

Chemical study on Bisphenol A

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Annex 1 Abbreviation list

Annex 2 Background information on aquatic toxicity

Preface

In the framework of the project "Investigating for chemicals in the future", the North Sea Directorate has put the department of Rijkswaterstaat Institute for Coastal and Marine Management (RIKZ) in charge, to start a study on unknown chemicals. The object of this project is to identify the most important contaminants, which present a threat to the North Sea and the identification of gaps in policy, management and knowledge. In the project monitoring data are evaluated and a number of "new" substances are proposed as a potential threat for the North Sea. On the 30th of June 2000 BKH Consulting Engineers has received the order to make a study on bisphenol A. This study will be directed on the whole track of bisphenol A in the environment. From production and emission to immission, waste and effects.

The project is coordinated by Mrs drs A.M.C.M. Pijnenburg of RIKZ. The project-leader of BKH is Mrs drs C.P. Groshart. The authors of the report are: Mr drs P.C. Okkerman and Mrs drs C.P. Groshart.

Summary

General

Bisphenol A is used as an intermediate (binding, plasticizing, hardening) in plastics, paints/lacquers, binding materials and filling-in materials. The substrate is mainly used for the production of polycarbonate resins (71%) and epoxy resins (27%). Furthermore bisphenol A is used as an additive for flame-retardants, brake fluids and thermal papers.

The current (1999) world-wide production of bisphenol A is approx. 2,000 ktonnes/year. Over the next 5 years, overall production is believed to grow to around 3,500 ktonnes/year in 2005.

Sources and emissions

The production of bisphenol A in the Netherlands in 1999 was around 280 ktonnes/year, which is approx. 35% of the total production in Europe and around 14% of the total world production. A review of all produced, used amounts and emissions is given in Table 1.

Over the years bisphenol A consumption has more than doubled. From 1993 to 1996, total consumption for polycarbonates grew with 11.6% per year and is expected to continue to grow at an average annual rate of 7.6% during the period 1996-2001. Bisphenol A consumption for the production of epoxy resins will also grow but more moderately.

In 1999 annual bisphenol A consumption in Europe is estimated at 680 ktonnes. Total polycarbonate consumption in the Netherlands is 14 ktonnes/year while other consumption of bisphenol A based products is 11 ktonnes.

Emissions of bisphenol A may occur during bisphenol A production, production of products using bisphenol A and from products in-use. Emission during bisphenol A production is around 2 tonnes/year to surface waters and 1 tonne to air. The most important emissions during bisphenol A product processing occur during production of phenoplast cast resins (43 tonnes to water in Europe), thermal paper production (151 tonnes to water in Europe) and the use of bisphenol A as inhibitor during PVC production (25 tonnes to water in Europe).

Total emissions are 2.1 tonnes to air, 199 tonnes to water and 30 tonnes to soil in Europe. The specific emissions for the Netherlands are unknown.

Emissions from products in-use are estimated at 160 kg from polycarbonates and <1 kg of epoxy resins used in can lining. Furthermore losses from PVC articles in-use are 20 tonnes to air and 30 tonnes to water.

Concerning emissions are the leaches of bisphenol A from baby bottles, cans and flasks to food. In baby bottles in a study an average of 56 ppm is found to leach and in another study a maximum of 20 mg BADGE/kg plastic leached from cans. Concentrations in food are not available.

Environmental characteristics and toxicity in aquatic systems

Bisphenol A has a moderately high water solubility (120 mg/l) and a low vapour pressure ($5.32 \cdot 10^{-5}$ Pa). The log K_{ow} value varies from 2.2 to 3.4. As a result of these characteristics bisphenol A has a tendency to partition into water and the rate of evaporation from soil and water will be low. The log K_{ow} indicates a low

bioaccumulative potential. Based on experimental data the BCF varies from 1 to 196, which also indicates a low potential to bioaccumulate in aquatic species. Bisphenol A is not susceptible to hydrolysis but has a potential to photolyse in water if not bound to organic matters (particulate phase) in water.

From biodegradation tests bisphenol A is found to be not readily biodegradable, but to be inherently biodegradable. However measured levels of bisphenol A before and after wastewater treatment suggest a high level of removal. After a short period of adaptation, bisphenol A seems to be readily biodegradable. The same goes for the biodegradation in natural waters after acclimatisation.

Bisphenol A is acutely moderately toxic to freshwater and marine algae, fish and crustaceans. Based on chronic tests bisphenol A is very slightly to slightly toxic in freshwater and moderately toxic in marine water. Based on 1 chronic study with endocrine effects (skewed sex-ratio) with an amphibian, bisphenol A is very toxic.

Occurrence and behaviour in aquatic systems

In the Netherlands concentrations of 21 to 40 ng/l have been found in fresh waters and of 3.5 to 23 ng/l in marine waters. The concentrations in industrial and urban wastewater are in the range of 300 to 700 ng/l but for two locations, where the concentration reached the 2 mg/l. Bisphenol A concentration in sewerage and wastewater sludge ranged from <116 to 7000 ng/l (15-270 ng/g dry matter). In sediments concentrations were below the detection limit of 0.05 - 0.25 µg/kg dry matter. There are no data on concentrations in other environmental compartments. In Japan concentrations of 60 to 1900 ng/l have been measured in surface water in 1974-1978.

All measured concentrations are considerable lower than the calculated HTBA value of 247 mg/kg and lower than the calculated iMPCs of 0.064 mg/l and 22.9 mg/kg for resp. surface water and sediment.

Policy

No specific quality standards are derived for bisphenol A. Bisphenol A is not regulated. However there are some regulations with regard to the maximum limits of bisphenol A in food and migration from materials that come into contact with food.

Conclusions and recommendations

From the results of this study can be concluded that bisphenol is widely used and therefore also widely spread in the environment. Current data on the release and distribution of bisphenol A are limited, but suggest that the substance will primarily be available in the aquatic phase in surface waters and probably will hardly bioaccumulate in organisms.

Estimates of emissions to the environment demonstrate that significant amounts may be released to surface water by discharge of treated wastewater.

For evaluation of the aquatic toxicity of bisphenol A, a limited amount of data was available.

Considering the large emission estimates to surface water, their high tendency to spread in aquatic systems and the fact that bisphenol A is moderately toxic to aquatic organisms, it is recommended to perform an additional study on these compounds with emphasis on collection and verification of emission factors and furthermore to generate new toxicity data. Especially in the area of endocrine disrupting effects more research should be done because these effects concentration may be a factor 100-1000 lower. Further research into

concentrations in food are also considered important in relation to the leaching of bisphenol A from baby bottles, flasks and cans.

Table 1:
Overview of consumption volumes and emissions in Europe

| Use Pattern and production Data | Tonnes/year | Emission to air In kg/year | Emission to water In kg/year | Emission to soil In kg/year |
|--|--------------------|-------------------------------|---------------------------------|--------------------------------|
| Bisphenol A production | 700,000 | 985 | - | 1996 |
| Polycarbonate production | 486,880 | 144.5 | 202..3 | - |
| Epoxy resin production | 171,095 | - | 403.25 | - |
| Phenoplast resins | 8,800 | - | 18,650 | - |
| Unsaturated polyester resin production | 3,000 | 0 | 0 | - |
| Can coating manufacture | 2,460 | 0 | 0 | - |
| Use PVC production and processing | 2,250 | - | - | - |
| Inhibitor during production process | - | - | 24,900 | - |
| Antioxidant during processing | - | 250 | 321 | - |
| Preparation of additive packages | - | - | 318 | - |
| Use of additive packages | - | 250 | 321 | - |
| Antioxidant in plasticiser | - | - | 636 | - |
| Plasticiser use | - | 500 | 42 | - |
| Alkyloxyated bisphenol A manufacture | 2,020 | 0 | 0 | - |
| Thermal paper manufacture | 1,400 | - | 106 | - |
| Thermal paper recycling | - | - | 151,600 | - |
| Polyols/Polyurethane manufacture | 950 | 0 | 0 | - |
| Modified polyamide production | 150 | 0 | 0 | - |
| Tyre manufacture | 110 | 0 | 0 | - |
| Brake fluid | 45 | 0 | 0 | - |
| Minor uses | 5,990 | - | - | - |
| Flame-retardant | (17,000) | 0 | 0 | - |
| EU Consumption of bisphenol A | 684,650 (~700,000) | 2,100 | 199,000 | 30,000 |

1 Introduction

1.1 Backgrounds

Bisphenol A is used as an intermediate (binding, plasticizing, hardening) in plastics, paints/lacquers, binding materials and filling-in materials.

About the effects of bisphenol A on the aquatic environment some information is available. This is alarming because bisphenol A is found in the aquatic environment. To get an opinion on the consequences of the occurrence of these chemicals in the aquatic environment, the underlying report is composed. This report gives an overview of the available knowledge on bisphenol A in regard to the aquatic environment. Important criteria for selecting this chemical is:

- it is used and/or produced in the Netherlands;
- it is on several attention lists;
- the production of these chemicals is growing;
- it is expected to be persistent and bioaccumulative;
- it is expected to present a danger to the environment.

This report is produced in the framework of the project "Investigating for chemicals in the future".

1.2 Objectives

The objectives of this study with regard to bisphenol A are:

To give an analysis of the problems in the aquatic environment: a description of the load, occurrence, behaviour and effects and a analysis of the problems which indicate how the presence of bisphenol A may disturb the functioning of the different water systems by effects on sensitive organisms. Furthermore giving an overview of the national and international policy.

