature. DIDP and DINP have recently been evaluated in relation to Entry 52 of Annex XVII to Regulation (EC) No 1907/2006 (REACH) and conclusions from this review will be cited here and only supplemented where new has been identified.

6.1.1 Classification

Of the selected phthalates only DIPP and DMEP are subject to harmonised classification. Both substances are classified as toxic to reproduction in category 1B. The harmonised classification is shown in Table 37.

TABLE 37
HARMONISED HUMAN HEALTH CLASSIFICATION ACCORDING TO ANNEX VI OF REGULATION (EC) NO 1272/2008 (CLP REGULATION)

Index No	International Chemical Identification	CAS No	Classification	
			Hazard Class and Category Code(s)	Hazard statement Code(s)
607-426-00-1	Diisopentylphthalate (DIPP)	605-50-5	Repr. 1B	H360FD
607-228-00-5	Bis(2-methoxyethyl) phthalate (DMEP)	117-82-8	Repr. 1B	H360Df

The remaining phthalates are self-classified by industry with the suggested human health classification shown in Table 12. As presented in the table, most notifiers have not classified the substances and indicated "data lacking" and "conclusive but not sufficient for classification". The table reflects the number of notifiers as of August 2013.

Two notifiers have suggested a classification as toxic to reproduction in category 2 (Repr. 2), for DEP and three notifiers have suggested a similar classification for DINP (CAS no. 68515-48-0). A few more notifiers suggest that DEP should be classified for specific target organ toxicity after single or repeated exposure. Other classification proposals reflect the acute toxicity, skin and eye irritation potential of the substances.

For DINP it should be noted that the suggested classifications for the two different CAS numbers are not the same. However, since only one out of 857 notifiers has suggested a classification for DINP (CAS 28553-12-0) and four out of 269 notifiers have suggested a classification for DIDP (CAS 68515-48-0), it is not relevant to draw any conclusions on that background.

6.1.2 DEP

Kinetics and metabolism

When DEP is administrated by oral gavage the major part is metabolised into the monoester and phthalic acid which is rapidly excreted in urine. Studies in rats and mice with ^{14}C-DEP have shown that 90% of the radioactivity was excreted with the urine within 48 hours with the majority being eliminated during the first 24 hours. Approximately 3% of the radioactivity was found in faeces over the same period of time (NICNAS, 2011).

When applied dermally, DEP penetrates the skin and is widely distributed in the body without accumulating in tissue. In an *in vitro* study with human and rat skin absorption of DEP was found to be 4.5 +/- 3.2% through human skin based on 24 samples. With rat skin the absorption was higher and found to be 37.5 +/- 4.0% based on 16 samples (ECHA, 2013a). In rats and rabbits it has been shown that around 25-50% of the administered doses is excreted within 24 hours in rats and 4 days in rabbits. Differences in dermal absorption between rats and humans may reflect species differences, differences in vehicle and/or differences in application. NICNAS reports that results from recent human studies indicate a dermal absorption with approximately 10% and 5.8% of dermally applied DEP found in serum and urine, respectively within 24 hours. On a weight of evidence basis, NICNAS assumes a dermal bioavailability for DEP of 10% in humans for the purposes of risk assessment (NICNAS, 2011).

Acute toxicity

Following oral administration of 14C-DEP the highest concentrations were observed in kidney and liver, followed by blood, spleen and adipose tissue and highest levels were noted within 20 minutes, followed by a rapid decrease to only trace amounts after 24 h (NICNAS, 2011). Distribution in female rabbits after dermal application of radioactively labelled DEP showed very little radioactivity in tissues 4 days after exposure with 0.004% of the dose in the liver, 0.003% of the dose the kidney and less than 1% of dose in the blood (NICNAS, 2011).

DEP has low acute toxicity in several animal species. LD50 values reported in rat studies range from >5600 to 31,000 mg/kg bw (NICNAS, 2011). In rabbit an oral LD50 of 1000 mg/kg bw is reported but the study is not evaluated as reliable in the ECHA registration information. Dermal toxicity in the rat is reported at >11,000 mg/kg bw and at 3000 mg/kg bw in guinea pig (NICNAS, 2011).

Irritation

Skin irritation studies are conducted in rats and rabbits. Undiluted DEP on intact and abraded rabbit skin in a 4-hour closed patch test (duration unknown) caused irritation at both sites after 24 hours but was reduced to 40% after 72 hours. Two other studies with undiluted DEP in rabbits under semi-occlusive conditions for 4 hours did not cause irritation. In rats application of undiluted DEP in a semi-occlusive patch test for 2 weeks, 6 hours/day resulted in erythema and/or slight desquamation (NICNAS, 2011). No dermal irritation was noted in 576 human subjects exposed dermally to DEP (US CPSC, 2010).

Overall the available animal studies and human data suggest that DEP causes minimal skin irritation.

Eye irritation was studied in rabbits. Application of undiluted DEP (0.1 mL) into the conjunctival sac of rabbit eyes resulted in transient slight redness of the conjunctivae and minimal eye irritation in two studies (NICNAS, 2011).
The key eye irritation study in the registration dossier is an older study in rabbits considered reliable with restrictions. 0.1 ml of 12.5% DEP in ethanol was installed in rabbit eyes. A severe conjunctival irritation was seen in all 3 tested animals including chemosis and discharge. All parameters were not fully reversible within 7 days. The results of the study were interpreted as if DEP is moderately irritating to eyes and requires classification as irritating to eyes (Category 2)

under GHS (Regulation 1272/2008). It is noted that historical data for eye irritation of ethanol shows similar reaction to that observed in this study (ECHA, 2013a).

Overall, the studies in rabbits showed that DEP causes minimal to moderate eye irritation.

Sensitisation
Skin sensitisation has been investigated using the local lymph node assay (LLNA), the Buehler test and in the open epicutaneous test, the Draize intradermal test and the Freund's complete adjuvant test. There was no evidence of sensitisation to DEP in any of the tests (ECHA, 2013a; NICNAS, 2011).

DEP caused no dermal sensitization reactions in normal volunteers as well as patients, including perfume-sensitive patients, contact dermatitis patients, children with dry plantar dermatosis, and others. Positive patch test reactions, have been reported in patients with contact dermatitis from eyeglasses frames and hearing aids, as well as from the plastic of a computer mouse known to contain phthalates (NTP, 2006). Although dermal sensitisation in humans has been described it seems to be rare.

No data on respiratory sensitisation is available.

Repeated dose toxicity
Several repeated dose toxicity studies have been conducted with DEP in rats and mice via the dermal and oral route. The liver appears to be the primary target organ for DEP in both short- and medium-term studies. Observed effects include increased organ weight, vacuolation, elevated serum and liver enzyme levels, and proliferation of mitochondria and peroxisomes. Hypertrophic effects (increased volume) have also been reported in other organs such as kidney, stomach and small intestine. The ECHA registration dossier and the NICNAS assessment both point to a 16-week dietary study in rats as the critical study for repeated dose toxicity. In this study rats were administered DEP in the diet at a concentrations of 0, 0.2, 1 and 5% (3,160 and 3,710 mg/kg-day for the males and females, respectively). According to NICNAS, effects included significantly depressed body weight (15–25% less than controls), and relative kidney and liver weights were increased significantly in both sexes at a dose of 5% (w/w) in the diet. In females, increases in relative liver weights were dose-dependent and statistically significant at all doses. In male rats, small intestine weights were increased at the 5% dose only, whereas stomach weights were increased at both the 1% and 5% dose levels. There was no abnormal histopathology of the liver, kidney or digestive organs and no significant effects on haematology, serum enzyme levels or urinary parameters. A conservative NOAEL of 0.2% (corresponding to 150 mg/kg bw/d) was established from this study based on dose-dependent increased relative liver weight in females and increased stomach weight in males at 1% (LOAEL of 750-770 mg/kg bw/d) (NICNAS, 2011). This is in line with the ECHA registration dossier.

Genotoxicity
DEP was negative in most bacterial mutagenicity tests with S. typhimurium with and without S9 activation and did not induce chromosomal aberrations in Chinese ovary cells either with or without exogenous metabolic activation at DEP concentrations up to 250–324 µg/mL. DEP induced sister chromatid exchanges in Chinese ovary cells in the presence (but not the absence) of exogenous metabolic activation at DEP concentrations of 167 and 750 µg/plate (US CPSC, 2010). Overall, these data do not support a genotoxic potential for DEP.

No *in vivo* data have been identified.

Chronic toxicity / carcinogenicity
Carcinogenicity studies are conducted in rats and mice by the oral and dermal route.

Evaluation of 2-year dermal studies in mice showed a statistically significant (but not dose-related) increase in basophilic foci in the liver in male mice dosed with 520 mg/kg bw/d. No effects were reported in female mice. Marginally increased incidences of combined hepatocellular adenomas and carcinomas were noted in both sexes but they were statistically significantly dose-related only in male mice. Due to lack of dose-response relationship in female mice and similar incidences of hepatocellular neoplasms between the high dose male mice and historical controls, these increases were considered equivocal evidence of carcinogenic activity for DEP (NICNAS, 2011).

In similar 2-year dermal studies in rats, no evidence of increased neoplasia was found other than treatment-related epidermal acanthosis (specific type of hyperpigmentation) at sites of DEP application, which was considered an adaptive response to irritation. No other lesions or neoplasms were noted in these 2-year studies in mice and rats. DEP did also not demonstrate any initiating or promoting activity in additional studies (NICNAS, 2011).

Overall, it is concluded that available data do not support a carcinogenic potential for DEP.

Reproductive toxicity

Several studies have been conducted with DEP in rats and mice to investigate reproductive toxicity endpoints. An overview is presented in NICNAS (2011) is shown in Table 45.

TABLE 38

OVERVIEW SUMMARY OF THE FERTILITY AND DEVELOPMENTAL EFFECTS OF DEP (NICNAS, 2011)

Study design	Species / route	Doses (mg/kg bw/d)	NOAEL (mg/kg bw/d)	LOAEL (mg/kg bw/d) and endpoint	References from NICNAS (2011)
Multigenerational dietary reproductive toxicity studies					
18 weeks (1 week prior to mating till weaning) 20/sex/group	Mice CD-1 Diet	0, 0.25, 1.25, 2.5% (0, 340, 1770, 3640)	Maternal: 3640 (F0) NE (F1) Fertility-related parameters: 3640 (F0) NE (m, F1) 3640 (f, F1) Developmental: 3640 (F1) NE (F2)	Maternal: 3640 (F1): ↓ body weight (m-f); ↑ liver & ↓ pituitary weights (f) Fertility-related parameters: 3640 (m, F1): ↓ sperm counts, ↑ prostate weight Developmental: 3640 (F2): ↓ no. of live pups/litter (combined sexes)	Lamb *et al.*, 1987
15-17 weeks per generation (10 weeks prior to mating till weaning) 24/sex/group	Rats SD Diet	0, 600, 3000, 15 000 ppm (0, 40-56, 197-267, 1016-1375) (m-f)	Maternal: 197-267 (m-f, F0, F1) Fertility-related parameters: 40 (m, F0, F1) 1375 (f, F0, F1)	Maternal: 1016-1375 (m-f): ↑ liver weight (F0, F1); ↑ kidney weight (f, F1) Fertility-related parameters: 197 (m): ↓ serum testosterone (F0), ↑ abnormal and tailless sperms (F0, F1) Developmental:	Fujii *et al.*, 2005

Study design	Species / route	Doses (mg/kg bw/d)	NOAEL (mg/kg bw/d)	LOAEL (mg/kg bw/d) and endpoint	References from NICNAS (2011)
			Developmental: 197-267 (m-f, F1, F2)	1016-1375 (m-f): ↓ pup weight on PND 21 (F1, F2) and PND 4-21 (f, F1), delayed pinna detachment (m, F1) & vaginal opening (f, F1)	
Studies on testes and testicular function					
4 days 12/group	Rats Male SD Intubation	0, 1600	*Fertility-related parameters:* 1600	NE	Foster *et al.*, 1980
7 days 10/group	Rats Male Wistar Diet	0, 2% (~2000)	NE	*Fertility-related parameters:* 2000: ↓ serum and testis testosterone	Oishi & Hiraga, 1980
2 days 12/group	Rats Male Wistar Gavage	0, 2000	NE	*Fertility-related parameters:* 2000: ultrastructural changes in Leydig cells	Jones *et al.*, 1993
150 days 6/group	Rats Male Wistar Diet	0, 10, 25, 50 ppm (0, 0.57, 1.43, 2.85)	NE	*Fertility-related parameters:* 0.57: ↓ testis weight, testicular antioxidant enzymes, serum testosterone and androstenedione	Pereira *et al.*, 2008b **ND**
28 days 6/group	Rats Male SD Gavage	0, 250 (MEP)	NE	*Fertility-related parameters:* 250: ↓ sperm counts & motility	Kwack *et al.*, 2009 **ND**
7 days 10/group	Rats Male Wistar Diet	0, 2% (~2000)	NE	*Fertility-related parameters:* 2000: ↓ serum and testis testosterone	Foster *et al.*, 1980
2 days 12/group	Rats Male Wistar Gavage	0, 2000	NE	*Fertility-related parameters:* 2000: ultrastructural changes in Leydig cells	Oishi & Hiraga, 1980
Prenatal developmental toxicity studies					
GD 5, 10, 15 5/group	Rats SD ip	0, 0.51, 1.01, 1.69 mL/kg (0, 500, 1000, 1500)	NE	*Developmental:* 500: ↓ pup weight, ↑ skeletal abnormalities	Singh *et al.*, 1972
GD 0-17 17-20/group	Mice Jcl:ICR Dermal	0, 500, 1600, 5600	*Maternal:* 1600 *Developmental:* 1600	*Maternal:* 5600: ↑ adrenal and kidney weights *Developmental:* 5600: ↓ pup weight, ↑ skeletal variations (rudimentary cervical and lumbar ribs)	Tanaka *et al.*, 1987* (reviewed by SCCNFP, 2002; IPCS, 2003)
GD 6-13	Mice	0, 4500	*Developmental:*	NE	Hardin *et al.*, 1987

Study design	Species / route	Doses (mg/kg bw/d)	NOAEL (mg/kg bw/d)	LOAEL (mg/kg bw/d) and endpoint	References from NICNAS (2011)
50/group	CD-1 Gavage		4500		
GD 6-15 27-32/group	Rats CD Diet	0, 0.25, 2.5, 5% (0, 200, 1900, 3200)	*Maternal:* 200 *Developmental:* 1900	*Maternal:* 1900: ↓ body weight & food consumption *Developmental:* 3200: ↑ skeletal variations (rudimentary lumbar ribs)	Field *et al.*, 1993
GD 12-19 5/group	Rats CD Gavage	0, 500	*Developmental:* 500	NE	Liu *et al.*, 2005
GD 8-18 5/group	Rats SD Gavage	0, 100, 300, 600, 900	*Maternal:* 900 *Developmental:* 900	NE	Howdeshell *et al.*, 2008 **ND**
Postnatal developmental toxicity study (one-generation study)					
GD 14 - PND 3 5/group	Rats SD Gavage	0, 750	*Developmental:* 750	NE	Gray *et al.*, 2000

F0 = parental generation; F1 = first filial/offspring generation; F2 = second filial/offspring generation;
m-f = male-female; ip = intraperitoneal; no. = number. ↓ = decreased; ↑ = increased;
GD = gestational day; NE = not established; PND = postnatal day; SD = Sprague-Dawley
* Quoted as secondary citations from the key documents listed in Section 1.3;
ND = new data since the release of the NICNAS DEP Hazard Assessment in 2008.

With regard to fertility parameters, it is concluded that associations are drawn between exposure to DEP and abnormal sperm parameters but no evidence of effects leading to decreased fertility in animals. Based on the multigeneration dietary reproductive toxicity study in rats NICNAS (2011) established NOAEL of 40 mg/kg bw/d was for fertility-related parameters based on the reduced testosterone levels and the increased incidence of abnormal sperms at 197 mg/kg bw/d.

Based on the same study, NICNAS (2011) concludes that the developmental NOAEL was 197 mg/kg bw/d and the LOAEL was 1016 mg/kg bw/d based on decreased pup weight and developmental delay.

Based on the same study in the registration dossier for DEP, the registrant has suggested a NOAEL for general toxicity and reproductive performance in parental animals at 15000 ppm (1016 mg/kg bw/d) as there were no adverse effects on these parameters. For development and growth of pups the NOAEL is considered to be 3000 ppm (197 mg/kg bw/d) due to decreased body weight gain in those given 15000 ppm (ECHA, 2013).

Endocrine disruption

The Danish Centre on Endocrine Disrupters (CEHOS, 2012) has provided a science based evaluation of the endocrine disrupting properties of the 22 substances on the SIN list[2] version 2.0. DEP is one of the substances which have been evaluated against the proposed Danish criteria for endocrine disrupters. The criteria are shown in Appendix XX. The result of the evaluation with relevance for human health was according to CEHOS (2012):

[2] List of substances identified by the NGO ChemSec as Substances of Very High Concern (SVHC) according to the criteria in REACH. http://www.chemsec.org/what-we-do/sin-list/sin-list-20

Di-ethyl phthalate (DEP), CAS 84-66-2
Associations between DEP exposure and clinical outcomes related to endocrine disruption (AGD in boys, infertility, and insulin resistance) have been reported in human studies. For some outcomes the same associations were seen as well for other phthalate metabolites present at the same time. Some in vitro studies show weak estrogenic effects, whereas others do not, i.e. results are conflicting.

In experimental animals findings of reduced testosterone levels, delayed vaginal opening and increased incidence of abnormal sperm in a two-generation study point to endocrine disruption. Several studies show that DEP does not share the same mode of action as DEHP, DBP, BBP, DPP and DiBP and does not affect e.g. anogenital distance, fetal testosterone production, fetal testicular gene expression, nipple retention, and reproductive organ weights. Two other studies describe effects of DEP on semen quality, but it is not the same parameters that are alteretered in the three studies. Other studies including an enhanced 28-day study did not detect any sperm quality changes. Thus, the possibility of effects of DEP on sperm quality is controversial and although evidence of endocrine disruption has been shown, any evidence of adverse effects is less clear.
Evaluation: Suspected ED in Category 2a.

Category 2a – Suspected ED

Substances are placed in category 2a when there is some evidence from humans or experimental animals, and where the evidence is not sufficiently convincing to place the substance in category 1. If for example limitations in the study (or studies) make the quality of evidence less convincing, category 2a could be more appropriate. Such effects should be observed in the absence of other toxic effects, or if occurring together with other toxic effects, the ED effect should be considered not to be a secondary non-specific consequence of other toxic effects. Substances can be allocated to this category based on:

- Adverse effects in vivo where an ED mode of action is suspected
- ED mode of action in vivo that is suspected to be linked to adverse effects in vivo
- ED mode of action in vitro combined with toxicokinetic in vivo data (and relevant non test information such as read across, chemical categorisation and QSAR predictions).

6.1.3 DIPP

The following data is available in the registration dossier for DIPP (ECHA, 2013):

- LD50, oral in rat: > 2000 mg/kg bw
- Not irritating in EPISKIN three dimensional human skin model
- Non corrosive/non severe eye irritant in Bovine Corneal Opacity and Permeability Test: An In Vitro Assay of Ocular Irritancy
- Sensitising in Mouse local lymphnode assay (LLNA). Considered a potential skin sensitiser
- Negative in Mutagenicity - Reverse Mutation Test Using Bacteria (s. typhimurium) with and without metabolic activation

DIPP is subject to harmonised classification and evaluated as requiring classification for reproductive toxicity in category 1B.

In Annex I to the Annex XV dossier, proposing DIPP as a SVHC substance, the following additional information is available (Environment Agency Austria, 2012):

- A good skin penetration potential can be expected as for the structurally related diisobutyl phthalate about 10 %
- Absorption via the gastrointestinal tract is substantiated by systemic effects in animal experiments. Alkyl phthalates are assumed to be absorbed via the respiratory tract. Since the vapour pressure is very low, inhalative exposure is only to be expected if DIPP is strongly heated or if aerosols are formed.
- Studies regarding metabolism of DIPP are not available

With regard to developmental toxicity and effects on fertility, the following information is available (Environment Agency Austria, 2012):

- According to recent and older studies there is strong evidence that dipentylphthalate (CAS 131-18-0) is an equal or even more potent testicular toxicant than DEHP. This is likely to be valid also for other structurally related pentyl phthalates, like DIPP. This is supported by results of from 1997. The mixture of pentyl phthalates caused a 100 % resorption at 1000 mg/kg/day while DEHP caused malformations in 70% of the litters at the same dose.
- There are no studies on fertility with DIPP available to date. A fertility reducing action is suspected because of the structural relationship to di-n-pentyl phthalate and dibutylphthalate and the findings available for these substances. The monoesters of phthalic acid esters of medium chain length (C4 – C6) cause damage to the germinal epithelium in the testis. Sertoli cells in the seminiferous tubules are the primary site of attack. They exhibit considerable vacuolization of the smooth endoplasmatic reticulum resulting in a reduced fertility. As a consequence the germinal epithelium may be lost. (ECBI/65/00 Add2).

No further information has been identified.

6.1.4 DPHP

The following data is available in the registrations dossier for DPHP (ECHA, 2013):

- The registration dossier reports results from a study of excretion following oral administration of DPHP in a healthy 63 year old male human volunteer. After a single oral application DPHP was hydrolysed to the respective monoester, which underwent further metabolic changes. 34 % of the applied dose was excreted in the urine, most of it as secondary metabolites. Only a minute amount of the applied dose was excreted in the form of the monoester (less than 1 %). It is noted that most of the metabolites were excreted within the first 24 hours after the dosing.
- LD50, oral in rat: >5000 mg/kg bw
- LC50: >5 mg/L air (4 hours). Clinical signs: Immediately after exposure the animals were wet, ruffled, agitated and raspy sounding. After 24 hours they appeared normal.
- LD50, dermal in rabbit: >2000 mg/kg bw. Clinical signs: There were no unusual behavioural signs noted.
- Not irritating to skin in rabbits according to EPA OPPTS 870.2500 (Acute Dermal Irritation)
- Non irritating to rabbit eyes according to OECD Guideline 405 (Acute Eye Irritation / Corrosion)
- Not sensitising in guinea pigs according to modified Buehler-test with 10 inductions
- Not sensitising in QSAR calculation

- The NOAEL in a repeated dose toxicity test in rats was established at 39 mg/kg bw/day based on effects on liver weight (peroxisomal proliferation) according to OECD Guideline 408 (Repeated Dose 90-Day Oral Toxicity in Rodents)
- Negative in chromosome aberration test according to OECD Guideline 473 (*In vitro* Mammalian Chromosome Aberration Test)
- Negative in Mutagenicity - Reverse Mutation Test Using Bacteria (s. typhimurium) with and without metabolic activation according to OECD Guideline 471 (Bacterial Reverse Mutation Assay)
- Negative in Chinese Hamster Ovary (CHO) cell gene mutation assay according to OECD Guideline 476 (In vitro Mammalian Cell Gene Mutation Test)
- A NOAEL of 8000 ppm (479.2 mg/kg bw/day (males); 619.6 mg/kg bw/day (females)) was established in a supporting carcinogenicity study based on organ weight and histopathology.
- Read-across from other high molecular weight (HMW) structural analogues (DINP/DIDP/DEHP/Di-C11 PE).The members of this category did not show potential for producing genetic effects. Liver tumours induced by peroxisome proliferation in rodents by HMW phthalate esters are not considered relevant in humans (ref. to SIDS, 2004).
- A NOAEL of 40 mg/kg bw/day (general systemic toxicity) was established in a Two-Generation Reproduction Toxicity Study in the rat according to OECD Guideline 416 based on peroxisome proliferation in the liver, bones, kidneys and thyroid; body weight; food consumption and compound intake. NOAEL for fertility was established at 600 mg/kg bw/day in parental and F1 animals based on overall effects; organ weights; histopathology; mating index; and fertility index. NOAEL in F1 and F2 animals was established at 200 mg/kg bw/day based on decreased pup body weights/pup weight gain. In conclusion DPHP did not influence fertility or reproductive parameters in parental animals and offspring.
- A NOAEL of 200 mg/kg bw/day for embryotoxicity, foetotoxicity and maternal toxicity was established in a developmental toxicity study in rats according to OECD Guideline 414 (Prenatal Developmental Toxicity Study). The NOAEL for teratogenicity was established at 1000 mg/kg bw/day. In a similar study with less animals the NOAEL for embryotoxicity, foetotoxicity, maternal toxicity and teratogenicity was established at the highest dose of 1000 mg/kg bw/day.

The Unites States Consumer Product Safety Commission (USCSPC, 2010) has assessed the potential health effects on consumers under the risk-based Hazardous Substances Act (FHSA) based on very much the same information as in the publicly available registration information for acute, repeat dose and reproductive and prenatal, perinatal, and post-natal toxicity. The overall conclusion was that *an insufficient amount of animal data and poorly described methodologies in studies using DPHP as a test substance supported the conclusion that there was* "insufficient evidence" for the designation of DPHP as a "hepatotoxicant", "adrenal toxicant", reproductive toxicant" and "developmental toxicant". No ADI was estimated for the general population or for other sensitive sub-populations because of lack of confirmatory data.

6.1.5 DMEP

No REACH registration dossier is available for DMEP.

Kinetics and metabolism

There is limited information about the toxicokinetics of DMEP. Studies in pregnant rats have shown that DMEP is hydrolysed to MMEP (mono-2-methoxyethyl phthalate) and 2-ME (2-methoxyethanol). 2-ME is further oxidised to MMA (methoxyacetic acid). DMEP injected intravenously is rapidly transferred across the placenta into the foetus which has little or no ability to hydrolyse DMEP to the monoester (NICNAS, 2008).

Based on an in vitro assay, DMEP is predicted to absorb very slowly into human skin, with a steady state absorption rate of 8 µg/cm2 /hour (USCPSC, 2011).

Acute toxicity
DMEP has low acute, dermal and inhalational toxicity. The oral LD50 in rats was reported to be 3200 – 6400 mg/kg bw (NICNAS, 2008). The dermal LD50 was > 11,710 mg/kg bw in guinea pigs (Environment Canada, 2009). LC50 (6 h) in rats was reported at > 770-1595 ppm (NICNAS, 2008).

Irritation
Based on a study in guinea pigs, where DMEP caused slight skin irritation when applied to depilated guinea pig abdomen under occlusive wrap for 24 hours, it was concluded that DMEP caused minimal skin irritation in guinea pigs. The same conclusion was made regarding eye irritation based on studies where DMEP was applied to rabbits eyes (NICNAS, 2008). No data regarding respiratory irritation have been identified. Due to DMEPs very low vapour pressure respiratory irritation is not expected.

Sensitisation
DMEP did not elicit a positive response when administered to ten guinea pigs using a standardised sensitisation procedure, but without further details of the test conditions (NICNAS, 2008)

Repeated dose toxicity
In subchronic repeated dose studies, DMEP caused decreases in absolute and relative thymus and testes weight with histological evidence of testes atrophy in rats (1000 mg/kg bw/day, gavage) and decreased relative testes weight in mice (250 mg/kg bw/day, intraperitoneal). In a rat 16-day gavage study, a LOAEL of 100 mg/kg bw/day was established based on decreases in haemoglobin and haematocrit values. No NOAEL could be established (NICNAS, 2008).

Genotoxicity
DMEP did not cause a significant increase in reverse histidine mutations in the presence of metabolic activation when treated in the *in vitro* Ames reverse mutation assay in *Salmonella typhimurium* strains ester strains TA98 and TA100 at concentrations up to 10,000 µg/plate with and without metabolic activation. With no activation, positive results were obtained in strain TA98 (US CPSC, 2011).

The genotoxicity of DMEP was also assessed in the *in vivo* dominant lethal assay. The high dose of DMEP statistically reduced the incidence of pregnancies and the number of implants per pregnancy compared to the control group, indicating a dominant lethal effect at this dose of 2785 mg/kg bw (US CSPC; 2011).

Chronic toxicity / carcinogenicity
A five-generation oral study with very limited study details did not reveal any chronic effects induced by DMEP in rats. The actual dosage was not stated and the dose was therefore estimated based on the assumption that DMEP was applied to rats in diet and administered up to 900 mg/kg diet per day (45 mg/kg bw per day). No signs of reproductive toxicity or carcinogenicity were observed in this old study from 1968 (Environment Canada, 2009). Carcinogenicity relevant for humans has also not been recognized for 2-ME (2-Methoxyetahnol) or other glycol ethers Although some phthalates induced various tumours in experimental animals, the relevance of these data to DMEP carcinogenicity and to humans is unclear (Environment Canada, 2011).

Reproductive toxicity
DMEP is subject to harmonised classification as toxic to reproduction in category 1B.

A NOAEL of 100 mg/kg for reproductive organ toxicity was established from an oral repeat dose study in rats based on decrease in testes weight at 1000 mg/kg bw/d. However, no reproductive toxicity studies were performed according to OECD guidelines (NICNAS, 2008).
There were no developmental studies following oral or inhalation administration of DMEP. Intraperitoneal injection induced marked embryotoxic, fetotoxic and teratogenic effects at doses above 1.03 mmol/kg (estimated 291 mg/kg bw). A NOAEL could not be established due to teratogenic effects at the lowest dose. The effects on the dams were unreported. Both 2-ME and MAA induced malformations, principally skeletal, in developmental studies. Overall, from available studies, it is anticipated that DMEP may cause fertility and developmental effects (Cited from NICNAS, 2008).

Endocrine disruption
In relation to the current re-assessment of the safety aspects of phthalates, e.g. DEHP, used in medical devices by the Scientific Committee on Emerging and Newly Identified Health Risks (SCENIHR) the Danish Ministry of Health has in 2012, encouraged the European Commission to consider having the SCENIHR study include an additional five phthalates suspected of having endocrine disrupting effects, including DMEP. The re-assessment is expected to be finalised early 2014 (Danish EPA, 2013).

No further information on endocrine disruption has been identified.

6.1.6 DINP and DIDP

DINP and DIDP are more extensively reviewed than the other selected phthalates for this study. In August 2013 ECHA issued a final review report with an Evaluation of new scientific evidence concerning DINP and DIDP in relation to entry 52 of Annex XVII to REACH Regulation (EC) No 1907/2006 (ECHA, 2013). Conclusions from this review are presented in the following (references included in the cited sections belong to the ECHA review).

Kinetics
Based on read-across from DEHP, it is assumed that humans orally absorb DINP and DIDP 100%. The oral absorption in adult rats was estimated to be in the order of 50-55%.

A bioavailability factor of 75% for inhalation can be assumed for adults and 100% for newborns and infants as a vulnerable subpopulation.

Based on a study with DEHP (Deisinger et al. 1998), and the assumption that DINP and DIDP are 10 times less absorbed through the skin than DEHP (Elsisi et al. 1989), a dermal absorption rate of 0.024 µg/cm2/h can be assumed.

Acute toxicity
Conclusions from the EU risk assessments are still considered valid:
DINP: "Most of the animal studies on acute toxicity were either not available for detailed study or performed prior to establishment of OECD or EU guidelines. However given the consistency of the results for oral, dermal and inhalation exposure, it can be considered that DINP has a low acute oral, dermal and inhalation toxicity. No LD50/LC50 was reported from acute exposure by those routes of exposure. Findings consisted of poor state, respiratory difficulties (laboured respiration, dyspnea) and alteretered appearance, following oral administration, even at very high level (up to 40,000 mg/kg). Acute inhalation studies, although poorly documented, did not report any body weight changes, any gross lesions or microscopic alterations of lungs, only slight tearing of the eye and slight clear nasal discharge following aerosol exposure of 4.4 mg/l of air during four hours. Therefore, no classification is indicated according to the EU criteria for acute toxicity." (EC 2003a).

DIDP: "Most of the animal studies on acute toxicity were either not available as detailed studies or performed prior to establishment of OECD or EU guidelines. However in view of the consistency of the results for all routes of exposure, it can be considered that DIDP has a low acute oral, dermal and inhalation toxicity. No classification is indicated according to the EU criteria for acute toxicity whatever the route of exposure." (EC 2003b)

Irritation and corrosivity
Conclusions from the EU risk assessments are still considered valid:

DINP: "On the whole, DINP may be considered as a very slight skin and eyes irritant, with effects reversible in short time. Thus no classification is indicated according to the EU criteria for those different end points." (EC, 2003a)

DIDP: "Results from animal studies following single skin exposure varying from 5 minutes to 24 hours lead to no or moderate effect, reversible with possible desquamation. Effects on eyes are weak and limited to conjunctiva. There is no indication of upper airways irritation in animal. In humans there is no indication of an irritating potential. Thus no classificationis indicated according to the EU criteria for those different end points." (EC 2003b).