In this study the most recent information on bisphenol A has been used. It is possible that in some attention areas the essential information is not yet available. In these cases recommendations for further research will be done.

The study is broadly set up. The next aspects will be handled. In chapter 2 the chemical characteristics of bisphenol A are described. In chapter 3 the production process is clarified and the use of these chemicals is described. In chapter 4 the sources of emissions, primarily to the aquatic environment, are estimated and specified. In chapter 5 and 6 the behaviour in the environment and the occurrence in the environment are described, respectively. In chapter 7 and 8 an overview is given of the toxicity data and the policy, respectively.

1.3 Limitations

In principle the study conforms itself to information that has a relation to aquatic systems. The situation around air or soil will be briefly described. Furthermore the emphasis lies on the situation in the Netherlands. In some cases the situation of the basins of Rhine, Meuse and Schelde will be commented. The information will be presented briefly. For more extensive information referred is to the concerned sources.

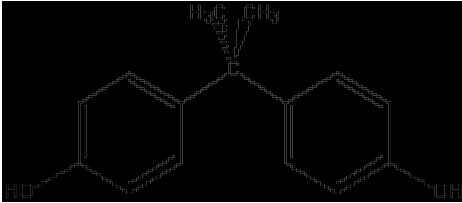
2 Physical chemical properties

2.1 Identification

In this study the risks of bisphenol A (BPA) for the aquatic environment are evaluated. Bisphenol A is extensively used in epoxy and polycarbonate resins (polymers), and furthermore in non polymers as flame retardant in the form of tetrabromobisphenol A, as a stabiliser in PVC and as an antioxidant in brake fluid, rubber and plastics.

The purity of bisphenol A varies from 99-99.8% depending upon the manufacturer. Impurities typically include phenol (<0.06%), ortho and para isomers of bisphenol A (<0.2%) and water (<0.2%) (UK, 2000).

Table 2.1:
Characteristics and physical properties of Bisphenol A (HSDB, 2000)

| | |
|--------------------|--|
| Substance | Bisphenol A (BPA) |
| CAS number | 80-05-7 |
| Chemical formula | C ₁₅ H ₁₆ O ₂ |
| Smiles notation | Oc(ccc(c1)C(c(ccc(O)c2)c2)(C)c1 |
| Molecular mass | 228.28 |
| Physical state | White to light brown flakes or powder |
| Chemical structure |  |

| | |
|--------------------|--|
| Synonyms | Bis(4-hydroxyphenyl) dimethylmethane; 2,2-bis(4-hydroxyphenyl)- propane; Bisphenol a ; P,p'- bisphenol a ; 4,4'-dihydroxydiphenyl-dimethylmethane; P,p'-dihydroxydiphenyl-propane; 2,2-di(4-hydroxy-phenyl)propane; Dimethyl bis(p-hydroxyphenyl)methane; Dimethyl-methylene-p,p'-diphenol; Diphenylolpropane; 2,2-di(4-phenylol)-propane; Isopropylidenebis (4-hydroxybenzene); P,p'-isopropylidenebisphenol; 4,4'-isopropylidenebisphenol; P,p'-isopropylidenediphenol; 4,4'-isopropylidenediphenol; 4,4'-(1-methyl-ethylidene)bisphenol; Phenol, 4,4'-dimethyl-methylenedi-; Phenol, 4,4'-isopropylidenedi-; Phenol, 4,4'-(1-methylethylidene)bis-; Propane, 2,2-bis(p-hydroxyphenyl)-; |
| Technical products | Dioan; Diano; Ipognox 88; Nci-c50635; Parabis a; Pluracol 245; Rikabanol; Ucar bisphenol hp ; |

2.2 Physico-chemical characterisation

Chemical and physical data for bisphenol A in table 2.2 indicate that the substance has the tendency to partition into water and that the rate of evaporation from soil and water will be low. Bisphenol A has a moderately high water solubility (120 mg/l at 25°C), a low vapour pressure (5.32×10^{-5} Pa at 25°C) and a low Henry's Law constant of 1.0×10^{-6} to 1×10^{-5} Pa m³ mol⁻¹. The log Kow indicates a moderate bioaccumulative potential.

It should be emphasized that the vapour pressure considerably increases at increasing temperature, potentially causing higher atmospheric concentrations under specific conditions such as production or processing. It is also possible that bisphenol A may enter the environment as dust particles, during production, processing or final use of the product.

Table 2.2:
Chemical and physical data of bisphenol A (HSDB, 2000; TemaNord, 1996; Iuclid, 1996; UK, 2000; CIS Envirofate, 2000; UBA, 1997; Staples, 1996)

| Compound | Bisphenol A | References |
|-------------------------------|---|---|
| CAS no | 80-05-7 | |
| Molecular formula | C ₁₂ H ₁₆ O ₂ | |
| Molecular mass (g/mol) | 228.31 | |
| Melting point (°C) | 153-157 | HSDB, 2000 |
| | 150 – 156.7 ^a | IUCLID, 1996 |
| Decomposition Point (°C) | 220 | HSDB, 2000 |
| Volatility (weight loss) | | |
| Vapour Pressure (Pa) | 25°C $5.32 \cdot 10^{-7}$ | TemaNord, 1996 |
| | 170°C 27 | TemaNord, 1996 |
| | 20°C = $1.6 \cdot 10^{-7}$ | IUCLID, 1996 |
| | 25°C = $4.1 \cdot 10^{-7}$ | IUCLID, 1996 |
| | 0.2 mm Hg at 170 °C, 1*10 ⁻⁸ mm Hg at 25°C estimated from Henry coefficient and water solubility | Dorn, et al., 1987 (Envirofate 2000) |
| Solubility H2O (25°C ; mg /l) | 120 – 300 | HSDB, 2000 |
| | 120 | Howard, 1990 (UK, 2000); Dorn, et al., 1987 (Envirofate 2000) |
| | 301 | Bayer, 1988 in UK, 2000 |
| Soluble in (28°C; g/kg) | CCl4 slightly | HSDB, 2000 |
| | Benzene soluble | HSDB, 2000 |
| Log K _{ow} | 3.32, 3.84, 2.2-3.4 | TemaNord, 1996 |
| | 3.32 | Howard, 1990 in UK, 2000 |
| | 2.2 | Eadsforth, 1983 in UK, 2000 |
| | 3.4 | Bayer, 1993 in UK, 2000 |

| | | |
|-----------------------------|---|--|
| Koc (calculated) | 293 – 1524 | UBA, 1997 |
| Melting point (°C) | 150-155 | HSDB, 2000 |
| Boiling point (°C) | 220 at 5 hPa | CRC, 1995 and Merck, 1989 in UK, 2000 |
| | 250-252 at 17 hPa | Von Braun, 1925 in UK, 2000 |
| Density (25°C/25°C) | 1.195 | HSDB, 2000 |
| Henry's Law Constant (25°C) | $1.0 \cdot 10^{-6}$ - $1.0 \cdot 10^{-5}$ Pa m ³ mol ⁻¹ | TemaNord, 1996 |
| | $1 \cdot 10^{-11}$ Atm.m ³ /mol at 25°C calc. | Syracuse research corp, 1998 (Envirofate 2000) |

- a. The melting point of the commercial material will be lower because of impurities. The melting point for the pure material will be reflected by higher values: 155-157°C (UK, 2000). 155°C will be used for calculations

2.3 References

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3 Applications, productions and use

3.1 Major applications

Bisphenol A is predominantly an intermediate for the production of other products. Main uses of bisphenol A are binding, plasticizing, and hardening functions in plastic products, paints/lacquers, binding materials and filling-in materials. The substance is used in the chemical industry, the iron/metal industry, the building and construction industry, the plastics industry and the service industry.

Bisphenol A is mainly used for the production of polycarbonate resins (71%); epoxy resins (27%); unsaturated polyester, polysulfone, polyetherimide and polyarylate resins (25%) (Chemexpo, 1999). Non-polymer BPA is used as an additive for a number of purposes such as flame-retardants, brake fluids and thermal papers.

3.1.1 Applications of Polycarbonate resins

Polycarbonate plastic is used for structural parts, impact-resistant glazing such as safety helmets and bullet resistant laminate, street-light globes, household appliance parts, sheet and glazing applications, components of electrical/electronic devices, compact discs, automotive applications, reusable polycarbonate bottles, food and drink containers, powder paints protective coatings and many other products.

In some overseas areas where drinking water is not readily available, polycarbonate is used for large 20 liter water bottles.

In the Netherlands, Germany, Switzerland, England, the U.S.A. and many other countries, polycarbonate is widely used for returnable milk bottles, which can withstand high temperature sterilization and repeated use, while contributing to the conservation of resources and reduction of waste materials.

3.1.2 Applications of epoxy, polyester and other resins

The diglycidyl ether of bisphenol A (BADGE) is used in the production of epoxy resins, which are liquid resins that cure to form hard, insoluble, chemical resistant plastics when hardening agents are added. Cured epoxy resin is used for coatings such as corrosion protectors, lacquers in the automotive industry, housings for electrical equipment, laminates, industrial floorings, construction parts, composites, adhesives, lacquers on food and beverage cans.

Bisphenol A is also the starting product for the manufacture of dental composites resembling epoxy resin (dental fillings and sealing agents).

3.1.3 Non polymer applications

A number of non polymer applications of bisphenol A are colour development component in thermal paper, antioxidant in high-temperature cables and tyres, reactant in the production of tetrabromo bisphenol A (flame retardant).

Bisphenol A is also used as an additive in thermal paper, in high-temperature cables and rubber tyres. In this application bisphenol A does not form a chemical bond with the host material and is therefore released more easily from the product.

3.2 Production processes

3.2.1 Bisphenol A

In commercial production bisphenol A (a white powder) is produced by the hydrochloric acid-catalyzed condensation reaction of two moles phenol with one mole of acetone while bubbling hydrogen chloride through the mixture.

In the production process phenol and acetone are injected into a reactor filled with a cation exchanger. Conversion to bisphenol A occurs at about 75°C. The mixture passes into a concentrator where it is freed of water and acetone under reduced pressure. Bisphenol A crystallises out when cooled and is then washed with phenol and distilled out under reduced pressure (UK, 2000).

Impurities are tri- or monohydroxy by products, which can be removed by distillation and extractive crystalliation under pressure (HSDB, 2000). Two grades of bisphenol A are produced. The more expensive (in terms of production cost) polycarbonate grade contains a maximum of 0.2% 2,4-isopropylidenediphenol to ensure superior optical and toughness properties. The epoxy grade may contain up to 5-7% 2,4- isomer, but in commercial practice generally contains less and may be essentially the same purity as polycarbonate grade.

3.2.2 Polymer processing

Processing of polycarbonate

Polycarbonate was first developed in Germany in 1958. Two processes are used for the production: Schotten-Baumann reaction of bisphenol A dissolved in a twentyfold excess of methyl chloride where carbonyl chloride (phosgene) is added and reacted at a specific processing temperature.

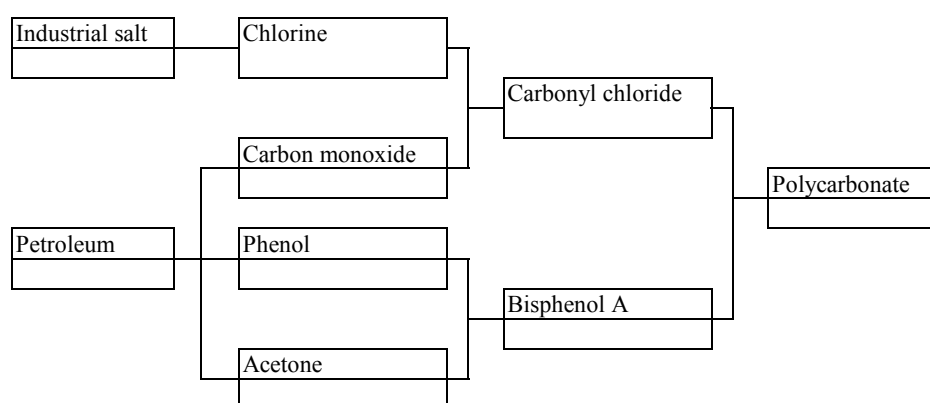


Figure 3.1:
Processing scheme for the production of polycarbonates

Another melt-phase continuous process that produces polycarbonate (PC) via transesterification route, requires no solvent. In this process, diphenylcarbonate is reacted with bisphenol A at 250-300°C in the presence of a proprietary catalyst. At such temperatures, the polymerization product is molten and can be pelletized directly from the reactor. Phenol, a by-product of the reaction, is used as a feedstock for bisphenol A production, thus closing the process loop (Chemical engineering 1993, from EnviroSense).

The residual bisphenol A content in polycarbonate products is typically less than 100 parts per million (ppm). When higher temperatures are used than in normal processing, there may occur thermal degradation of polycarbonate resin in melt

condition and increase residual bisphenol A in polycarbonate products (PRM, 1999).

For further processing polycarbonate can be cured from solutions to fibres or foils or thermoplastic in moulded cast work or extrusion from granulate to produce laminates or foils. The bisphenol A content in polycarbonate is estimated at 89% (Bayer\Dow, 1996).

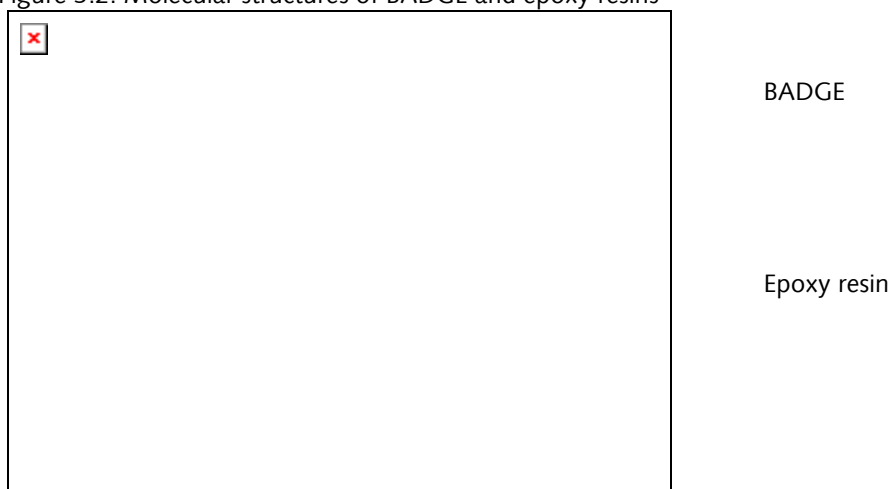
Processing of epoxy resins

Epoxy resins are a family of synthetic resins including products, which range from liquids to solids. Standard epoxy resins are produced using one mole of bisphenol A and two moles of glycidyl ether (epichlorhydrin) in the presence of an alkaline catalyst to form bisphenol A diglycidylether (BADGE). In the next step BADGE undergoes dehydrohalogenation with an alkali. Approximately 80% of all epoxy resins are produced using this two step process (Muskopf/McCollister, 1987).

An alternative production process is the Taffy process. In this process bisphenol A reacts directly with epichlorohydrin in the presence of caustic soda. At the completion of the reaction, the mixture consists of an alkaline brine solution and water-resin emulsion and recovery of the product is accomplished by the separation of phases, washing the resin with water and removal of water under vacuum conditions (Kirk-Othmer, Vol 9, 1994).

Whereas polycarbonate is almost completely produced on the basis of bisphenol A, in epoxy resins the bisphenol A content is lower and more variable (75-80%) (Bayer/Dow, 1996, Muskopf/ McCollister, 1987; Serini, 1992). UBA (1997) assumed an average bisphenol A content of 70%.

Figure 3.2: Molecular structures of BADGE and epoxy resins



Curing of epoxy resins generally occurs at ambient temperatures and is achieved by the chemical reaction of the epoxy with a second reactant such as amines, polyamines, polyamides, amine products, or other reactants. Cure can occur at higher temperatures when reacted with anhydrides, carboxylic acids, phenol or novolac (phenol-formaldehyde) thermoplastic resins.

Each of the above mentioned reactants impart a different performance characteristic to the cured epoxy compound. Rigidity and upper temperature performance can be controlled. The cross-linking reaction is exothermic and

irreversible. The mixed reactants have a limited time in which they are suitable for processing. Cured materials are amorphous.

Physical and mechanical properties vary as the temperature increases. Upper temperature is limited by the glass transition temperature and varies from 49-249°C. The primary use of epoxies in the chemical process industries is in the manufacture of reinforced composites (Benjamin et al., 1994).

Bisphenol A is also used in the production of ethoxylated bisphenol A, which is used as an intermediate in the manufacture of some forms of epoxy resins. In the process bisphenol A is charged to the first vessel and melted out at 140°C. A catalyst is added under vacuum and the bisphenol is then ethoxylated. Production is done on a batch wise basis.

Epoxy can coatings are based on high molecular weight epoxy resins made by advancing liquid epoxy resin with bisphenol A.

Processing of polyester and other resins

As well as epoxy resins bisphenol A may be used in the production of a number of other resins including phenoplast resins, phenolic resins, unsaturated polyester resins, polyols, PVC, fumarates, dimethacrylates, modified polyamides. Often resin manufacturers group all the resins they produce as epoxy resins, so it is difficult to determine the total amount of the other resins produced.

Phenoplast resins are epoxy resins that are cross-linked with phenol to give a higher molecular weight solid epoxy resin (Kirk-Othmer, 1994).

Phenolic resins are based upon the reaction products of phenols (bisphenol A in this case) with formaldehyde. The phenolic resins formed using bisphenol A are used in low colour moulding compounds and coatings (Kirk-Othmer, 1996a).

There are two unsaturated polyester resin groups based upon bisphenol A; bisphenol fumarates which are used in applications involving highly corrosive environments; and bisphenol A epoxy dimethacrylates which have high flexural properties and high tensile elongation (Kirk-Othmer, 1996b).

Bisphenol A fumarate plastics are formed by reacting bisphenol A with propylene oxide to form a glycol, which is then reacted with fumaric acid to produce a resin. These resins have better resistance to acids than other polyesters and better resistance to alkali than vinyl ester. Temperature resistance is acceptable to 232°C. Typical applications are fiber-reinforced tanks and piping (Benjamin et al., 1994).

Bisphenol A is also used in the production of modified polyamide. The modified polyamide grades produced have reduced moisture absorption conferring improved dimensional stability to the finished parts. The modified polyamide is produced via a dry process in closed systems. Bisphenol A is introduced into polyamide at an average concentration of less than 8% by means of a compounding extruder. Bisphenol A functions as an additive, being tightly bound within the polar polyamide matrix. The modified polyamide is used for finished parts with improved dimensional stability mainly in electrotechnical applications.