Sensitisation - DINP and DIDP
In general, phthalates (including DINP and DIDP) lack intrinsic sensitising potential. However, both DINP and DIDP share at least some of the adjuvant properties demonstrated for phthalates and an effect on atopic responses in humans cannot be excluded. An association has been shown between exposure to phthalates and asthma and allergic disease in epidemiological studies. However, a causal relationship remains to be established.

Repeated dose toxicity - DINP
A NOAEL of 15 mg/kg bw/day with a LOAEL of 152 mg/kg bw/day (Exxon 1986) and a NOAEL of 88 mg/kg/day with a LOAEL of 359 mg/kg bw/day (Aristech 1994) were identified in the two key repeated dose toxicity studies based on statistically significant increases of incidence of spongiosis hepatis together with other signs of hepatotoxicity.

As a result of the methodological difference (amount of examined liver sections), the Exxon (1986) study was considered the most appropriate to use. Thus a NOAEL of 15 mg/kg bw/day was selected for repeated dose toxicity of DINP. This conclusion was supported by RAC (ECHA 2013a). RAC however noted that the NAEL could be higher given the large dose spacing in the Exxon study.

Repeated dose toxicity - DIDP
Subchronic studies in respectively the dog (Hazleton 1968b) and rat (BASF 1969) were available. From the rat study, a NOAEL of 60 mg/kg bw/day can be assumed based on dose-related increase of relative liver weights in females. A NOAEL of 15 mg/kg bw/day can be derived for the study in dog on the basis of hepatic effects. However, the large limitations of the study need to be emphasised.

In a new 2-year rodent carcinogenicity study by Cho et al. (2008, 2010) a LOAEL of 22 mg/kg bw/day based on spongiosis hepatis in a 2-year study in rat could be derived. However, there are some questions related to the reliability of these findings.

In line with the opinion of RAC (ECHA 2013a,b), a weight of evidence approach was used for DNEL calculation on the basis of a LOAEL of 22 mg/kg bw/day (Cho et al. 2008, 2010), a NOAEL of 15 mg/kg bw/day (Hazleton 1968b) and a NOAEL 60 mg/kg bw/day (BASF 1969b).

Mutagenicity
Conclusions from the EU risk assessments are still considered valid:

"DINP is not mutagenic in vitro in bacterial mutation assays or mammalian gene mutation assay (with and without metabolic activation) and is not clastogenic in one cytogenetic assay in vitro on CHO cells and in one in vivo assay on bone marrow cell of Fisher 344 rats. This suggests that DINP is not genotoxic in vivo or in vitro." (EC 2003a)

"DIDP is not mutagenic in vitro in bacterial mutation assays (with and without metabolic activation) and is negative in a mouse lymphoma assay. It is not clastogenic in a mouse micronucleus assay in vivo. This indicates that DIDP is a non-genotoxic agent." (EC 2003b)

Carcinogenicity – DINP
The renal tumors seen in rats are assumed to stem from an alpha-2u-globulin mode of action which is not considered to be relevant for humans.

Liver neoplasia were seen in rats and mice with a NOAEL of 112 mg/kg bw/day. It is believed that peroxisome proliferation is the underlying mode of action for development of liver tumors with DINP, and that PPARα[3] is involved in hepatic tumour formation. However, the more recent literature indicates that the mechanisms of liver carcinogenicity in rodents with peroxisome proliferators have not entirely been elucidated and that multiple pathways seem to exist. Some of those pathways seem to be PPARα-independent, which might indicate a need for some caution when interpreting the relevance of rodent carcinogenicity with DINP to humans.

The increased incidences in MNCL (mononuclear cell leukemia) seen in rats with a NOAEL of 15 mg/kg bw/day might have a human counterpart. The available information does not allow to draw definite conclusions on the relevance of the findings. As MNCL is likely to follow a threshold mode of action with a NOAEL equal to that for repeated dose toxicity, the finding would not be a driver for the risk assessment. Therefore, the endpoint is not taken further to the risk characterisation step.

Carcinogenicity – DIDP
*Although no treatment-related tumours were observed in a 2-year carcinogenicity study with rats, DIDP has been shown to induce liver adenomas in a 26-week study in rasH2 mice (NOAEL of 0.33% in feed, estimated to correspond to approximately 500 mg/kg bw/day). It is assumed that the increased incidence of liver adenomas in mice is related to peroxisome proliferation, and that PPARα is involved in hepatic tumour formation. However, the more recent literature indicates that the mechanisms of liver carcinogenicity in rodents with peroxisome proliferators have not entirely been elucidated and that multiple pathways seem
to exist. Some of those pathways seem to be PPARα-independ nt, which might indicate a need for some caution when interpreting the relevance of rodent carcinogenicity with DINP to humans.*

The increased incidences in MNCL seen in a 2-year carcinogenicity study with rats (NOAEL of 110 mg/kg bw/day) might have a human counterpart. The available information does not allow to draw definite conclusions on the relevance of the findings. As MNCL is likely to follow a threshold mode of action with a NOAEL well above that for repeated dose toxicity, the finding would not be a driver for the risk assessment. Therefore, the endpoint is not taken further to the risk characterisation step.

[3] PPAR = peroxisome proliferator activated receptor

Reproductive toxicity- DINP

Decreases foetal testicular testosterone concentration during critical time window of masculinisation and increased incidence of multinucleated gonocytes and Leydig cell aggregates were observed with a NOAEL of 50 mg/kg bw/day. In a two-generation reproductive toxicity study the offspring bodyweight was decreased with a LOAEL of 159 mg/kg bw/day (no NOAEL) and increased skeletal variations were observed in a prenatal developmental toxicity study with a NOAEL of 100 mg/kg bw/day. The in vivo findings indicate that DINP has anti-androgenic potency but may also exhibit its effects through other modes of action.

Effects on fertility occur at higher dose levels, with a NOAEL for decreased live birth and survival indices of 622 mg/kg bw/day and a NOAEL of 276 mg/kg bw/day for decreased testicular weights.

Reproductive toxicity - DIDP

The most critical reproductive effect for DIDP is the decreased survival of F2 pups observed in both two-generation reproductive toxicity studies with rats, leading to a NOAEL of 33 mg/kg bw/day. A NOAEL of 40 mg/kg bw/day can be derived for foetal variations from prenatal developmental toxicity studies.

DIDP did not induce substantial anti-androgenic activity in available studies; in particular it did not reduce foetal testicular T levels or affect gene expression levels related to masculinisation during critical time window during development. DIDP seems to have a partly different spectrum and/or potency of toxicological properties than several other phthalates, such as DINP, DEHP and DBP.

Other effects on fertility occurred at higher doses with a NOAEL of 427 mg/kg bw/day (0.8% dietary level) based on a two-generation reproductive toxicity study.

Endocrine disruption

The ECHA review concludes regarding estrogenic activity that DIDP and DINP do not seem to be active. It is however noted that certain phthalates, such as DEHP, have suggested affecting also female reproductive health but as whole the effects of phthalates on reproduction in females have been studied much less than in males (ECHA, 2013).

The ECHA review also emphasises that for both males and females, other relevant human health endpoints concerning endocrine disruption such as developmental neurotoxicity, thyroid system, arylhydrocarbon receptor signalling and obesity have not been clearly associated with phthalate exposure according to other recent reviews.

According to the Danish Phthalate Strategy (Danish EPA, 2013) Denmark will in 2013 assess whether the evidence of endocrine disrupting effects observed at high doses of DINP provides a basis for a harmonised classification or other measures (Danish EPA, 2013).

6.2 Human exposure

Humans are potentially exposed to phthalates through ingestion, inhalation, and dermal contact. Quantification of the exposure can be based on indirect methods where the exposure is based on estimations of the concentration of phthalates in different sources (air, soil, diet, articles, etc.) or direct methods based on results from biomonitoring studies of relevant biomarkers.

According to Clark *et al.* (2011), the indirect and biomarker methods generally are in agreement within an order of magnitude and discrepancies are explained by difficulties in accounting for use of consumer products, uncertainty concerning absorption, regional differences, and temporal changes. No single method is preferred for estimating intake of all phthalate esters. It is suggested that biomarker estimates be used for low molecular weight phthalates for which it is difficult to quantify all sources of exposure and either indirect or biomarker methods be used for higher molecular weight phthalates. The indirect methods are useful in identifying sources of exposure while the biomarker methods quantify exposure (Clark *et al.*, 2011).

For the selected phthalates, most data are available for DINP, DIDP and DEP. As DMEP is not on the market in Europe exposure is expected to be related to imported articles only.

6.2.1 Direct exposure pathways

Based on the identified uses in Denmark for the selected phthalates, possible direct exposures are suggested in Table 39.

TABLE 39
OVERVIEW OF POSSIBLE DIRECT EXPOSURE FROM THE SELECTED PHTHALATES IN DENMARK

Phthalate	Consumers		Working environment	
	Route	Source	Route	Source
DINP	Dermal, ingestion, inhalation (dust)	Various flexible PVC products indoors and outdoors (by touch, ingestion of foods packed or kept in plasticised food contact plastics	Dermal, inhalation (dust, aerosols)	Various flexible PVC products indoors and outdoors, sealants and paints (by application and other handling)
DIDP	Dermal, inhalation (dust)	Wire and cable, tarpaulins (at application and other handling)	Dermal, inhalation (dust, aerosols)	Wire and cable, tarpaulins, roof membranes, geo-membranes, sealants, paints (by application and other handling)
DPHP	do	do	do	do
DEP	Dermal, ingestion, inhalation (aerosols)	Cosmetics and personal care products (+others?); at personal use or indirectly at contact with persons using them	Dermal, ingestion, inhalation aerosols	Cosmetics and personal care products (+others?) from personal use or indirectly by contact with persons using them
DIPP	-	-	Dermal	Explosives?
DMEP	-	-	-	-

Legend: - : Exposure deemed absent or marginal; ?: Uncertain, cannot be ruled out completely;

The Danish eight-hour average occupational exposure limits for DEP, DINP (CAS No. 28553-12-0) and DIDP (CAS No. 26761-40-0) are 3 mg/m3 workplace air.

6.2.2 Indirect exposure pathways

Based on the identified uses in Denmark for the selected phthalates, possible indirect exposures are suggested in Table 40 based on general background knowledge.

TABLE 40
OVERVIEW OF POSSIBLE INDIRECT EXPOSURE FROM THE SELECTED PHTHALATES IN DENMARK

Phthalate	Indoor climate	Via external environment				Remarks
		Food and drink	Air	Soil	Water	
DINP	X	X	-	-	-	Various product uses (via evaporation + dust)
DIDP	X	-	-	-	-	Wire and cable (via evaporation + dust)
DPHP	x	-	-	-	-	Wire and cable (via evaporation + dust)
DEP	x	-	-	-	-	Cosmetics and personal care products (via evaporation + dust)
DIPP	-	-	-	-	-	Use may be limited to some explosives and some ammunition charges; no data indicating significant environmental concentrations were found
DMEP	?	?	-	-	-	May be contained in imported articles, but exposure is expected to be limited; no data indicating significant environmental concentrations were found

Legend: X : Possible exposure; x: possible exposure, but likely smaller relatively; ?: Uncertain, cannot be ruled out completely; - : Exposure deemed absent or marginal.

Indirect exposure of vulnerable groups to DINP considering Danish exposure situations are estimated in two recent projects from the Danish EPA.

In a survey and health assessment of the exposure of 2-year-olds to chemical substances in consumer products (Danish EPA, 2009) the contribution from foods is estimated at a maximum of 10 µg/kg bw/day of DINP and the contribution to ingestion of DINP from the indoor climate (dust and air) is estimated at 0.0003 µg/kg bw/day (worst case/winter scenario based on ingestion of 100 mg dust).

In a project on exposure of pregnant consumers to suspected endocrine disruptors (Danish EPA, 2012) the exposure of women in the child-bearing age to a number of suspected endocrine disruptors including DINP was investigated. The total, maximum exposure from consumer products, indoor environment and food was estimated at 2.2042 µg/kg bw/day.

No data specific for Danish conditions on the other selected phthalates were identified.

DMEP is not registered for use in Europe but may be imported in articles containing e.g. cellulose acetate lamination films. The Annex XV dossier for DMEP (BAUA, 2011) includes a reference to recent Austrian unpublished results where DMEP was analysed in 10 products and 10 house dust samples (commercial and private) and was not detected above the detection level of 0.04 mg/kg. DMEP has been detected in an older German study conducted in 65 apartments in Hamburg, Germany between 1998 and 2000 and analysing indoor dust (<63 µm) collected from vacuum cleaner bags. DMEP was detected in 49 samples in concentrations up to 17 mg/kg (50th percentile = 2 mg/kg; 95th percentile = 8 mg/kg) and it was speculated that the phthalates originated from use of consumer products.

6.3 Bio-monitoring data

For phthalates most biomonitoring studies used for estimation of exposure have investigated levels of metabolites in urine and to a much lesser extent levels in blood and breast milk. Although parent phthalates can be detected in blood, fast cleavage of the first ester bond by serum esterase, results in a very short half-life, which makes the parent compound unsuitable as a biomarker (ECHA, 2013). Urinary concentrations in nursing mothers are not considered useful for estimating exposure to phthalates through milk ingestion by breast-fed infants (Högberg *et al.*, 2008)

Danish biomonitoring data specifically relevant for the phthalates selected for this study have been identified for DINP and DEP.

DINP and DIDP

Danish biomonitoring data are available for DINP. Estimated DINP intakes (µg/kg bw/day) based on urinary metabolite data from Denmark are shown in Table 41. Exposures calculated from 24 hour samples are based on the urinary metabolite concentration (µmol/l). In the case of exposures calculated from spot urine samples the urinary metabolite concentration is normalised against creatinine or urinary volume references in order to estimate the daily excretions.

TABLE 41
ESTIMATED DINP INTAKES (µG/KG BW/DAY) BASED ON URINARY METABOLITE DATA FROM DENMARK (ECHA, 2013)

Country	No. of subjects	Age (y)	year	Intake µg/kg bw/day		Basis of estimated intake
				50th percentile	95th percentile (max)	
DK N=129	25 26 14 24 29 11	Boys 6-10 11-16 17-21 Girls 6-10 11-16 17-21	2006-2008	2.04 1.42 1.52 1.93 1.53 1.01	9.02 (9.88) 5.26 (5.36) N.R. (3.63) 10.4 (11.9) 6.99 (7.96) N.R. (2.49)	24 hour urine samples Based on urine levels of MiNP, MHiNP, MOiNP and MCiOP intake based on fractions of dose excreted in urine in adult volunteer experiment (Anderson *et al.* 2011) using child specific model (Koch, 2007; Wittassek *et al.* 2007)
DK	60	18-26	2006	1.26	3.48	Spot samples Based on urine levels of MiNP, MHiNP, MOiNP and MCiOP Calculation by Kransler *et al.* (2012)
DK	250 girls 250 boys	4-9 4-9	2006-7	2.13 2.25	3.03 3.41	Spot samples Based on urine levels of MiNP, MHiNP, MOiNP and MCiOP Fractional urinary excretion values from Anderson *et al.* (2011) Calculation by Kransler *et al.* (2012)

N.R. = not reported

The estimated median adult exposure in Denmark is around 1.3 µg/kg bw/day and 95th percentile intakes estimated at around 3.4 µg/kg bw/day. As shown in Table 41 the estimated exposure results for DINP indicate a decrease in exposure with an increase in age, assumed to be a result of higher dust and food intakes combined with lower body weights (ECHA, 2013). Differences in study approach and methodology result in significant variability between studies and this makes comparison of the outcome from different EU countries more difficult. According to ECHA (2013), there are no biomonitoring data for children under three years of age. Due to the restriction of the use of phthalates in toys, such monitoring data would not reflect exposure from toys and childcare articles which can be placed in the mouth, but could be indicative of exposure from other sources.

Similar data for estimated DIDP exposure in Denmark have not been identified. Estimations based on data from other countries indicate a lower intake of DIDP compared to DINP (ECHA, 2013).

In a newly published study with results from human biomonitoring on a European scale, all 17 participating countries analysed 4 human biomarkers including metabolites of some phthalates in urine. DINP was part of the study. Samples were taken from children aged 6-11 years and their mothers aged 45 years and under. Results of urinary metabolites of DEP, DINP and DIDP measured in Danish mother-child pairs are shown in Table 42 (Frederiksen *et al.*, 2013). The results showed higher levels in children compared to mothers, with the exception of MEP, a metabolite of DEP, which is not regulated and is mainly used in cosmetics. A possible explanation for the generally higher levels in children is children's relatively higher intake: they are more exposed to dust, playing nearer the ground, and have more frequent hand-to-mouth contact; and they eat more than adults in relation to their weight. Consumption of convenience food, use of personal care products and indoor exposure to vinyl floors and wallpaper have all been linked to higher phthalate levels in urine (DEMOCOPHES, 2013; Frederiksen *et al.*, 2013).

TABLE 42
UNIRARY PHTHALATE METABOLITES IN DANISH MOTHER-CHILD PAIRS (FREDERIKSEN *ET AL.*, 2013)

Diester phthalate	Phthalate metabolite	Limit of detection	Mother (n=145)			Child (n=143)		
		LOD	Mean	50th percen-tile	95th percen-tile	Mean	50th percen-tile	95th percen-tile
Concentration (ng/ml)								
DEP	MEP	0.53	74	29	359	28	20	68
DINP	MiNP	0.61	0.30		1.9	0.88		3.2
	HMiNP	0.26	5.3	2.7	19	123	5.0	38
	MOiNP	0.25	2.9	1.4	13	7.2	2.6	17
	MCiOP	0.11	9.8	6.2	35	22	7.8	46
	∑DiNPm		24	13	100	58	20	111
DIDP	MiDP	0.69	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Creatine adjusted concentration (µg/g crea)								
DEP	MEP		64	29	*298*	28	19	93
DINP	MiNP		0.3		1.6	0.91		2.7
	HMiNP		5.1	2.6	17	14	5.0	28
	MOiNP		2.7	1.3	9.9	7.6	2.7	14
	MCiOP		9.9	5.2	37	24	8.2	7
	∑DiNPm		24	12	81	61	22	102

The study also concludes that the sum of DEHP-metabolites in Danish children participating in the study was lower than the average adjusted for urinary creatinine, age and gender for the 17 involved EU countries.

DEP

A recent study has investigated children's phthalate intakes (DEP, DnBP, DiBP, BBzP and DEHP) and resultant cumulative exposures estimated from urine compared with estimates from dust ingestion, inhalation and dermal absorption in their homes and daycare centers. Based on the results, it was concluded that the exposure to the low-molecular-weight phthalates such as DEP (and DnBP and DiBP) occurring indoors via dust ingestion, inhalation and dermal absorption can meaningfully contribute to the total intake of these substances. Dermal absorption and inhalation appear to be the most important routes of environmental exposure for these chemicals. None of the children had intakes that exceeded the TDI of 500 mg/kg bw for DEP taken from a statement on dietary exposure to phthalates by the independent Committee on Toxicity of Chemicals in Food, Consumer Products and Environment in the UK[4] (Bekö *et al.*, 2013). The study involved dust samples collected between March and May 2008 from the homes of 500 children and from the 151 day care centers in a major city in Denmark. Morning urine samples from 441 children were collected between August 2008 and April 2009.

Several biomarker studies from different parts of the world report on phthalate ester metabolites in urine and present estimates of daily intake based on these results. In a study estimating the range of adult intake of DEP based on both the biomarker method and a scenario-based approach (indirect), and results from USA, Japan, Taiwan and Europe, the daily intake estimated from urinary metabolites was in the range of 0.77 to 12.3 µg/kg/day with a median value of 5.5 µg/kg/day (Clark *et al.*, 2011). Most data were retrieved from the US National Health and Nutrition Examination Survey with data on urinary metabolites obtained from 2001-2002 (Clark *et al.*, 2011). The adult daily intakes based on indirect studies were reported at (Clark *et al.*, 2011):

- 0.007 - 0.13 µg/kg/day from the diet only,
- 0.051 – 0.46 µg/kg/day from diet, air and dust, and
- 4.27 µg/kg/day from diet, air, dust and consumer products excluding personal care products

These figures indicate that the major contribution of DEP is from consumer products. It should however be noted, that most data for individual foods are more than 20 years old. Based on the biomarker data, intake of DEP is highest in the USA, followed by Germany, Taiwan, and Japan. This difference between regions is also apparent in the measured concentrations of DEP in indoor air; in the USA, the average concentration is approximately two times the average concentration in Europe and six times the average concentration in Japan (Clark *et al.*, 2011).

DEP has been measured in human milk in a study investigating phthalate diesters and their metabolites in human breast milk, blood or serum, and urine as biomarkers of exposure in vulnerable populations in a small study population in Sweden (Högberg *et al.*, 2007). Identified phthalate diesters and metabolites in milk and blood or serum, were present at concentrations close to the limit of detection. Most phthalate metabolites were detectable in urine at concentrations comparable to results from the United States and Germany. No correlations could be established between urine concentrations and those found in milk or blood/serum for single phthalate metabolites. Data from the study were comparable with previous results showing comparatively high concentrations of phthalate metabolites in Finnish and Danish mothers' milk. The concentrations of DEP in milk was measured in the range of 0.22 – 1.45 ng/ml with a mean value of 0.30 ng/ml. It is concluded that concentrations of phthalate metabolites in urine are more informative than those in milk or serum, but urine metabolite estimates are not suitable to estimate exposure to phthalates through milk ingestion by breast-fed infants.

[4] http://cot.food.gov.uk/

DIPP and DPHP
Specific biomonitoring data for DIPP and DPHP have not been identified.

6.4 Human health impact

DEP
The Scientific Committee on Consumer Products (SCCP) has re-evaluated its opinion from 2002 on the safe use of DEP in cosmetics in 2006 and found no reason to update the opinion. It is concluded that DEP may be used as fragrance solvent at a maximum concentration of 50% (hypothetical usage volume of 1 ml). This results in a potential exposure of 28 mg/day giving a Margin of Safety (MoS) of 321 or as an ethanol denaturant at a maximum concentration of 1% (hypothetical usage volume of 10 ml), resulting in a potential exposure of 5.6 mg/day giving a MoS of 1607. The worst case MOS calculation made by the Scientific Committee on Cosmetics Products and Non-Food Products intended for Consumers (SCCNFP) for all cosmetics was 161, assuming 10% of diethyl phthalate in all cosmetic products (SCCP, 2006).

DINP/DIDP
Risk assessment is carried out for DINP and DIDP in the ECHA review.

The overall conclusions from the ECHA review regarding the risk from DIDP and DINP are as follows: ECHA concluded that a risk from the mouthing of toys and childcare articles with DINP and DIDP cannot be excluded if the existing restriction were lifted. No further risks were identified. These conclusions were supported by ECHA's Committee for Risk Assessment. Based on the risk assessment in this report, it can be concluded that there is no evidence that would justify a re-examination of the existing restriction on DINP and DIDP in toys and childcare articles which can be placed in the mouth by children (restriction entry 52 in Annex XVII to REACH).

For children the reasonable worst case RCRs ranging from 1.3 to 2.0 indicate a risk of liver toxicity for children of 0-18 months old from mouthing toys and childcare articles containing DINP or DIDP. Thus, it is concluded that a risk from the mouthing of toys and childcare articles with DINP and DIDP cannot be excluded if the existing restriction were lifted (i.e. in the scenario where DINP or DIDP would be present in toys and childcare articles). This conclusion was supported by RAC (ECHA 2013a,b).

For adult consumers RCRs of 0.4 in the reasonable worst case use of sex toys, it seems not likely that the use of sex toys with DINP or DIDP would result in a risk. This conclusion is subject to substantial uncertainties with regard to exposure duration and migration rates of the phthalates from sex toys.

Dermal exposure from for instance PVC garments is not anticipated to result in a risk for the adult population. Exposure from food and the indoor environment are not very significant in the adult population, which is confirmed by the available biomonitoring data.

Based on the risk assessment in this report, it can be concluded that no further risk management measures are needed to reduce the exposure of adults to DINP and DIDP.

In the survey and health assessment of the exposure of 2-year-olds to chemical substances in consumer products (Danish EPA, 2009) referred to in 6.2.2, the DNEL for DINP was calculated at 1.6 mg/kg BW/day (NOAEL/AF) based on a NOAEL of 276 mg/kg bw/day for antiandrogenic effects (reduced testicular weight in mice) and an assessment factor of 175. The combined daily ingestion of DINP from both direct and indirect exposure pathways, including exposure to toys which are no longer allowed to contain more than 0.05 %(w/w) DINP, resulted in total ingestion (95th percentile) of 31.23 µg/kg bw/day for the summer scenario and 37.54 µg/kg bw/day for the winter scenario and risk characterisation ratios (RCRs) of 0.020 and 0.023 respectively. The resulting RCRs indicates that DINP does not constitute a risk under the assumptions made in the report.

In the project on exposure of pregnant consumers to suspected endocrine disruptors (Danish EPA, 2012) referred to in 6.2.2 the $DNEL_{AA}$ (for substances mainly with antiandrogenic effect) of 1500 µg/kg bw/day based on a NOAEL of 300 mg/kg bw/day in a study showing reduced semen quality and increased nipple retention in male rats exposed during pregnancy and lactation was used to calculate a risk characterisation ratio of 0.0015. The resulting RCR indicated that DINP does not constitute a risk under the assumptions made.

No risk assessments have been identified for DIPP, DMEP and DPHP.

Combined risk assessment
The Danish EPA has used the concept of dose addition in a cumulative risk assessment in relation to the proposal for restrictions on four phthalates (Annex VX dossiers for DEHP, DBP, BBP, and DIBP) in 2012, and in relation to risk assessment of the total exposure of two-year-olds to chemical substances (Danish EPA, 2009) and in other projects addressing risk to vulnerable groups such as pregnant women. A study by Christen *et al.* (2012) demonstrates that concentration addition is an appropriate concept to account for mixture effects of antiandrogenic phthalates.

On the other hand, in the case of possible combination effects from exposure to e.g. anti-androgens and estrogens simultaneously, there is not sufficient information available.

The ECHA review of DINP and DIDP addresses the need for considering combined effects of phthalates with same mode of action in the risk assessment of the substances: *Based on the available information from in vitro studies, different phthalates seem to exhibit various effects – stimulatory, inhibitory or no effects – on certain endocrine parameters. Phthalates having the same mode of action or the same adverse outcome are likely candidates for combined risk assessment. However, the mode of action should always be carefully considered in selecting candidates for combined risk assessment.*

DINP has anti-androgenic properties and it could be appropriate to include this substance in a combined risk assessment of phthalates with anti-androgenic properties. DIDP, on the other hand, does not have similar properties/potency and it would not be justified to group DIDP in a combined risk assessment of phthalates on the basis of anti-androgenic properties.

There seem to be sufficient grounds to assess combined effects of DINP and DIDP (as well as DEHP and possibly other substances) on the basis of liver toxicity (spongiosis hepatis) (ECHA, 2013).

Cumulative risk assessment should also be considered in relation to the other selected phthalates. Although they are not all equivalent in terms of severity of their effects, e.g. the ability to cause adverse effects on the development of the male reproductive system should be considered.

6.5 Summary and conclusions

DIPP and DMEP are subject to harmonised health classification and both substances are classified for reproductive toxicity in Category 1 B. The four other phthalates selected for the study are self-classified by industry. No classification is suggested for DPHP and although much data is available for DEP, DINP, and DIDP, only few of the notifiers have self-classified these substances. The reasons provided by the notifiers not suggesting a classification of the substances are typically "data lacking" and "conclusive but not sufficient for classification". Denmark will in 2013 assess whether there is sufficient evidence of endocrine disrupting effects of DINP to provide a basis to support a harmonised classification or other measures.

The six phthalates are generally of low acute toxicity via all routes and with low the skin and eye irritation potential. There are case reports referring to skin sensitisation to plastic articles in patients with dermatitis, e.g. in relation to DEP, but in general phthalates are not considered sensitising. The main reason for concern in relation to phthalates and health hazards are adverse effects on the reproductive system of in particular male animals and endocrine disruption. Of the selected phthalates DEP has been evaluated against the proposed Danish criteria for endocrine disrupters as a suspected endocrine disrupter in category 2a.

No significant exposure to DMEP is expected as the substance is not registered for use in the EU. DEP has not been identified as an ingredient in cosmetic and personal care products in Denmark but may be imported from other countries.

Occupational exposure is primarily expected via dermal contact in relation to handling of flexible PVC products, formulation and use of sealants and paints, and contact with cosmetics and personal care products. Direct consumer exposure is expected from dermal contact with various flexible PVC products, wires and cables and in particular imported cosmetics and personal care products. Indirect exposure of consumers occurs in relation ingestion of food, and inhalation and ingestion of dust in the indoor climate.

In a newly published study with results from human biomonitoring on a European scale, all 17 participating countries analysed among others metabolites of DEP, DINP and DIDP, in urine. Samples were taken from children aged 6-11 years and their mothers aged 45 years and under. The results showed higher levels in children compared to mothers, with the exception of MEP, a metabolite of DEP, which is not regulated and is mainly used in cosmetics. A possible explanation is children's relatively higher intake: they are more exposed to dust, playing nearer the ground, and have more frequent hand-to-mouth contact; and they eat more than adults in relation to their weight. Consumption of convenience food, use of personal care products and indoor exposure to vinyl floors and wallpaper have all been linked to higher phthalate levels in urine.

DINP and DIDP have been reviewed by ECHA in relation to entry 52 in Annex XVII to REACH. It was concluded that a risk from the mouthing of toys and childcare articles with DINP and DIDP cannot be excluded if the existing restriction were lifted. No further risks were identified. These conclusions were supported by ECHA's Committee for Risk Assessment.

The ECHA review also addressed the need for considering combined effects of phthalates with same mode of action in the risk assessment of the substances. This is relevant e.g. in relation to antiandrogenic properties of DINP and in relation to liver toxicity (spongiosis hepatis) for DINP and DIDP but should be considered in genetal for substances with same endpoint and mode of action.

Data gaps

Data gaps or areas where an improved understanding would be useful are identified as follows based on the reviewed literature:

- Identification of the most important metabolites to be used as a biomarker for human exposures
- Further research addressing the cumulative exposure to multiple phthalates and other antiandrogenic and estrogenic substances seem to be warranted
- Limited information on endocrine specific end-points for some phthalates
- Better understanding of combination effects of antiandrogens at different levels

7. Information on alternatives

7.1 Alternatives to DINP, DIDP and DPHP use in PVC

Alternatives to the phthalates in flexible PVC can be grouped into two types:

- Alternative plasticisers for flexible PVC
- Alternative plastics with similar properties as flexible PVC.

Here, we primarily deal with alternative plasticisers, as they require the least adaption efforts by industry.

7.2 General features of plasticisers relevant in substitution efforts

When considering the possibilities for substitution of specific plasticisers, it is important to note that a vast number of organic substances can act as plasticisers in polymers. Contrary to many other substitution efforts, plasticising is not dependent on highly specific chemical bonding, but rather on a series of characteristics which the plasticiser must have to meet functional demands. Finding the good plasticiser is therefore not a distinct theoretical science, but rather an empiric process supported by a large number of measuring methods designed for this purpose.

To get an impression of the many possibilities for plasticising polymers, it has therefore been chosen to present extracts from an introduction given by Maag *et al.* (2010) to the basic functions of plasticisers:

"*We describe here the basics of external plasticisation of PVC, the major use of plasticisers. The word "external" denotes plasticisers that are not bound chemically in the polymer matrix, and can therefore migrate out of the polymer at certain conditions. Polymers can also be plasticised "internally" by incorporation of functional groups into the polymer itself, which imparts flexibility. Phthalates are external plasticisers, as are their direct substitutes, and external plasticisation is described in this section.*

PVC consists of long chains of the basic vinyl building block. The polymer is bound together in three dimensions by two overall types of forces. In some points the polymer is crystallised into a fixed geometric pattern with strong chemical bonds. In the rest of the polymer matrix, the polymer chains are somewhat more randomly organised and bound together by weaker forces based on attraction between polar parts of the polymer chain with different polarity. The ideal plasticiser works in these less strictly organised parts of the polymer.

In the hard polymer, the chains are packed closely together, also in the randomly organised parts, and the weak attraction forces bind the polymer together to a rigid structure with no flexibility. The (external) plasticiser has solvent capabilities and penetrates the less strongly bound parts of the polymer in the so-called swelling, where plasticiser and polymer resin is mixed. In the polymer, the plasticiser acts as a kind of sophisticated lubricant, as it creates distance between the freely organised polymer chain parts, and shields the attraction forces between polar parts of the chain, and thereby weakens the attraction between the chain parts. This allows for more free movement amongst the weakly bound chain parts, which means that the material becomes flexible.