Processing of non-polymer products

Bisphenol A is also used in PVC manufacture and processing. There are four reported uses of bisphenol A within this industry: as an inhibitor or reaction 'killing' agent during the polymerisation stage of PVC production; as an antioxidant in PVC processing; as a constituent of an additive package used in PVC processing; and as an antioxidant in the production of plasticisers used in PVC processing. Bisphenol A

diglycidylether (BADGE) is also used as additive for stabilizing PCV-organosol lacquers (UBA, 1997).

Bisphenol A is furthermore used in the production of polyols that are used in the production of polyurethane. This use is only thought to occur at one site within the EU. In the process bisphenol A is a reactant in the production of rigid polyols. The hydroxyl group of the bisphenol A molecule reacts with propylene oxide to form a polyether binding. The polyol is then reacted with isocyanate to form a rigid polyurethane foam. Any residual bisphenol A in the polyol reacts with the isocyanate. The production process is dry.

Bisphenol A is used as a compounding ingredient for the manufacture of car tyres. The highly automated compounding step usually involves the blending of styrene butadiene rubber with highly aromatic extender oils, carbon black and various amine accelerators for the curing process. The compounding process is a dry operation with no aqueous effluents. The role of bisphenol A, which is used in small quantities, as an antioxidant, is not fully understood in terms of imparting technological advantage to the cured elastomers. In the presence of the other compounding ingredients and during the curing process, the bisphenol A becomes incorporated into the polymer matrix. Although it is used as an anti-oxidant this appears to be specifically for the compounding phases and it is presumably intended to protect the materials at this stage. There is no indication that it is intended to be the major anti-oxidant in the actual tyres, and so it is not expected to be present at significant levels in the finished product. As an anti-oxidant it will also react to give complex products so a proportion will be used up in this way.

Non-polymer BPA is used as additive such as organic colouring component in thermal paper as anti-oxidant in brake fluid and as flame retardant after bromination to tetrabromo-bisphenol A (TBBPA).

Bisphenol A is used as an additive in the coating that is applied to thermal paper, and its main function is as a developing agent when the paper is heated. The bisphenol A in the paper reacts when it is heated; however if the paper is not completely developed, residual bisphenol A may remain. 1 Tonne of bisphenol A is necessary for the production of approximately 75 tonnes/year of thermal paper. Based upon a total usage of 1,400 tonnes/year bisphenol A the total amount of thermal paper manufactured that contains bisphenol A is 105,000 tonnes/year. In tetrabromo-bisphenol A (TBBPA) production methylene chloride is used as reaction solvent to dissolve BPA. The reagent mixture is heated in a closed reaction vessel at temperatures between 40 and 60°C, the latter being the boiling point of bromine. The reactor is equipped with a reflux condenser which operates at 10-20°C, to recycle bromine vapours. Non-condensable reaction products such as hydrogen bromide are removed in serial scrubbing towers. In TBBPA production, hydrogen bromide is converted into bromine by hydrogen peroxide addition. At the end of each process cycle, a solvent is added to the reaction mixture to dissolve the polybrominated products. Excess bromine is distilled from the reaction vessel, condensed and recycled for subsequent use in following production cycles. After completion of the bromine recovery, the reaction mixture is mixed with water to dissolve hydrogen bromide and other water-soluble products. The reaction mixture is subsequently decanted to separate solvent and water layers. Wastewater is sent to the production site's effluent treatment plant.

3.3 Major producers

The bisphenol A industry currently consists of around 19 major companies in the United States, Western Europe and Japan.

Table 3.1:
Major producers of Bisphenol A (Chemexpo, 1999)

| Country | Producer | Location | Capacity (ktonnes/year) |
|---------------------|--|-----------------------|-------------------------|
| The Netherlands | Shell | Pernis | 110 |
| | GE Plastics | Bergen op Zoom | 210 |
| Belgium | Bayer Antwerpen N.V. | Antwerp | 220 |
| Germany | Bayer AG | Krefeld-Uerdingen | 160 |
| | Dow Deutschland Inc. | Rheinmunster | 100 |
| Spain | GE Plastics | Cartagena | 110 |
| Romania | Petro Borzesti | Borzesti | 10 |
| Poland | ZC | Blachownia | 10 |
| <i>Total Europe</i> | | | <i>930</i> |
| USA | Aristech | Haverhill, Ohio | 104 |
| | Dow | Freeport Texas | 166 |
| | GE Plastics | Burkeville, Alabama | 75 |
| | GE Plastics | Mount vernon, Indiana | 265 |
| | Shell | Deer Park, Texas | 249 |
| | Bayer | Bayport, Texas | 159 |
| <i>Total USA</i> | | | <i>1018</i> |
| Japan | Idemitsu | Chiba | 70 |
| | Mitsubishi | Kashima | 80 |
| | Mitsui | Nagayo and Osaka | 80 / 60 |
| | Shin Nihon (Mitsubishi chem./Nippon steel) | Kyusu | 95 |
| | | | |
| India | Kesar | Loteparhuram | 7.5 |
| Taiwan | Nan Ya | Mailiao | 72 |
| | Chang Chun | Mailiao | 20 |
| | Taiwan Prosperity | Linyuan | 25 |
| Singapore | Mitsui | Pulau Sakra | 70 |
| Korea | Kumho P & B | Yeochon | 30 |
| China | Wuxi Resin | Wuxi | 10 |
| <i>Total Asia</i> | | | <i>619.5</i> |
| <i>Total world</i> | | | <i>2567.5</i> |

3.4 Production volumes and developments

Over the different years and regions in literature several figures are available on the production volumes of bisphenol A: The global production of bisphenol A was estimated at 1,100,000 tonnes/year in 1993 and 1,600,000 tonnes/year in 1996 (SRI, 2000).

The bisphenol A production in Europe was estimated at 350,000 tonnes/year in 1993, 420,000 tonnes/year in 1995 (UBA, 1997) and 700,000 tonnes/year in 1999 (CEFIC data, from UK, 2000).

The production in the USA was estimated at 788,000 tonnes/year in 1997 (1.73 billion pounds) and 820,000 tonnes/year in 1998 (1.8 billion pounds); extrapolated to 2002: 1,040,000 tonnes/year (2.3 billion pounds). These data include USA exports, which amounted to 60,000 tonnes/year (132 million pounds) in 1996 and averaged 70,000 tonnes/year (161 million pounds per year) in the 1994-96 period (imports are considered negligible) (Chemexpo, 1999).

In Japan, 1995 approximately 300,000 tonnes were produced annually.

In figure 3.3 the global production of bisphenol A is reflected as well as the expected production.

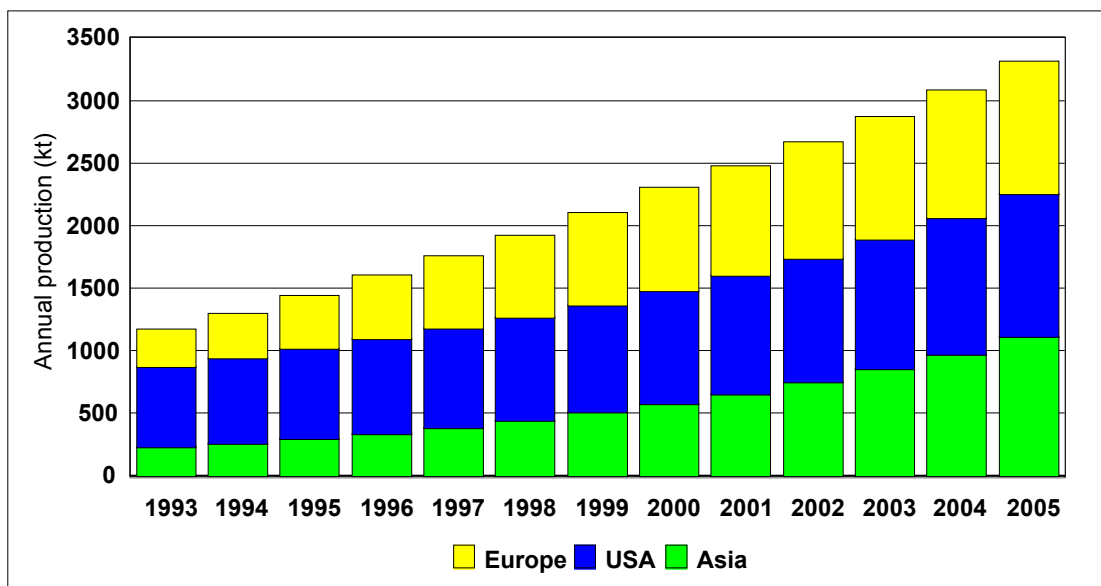


Figure 3.3:
Global production of Bisphenol A

3.4.1 Production in the Netherlands

Main producers of bisphenol A in the Netherlands are GE Plastics and Shell in Pernis with an capacity of 320,000 tonnes/year and an estimated total production of 280,000 tonnes/year in 1999 (BKH estimate), which is approximately 35% of the total production in Europe.

3.5 Development of consumption

Bisphenol A consumption has more than doubled during the past decade, driven primarily by heavy demand for polycarbonate resins. Polycarbonates (PC), with major outlets in automotive parts, compact discs, and sheet and glazing applications, have consistently grown at near double-digit rates and now account for more than 60 percent of bisphenol A's end-uses.

Total consumption in Europe, USA and Japan regions grew at an average rate of 11.6% per year, from 1993 to 1996. Bisphenol A demand in the polycarbonate market is expected to grow at an average annual rate of 7.6% during 1996-2001 in Europe USA and Japan. Epoxy resins have also experienced considerable growth, but are expected to grow only moderately over the next few years (SRI, 2000).

The annual bisphenol A consumption in the EU is estimated at 380,000 tonnes/year in 1995 (Bayer/Dow, 1996). In 1999 the bisphenol A consumption in Europe is estimated at 680,000 tonnes (UK, 2000) (see table 3.2).

Remarkable, is the increasing PC-use for the production of packaging materials (3% in Western Europe, 7000 tonnes): especially for milk and dairy products and large water flasks (20 l). In 1995 in Europe the PC demand for milk flasks is estimated approximately 1,000 tonnes/year. PC in households is used for household machines, place mats, kitchen utensils, coffee filters, flasks/cans, and baby-milk-flasks. In 1995 the PC use in households is estimated at 3.500 tonnes in Western Europe.

Based upon submissions to CEFIC over the period 1996-1999 made by bisphenol A manufacturers and end users, the following use pattern can be extracted (UK, 2000).

Table 3.2:
Bisphenol A use pattern data (UK, 2000)

| Use Pattern Data | Tonnes/year | Percentage of EU consumption |
|--|-------------|------------------------------|
| Polycarbonate production | 486,880 | 71.1 |
| Epoxy resin production | 171,095 | 25.0 |
| Phenoplast resins | 8,800 | 1.3 |
| Unsaturated polyester resin production | 3,000 | 0.4 |
| Can coating manufacture | 2,460 | 0.4 |
| Use PVC production and processing | 2,250 | 0.3 |
| Alkyloxyolated bisphenol A manufacture | 2,020 | 0.3 |
| Thermal paper manufacture | 1,400 | 0.2 |
| Polyols/Polyurethane manufacture | 950 | 0.1 |
| Modified polyamide production | 150 | <0.1 |
| Tyre manufacture | 110 | <0.1 |
| Brake fluid | 45 | <0.1 |
| Minor uses | 5,990 | 0.9 |
| EU Consumption | 684,650 | |

Information on the bisphenol A content in the different types of products, presented in Table 3.3, has been obtained from the Danish Product Register prepared in 1998 (UK, 2000). In the Danish Product Register 915 products are reported as containing bisphenol A. The total quantity of bisphenol A used in products is reported as 151 tonnes/year.

Table 3.3:
Information from Danish Product Register (June 1998)

| Product Type | Bisphenol A concentration in product | Number of products | Quantity of bisphenol A (Tonnes/year) |
|--------------------------------|--|--------------------|---------------------------------------|
| Insulation materials | 0-1% | 3 | <1 |
| Process regulators (Hardeners) | 0-1% | 60 | <1 |
| | 1-5% | 39 | 2 |
| | 5-10% | 15 | 1 |
| | 10-20% | 22 | <1 |
| | 20-50% | 23 | 17 |
| Fillers | 0-1% | 42 | <1 |
| | 1-5% | 3 | 16 |
| Softeners | Information classified as confidential on register | | |
| Adhesives, binding agents | 0-1% | 180 | <1 |
| | 5-10% | 3 | <1 |
| | 20-50% | 3 | <1 |
| Construction materials | 0-1% | 29 | <1 |
| | 10-20% | 3 | <1 |
| | 20-50% | 9 | 2 |

Note to table 3.3. If the number of products within a category is sufficiently low the information is considered to be confidential and is marked as such. If the number of products within a given concentration interval is too small the line is deleted. This can result in totals larger than the sum of the above mentioned numbers.

In 1995 in Germany domestic consumption in final products was in total 119,500 tonnes/year and consisted of PC: 77,000 tonnes/year, EpR: 41,000 tonnes/year and other uses 1,450 tonnes/year (UBA, 1997).

In recent years, the use of polycarbonate products has increased, especially as an alternative to metal or melamine-formaldehyde resin tableware for school lunches.

A substantial increase in use of bisphenol A's is expected, based on the high growth expected for CDs during the next few years and the emergence of new markets, such as polycarbonates for auto-glazing. Epoxies are projected to grow at a more modest annual rate of 3 to 4 percent, based on continued wide acceptance in adhesives, powder coatings, and electrical and electronic applications.

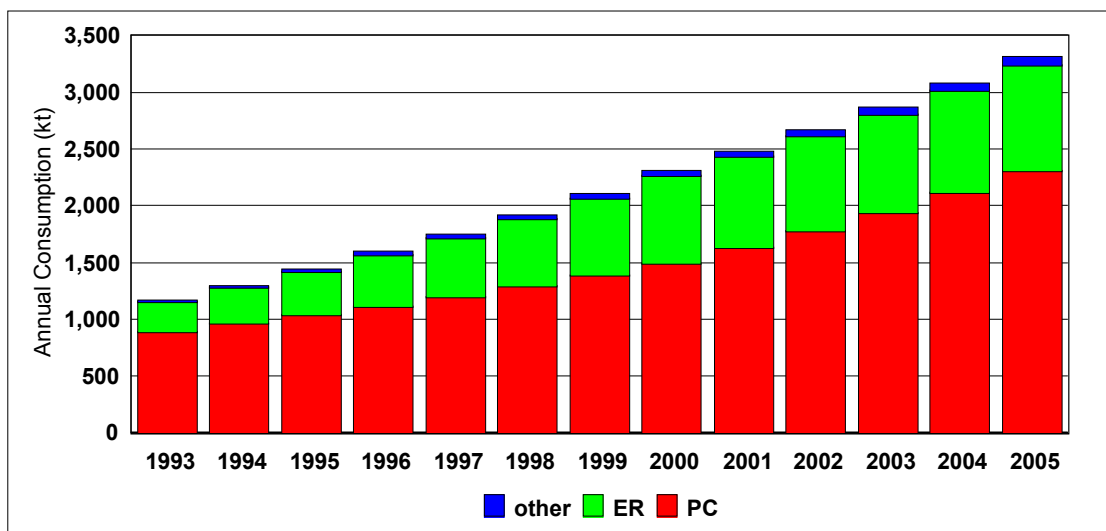


Figure 3.4: Global consumption of bisphenol A in polycarbonates (PC), epoxy resins (ER) and brominated TBBPA flame-retardants

3.5.1 Specific demands in the Netherlands

No consumption data on bisphenol A are available for the Netherlands. Assuming a proportionate relationship between the consumption in the Netherlands and Europe, combined with a related growth rate (growth PC and EpR consumption of 10% and 5.5%, respectively), the bisphenol A consumption data in the Netherlands as presented in table 3.4 is estimated:

Table 3.4: Estimated bisphenol A consumption in the Netherlands (tonnes/year)

| | | | | | |
|---|--------|--------|--------|--------|--------|
| Bisphenol A consumption in products | 1996 | 1997 | 1998 | 1999 | 2000 |
| PC consumption | 9,600 | 10,500 | 11,500 | 12,700 | 14,000 |
| EpR plastic and non-plastic bisphenol A consumption | 8,900 | 9,400 | 10,000 | 10,500 | 11,100 |
| Flame Retardant BPA consumption | 330 | 350 | 380 | 410 | 450 |
| Total BPA consumption | 18,800 | 20,300 | 21,900 | 23,600 | 25,600 |

3.6 Waste disposal

3.6.1 General

Polycarbonate and epoxy resin wastes are either generated in the form of used consumer goods or as industrial waste materials. Plastic wastes are mainly materials from cars, boats, computers and consumer electronics such as TV sets, audio equipment, etc. and non-plastic materials such as paint, textiles, lacquers.

Being constituents of regular industrial, company and municipal waste, these plastic and non-plastic materials are currently disposed of with these waste streams.

3.6.2 Incineration

Polycarbonates en epoxy resins

Incineration of polycarbonates and epoxy resins will result in a complete removal of all bisphenol A.

3.6.3 Waste separation and recycling

Recycling of polycarbonates and epoxyresins are of minor importance. Nevertheless some experiments have been carried out in recycling computer housings and the reuse of CDs (UBA, 1997).

3.7 Conclusions and recommendations

Bisphenol A production in 1999 was approx. 2,000 ktonnes/year worldwide, 680 ktonnes/year in Europe and 280 ktonnes in the Netherlands (14% of world production). Bisphenol A is primarily utilised as an intermediate for the production of polycarbonates and epoxy resins. The bisphenol A consumption has grown with 11% (1993-1996) and will remain to grow with about 7.6%. Total polycarbonate consumption in the Netherlands is 14 ktonnes/year and for other consumption products 11 ktonnes/year is used.

Conclusive data on the use of bisphenol A in the Netherlands are not available. According to proportional estimates from European figures, the consumption of Bisphenol A in the Netherlands is estimated at 25,600 tonnes/year.

With respect to the use of polycarbonates and epoxy resins it was established that between 1992 and 1998 global demand for these compounds has roughly doubled. For a conclusive insight in current amounts in Europe and the Netherlands, an extended market survey by a specialised company is recommended.

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4 Emissions to aquatic environment

Based on the high world-wide production volume of bisphenol A, and the fact that it is used at many sites and in many types of products, it is likely that bisphenol A enters the environment. Both diffuse sources (products in use, rest and waste products) and point sources (accidental spills, industrial wastewater discharges) may contribute to the emission of bisphenol A to the environment.

The following emission sources/ activities are identified:

1. Emissions from production of bisphenol A and manufacturing processes involving bisphenol A;
2. Emissions of bisphenol A, from products in use;
3. Emissions from discharged products.

4.1 Emissions from production and manufacturing processes

Emissions of bisphenol A during production of the pure chemical are considered to be minimal because the production occurs in a closed system (EPA 1984). Furthermore this emission is of low importance (because of the low vapour pressure), as compared to the atmospheric emission of BPA dust during trans-shipment and transport (Staples, 1996 and BUA, 1997). However, inadvertent and accidental spills may occur during manufacturing, processing, handling and distribution of the chemical.