The properties of the plasticiser have immense influence of how well it plasticises the polymer, and on the performance characteristics of the plasticised material. It is however important to understand that the plasticiser (with a few exceptions) does not form specific chemical bonds with the polymer, and there is therefore in principle a flexibility in which type and configuration of plasticisers that actually can be used to obtain the desired plasticising performance characteristics.

External plasticisers may be separated from the PVC matrix due to extraction by solvents, oils, water, surface rubbing, volatility, migration into adjacent media, or degradation mechanisms."

The key functional characteristics involved in plasticiser selection include:

- Solvency in the polymer resin (also called compatibility or miscibility)
- Efficiency (defined as the flexibility it gives in the polymer compared to DEHP)
- Volatility
- Diffusivity
- Low temperature performance

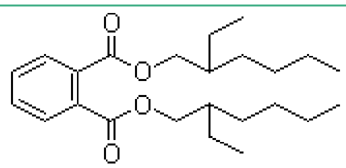
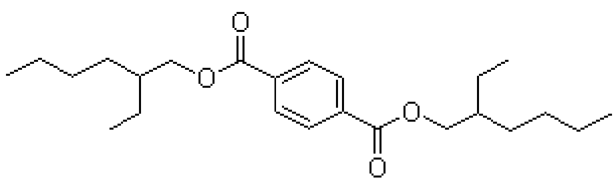
Structure of some plasticiser families

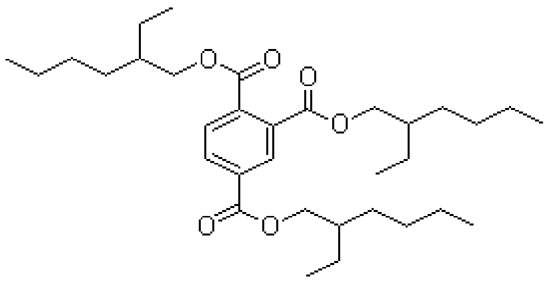
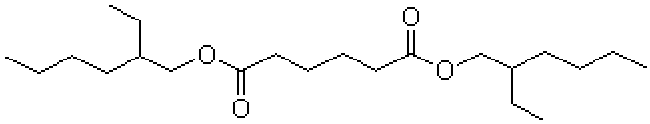
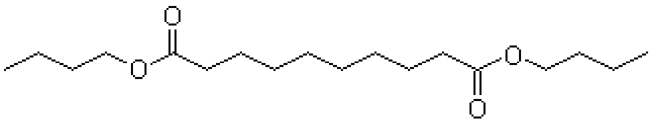
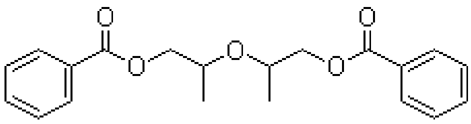
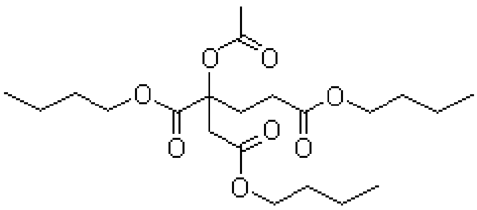
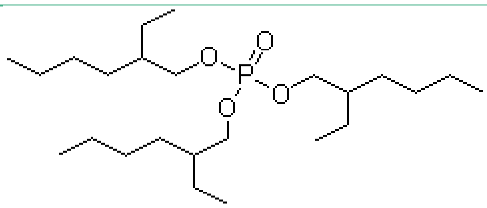
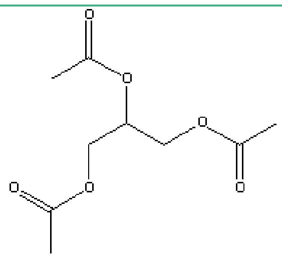
Many families of plasticisers are available. Most of them have however certain chemical functionalities in common with the phthalates family. This can be seen in Figure 3, which shows representatives of some different plasticiser families, of which several are relevant as plasticiser alternatives to the phthalates dealt with in this report. They are typically branched, quite "voluminous" molecules, with many oxygen bonds (= carbonyl groups). Many have benzyl rings or the hydrogenated counterpart, cyclohexane.

Many similar plasticisers have however distinctly different impacts on health and environment, and are therefore relevant alternatives to phthalates. This is probably primarily due to the fact that many types of interactions with biological systems are substance specific, and even structure-specific meaning that substances with identical chemical composition may work differently, if just a part of the molecule has shifted position from one place to another (as the case is for DEHP and DEHT).

The substance family of the plasticiser influences its performance significantly, but some functional groups in the molecules also influence the performance across families, and plasticisers can therefore to a certain extent be tailor-made to suit different performance needs. In addition, plasticisers can be mixed to achieve desired properties. For more information on the defining characteristics of plasticisers, see Maag *et al.* (2010).

FIGURE 3
CHEMICAL STRUCTURE OF REPRESENTATIVES OF DIFFERENT PLASTICISER FAMILIES (FROM MAAG *ET AL.* 2010).

Ortho-phthalates (Example: DEHP, DOP; di 2-ethylhexylphthalat)	
Terephthalates, (Example: DEHT, DOT DOTP; di 2-ethylhexyl terephthalate)	

Trimellitates (Example: TOTM; tri (2-ethylhexyl) trimellitate)	
Aliphatic dibasic esters, adipates (Example: DEHA, DOA = di (2-ethylhexyl) adipate)	
(DBS = Dibutyl sebacate)	
Benzoates (Example: DGD; dipropylene glycol dibenzoate)	
Citrates (Example: ATBC; acetyl tributyl citrate)	
Phosphates (Example: tri(2-ethylhexyl) phosphate)	
Glyceryl triacetate (GTA, Triacetin)	

7.3 Possible plasticiser alternatives to DINP, DIDP and DPHP in PVC

According to ECPI (2013), DPHP is often used as a phthalate alternative to DIDP because only minor compound changes are needed to adapt wire formulations for example to DPHP. It also matches DIDP performance in automotive applications.

It has not been possible to identify any studies specifically focussing on alternatives to DINP, DIDP and DPHP. Most available information on alternatives to primary plasticisers like DINP, DIDP and DPHP has therefore been reviewed based on results from the search for substitutes for the classic general plasticiser DEHP (to which DINP and to as lesser extend DIDP and DPHP are the key alternatives today).

Several studies of alternatives to the classified phthalates DEHP, DBP and BBP have been undertaken and some studies lists the DINP and DIDP together with other alternatives to the classified phthalates while other of the studies focus on non-phthalate alternatives. From the studies which include both DINP and DIDP and non-phthalate alternatives it is possible to extract some information which can indicate to what extent the non-phthalate alternatives can be considered alternatives to DINP, DIDP and DPHP. A closer analysis would however be needed as the properties of DINP, DIDP and DPHP are not exactly the same as those of DEHP. DINP, DIDP and DPHP are more expensive that DEHP, but also have some advantages for some applications, and experience with substitution of non-phthalate alternatives for DEHP does not necessary imply that the substances can substitute for DINP, DIDP and DPHP without research and development and changes in process conditions and machinery.

Maag *et al.* (2010) focus in a study for the Danish EPA on non-*ortho*-phthalate alternatives to DEHP, DBP and BBP. Based on information on the plasticisers found in toys and childcare articles and initial information from manufacturers, a gross list of 25 potential non-phthalate alternatives was compiled and from this list 10 plasticisers were selected for further assessment.

The study included a survey of plasticisers applied in toys and childcare products with restriction on the use of DINP and DIDP. Three of the non-*ortho*-phthalate plasticisers were found in a significant percentage of surveys of phthalates in toys and are reported by all responding Danish manufacturers of toys as used as alternatives to phthalates: DINCH, DEHT and ATBC. All three are marketed as general plasticiser alternatives to DEHP. Among the non-phthalate plasticisers, only DEHT may candidate to be a one-to-one substitution for all traditional applications of DEHP, but not necessarily for DINP, DIDP and DPHP. Which substitutes are suitable depends on the actual processing conditions and the desired properties of the final product. Finding the right plasticiser for a given application is often a complex process, as described above. Many technical criteria have to be met simultaneously and comprehensive testing of the performance of the polymer/plasticiser system is often required. By way of example one Danish manufacturer reported that the development led to the use of a mixture of ATBC, DINCH and DEHT, which could be blended in a variety of combinations to achieve softened PVC that performed to the required standards with the existing production setup (Maag et al, 2010).

A summary of the findings of the study is shown in Table 43 below. The price of the alternatives is indicated as compared with DEHP. The price of DINP and DIDP is approximately 15% higher than the price of DEHP. Similar price data has not been found for DPHP.

TABLE 43
SUMMARY OF THE TECHNICAL ASSESSMENT OF ALTERNATIVE PLASTICISERS (IN ALPHABETICAL ORDER), AND THEIR PRICES RELATIVE TO DEHP (MAAG *ET AL.*, 2010)

Abbreviation	Substance name	CAS No	Overall technical assessment	Price relative to DEHP *1
ASE	Sulfonic acids, C10 – C18-alkane, phenylesters	91082-17-6	ASE is a general plasticiser alternative to DEHP. The producer has indicated significant market experience for most traditional DEHP, DBP and BBP uses.	+

Abbreviation	Substance name	CAS No	Overall technical assessment	Price relative to DEHP *1
ATBC	Acetyl tributyl citrate	77-90-7	The performance of ATBC on some parameters seems similar to DEHP, indicating technical suitability for substitution of DEHP for some applications. The higher extractability in aqueous solutions and the higher volatility may reduce the performance of ATBC as a plasticiser in PVC. The data available does not allow a closer assessment of ATBC's technical suitability as alternative to DEHP, DBP and BBP	++
Mixture of benzoates incl. DEGD	Benzoflex 2088	Mix of 120-55-8, 27138-31-4, 120-56-9	The producer has indicated significant market experience in several of the traditional DBP and BBP specialty plasticiser applications and certain DEHP applications, notably in the non-polymer (adhesives, sealants, etc.) and PVC spread coating (plastisol) application fields. According to the producer, Benzoflex 2088 (with DEGD) has become the main non-phthalate alternative to DBP or BBP in vinyl flooring production in Europe. The higher extractability in water may limit its use for some applications.	≈
COMGHA	Mixture of 12-(Acetoxy)-stearic acid, 2,3-bis(acetoxy)propyl ester and octadecanoic acid, 2,3-(bis(acetoxy)propyl ester	Mix of 330198-91-9 and 33599-07-4	According to the producer, COMGHA still has relative moderate market experience, albeit with many examples of full scale usage and pilot/lab scale tests, and significant market experience in some plastisol application and cosmetics. The producer found good performance on key technical parameters indicating a potential for substituting for DEHP and perhaps for DBP and BBP in some traditional uses of these substances.	++
DEHT	Di (2-ethyl-hexyl) terephthalate	6422-86-2	DEHT is a general plasticiser alternative to DEHP. Today, terephthalates like DEHT are more commonly used in the USA than in Europe.	≈
DINA	Diisononyl adipate	33703-08-1	DINA has mostly been used for low temperature PVC applications and in PVC film/wrapping. The data available for this study does not allow clear-cut conclusions as regards DINA's suitability as alternative to DEHP	+

Abbreviation	Substance name	CAS No	Overall technical assessment	Price relative to DEHP *1
DINCH	Di-isononyl-cyclohexane-1,2dicarboxylate	166412-78-8	The producer's sales appraisal indicates a relatively wide usage of DINCH for general plasticiser purposes. DINCH was the most frequently found plasticiser in two European surveys of plasticisers in toys and childcare articles. The data available does not allow a closer assessment of DINCH's technical suitability as alternative to DEHP, DBP and BBP.	+
DGD	Dipropylene glycol dibenzoate	27138-31-4	The fact that DGD for many years has been a well known and much used competitor to BBP, especially in PVC flooring and in PVA adhesives, indicates a clear potential for substituting DGD for BBP, from a technical point of view. DGD may probably also substitute for some traditional uses of DEHP and DBP.	≈
GTA	Glycerol Triacetate	102-76-1	According to a producer, GTA can substitute for DBP and BBP in adhesives, inks and coatings. The data available does not allow a closer assessment of GTA's technical suitability as alternative to DEHP, DBP and BBP.	+
TXIB	Trimethyl pentanyl diisobutyrate	6846-50-0	TXIB was found in more than 10% of the samples in surveys of plasticisers in toys and childcare articles. However, the producer does not consider TXIB an alternative to DEHP, DBP or BBP, and the usage of TXIB in vinyl flooring has declined in the 1990's due to high emissions from end products. Consequently, TXIB seems not to be a suitable alternative to DEHP, DBP or BBP.	NA

*1 Based on comparison with DEHP, but DBP and BBP are reported to have similar price and the notation therefore serves as indicating price relative to DBP and BBP as well. The price of DINP and DIDP is approximately 15% higher than the price of DEHP. "≈" means similar price or slightly lower or higher than DEHP; "+" means somewhat higher price (10-50% higher) than DEHP and "++" means significantly higher price than DEHP. The report provides actual price examples.

In a study on cost curves of reducing the use of DEHP, BBP and DBP for the European Chemicals Agency (ECHA) Lassen *et al.* (2013) have indicated the costs of the replacement of the three phthalates with DINP, DIDP and a number of non-phthalate alternatives.

As shown in Table 44, the effective price of the non-*ortho*-phthalate alternative DEHT was in the same price range as the price of DINP and DIDP, whereas ASE and DINCH were somewhat more expensive. It is in general very difficult to obtain precise information on the prices of the plasticisers and this information is considered confidential.

The effective price difference depends on the price of the alternative and a substitution factor (also called "efficiency"), which indicates the amount of the alternatives needed as compared with DEHP in order to obtain the same plasticising properties. According to Lanxess (as cited by Lassen *et al.*, 2013), the substitution factors may typically vary by less than ±5% for the most used direct alternatives to DEHP. The factor varies with the specific processing conditions, but it is not possible to indicate some general differences between the different processing types (e.g. plastisol processing vs. calendering).

The content of DEHP in plasticised PVC varies with the application but is typically in the range of 20-40% of the plastics and an increase in the price of the plasticiser of e.g. 30% will result in a material price increase of 10% for the plastic material.

Prices of chemicals (and other industrial products) tend to decrease as production capacity and competition is increased. Different chemicals are however based on different raw materials and more or less complex and resource demanding chemical synthesis technologies. This of course sets limits to the minimum prices attainable even in a mature market, and some of the alternative plasticisers described may remain at higher price levels.

Besides the price of the plasticisers, the substitution of the phthalates may imply some costs of research and development for reformulation and process changes which is discussed further below.

TABLE 44
PRICE OF ALTERNATIVES AS COMPARED WITH DEHP FOR USE IN PVC (LASSEN *ET AL.*, 2013)

Alternative	CAS No	Price compared to DEHP	Substitution factor, %	Effective price compared to DEHP	Source of information
DINP (Jayflex™ DINP)	68515-48-0	+13-16%	up to 106 *1	+13-20%	ExxonMobil, manufacturer of alternative / ICIS pricing
DIDP (Jayflex™ DIDP)	68515-49-1	+13-16%	up to 110 *1	+13-24%	-"-
DINP	68515-48-0	+5%	107	+12%	DSU, extrusion and injection moulding PVC
DINP	68515-48-0	+15%	106	+18%	DSU, extrusion PVC
DIDP	68515-49-1	+5%	110	+16%	-"-
Hexamoll® DINCH Di-isononyl-cyclohexane-1,2-dicarboxylate,	166412-78-8	+50%	107	+61%	-"-
DEHT, DOTP Di(2-ethylhexyl) terephthalate	6422-86-2	+10%	107	+18%	-"-
DEHT, DOTP 1,4-Di(2-ethylhexyl) terephthalate	6422-86-2	+15%	100-103	+15-18%	Eastman, manufacturer of alternative

Alternative	CAS No	Price compared to DEHP	Substitution factor, %	Effective price compared to DEHP	Source of information
Citroflex® A-4 Acetyl Tributyl Citrate,	77-90-7	+50-100%	100	+50-100%	Vertellus, manufacturer of alternative
Citroflex® n-Butyryltri-n-hexyl citrate	82469-79-2	+>50-100%	not indicated	+>50-100%	Vertellus, manufacturer of alternative
Mesamoll® (ASE) Sulfonic acids, C10 – C18-alkane, phenylesters,	70775-94-9	not indicated [+75% *2]	not indicated	not indicated	Lanxess, manufacturer of alternative
Unimoll AGF® Multi-constituente substance - mixture of acylated glycerides,	mixture	not indicated	not indicated	not indicated	-“-
DOA Di-2-ethylhexyl adipate, Adimoll® DO	103-23-1	*3	95	*3	-“-
ODS n-Octyl n-decyl succinate mixture, Uniplex® LXS TP ODS)	mixture	*3	100	*3	-“-
BEHS Benzyl-2ethylhexyl succinate mixture, Uniplex® LXS TP BEHS	mixture	*3	95	*3	-“-

*1 The substitution factor depends on the concentration of phthalates in the material. The 106% and 110% represent the typical situation e.g. in cable, film and sheet, but it may be less for some applications.