Important point sources for the emission of bisphenol A to the surrounding environment may be the large volumes of waste waters from industries manufacturing epoxy-, polycarbonate- and polysulphone hardeners and from industries involved in rubber production (EPA 1984, Hanze 1994, Lobos et al. 1992). Matsumoto (1982) considered the bisphenol A detected in polluted Japanese rivers to originate mainly from industrial products such as epoxy and polycarbonate resins and their degradation products (Temanord, 1996).

Hedin & Perenius (1993) emphasised that the spread of bisphenol A may be considerable due to its presence in PVC products produced by numerous industries and because many PVC products are used so extensively in modern society.

The UBA (UBA, 1997) assumed 1 tonne/year bisphenol A emission in Germany in 1995, due to emissions during production, processing and transport of BPA and BPA-Products. This is only a very rough estimate as data on the release from BPA products are hardly available.

Total BPA production in Europe at 6 sites is estimated at 698,000 tonnes/year (UK, 2000). Environmental release data of BPA from these production sites in Europe indicate that the highest releases to air and receiving waters are 575 kg/year (dust) and 860 kg/year, respectively (see table 4.1).

Table 4.1:
Summary of environmental releases data from bisphenol A production sites (UK, 2000)

| Site | Air | | Effluent (After wastewater treatment) | | Receiving waters |
|--------------------|---|---|--|------------------------------|---|
| | Measured levels | Release | Measured levels | Release | |
| BPA1 ^b | <0.2 mg/Nm ³ (outlet) <0.5 µg/Nm ³ (50 m from site) | <0.012 kg/day <4.4 kg/year | 0.146 mg/l | 1.59 kg/day 580 kg/year | Flow rate 8.64×10 ⁶ m ³ /day |
| BPA2 ^b | 2.9 mg/Nm ³ (outlet discontinuous) 0.1 µg/Nm ³ (outlet) | 0.00017 kg/day 0.0605 kg/year | 0.69 µg/l | 0.017 kg/day 6.1 kg/year | Flow rate 2.068×10 ⁸ m ³ /day |
| BPA3 ^b | <1 mg/Nm ³ (dust) | <1 kg/day (dust) <365 kg/year (dust) | ~0.005 mg/l | 0.31 kg/day 113 kg/year | Flow rate 8.08×10 ⁷ m ³ /day |
| BPA4 ^b | | 0.03 kg/day 10 kg/year | | 0.19 kg/day 70 kg/year | River estuary 2.49×10 ⁷ m ³ /day |
| BPA5 ^b | | 1.58 kg/day (dust) 575 kg/year (dust) | | 1.01 kg/day 367 kg/year | River estuary 2.59×10 ⁶ m ³ /day |
| BPA 6 ^b | 10 mg/Nm ³ (dust) | 0.08 kg/day (dust) 31.2 kg/year (dust) | <1 ppm (1 mg/l) (Detection limit) | <2.36 kg/day <860 kg/year | Sea |
| Total | - | - | - | ~2000 kg/year | - |

a. Nm³: volume in m³ at standard temperature and pressure.

b. The six production sites within the EU, data are confidential and therefore coded.

Bisphenol A emissions may occur during the following polycarbonate and epoxy resin production processes.

Table 4.2:

Activities related to the production and processing of polycarbonates and epoxy resins

| Activity | Emission potential |
|---|--|
| Filament Winding/Pultrusion | - |
| Resin Transfer Molding | - |
| Pre-preg and Laminate Production | - |
| Flooring, Grouting and Hand Applications | Large surface areas and high temperatures may increase possible emission |
| Coating | Spraying these coatings causes generation of aerosols which increase emission |
| Unloading/Mixing/Pouring - hose connect/disconnect - drum pump cleaning/handling - dumping/pouring | - |
| Cutting/Machining/Fashioning | These tasks generate dust which increases the potential of emission |
| Clean Up | High Potential of emission |
| Maintenance | - |
| Spraying | Spraying the coatings causes generation of aerosols which increase the potential of emission |
| Brushing | - |
| Hand Layup | - |

4.1.1 Releases during polycarbonate processing

Bisphenol A is used in the production of polycarbonate at 6 sites within the EU. At 5 of these sites bisphenol A production also occurs. The total amount of bisphenol A used in the production of polycarbonate is estimated from company submissions to be 486,880 tonnes/year. One site produces polycarbonate from bisphenol A in a continuous wet process in closed systems. The plant operates for 289 days/year. No other use of bisphenol A is reported at this site. The release of bisphenol A to air is estimated as 0.5 kg/24 hours (based upon measured data). This gives a yearly release to air of 144.5 kg/year.

The release of bisphenol A to water is estimated as 0.7 kg/24 hours (based upon measured data). This gives a yearly release of 202.3 kg/year. The effluent from the production plant is released directly to receiving waters. The dilution in the receiving waters is 200.

Ligon et al. (1997) studied the evolution of volatile organic compounds from polymers during extrusion operations. The study looked at three polycarbonate polymers containing between 94-99.5% polycarbonate. For all the polycarbonate blends studied bisphenol A was not detected in the vent gases from the extrusion apparatus.

In further work Ligon et al. (1998a) studied the evolution of volatile organic compounds from polymers during moulding operations. The study, which looked at several polymer blends, included three polycarbonate polymers (94-99.5% polycarbonate). For all the polycarbonate blends studied bisphenol A was not detected in the vent gases from the moulding apparatus.

Processing of polycarbonate may increase residual bisphenol A levels if the incorrect operating conditions are employed. The major causes of polycarbonate degradation during processing are: the presence of water in the polycarbonate before processing; the use of too high a processing temperature; and use of additives that promote degradation. To overcome these problems polycarbonate manufacturers provide information on proper processing conditions and handling information. As long as these guidelines are followed, the formation of bisphenol A due to degradation during processing should be negligible under normal conditions of processing and use.

4.1.2 Releases during epoxy resin production

Bisphenol A is used in the production of epoxy resins within the EU, and information on releases has been received from eight sites. Of the eight sites for which information is available, two sites are also bisphenol A production sites and excluded here. The total amount of bisphenol A used in the production of epoxy resins is estimated at 171,095 tonnes/year from company submissions. Of this amount 158,007 tonnes/year (92% of total tonnage) are used at the sites for which site specific information is available. Small volume sales account for the remaining tonnage. These sales are to approximately 20 customers with the amount sold being in the range of 200-800 tonnes/year per site. As site specific information is available covering 92% of the total tonnage of bisphenol A used in the production of epoxy resins this data will be taken as representative of releases from all epoxy resin sites (UK, 2000).

At three sites Bisphenol A is handled in closed systems and there are no releases to air or water from the process. For the three other sites effluent concentrations were measured at <5µg/l, 0.5 µg/l (predicted) and 30 µg/l. Daily release to the effluent is estimated at <0.075, 0.16 and 0.72 kg/day. The highest release was estimated at 216 kg/year.

The remaining releases from the other specific sites (187.25 kg/year) are considered as continental releases. These releases are after wastewater treatment.

4.1.3 Releases during phenoplast cast resins production

8,800 tonnes/year of bisphenol A are used in the production of phenoplast cast resins. No information is available as to the number of sites or amount used per site where this process takes place. Therefore a generic scenario is used based upon the total tonnage reported being used at one site.

Applying EUSES release factors of 0 for the release to air (vapour pressure <1 Pa) and 0.007 (>1000 tonnes per year) for the release to wastewater, results in a release to wastewater of 205 kg/day (61.5 tonnes/year).

Regional and continental release is calculated at 10% and 90% of the total release, respectively. Resulting in 6.15 tonnes/year and 55.35 tonnes/year, respectively. Of the 6.15 tonnes regional release 70% (= 4.305 tonnes/year) goes to wastewater and 30% (= 1,845 tonnes/year) to receiving waters. Of the 55.35 tonnes continental release 70% (= 38.745 tonnes/year) goes to wastewater and 30% (= 16,805 tonnes/year) to receiving waters.

4.1.4 Releases during unsaturated polyester resins production

3,000 tonnes/year of bisphenol A are sold annually for use in unsaturated polyester resin production. There are thought to be between 5 to 10 sites within the EU using bisphenol A in this application.

No information on releases to air is available, but it is probably reasonable to assume that any losses to air are volatile losses during processing. The default release factor for use as a chemical intermediate for a low volatile substance is 0. Therefore releases to air will be assumed to be negligible.

Since the process is dry and does not produce any liquid effluent it is not be considered further.

4.1.5 Releases during can coating production

Can coatings are produced by the reaction of an epoxy resin with bisphenol A. The total amount of bisphenol A used at the five known sites is 2460 tonnes/year (UK, 2000).

There are no aqueous emissions of bisphenol A, and so they will not be considered further.

No information on releases to air is available, but it is probably reasonable to assume that any losses to air are volatile losses during processing. The default release factor for use as a chemical intermediate for a low volatile substance is 0. Therefore releases to air will be assumed to be negligible.

4.1.6 Releases during thermal paper production

Information has been received from six thermal paper manufacturers operating at seven sites within the EU on the use and release of bisphenol A. The usage from these six manufacturers accounts for approximately 1,400 tonnes bisphenol A per year. The data from these companies are taken as representative for the use of bisphenol A in thermal paper manufacture.

The sum of all the emissions to receiving waters after wastewater treatment is 106 kg/year. The highest value from a site (36 kg/year) is used for the regional emission. The sum of emissions from the remaining sites (70 kg/year) is used for the continental emission (UK, 2000).