*2 Price difference indicated by Maag *et al.*, 2009.

*3 Price reported, but considered confidential.

The experience with substitution of DEHP by product group, as reported by the manufacturers of the alternatives, is shown in Table 45. As indicated in the note to the table, the manufacturer of DEHT, Eastman has indicated that DEHT has more typically been used for substitution of DINP, and DEHT can technically replace both DEHP and DINP in all flexible PVC products. DEHP is widely used in the USA for the same applications as DINP is applied in Europe. Eastman indicates that DEHT is a drop-in alternative for DEHP for most applications and no significant costs of R&D and process changes are foreseen (Lassen *et al.*, 2013). The same is probably the situation as concern substitution of DEHT for DINP.

Lanxess indicates according to Lassen *et al.* (2013) that they believe that ASE and DOA can replace DEHP without any changes to the existing equipment. Additional costs may be incurred by minor one-off reformulating work, the costs of this is indicated as “insignificant” by the manufacturer. The company has indicated that the main part of the R&D will take place by the manufacturer of the alternatives in order to ensure that the plasticiser blend has the desired properties.

TABLE 45
EXPERIENCE WITH SUBSTITUTION OF DEHP BY PRODUCT GROUP AS REPORTED BY THE MANUFACTURERS; SEE DEFINITION OF SCORES USED IN NOTES (LASSEN *ET AL.*, 2013)

Application	DINP	DIDP	DEHT / DOTP *2	Citroflex ® A-4	ASE	DOA	ODS
	Exxon Mobil		Eastman	Vertellus	Lanxess		
Calendering of film, sheet and coated products *1	1	1		3	2	2	
Calendering of flooring and roofing *1	1	1			4		4
Extrusion of hose and profile *1	1	1		3	2	2	
Extrusion of wire and cable	1	1	3		2	2	
Extrusion of miscellaneous products from compounds	1	1		2	2	2	
Injection moulding of footwear and miscellaneous	1	1			?	2	
Slush/rotational moulding *1	1				?		
Spread coating of flooring *1	1				2		
Spread coating of coated fabric, wall covering, coil coating, etc. *1	1	1	1		2	2	4
Car undercoating *1	1	1			2		4
Non-PVC polymer applications (acrylics)	1		2		?	2	
Adhesives/sealant (e.g. PU), rubber	1		2	2	2	1	
Lacquers and paint			2		2	2	
Printing ink			1	2	2	1	

Notation used: 1) main alternative on market; 2) Significant market experience, 3) Some examples of full scale experience, 4) Pilot/lab scale experience

*1 According to ExxonMobil, DEHP is no longer used in most of those end-uses but has been replaced by high phthalates (DINP and DIDP). However this may not be true when considering the use of DEHP in Eastern Europe.

*2 The manufacturer Eastman has indicated for this study a relatively small number of applications where they have experience in substituting DEHT for DEHP. According to the company, DEHT has more typically been used for substitution of DINP and DEHT can technically replace both DEHP and DINP in all flexible PVC products.

Costs of Research and Development

According to (Lassen *et al.*, 2013) some adjustment is often necessary when replacing the plasticisers and this is typically done in cooperation between the manufacturer and the downstream user, but the one-of costs of research and development (R&D) and investments in equipment is generally low compared to the costs of the plasticisers. Particular high costs of research and development is expected for layered flooring, because of its technical complexity. In the models of Lassen *et al.* (2013) it is assumed that the costs of R&D for per manufacturing site is 300,000 € while it for other applications areas is 60,000 €.

7.4 Alternatives to DEP, DMEP and DIPP

Information on specific alternatives to DEP, DMEP and DIPP has been searched for on the Internet in this study, but aggregated information was scarce.

As mentioned in Section 3.3, a survey of 23 nail polishes/lacquers marketed in California in 2012 (focusing on DBP, toluene and formaldehyde), found no DEP with the analysis methods used, but DBP in 9 products and no DBP but other plasticisers in other 9 products. In 5 products, no plasticisers were observed with the use analytical methods. The other plasticisers observed were camphor (mentioned as a secondary plasticiser as well as a fragrance), dioctyl adipate, tributyl phosphate, butyl citrate, triphenyl phosphate, N-ethyl-o-toluene sulfonamide, N-ethyl-p-toluene sulphonamide, P-toluene sulphonamide (tosylamide) (California EPA, 2012).

As regards denaturing of alcohol, a former DEP use in the EU, Regulation 162/2013 lists the following substances as allowed denaturants (of which most are only allowed in certain countries specified in the regulation); it should be noted that several of them have substantial adverse effects on human health or the environment. The denaturing mixture prescribed for all Member States without national rules is based on the three substances isopropyl alcohol (IPA), methyl ethyl ketone (MEK) and denatonium benzoate. DEP must thereby be considered as obsolete as a denaturant in the EU and with many actual alternatives available. It has not been possible to evaluate the environment and health characteristics of these substances within the framework of this review.

TABLE 46
DENATURANTS LISTED IN EU REGULATION 162/2013 OF 21 FEBRUARY 2013

Substance name	CAS no.
Acetone	67-64-1
CI reactive red 24	70210-20-7
Crude pyridine	not available
Crystal violet (C.I. No 42555)	548-62-9
Denatonium benzoate	3734-33-6
Ethanol	64-17-5
Ethyl acetate	141-78-6
Ethyl sec-amyl ketone	541-85-5
Ethyl tert-butyl ether	637-92-3
Fluorescein	2321-07-5
Formaldehyde	50-00-0
Fusel oil	8013-75-0
Gasoline (including unleaded gasoline)	86290-81-5
Isopropyl alcohol (IPA)	67-63-0
Kerosene	8008-20-6
Lamp oil	64742-47-8 to 64742-48-9

Substance name	CAS no.
Methanol	67-56-1
Methylethyl ketone (butanone) (MEK)	78-93-3
Methyl isobutyl ketone	108-10-1
Methyl isopropyl ketone	563-80-4
Methyl violet	8004-87-3
Methylene blue	61-73-4
Mineral naphtha	not available
Solvent naphtha	8030-30-6
Pyridine (or Pyridine bases)	110-86-1
Spirit of turpentine	8006-64-2
Technical petrol	92045-57-3
tert-butyl alcohol	75-65-0
Thiophene	110-02-1
Thymol blue	76-61-9
Wood naphtha	not available

Maag *et al.* (2010) list the non-*ortho*-phthalate plasticisers/solvents shown in Table 47 as usable in traditional applications of these substances. While plasticiser (and solvent) use may be very specific to the polymer and application in question, the information summarised here indicates however that there may be technically viable alternatives to DEP, DMEP and DIPP available.

As regards base oils for fragrances, a DEP application, a quick Internet search of the market indicates that many options are available, including also natural oils like avocado oil, almond oil, etc.

TABLE 47
NON-*ORTHO*-PHTHALATE PLASTICISERS USABLE IN TRADITIONAL DEP, DMEP AND DIPP APPLICATIONS (BASED ON MAAG ET AL, 2010).

Application	Alternative substance *1	Remarks on the alternative's application (if any)
DEP applications		
Cosmetics	COMGHA	A non-phthalate substitute for general plasticisers in sensitive applications. Indicated as used for cosmetics.
	DINCH	Used in cosmetics (e.g. nail polish).
	GTA	GTA has a variety of applications including as a plasticizer for cigarette filters and cellulose nitrate, solvent for the manufacture of celluloid, photographic films, fungicide in cosmetics, fixative in perfumery, support for flavourings and essences in the food industry, component in binders for solid rocket fuels and a general purpose food additive.

Application	Alternative substance *1	Remarks on the alternative's application (if any)
	ATBC	Acetyl tributyl citrate is used in inks, hair sprays and aerosol bandages.
Packaging film	DINA	DINA has mostly been used for low temperature PVC applications and in PVC film/wrapping.
	ATBC	ATBC is widely used in food contact polymers.
DMEP applications		
Nitrocellulose	GTA	According to the producer, GTA is used as a plasticizer for cellulosic resins and is compatible in all proportions with cellulose acetate, nitrocellulose, and ethyl cellulose. GTA is useful for imparting plasticity and flow to laminating resins, particularly at low temperatures, and is also used as a plasticizer for vinylidene polymers and copolymers. It serves as an ingredient in inks for printing on plastics, and as a plasticizer in nail polish. GTA is approved by the FDA for food packaging and many other food-contact applications.
	ATBC	Indicated as used for nitrocellulose paints.
	DGD	DGD is a high solvating plasticizer that has been used for many years in a wide variety of applications. Indicated as used for nitrocellulose.
	ASE	Good gelling capacity with a large number of polymers. Indicated as used for nitrocellulose paints.
	"Benzoflex 2088"	According to the manufacturer this is a high solvating plasticizer primarily known for its use in polyvinyl acetate, water-based adhesive systems and PVC flooring. Indicated as also used for nitrocellulose paints.
Cellulose acetate, vinylidene polymers	GTA	See above
Polyvinyl acetate	DEGD	According to the manufacturer a high solvating plasticizer primarily for polyvinyl acetate and water-based adhesive systems.
Pesticide inerts	ATBC	Industrial uses include children's toys; animal ear tags; ink formulations; adhesives; pesticide inerts.
DIPP applications		
Explosives and propellant (ammunition charge)	ATBC	According to manufacturer: Cellulosics: Nitrocellulose-based explosives/ propellants.

Note: *1: See chemical names and CAS numbers in table below.

Environment and health assessment of alternatives

A summary of the inherent properties for the alternative plasticisers investigated by Maag et al. (2010) is shown in

Table 48 using key parameters: acute and local effects, sensitisation, carcinogenicity, mutagenicity, reproductive toxicity, persistence, bioaccumulation and aquatic toxicity. Maag et al. concludes as follows:

"From the overview it can be seen that all ten substances are expected to have low acute toxicity based on animal studies. With regard to local effects most substances are non-irritating to skin and eyes or only produce slight irritation which would not lead to classification. None of the tested substances are sensitising.

Effects from repeated dose toxicity studies mainly include reduced body weight gain, increased organ weights (liver and/or kidney) and for some substance also changes in clinical chemistry or clinical pathology parameters. However, more serious pathological effects were not observed. Studies to evaluate the potential for reproductive/developmental toxicity primarily show toxic effects on parents and offspring. For TXIB statistically significant reproductive and developmental toxicity is observed.

Carcinogenicity has only been evaluated for three substances in combined studies. For all three substances the outcome was negative (no carcinogenicity effect). However, the studies cannot be considered sufficient to exclude possible carcinogenic effects.

The assessment in this study of the toxic properties of ATCB, COMGHA, DINCH and DEHT is in line with the recent assessment from the Scientific Committee on Emerging and Newly-Identified Health Risks (SCENIHR).

All substances have been tested for acute toxicity for at least one exposure route, sensitisation (except ASE), subchronic toxicity and mutagenicity. All substances except ASE, COMGHA and DINA have been tested for both reproductive and developmental toxicity.

With regard to carcinogenicity only ATBC, DEHT and DINCH have been tested in combined chronic toxicity and carcinogenicity studies. For DEGD, DGD and DEHT estrogenic activity has been tested in a uterotrophic assay without positive response.

Most data used for the evaluation are considered of good quality, i.e. studies following accepted guidelines (OECD or US EPA) or studies considered acceptable at the time they were carried out. For some of the studies little information is available to evaluate the quality. However, key information is obtained from IUCLID data sheets, USEPA or OECD HPV robust summaries.).

With regard to environmental properties, none of the 10 studied alternatives meet the criteria for being a PBT or vPvB substance, although all substances except GTA show one or two of these properties. GTA (triacetin) appears to be easily biodegradable, it does not bioaccumulate and has very moderate toxicity in the aquatic environment.

DEGD, DGD and DINA also come out rather favourable, while ATBC and COMGHA come out negatively despite their degradability because of their aquatic toxicities and bioaccumulative properties. ASE and DINCH both have low acute toxicities to aquatic organisms, but are not easily degradable and have high log KOW values. DEHT is also not easily biodegradable and is bioaccumulative but its aquatic toxicity cannot be fully evaluated based on the data available. Useful fate data regarding biodegradability (in water) and bioaccumulative properties (either as BCF or log KOW) are available for all alternatives while other fate data are incomplete for some substances. With regard to ecotoxicological effect data, results from short-term tests with the base-set of organisms - fish, crustaceans and algae - exist for all 10 substances although the duration of some studies deviate from the current OECD standard.

Overall, the data identified are of good quality i.e. they are mostly based on studies performed according to accepted guideline procedures, and the studies have been evaluated to be reliable without restrictions or reliable with restrictions (e.g. in the USEPA HPV robust summaries)."

TABLE 48

OVERVIEW OF MAIN TOXICOLOGICAL AND ECOTOXICOLOGICAL PROPERTIES OF POTENTIAL ALTERNATIVES

Name of substance	CAS No.	Health					Environment			Data quality / data completeness (CMR and PBT)
		Acute, local and sens. effects (A/L/S)	Carcinogenic (C)	Mutagenic (M)	Repro-toxic (R)	Subchronic toxicity	Persistence *1	Bioaccumulation *2	Aquatic Toxicity *3	*4
ASE	91082-17-6	○/○/○	-	○	○	●	● (not readily)	● P_{ow}	○	2 / 2
ATBC	77-90-7	○/(○)/○	○	○	○	[●]	○	● BCF	●	1 / 2
COMGHA	330198-91-9	○/○/○	-	○	-	(●)	○	● P_{ow}	●	1 / 2
DEGD	120-55-8	○/(○)/○	-	○	(●)	●	○	(○) BCF	●	1 / 2
DGD	27138-31-4	○/(○)/○	-	○	(●)	●	○	● P_{ow}	●	1 / 2
DEHT / DOPT	6422-86-2	○/(○)/○	○	○	○	●	● (inherently)	● P_{ow}	(●)	1 / 2
DINA	33703-08-1	○/○/○	-	○	-	●	○	(●) (conflicting)	○	1 / 2
DINCH	166412-78-8	○/(○)/○	○	○	○	●	● (not readily)	● P_{ow}	○	1 / 2
GTA	102-76-1	○/○/○	-	○	○	○	○	○	○	1 / 2
TXIB	6846-50-0	○/(○)/○	-	○	●	●	● (inherently)	○ BCF	●	1 / 2

Notes:

The inherent properties for the investigated substances are summarised using key parameters: acute and local effects, sensitisation, carcinogenicity (C), mutagenic toxicity (M), reproductive toxicity (R), persistence, bioaccumulation and aquatic toxicity. If data are not available for all parameters or only from non standard test results a tentative assessment is given (shown in parentheses). The symbols: ● identified potential hazard, ○ no identified potential hazard, and – no data available. [] indicate the effects are considered of minor significance.

*1 The terms refer to different biodegradability tests:

Inherently biodegradable: Not meeting the criteria in an "inherent biodegradability" test

Not readily biodegradable: Not meeting the criteria in "ready biodegradability" tests.

*2 ● is based on BCF > 100 or Pow > 3 (BCF prevails over Pow where both values exist).

*3 ●● is used for very toxic and toxic < 10 mg/L.

*4 The following notation is used:

Data quality (first number):

1 Data summaries from recognised, peer reviewed sources (e.g. EU HVP programme, SIDS, SCHENIR, NICNAS) or reliable test data.

2 Data summaries from not peer reviewed sources, considered reliable with restrictions (e.g. IUCLID).

3 Data summaries which do not give sufficient experimental details for the evaluation of the quality.

Data completeness (second number):

1 Data considered sufficient for classification of CMR effects and according to PBT criteria.

2 Data available about the endpoint, but not considered sufficient for classification.

3 Data not available or relevant for classification of the endpoint.

An average score is assigned based on the sum of scores for C, M, R, P, B and T properties as follows: Sum 6-8 =1, Sum 9-14=2 and Sum 14-18=3

7.4.1 Alternative polymers

Many alternative materials to flexible PVC exist and the subject is complicated. Examples of alternatives include such diverse materials as linoleum and wood for flooring, woven glass fibre and paper for wall coverings, and glass for medical appliances.