Recycling thermal paper

An important source of emission is the recycling of used paper. In the process of deinking of waste paper also the bisphenol A will be released. The BUA estimated that in Germany in 1995 36 to 54 tonnes of bisphenol A have been released from the waste paper, of which 80% (approx. 36 tonnes) was absorbed in the activated sludge of sludge treatment plants and 20% (approx. 9 tonnes) was discharged in effluent waters (BUA, 1997). In 1997 approx. 64 tonnes bisphenol A were

absorbed in activated sludge and 16 tonnes was discharged in the effluent. If this is proportionally extrapolated to the Netherlands, this would lead to an absorption of 13 tonnes bisphenol A to activated sludge and 3.2 tonnes bisphenol A discharge in the effluent.

The UK risk assessment reports uses the 1,400 annual usage of thermal paper as starting point. Conform the Technical guidance document it is assumed as worst case assumption, that during alkaline pulping 100% of all bisphenol A is released to water. The emission scenario document also states that at least primary sedimentation is carried out at all paper mills and that this process will remove 50% of poorly water soluble substances. and that the total amount of paper is recycled at 10 sites (i.e. a maximum of 10% of the substance at a site). The default recycling rate is given as 50% of the total paper use. Thus the amount of bisphenol A in thermal paper at a paper mill using recycled paper is 70 tonnes/year. 50% of the release is adsorbed during primary treatment.

Using the above data the emissions of bisphenol A after on site primary treatment from recycling of thermal paper are as follows:

| | |
|-------------|--|
| Local | 35,000 kg/year (140 kg/day) to wastewater |
| Regional | 35,000 kg/year (95.8 kg/day) to wastewater |
| Continental | 315,000 kg/year (863 kg/day) to wastewater |

Assuming the same removal rate (43%) as in other STPs, the release to receiving water is calculated at 15,000 kg/year on regional basis and 136,600 kg/year on continental basis.

4.1.7 Releases during PVC production and processing

The total amount of bisphenol A used in the PVC industry is approximately 2250 tonnes/year. There are four possible uses of bisphenol A associated with PVC production and processing. These are as follows:

1. Use as an inhibitor or reaction 'killing' agent during the polymerisation stage of PVC production. The total tonnage of bisphenol A used is 200-250 tonnes/year. Use occurs at approximately 10 PVC production sites within the EU (20% of PVC producers).
2. Use as an antioxidant during the processing of PVC. The total tonnage of bisphenol A used is 500 tonnes/year. There are a large number of sites using bisphenol A for this purpose, industry estimates vary from 200-500 sites within the EU. The amount of bisphenol A used per site is approximately 1-3 tonnes/year.
3. Incorporation into an additive package which is subsequently sold onto PVC processors for use. The total tonnage of bisphenol A used is 500 tonnes/year. There are approximately 10-20 sites within the EU making additive packages that incorporate bisphenol A. No information on the end use of these additive packages is known, though usage is thought to be similar to direct use of bisphenol A as an antioxidant.
4. Use as an antioxidant in the production of plasticisers used in PVC processing. The total tonnage of bisphenol A used is 1000 tonnes/year. There are approximately 12 sites within the EU that undertake this process.

Highest bisphenol A emissions are reported for the use as inhibitor of PVC during the production process (see Table 4.3). Regional emissions to receiving water are calculated at 2490 kg/year. Continental emissions are 22,410 kg/year (UK, 2000). Emissions to surface waters due to other bisphenol A uses such as antioxidant

during PVC processing, preparation and use of additive PVC packages, antioxidant in plasticiser and plasticiser use are only 6.5% of the main emission.

4.1.8 Polyols/polyurethane

950 tonnes/year of bisphenol A are used at one site in the production of polyols that are used in the production of polyurethane. The site is also a bisphenol A production site. Hence, emissions are included in the production section. No other sites using bisphenol A in this application are known. The polyol production process is a dry process.

Since the process is dry and does not produce any liquid effluent it is not be considered further.

4.1.9 Brake fluid manufacture

Bisphenol A is used in the production of brake fluids at one site that is also a bisphenol A production site. Hence, the emissions from this site are included in the production section. The concentration of bisphenol A in the effluent from the brake fluid operations at the production site is measured as <0.1 mg/l, which is before any wastewater treatment.

In use the brake fluid is likely to be subjected to heat and pressure. As it is added to the brake fluid as an antioxidant, bisphenol A may also be expected to react during product use, effectively being destroyed. Spent brake fluid is usually disposed of by professional personnel as chemical waste. It is therefore assumed probable that the amount of bisphenol A reaching the environment during product use and disposal is very low. Therefore, the potential for release during brake fluid use will not be considered further.

4.1.10 Tyre manufacture

110 Tonnes/year of bisphenol A are used as a compounding ingredient in tyre manufacture. This is assumed to be all used by one manufacturer within the EU at one site. The compounding process is a dry operation with no aqueous effluents.

In the presence of the other compounding ingredients and during the curing process, the bisphenol A becomes incorporated into the polymer matrix. Although it is used as an anti-oxidant this appears to be specifically for the compounding phases and it is presumably intended to protect the materials at this stage. There is no indication that it is intended to be the major anti-oxidant in the actual tyres, and so it is not expected to be present at significant levels in the finished product. As an anti-oxidant it will also react to give complex products so a proportion will be used up in this way. As a consequence, during the life time use of car tyres, there should be no significant environmental release of bisphenol A.

4.1.11 Polyamide production

150 Tonnes/year of bisphenol A is used at one site for the production of modified polyamide grades. The production of the modified polyamide is a dry process in a closed system. Therefore releases are considered as negligible.

4.1.12 Alkoxylated bisphenol A

One company has reported using 2,020 tonnes/year bisphenol A in the production of alkoxylated bisphenol A, which is subsequently sold as an intermediate in the production of epoxy resins. The company operates two sites within the EU.

Releases to the environment during production of the alkoxylated bisphenol A appear to be negligible and this use will not be considered.

4.1.13 Tetrabromobisphenol A production

Bisphenol A is used in the production of tetrabromobisphenol A (TBBPA) at three sites. In 2000 in Europe the use of TBBPA is estimated at 40,000 tonnes (RIKZ, 2000) indicating a bisphenol A use of 17,000 tonnes/year. The use of bisphenol A occurs in closed vessels. Releases of bisphenol A from the process are therefore taken as negligible and will not be considered further in this assessment.

4.1.14 Summary environmental releases during production and processing

Table 4.3:

Summary of regional and continental releases due to production processes

| Process | Air (kg/year) | | Emission to wastewater treatment plants (kg/year) | | Emission to receiving waters (kg/year) | |
|---|---------------|-------------|---|-------------|--|-------------|
| | Regional | Continental | Regional | Continental | Regional | Continental |
| Bisphenol A production | 575 | 410 | | | 860 | 1136 |
| Polycarbonate production | 144.5 | | | | 202.3 | |
| Epoxy resin production | | | | | 216 | 187.25 |
| Phenoplast cast resin production | | | 4305 | 38,745 | 1845 | 16805 |
| Thermal paper production | | | | | 36 | 70 |
| Thermal paper recycling ^b | | | 35,000 | 315,000 | 15,000 | 136,600 |
| PVC -Inhibitor during production process ^a | | | 5810 | 52,290 | 2490 | 22,410 |
| PVC - Antioxidant during processing ^a | 25 | 225 | 75 | 674 | 32 | 289 |
| PVC - Preparation of additive packages ^a | | | 74 | 668 | 32 | 286 |
| PVC -Use of additive package ^a | 25 | 225 | 75 | 674 | 32 | 289 |
| PVC - Antioxidant in plasticiser ^a | | | 148 | 1336 | 64 | 572 |
| PVC - Plasticiser use ^a | 50 | 450 | 10 | 88 | 4 | 38 |
| Total | 820 | 1310 | 45,497 | 409,475 | 20,813 | 178,482 |
| Total in kg/day (Averaged over 365 days) | 2.2 | 3.6 | 125 | 1122 | 90 (16) | 489 (115) |

a. Releases to waste water calculated in the text; these are split 70:30 between STP and receiving waters in the table

In addition to the releases in the table, there are also releases to soil of 3000 kg/year in the regional environment, and 27,000 kg/year in the continental environment (UK, 2000).

An estimate of actual emissions for durable products such as plastics must be based not only on the amounts produced and processed but also on the volume of existing products in use. This exceeds the annual volume of new products and the annual volume of products discarded and withdrawn from use. It was not considered for bisphenol A, since no data were available on existing products and the emissions resulting from them.

Summing up, the estimate of actual bisphenol A emissions from products is likely to be on the low side, since it does not take sufficient account of products in use. The figures do not include emissions from durable plastics applications. It should include all PC products in the consumption process. The average lifetime of PC products differs with the application, but is more in the range of 10ths of years than years (UBA, 1997). The amount of PC-products in use exceeds considerably the yearly production. However, the magnitudes of the respective emission flows are not likely to be greatly distorted.

Emissions of bisphenol A from products are not significant in absolute terms. They originate mainly from one specific use (recycling of thermal paper) for which the available figures are relatively accurate.

4.2 Emissions of bisphenol A, from products in use

Bisphenol A release from polycarbonates

Krishnan et al. (1993) found that bisphenol A is released from polycarbonate flasks during autoclaving. Polycarbonate is produced by condensing monomer bisphenol A with phosgene gas to yield carbonate linkages that form the polycarbonate polymer. The carbonate linkages are subject to hydrolytic attack at high temperatures; such degradation is accelerated in alkaline pH and retarded at pH 5 or below. Krishnan et al. (1993) reported that bisphenol A leaches out of polycarbonate flasks during autoclaving in concentrations up to 10-15 nM (~ 2.3-3.4 µg/l).