Focusing on alternative materials with characteristics similar to the characteristics of flexible PVC, the following flexible polymers are among the principal alternatives to flexible PVC (Maag *et al.*, 2010):

- Ethylene vinyl acetate, EVA;
- Low density polyethylene, LDPE;
- Polyolefin elastomers (polyethylene and polypropylene elastomers);
- Several types of polyurethanes (may in some cases be plasticised with
- phthalates);
- Isobutyl rubber;
- EPDM rubber (may in some cases be plasticised with phthalates);
- Silicone rubber.

The ECHA study on DEHP (COWI *et al.*, 2009) concludes that available studies demonstrate that for many applications of DEHP/PVC, alternative materials exist at similar price. Many of the materials seem to have equal or better environment, safety and health performance and cost profiles, but clear conclusions are complicated by the fact that not all aspects of the materials' lifecycles have been included in the assessments.

Maag et al (2010) concluded that a number of flexible polymers are available which can substitute for many traditional uses of flexible PVC. Polyethylene (PE), polyolefin elastomers, different polyurethane (PU) qualities, ethylene vinyl acetate (EVA) and different rubber types are examples among others. For many flexible PVC uses, also other substitute materials than flexible polymers exist. The LCA-based, application-focused assessments are few, and often clear-cut conclusions could not be made. But many materials exist with seemingly equal or better environmental, health and safety, performance and cost profiles. The assessment made Maag *et al.* (2010) did not allow for a more detailed analysis of possibilities and limitations in the coverage of alternative flexible polymers. For more detailed summaries of the identified studies of alternative materials to flexible PVC, see (Maag *et al.* 2010).

7.5 Historical and future trends

With the increased focus in regulation of phthalates with observed adverse effects, substitution efforts have taken place over the last two decades. Especially for sensitive purposes like polymer articles/materials for children, for food contact and for some medical applications, a series of non-*ortho*-phthalates has gained more ground, the most dominant substance families being represented in the description above. From recent COWI studies of phthalates and alternatives, it was observed that while the traditional phthalates are more dominant in articles imported from Asia, also Chinese producers are now familiar with providing PVC materials plasticised without the phthalates most often addressed by regulation; for example so-called "3-P-free" flexible PVC (without DEHP, DBP and BBP) and "6-P-free" (without DEHP, DBP, BBP, DINP, DIDP and DNOP]).

For general applications of flexible PVC (the dominant plasticiser use), the primary move has been away from DEHP towards DINP and DIDP (and DPHP), which are closest to "drop-in" alternatives requiring the least process modifications by manufactures of flexible PVC articles. Please see more description of this issue in Section 3.4 on historical trends in use.

7.5.1 Summary and conclusions

When considering the possibilities for substitution of specific plasticisers, it is important to note that a vast number of organic substances can act as plasticisers in polymers. Contrary to many other substitution efforts, plasticising is not dependent on highly specific chemical bonding, but rather on a series of characteristics which the plasticiser must have to meet functional demands. Finding the good plasticiser is therefore not a distinct theoretical science, but rather an empiric process supported by a large number of measuring methods designed for this purpose.

Many families of plasticisers are available. Most of them have however certain chemical functionalities in common with the phthalates family. They are typically branched, quite "voluminous" molecules, with many oxygen bonds (= carbonyl groups). Many have benzyl rings or the hydrogenated counterpart, cyclohexane.

The substance family of the plasticiser influences its performance significantly, but some functional groups in the molecules also influence the performance across families, and plasticisers can therefore to a certain extent be tailor-made to suit different performance needs. In addition, it is common to mix plasticisers to achieve desired properties.

Many similar plasticisers have however distinctly different impacts on health and environment, and are therefore relevant alternatives to phthalates. This is probably primarily due to the fact that many types of interactions with biological systems are substance specific, and even structure-specific meaning that substances with identical chemical composition may work differently, if just a part of the molecule has shifted position from one place to another (as the case is for DEHP and DEHT).

Most available information on alternatives to **primary plasticisers** like DINP, DIDP and DPHP has been reviewed as part of the search for substitutes for the classic general plasticiser DEHP (to which DINP and to as lesser extend DIDP and DPHP are the key alternatives today). Several alternatives are however available, both *ortho*-phtalates (with basic structure similar to DINP, DIDP and DPHP) and others. The one non-*ortho*-phthalate with the widest coverage for traditional DEHP applications is likely its terephthalate counterpart DEHT, which has the same chemical composition, but a different form, and therefore different environmental characteristics. Otherwise, no single non-*ortho*-phthalate plasticiser covers all traditional applications of DEHP (and thus DINP, its main alternative). Together, however, the reviewed non-*ortho*-phthalates cover most or all the key applications. The non-*ortho*-phthalate alternatives best described include besides DEHT: DINCH, ASE, DGD, DEGD (in mixtures), COMGHA, DINA, ATBC and GTA. While most of these have their own environmental issues, many of them are deemed to have overall better environmental performance than DEHP based on the available information. A direct environmental comparison of DINP, DIDP and DPHP and their alternatives has not been found. Besides alternative plasticiser use, alternatives to the plasticised materials exist; this has however not been dealt with in much detail in this review. Some flexible polymer alternatives to flexible PVC include PU elastomers, various rubber types, silicones, EVA and LDPE, all with different performance characteristics (note that some rubbers are in some cases plasticised with phthalates).

A wide search of alternatives to the phthalates DEP, DIPP and DMEP has not been possible within this project. For the use of DEP as a denaturant, many alternatives exist, and DEP is not a part of the 2013 list of denaturants required used for attaining tax exemptions in EU Member States (including Denmark). Based on a 2010 review of alternatives to DEHP, DBP and BBP, there are however clear indications that non-*ortho*-phthalate alternatives to key applications of DEP, DIPP and DMEP. Examples include GTA, ATBC, COMGHA, DINCH, DINA, DGD, ASE and a mix with DEGD as a major component.

Focusing on **alternative materials** with characteristics similar to the characteristics of flexible PVC, the following flexible polymers are among the principal alternatives to flexible PVC (Maag *et al.*, 2010):

- Ethylene vinyl acetate, EVA;
- Low density polyethylene, LDPE;
- Poly olefin elastomers (polyethylene and polypropylene elastomers);
- Several types of poly urethanes (may in some cases be plasticised with
- phthalates);
- Isobutyl rubber;
- EPDM rubber (may in some cases be plasticised with phthalates);
- Silicone rubber.

Data gaps
- Information on direct alternatives to DEP, DIPP and DMEP in different uses.
- Direct comparisons of DINP, DIDP and DPHP with available alternatives in relevant uses.

8. Abbreviations and acronyms

ASE	Alkylsulphonic phenyl ester
ATBC	Acetyltributyl citrate
BBP	Butylbenzyl phthalate
BCF	Bioconcentration factor
BEHS	Benzyl-2 ethylhexyl succinate mixture
CLP	Classification, Labelling and Packaging Regulation
DEHAtere	Di-2-ethylhexyl adipate
DEGD	Diethylene glycol dibenzoate
DEHP	Bis(2-ethylhexyl)phthalate
DEHT	Di(2-ethylhexyl) terephthalate (same as DOTP and DEHTP)
DGD	Dipropylene glycol dibenzoate
DIDP	Diisodecyl phthalate
DINCH	Diisononylcyclohexane dicarboxylate
DINP	Diisononyl phthalate
DNEL	Derived No Effect Level
DOA	Di-2-ethylhexyl adipate (same as DEHA)
DOTP	Di(2-ethylhexyl) terephthalate (same as DEHT)
DPHP	Di(2-propylheptyl) phthalate
ECB	European Chemicals Bureau
ECHA	European Chemicals Agency
ECPI	European Council for Plasticisers and Intermediates
EFSA	European Food Safety Authority
EPA	Environmental Protection Agency
EU	European Union
GTA	Glycerol triacetate
HELCOM	The Baltic Marine Environment Protection Commission (Helsinki Commission)
HMW	High Molecular Weight
Kow	Octanol/water partitioning coefficient
LOUS	List of Undesirable Substances (of the Danish EPA)
LMW	Low Molecular Weight
MWWTP	Municipal waste water treatment plant
NOAEL	No observable adverse effect level
NOVANA	Danish national monitoring and assessment programme
ODS	n-Octyl n-decyl succinate mixture
OECD	Organisation for Economic Co-operation and Development
OSPAR	Convention for the Protection of the Marine Environment of the North-East Atlantic
PVC	Polyvinylchloride
QSAR	Quantitative Structure and Activity Relationship
R&D	Research & development
RAR	Risk Assessment Report

REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals (Regulation EC 1907/2006)
SCCP	Scientific Committee on Consumer Products
SCCNFP	Scientific Committee on Cosmetics Products and Non-Food Products intended for Consumers
SCENIHR	The Scientific Committee on Emerging and Newly Identified Health Risks
SPT	Association of Danish Cosmetics, Toiletries, Soap and Detergent Industries
SVHC	Substance of Very High Concern
TDI	Tolerable daily intake
WWTP	Waste water treatment plant

References

Anderson WA, Castle L, Hirds, Jeffrey J and Scotter MJ (2011): A twenty-volunteer study using deuterium labelling to determine the kinetics and fractional excretion of primary and secondary urinary metabolites of di-2-ethylhexylphthalate and di-iso-nonylphthalate. Food Chem Toxicol. 2011 Sep;49(9):2022-9. (Abstract only)

ATSDR (1995): Toxicological profile for diethyl phthalate. Accessed August 2013 at http://www.atsdr.cdc.gov/toxprofiles/tp73.pdf

Babich MA and Osterhout A (2010). Toxicity review of diisononyl phthalates (DINP). U.S. Consumer Product Safety Commission. Available at: http://www.cpsc.gov/about/cpsia/toxicityDINP.pdf

BASF (2008): Technical Leaflet on Palatinol® A (R). Accessed August 2013 at http://www.csc-jaekle.de/fileadmin/MeBl/485/MeBl_485632_EN.pdf

BAuA (2011): Annex XV dossier - Proposal for identification of a substance as a CMR (1a or 1b), PBT, vPvB or a substance of an equivalent level of concern - Bis(2-methoxyethyl)phthalate. Accessed March, 2013 at http://echa.europa.eu/documents/10162/13640/svhc_axvrep_germany_cmr_bis2-methocxyethylphthalate_20110829_en.pdf

Baumann W and Rothardt T (1999): Druckereichemikalien, Daten und Fakten zum Umweltschutz, 2. Aufl. Springer Verlag. As cited by BaUA (2011).

Bayrishes Landesamt für Gesundheit und Lebensmittelsicherheit (2012): Diethylphthalat in kosmetichen Mitteln - Untersuchungsergebnisse 2003 und 2006 (in German: Diethylphthalate in cosmetics – results from 2003 and 2006). Accessed August 2013 at http://www.lgl.bayern.de/produkte/kosmetika/kosmetische_mittel/ue_2006_diethylphthalat_kosmetika.htm)

Bekö G, Weschler CJ, Langer S, Callesen M, Toftum J and Clausen G (2013): Children's Phthalate Intakes and Resultant Cumulative Exposures Estimated from Urine Compared with Estimates from Dust Ingestion, Inhalation and Dermal Absorption in Their Homes and Daycare Centers. PLoS ONE 8(4): e62442. doi:10.1371/journal.pone.0062442 (open access)

Borling P, Engelund B, Sørensen H and Cohr KH (2006): Survey, migration and health evaluation of chemical substances in toys and childcare products produced from foam plastic. Survey of Chemical Substances in Consumer Products, No. 70, 2006, DHI for DEPA. Accessed August 2013 at http://www2.mst.dk/udgiv/publications/2006/87-7052-098-4/pdf/87-7052-099-2.pdf

Boutrup S, Svendsen LM: Tilførsel af syntetiske stoffer samt ikke-syntetiske stoffer og forbindelser til danske farvande (Danish: Addition of synthetic substances and non-synthetic substances and compounds to Danish waters.. Notat 2.7. DCE, August 2012

Brandt UK, Hansen E. (2009): Ftalater i afgiftsbelagte produkter (Danish: Phthalates in products subject to taxation). Environmental Project No. 1290 2009. Danish Environmental Protection Agency, Copenhagen.

California EPA (2012): Summary of data and findings from testing of a limited number of nail products. California Environmental Protection Agency, Department Of Toxic Substances Control. Accessed September 2013 at http://www.dtsc.ca.gov/pollutionprevention/upload/nailsalon_final.pdf

Calvin, E. (2011); Plasticizer Market Update. BASF Corporation. Presentation at the 22nd Annual Vinyl Compounding Conference, Burlington, July 10-13, 2011. Accessed September 3, 2011 at: Accessed July 2013 at: http://spi.files.cmsplus.com/about/VPD/Tuesday%201.%20Calvin%20Emmanual-%20BASF%20%3D%20Global%20Plasticizer%20Update.pdf

CEHOS (2012): Evaluation of 22 SIN List 2.0 substances according to the Danish proposal on criteria for endocrine disruptors, Danish Centre on Endocrine Disrupters, May 2012

Clark,KE, David, RM, Guinn,R, Kramarz, KW, Lampi, MA and Staples CA. (2011): Modeling Human Exposure to Phthalate Esters: A Comparison of Indirect and Biomonitoring Estimation Methods. Human and Ecological Risk Assessment, 17: 923–965.

COWI, IOM and Entec (2009): Data on manufacture, import, export, uses and releases of bis(2-ethylhexyl)phthalate (DEHP) as well as information on potential alternatives to its use. For ECHA. Revised version of 29 January 2009

COWI *et al.* (2012): Volumes of DINP and DIDP. COWI, IOM Consulting and AMEC for the European Chemicals Agency (ECHA).

CPSC (2011): CPSC staff review of two phthalates and one phthalate alternative for consideration by the Chronic Hazard Advisery Panel – 2011. Accessed August 2013 at http://www.cpsc.gov/PageFiles/125715/DMEP.pdf.

Danish EPA (2005a). Punktkilder 2004 (Point Sources 2004). Orientering fra Miljøstyrelsen nr. 9, 2005.

Danish EPA (2005b). Punktkilder 2003 – revideret udgave (Point Sources 2004 – Revised Edition). Orientering fra Miljøstyrelsen nr. 1, 2005

Danish EPA (2009): Survey and Health Assessment of the exposure of 2 year-olds to chemical substances in Consumer Products. Survey of Chemical Substances in Consumer Products, No. 102 2009

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

Danish EPA (2012): Exposure of pregnant consumers to suspected endocrine disruptors. Survey of chemical substances in consumer products no. 117, 2012.

Danish EPA (2013): Phthalate Strategy. Environmental Project No. 1488, 2013.

DEMOCOPHES (2013): Human biomonitoring on a European scale. Layman's Report. http://www.eu-hbm.info/euresult/media-corner/press-kit

DFL (2013): Personal communication from Anette Harboe Dahl, September 2013.

DVFA. (2010): Phthalater i fødevarekontaktmaterialer, Projekt J. nr.: 2010-20-64-00230 2010. Danish Veterinary and Food Administration, Copenhagen. [in Danish]

EC (2003a).: 1,2-benzenedicarboxylic acid, di-C9-11-branched alkyl esters, C10-rich and di-"isodecyl" phthalate (DIDP). European Union Risk Assessment Report. Volume 36. European Chemicals Bureau. Office for Official Publications of the European Communities, Luxembourg.

EC (2003b): 1,2-benzenedicarboxylic acid, di-C8-10-branched alkyl esters, C9-rich and di-"isononyl" phthalate (DINP). European Union Risk Assessment Report. Volume 35. European Chemicals Bureau. Office for Official Publications of the European Communities, Luxembourg.

ECBI/65/00 Add 2. Rationale for Classification.
http://apps.kemi.se/hclass/SubstanceSheet.aspx?ID=7989

ECHA (2012a): ECHA proposal to Member States. Draft Community Rolling Action Plan (CoRAP) update for years 2013-2025. European Chemicals Agency, 23 October 2012.

ECHA (2013); Evaluation of new scientific evidence concerning DINP and DIDP in relation to Entry 52 of annex xvii to regulation (EC) No 1907/2006 (REACH). Final review report. August 2013

ECHA (2013a): Registered substances. Information on ECHA's website at: Available at: http://echa.europa.eu/web/guest/information-on-chemicals/registered-substances.

ECHA (2013b): Candidate List of Substances of Very High Concern for Authorisation. Available at: http://echa.europa.eu/da/candidate-list-table

ECHA (2013c): Fourth Annex XIV recommendation - 17 January 2013. Available at: http://echa.europa.eu/documents/10162/13640/4th_a_xiv_recommendation_17jan2013_en.pdf

ECHA (2013d): C&L Inventory database. Available at:
http://echa.europa.eu/web/guest/information-on-chemicals/cl-inventory-database

ECPI (2009): Information from the website of the European Council for Plasticisers and Intermediates (ECPI), Brussels at: www.ecpi.org. As cited by Maag et al (2010).

ECPI (2013a): High phthalates. European Council for Plasticisers and Intermediates (ECPI). European Council for Plasticisers and Intermediates (ECPI). Accessed June 2013 at: http://www.plasticisers.org/en_GB/plasticisers/high-phthalates

ECPI (2013b): DINP Information Centre. European Council for Plasticisers and Intermediates (ECPI): Accessed June 2013 at http://www.dinp-facts.com

ECPI (2013c): DIDP Information Centre. European Council for Plasticisers and Intermediates (ECPI): Accessed June 2013 at http://www.didp-facts.com

ECPI (2013d): DPHP Information Centre. European Council for Plasticisers and Intermediates (ECPI). Accessed June 2013 at http://www.dphp-facts.com

ECPI (2013e): Seykali M, personal communication, 20 June 2013.

ECPI (2013f): Danish National Phthalates Strategy. Background info and comments from ECPI. Meeting between ECPI and the Danish EPA, Copenhagen, July 2nd, 2013.

Environment Canada (2009): Canadian Screening Assessment - Existing substances evaluation: Screening assessment for the challenge 1,2-benezenedicaboxylic acid, bis(2-methoxyethyl) ester, Chemical Abstracts Service registry number 117-82-8. Environment Canada, Health Canada. November 2009. As cited by BaUA (2011).

Environment Agency Austria (2012): Annex XV – Identification of diisopentylphthalate (DIPP) as SVHC. Accessed March 2013 at http://www.echa.europa.eu/documents/10162/b33d9431-e823-43fd-bf4b-d554b6aef968

Eurostat (2013): Eurostat 2012. External trade by CN8 database.

FDA (2013): Phthalates and cosmetic products. Accessed Aug 2013 at http://www.fda.gov/Cosmetics/ProductandIngredientSafety/SelectedCosmeticIngredients/ucm128250.htm

Frederiksen H, Nielsen JK, Mørck TA, Hansen PW, Jensen JF, Nielsen O, Andersson AM, and Knudsen LE: Urinary excretion of phthalate metabolites, phenols and parabens in rural and urban Danish mother-child pairs. Int J Hyg Environ Health. 2013 Nov;216(6):772-83.

Högberg J, Hanberg A, Berglund M, Skerfving S, Remberger M, Calafat AM, Filipsson AF, Jansson B, Johansson N, Appelgren M, Håkansson H. (2008): Phthalate diesters and their metabolites in human breast milk, blood or serum, and urine as biomarkers of exposure in vulnerable populations. Environ Health Perspect. 2008 Mar;116(3):334-9.

Høibye L, Maag J, Hansen E (2011): Background data for Annex XV dossier - DEHP, BBP, DBP and DIBP. Environmental Projevt No. 1362. Danish Environmental protection Agency, Copenhagen.

Hyldgaard JG (2013): Personal communication, September 2013. Hygade, Denmark, www.hygade.com)

KemI (2013): Assignment to phase out phthalates in Sweden. http://www.kemi.se/en/This-is-KemI/Government-assignments-in-2011/Reported-commissions-2010-2011/Assignment-to-phase-out-phthalates-in-Sweden/

Kjølholt, J. *et al.* (2011): Nøgletal for miljøfarlige stoffer i spildevand fra renseanlæg (mean nation concentrations of hazardous substances in effluents from WWTPs). Rapport. Naturstyrelsen, 2011.)

Kransler KM, Bachman AN, McKee RH. (2012): A comprehensive review of intake estimates of di-isononyl phthalate (DINP) based on indirect exposure models and urinary biomonitoring data. Regul Toxicol Pharmacol. 2012 Mar;62(2):248-56.

Labunska and Santillo (2004) [Greenpeace] (5 pp.). http://www.greenpeace.to/publications_pdf/DEP_2004.pdf. As cited by NIEHS, 2006.

Larsen HF, Helweg C, Pedersen AR, Boyd HB, Lauresen SE and Hansen J (2000): Kemikalier i tekstiler [Chemicals in textiles]. Miljøprojekt Nr. 534 2000. Miljøstyrelsen (DEPA; - in Danish). Accessed August 2013 at http://www2.mst.dk/udgiv/publikationer/2000/87-7909-800-2/pdf/87-7909-801-0.pdf

Lassen S, Maag J, Sørensen MM (2013): Abatement cost curves for the four phthalates DEHP, BBP, DBP and DIBP. COWI A/S for the European Chemicals Agency, ECHA, Helsinki.

Lowell (2011): Phthalates and their alternatives: Health and environmental concerns. Lowell Center for Sustainable Production at the University of Massachusetts Lowell.

Maag J, Lassen C, Brandt UK, Kjølholt J, Molander L and Mikkelsen SH (2010): Identification and assessment of alternatives to selected phthalates. Environmental Project No. No. 1341 2010. COWI for the Danish Environmental Protection Agency, Copenhagen.

Maag, J., C. Lassen, U.K. Brandt, J. Kjølholt, L. Molander and S.H. Mikkelsen. (2010). Identification and assessment of alternatives to selected phthalates. Environmental Project 1341. Danish Environmental Protection Agency, Copenhagen.

Müller AK, Nielsen E, Ladefoged O, Dalgaard M, Hass U. (2006): Evaluation of the health risk to animals playing with phthalate containing toys. Survey of Chemical Substances in Consumer Products, No. 74. Danish Environmental Protection Agency, Copenhagen.

Australian NICNAS, 2008. Existing Chemical Hazard Report, Bis(2-methoxyethyl) Phthalate, June 2008. http://www.nicnas.gov.au/publications/car/other/dmep%20hazard%20assessment.pdf, as cited by BAuA (2011).

NICNAS (2011): Priority Existing Chemical Assessment Report No 33, Diethyl Phthalate. Australian Government, Department of Health and Ageing, Noovember 2011.

NIEHS (2006): Chemical Information Profile for Diethyl Phthalate. National Institute of Environmental Health Sciences, USA. Accessed March 2013 at http://ntp.niehs.nih.gov/ntp/htdocs/Chem_Background/ExSumPdf/Diethyl_phthalate_508.pdf

Nilsson NH, Malmgren-Hansen B, Bernth N, Pedersen E and Pommer K (2006): Survey and health assesment of chemicals substances in sex toys. Survey of Chemical Substances in Consumer Products, No. 77, 2006. Danish Technological Institute for DEPA. Accessed August 2013 at http://www2.mst.dk/udgiv/publications/2006/87-7052-227-8/pdf/87-7052-228-6.pdf

Nilsson NH, Malmgren-Hansen B, Bernth N, Pedersen E and Pommer K (2006): Survey and health assessment of chemicals substances in sex toys. Survey of Chemical Substances in Consumer Products, No. 77. Danish Environmental Protection Agency, Copenhagen.

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

NTP (2006): Chemical Information profile for Diethyl Phthalate [CAS No. 84-66-2]. Supporting Nomination for Toxicological Evaluation by the National Toxicology Prrogram. November 2006.

Ormby, M (2005): Analysis of laminated documents using solid-phase microextraction. Journal of the Amercian Institute for Conservation,44(1): 13-26. As cited by BaUA (2011).

Remberger M, Kaj L, Hansson K, Andersson H, Brorström-Lundén E, Lunder H and Schlabach M (2013): Selected Plasticisers and Additional Sweeteners in the Nordic Environment. TemaNord 2013:505, Nordic Council of Ministers 2013http://dx.doi.org/10.6027/TN2013-505.

Polynt (2010): Specialty esters. Polynt S.p.A, Scanzorosciate, Italy. Accessed Aug. 2013.

Pors J, Fuhlendorf R. (2001): Phthalates and organic tin compounds in PVC products. Survey of Chemical Substances in Consumer Products, No. 1. Danish Environmental Protection Agency, Copenhagen.

Poulsen PB, Schmidt A. (2007): A survey and health assessment of cosmetic products for children. Survey of Chemical Substances in Consumer Products, No. 88. Danish Environmental Protection Agency, Copenhagen.

Skat (2013): Ny formel til fuldstændig denaturering af alkohol – Styresignal (in Danish: New formula for complete denaturation of alcohol – guiding signal). Accessed September 2013 at http://www.skat.dk/SKAT.aspx?oID=2111895)

Skårup S, Skytte L (2003): Forbruget af PVC og phthalater i Danmark år 2000 og 2001. [Consumption of PVC and Phthalates in Denmark in year 2000 and 2001]. Kortlægning af Kemiske Stoffer i Forbrugerprodukter nr. 35. Danish EPA, Copenhagen [In Danish]

SPT (2013): Cathrine Berliner Boteju, SPT, personal communication, September 2013. www.spt.dk.

Statistics Denmark (2013): Udenrigshandel, produktion og forsyning. Available at: http://www.dst.dk/da/informationsservice/oss/UHprod.aspx

Svendsen N, Bjarnov E, Poulsen PB (2007): Survey as well as health assessment of chemical substances in school bags, toy bags, pencil cases and erasers. Survey of Chemical Substances in Consumer Products, No. 84. Danish Environmental Protection Agency, Copenhagen.

Svendsen N, Pedersen SF, Hansen OC, Mossing JT, Bernth N (2004): Survey of chemical substances in toothbrushes. Survey of chemical substances in consumer products no. 42, 2004. Danish Environmental Protection Agency, Copenhagen.

Tønning K, Jacobsen E, Pedersen E, Strange M, Poulsen PB, Møller L and Boyd HB (2009): 2-åriges udsættelse for kemiske stoffer [The exposure of 2-year olds to chemicals]. Kortlægning af kemiske stoffer i forbrugerprodukter Nr. 103, 2009. DEPA (in Danish). Accessed August 2013 at http://www2.mst.dk/udgiv/publikationer/2009/978-87-92548-83-2/pdf/978-87-92548-84-9.pdf

Tønning K, Jacobsen E, Pedersen E, Strange M, Poulsen PM, Møller L, Boyd PB. (2009) Survey and health assessment of the exposure of 2 year-olds to chemical substances in consumer products. Survey of Chemical Substances in Consumer Products, No. 102. Danish Environmental Protection Agency, Copenhagen.

Tønning K, Malmgren-Hansen B, Jacobsen E, Pedersen E and Nilsson NH (2010): Phthalates in plastic sandals. Survey of Chemical Substances in Consumer Products, No. 107, 2010. Danish Technological Institute for DEPA. Accessed August 20123 athttp://www2.mst.dk/udgiv/publications/2010/978-87-92708-67-0/pdf/978-87-92708-66-3.pdf

Tønning K, Pedersen A, Lomholt AD, Malmgren-Hansen B, Woin P, Møller L and Bernth N (2008): Survey, emission and health assessment of chemical substances in baby products. Survey of Chemical Substances in Consumer Products, No. 90, 2008. Danish Technological Institute for DEPA. Accessed August 2013 at http://www2.mst.dk/udgiv/publications/2008/978-87-7052-717-0/pdf/978-87-7052-718-7.pdf

Ullmann´s (2012): Encyclopedia of Industrial Chemistry.Wiley-VCH Verlag GmbH & Co KGaA. As cited by Environment Agency Austria (no year).

US CPSC (2010): Toxicity Review of Diethyl phthalate (DEP). Memorandum. United States Consumer product Safety Commission.

US FDA, 2013): Nail Care Products - Safety and Regulatory Information. Accessed September 2013 at http://www.fda.gov/Cosmetics/ProductandIngredientSafety/ProductInformation/ucm127068.htm

Wilkes CE, Summers JW, Daniels CA, Berard MT (2005): PVC handbook. Carl Hanser Verlag, Munich 2005

Wittassek M, Koch HM, Angerer J, Brüning T. (2010): Assessing exposure to phthalates - the human biomonitoring approach. Mol Nutr Food Res. 2011 Jan;55(1):7-31.

Appendix 1: Background information to chapter 3 on legal framework

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

EU and Danish legislation
Chemicals are regulated via EU and national 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[5] and the CLP Regulation[6] are the overarching pieces of EU chemicals legislation regulating industrial chemicals. The below will briefly summarise the REACH and CLP

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

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 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:

1. It has to be identified as a SVHC leading to inclusion in the candidate list[7]
2. It has to be prioritised and recommended for inclusion in ANNEX XIV (These can be found as Annex XIV recommendation lists on the ECHA web-site)
3. It has to be included in REACH Annex XIV following a comitology procedure decision (substances on Annex XIV appear on the Authorisation list on the ECHA web-site).

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

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

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

This is done as a REACH Annex XV proposal.

The 'registry of intentions' gives an overview of 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

for the three types of Annex XV dossiers.

International agreements

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

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.

8.1.1.1 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).

Appendix 2: Danish proposal on criteria for endocrine disruptors

The following criteria for endocrine disruptors are suggested by the Danish Centre on Endocrine Disrupters (CEHOS, 2012).

Category 1 - Endocrine disrupter

Substances are placed in category 1 when they are known to have produced ED adverse effects in humans or animal species living in the environment or when there is evidence from animal studies, possibly supplemented with other information, to provide a strong presumption that the substance has the capacity to cause ED effects in humans or animals living in the environment. The animal studies shall provide clear evidence of ED effect in the absence of other toxic effects, or if occurring together with other toxic effects, the ED effects should be considered not to be a secondary non-specific consequence of other toxic effects. However, when there is e.g. mechanistic information that raises doubt about the relevance of the adverse effect for humans or the environment, category 2a may be more appropriate.

Substances can be allocated to this category based on:
Adverse in vivo effects where an ED mode of action is highly plausible
ED mode of action in vivo that is clearly linked to adverse in vivo effects (by e.g. readacross)

Category 2a - Suspected ED

Substances are placed in category 2a when there is some evidence from humans or experimental animals, and where the evidence is not sufficiently convincing to place the substance in category 1. If for example limitations in the study (or studies) make the quality of evidence less convincing, category 2a could be more appropriate. Such effects should be observed in the absence of other toxic effects, or if occurring together with other toxic effects, the ED effect should be considered not to be a secondary non-specific consequence of other toxic effects.

Substances can be allocated to this category based on:
Adverse effects in vivo where an ED mode of action is suspected
ED mode of action in vivo that is suspected to be linked to adverse effects in vivo
ED mode of action in vitro combined with toxicokinetic in vivo data (and relevant non test information such as read across, chemical categorisation and QSAR predictions)

Category 2b – Substances with indications of ED properties (indicated ED)

Substances are placed in category 2b when there is in vitro/in silico evidence indicating potential for endocrine disruption in intact organisms. Evidence could also be observed effects in vivo that could be ED-mediated.

¶

Survey of selected phthalates
This survey is part of the Danish EPA's review of the substances on the List of Undesirable Substances (LOUS). This survey concerns the phthalates DINP, DIDP, DPHP, DEP, DMEP and DIPP. The report presents information on the use and occurrence of the selected phthalates, internationally and in Denmark, information on environmental and health effects, releases and fate, exposure and presence in humans and the environment, on alternatives to the substances, on existing regulation, waste management and information regarding on-going activities under REACH, among others.

Kortlægning af udvalgte ftalater
Denne kortlægning er et led i Miljøstyrelsens kortlægninger af stofferne på Listen Over Uønskede Stoffer (LOUS). Denne kortlægning vedrører ftalaterne DINP, DIDP, DPHP, DEP, DMEP and DIPP. Rapporten indeholder blandt andet en beskrivelse af brugen og forekomsten af de udvalgte ftalater, internationalt og i Danmark, en beskrivelse af miljø- og sundhedseffekter af stofferne, udslip of skæbne, eksponering og forekomst i mennesker og miljø, viden om alternativer, eksisterende regulering, affaldsbehandling og igangværende aktiviteter under REACH.

Danish Ministry of the Environment
Environmental Protection Agency

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

www.mst.dk