Bisphenol A is strongly incorporated in the polymer product. The fraction monomer in PC product is considered to be maximal 100-150 ppm, typical < 25 ppm (Bayer, 1996; Bayer/Dow 1996).

Mountfort (et al. 1997) studied the real monomer content in baby bottles (detection limit 10 ppm). In 14 out of 22 bottles the rest-bisphenol A concentrations were below detection limit; In 8 bottles the bisphenol A content was 18 to 139 mg/kg plastic (ppm), with an average of 56 ppm.

The BUA (BUA, 1997) assumes a bisphenol A-rest-monomer content in PC of <100 ppm and a migration rate of 10 %. On the basis of a year production of 15,700 tonnes PC, the rest-bisphenol A content is then 1,600 kg and the diffuse input (10%) in the environment 160 kg. Producers indicate that this is an upper limit as the rest-bisphenol content is approximately 25 ppm (Bayer/Dow 1996).

For the migration into foods, BUA estimated a level below 20 ppb bisphenol A (BUA, 1997). This is also considered to be an upper limit. According to PC producers a migration level of < 10 ppb is more realistic (Bayer/Dow 1996). The migration level is based on 1 kg food for 10 days in contact with a plastic surface of 6 dm² at 40°C (or 30 minutes at 120°C). PC with an assumed "wall strength" of 0.2 cm and a density of 1.2 g/cm³ corresponds to 144 g PC. A migration of 20 µg bisphenol A out of 144g PC equals a migration of 0,14 ppm (µg/g) bisphenol A.

Bisphenol A release from epoxy resins products

Emission of bisphenol A from products in use has been reported by a few authors. Krat et al. (1986), cited in Sheftel (1995), determined the migration of bisphenol A into water from epoxy coatings during a 7 day period to be 4 µg/l at 37°C. Buczowska & Jarnuszkiewicz (1971) showed that bisphenol A and other components from epoxy resins used as corrosion resistant coatings in ship water-tanks migrated into the water if the epoxy had not been properly hardened.

Leakage of bisphenol A and the related compound BADGE (bisphenol A diglycidylether) into food-simulant liquids (distilled water, 15% ethanol, 3% acetic acid, olive oil) has been reported by Philo et al. (1994). Bisphenol A underwent 40% decomposition in 1 hour at 100°C and 3% acetic acid. BADGE underwent 90-100% decomposition in all aqueous simulants and 15-25% decomposition in olive oil at 175°C. Brotons et al. (1995) reported migration of bisphenol A into canned food from the lacquer coatings of the cans. Up to 33 µg bisphenol A per can were detected (Brotons et al. 1995). This amount was confirmed by others (Haase-Asdorf, 1997, unpublished data).

In 1996 in Switzerland the oil of 142 cans was analysed for BADGE. In 17% of the cases no BADGE could be detected (Detection limit 0.02 mg/kg). In 42% the BADGE level was beyond 0.2 mg/kg. Highest measured concentrations were approximately 20 mg/kg (Biederman et al., 1996).

The bisphenol A-rest monomer content of cured epoxy resins (lacquers) varies depending on the resin type, lacquer-formulation, curing conditions and layer thickness. According to the lacquer producing industry the bisphenol A content is ranging between 20-40 ppb. The BADGE content in organosol lacquers is ranging between 20-80 ppb (BASF, 1997; ICI, 1997 and Shell chemicals 1997) and always below 1 ppm. It should be emphasised that in lacquers, except for BADGE also BADGE-primers are found (semi-BADGE), which may have a content up to 10%. It is observed that heating of organosol lined cans with fatty contents causes increased bisphenol A concentrations in foods, indicating hydrolysis of BADGE in the lining (UBA, 1997).

Because of the many uses and applications, that influence the release, the amount of bisphenol A monomer in the epoxy resin, the variable curing, make it impossible to make a reliable estimation of the migration of bisphenol A from epoxy resins.

The rest bisphenol monomer content in can linings is on average 100 ppb and is therefore about a magnitude of 1000 below the monomer content in polycarbonates (information from producers, UBA, 1997). The producers indicate that under normal conditions no migration occurs (detection limit 50 ppb). Using these data, a consumption volume of 16,000 tonnes/year would lead to a rest monomer content of less than 20 kg and a migration of less than 1 kg. It is questionable, whether these data are representative for all epoxy resins applications.

The atmospheric release of bisphenol A due to thermal processing of lacquers is to be expected. However no data are available on the amounts of emission.

In table 4.4 the release data from polycarbonate and epoxy resin products are summarised.

Table 4.4:
Releases from polycarbonate and epoxy resin products (summary)

| Process | | Bisphenol A leaches from product | Monomer in product | Reference |
|----------------|-------------------|---|--|--|
| Polycarbonates | PC-flasks | 2.3 - 3.4 µg/l | | Krishnan, et al., 1993 |
| | PC-product | | 100 – 150 ppm bisphenol A <25 ppm bisphenol A | Bayer, 1996 |
| | Baby bottles (22) | 14 bottles <10 ppm (dl) 8 bottles 18 - 139 ppm average 56 ppm | | Mountfort, 1997 |
| | PC | | <100 ppm bisphenol A 10% migration 1600 kg monomer of 15,700 t = 160 kg to environment | BUA, 1997 |
| | PC- cans > Food | <20 ppb/ 144g (0.14 ppm) <10 ppb | | BUA, 1997 Bayer/Dow, 1996 |
| Epoxy resins | To water | 4 µg/l in 4d | | Krat et al., 1986 |
| | To canned food | 33 µg/can | | Broton, et al., 1995 Haase-Asdorf, 1997 |

| | | | | |
|--|----------------------------|--|--|--|
| | From cans (142) | 17% no BADGE 42% < 0.2 mg BADGE/kg max. 20 mg BADGE/kg | | Biederman, et al., 1996 |
| | Laquer Organosol laquer | | 20 – 40 ppb BADGE 20 – 80 ppb BADGE < 1 ppm always | BASF,1997 ; ICI,1997; Shell chemicals, 1997 |
| | Laquer | | =10% BADGE primers | BUA, 1997 |
| | Can lining | | 100 ppb bisphenol A= 20 kg monomer of 16,000 t = < 1 kg to environment | BUA, 1997 |

DI = detection limit

Bisphenol A release from other non polymer applications

In table 4.5 the estimated releases, from PVC articles in use, are given.

Table 4.5:
Releases

| Process | Air (kg/year) | | Emission to wastewater treatment plants (kg/year) | | Emission to receiving waters (kg/year) | |
|---------------------------------|---------------|-------------|---|-------------|--|-------------|
| | Regional | Continental | Regional | Continental | Regional | Continental |
| Losses from PVC articles in use | 2000 | 18000 | | | 3000 | 27000 |

4.3 Emissions from discharged products

Yamamoto and Yasuhara (1999) studied the leaching of bisphenol A from plastic waste samples.

To quantify the leaching of bisphenol A into water, various samples of plastic waste were cut into small pieces, soaked in water for two weeks at room temperature in the dark, and the concentration of bisphenol A in the water determined by gas chromatography /mass spectrometry (GC/MS). The amount of bisphenol A leached from the plastic wastes varied from undetectable to 139 µg/g. The detection limit was 2 ng/g when 100 g of plastic waste was used. A sample of synthetic leather, presumed to consist PVC yielded the highest concentrations. Around 11% of the amount of BPA in this material leached to water in two weeks. Wenzel et al. (1998) measured bisphenol A in leachate water from three landfill sites in Germany with an average concentration of 81 µg/l.

Kjølholt et al. (1994) measured concentrations of various organic pollutants including phthalates and bisphenol A in percolates and gas from different Danish waste disposal sites. In percolate from a waste dump, which receives moderate amounts of organic material a concentration of 30 µg/l bisphenol A was determined. However, no bisphenol A was detected in percolates from another waste disposal site, which receives large amounts of organic material. Bisphenol A was not detected in gas produced at the two waste dumpsites.

Based on the concentration of bisphenol A in percolates from Danish waste dump sites (30 µg/l) and a yearly percolate estimate of approximately 1 million m³ Kjølholt et al. (1994) estimated the emission of bisphenol A from waste disposal sites in Denmark to be 30 kg/year.

Kjølholt et al. (1994) was unable to detect any bisphenol A in flue gas, cinders, fly ash, wash water and flue gas cleaning residue from a Danish waste incinerator plant. Neither was bisphenol A found in compost from a Compost Treatment Plant in Denmark or in gas produced from the compost.

The formation of bisphenol A during the use of alkoxylated bisphenol A is not expected to occur to any significant extent. The alkoxylated bisphenol A is chemically bound into the resin produced and so environmental releases of bisphenol A are expected to be negligible.

4.4 Overall emissions to the environment

In order to evaluate the contributions of the various emission sources in the production/processing and from the use of product, emissions from the individual stages are summarised in table 4.5 and 4.4. The emissions to the Netherlands environment are largely related to the production stage. Total emissions in Europe amount to 67,130 kg/y regional releases divided into 45,497 kg to wastewater treatment plants, 20,813 kg to the surface water, 820 kg to the atmosphere. Furthermore total continental releases amount to 589,267 kg/y divided into 409,475 kg to wastewater treatment plants, 178,482 kg to the surface water, 1310 kg to the atmosphere. Besides these emissions in waste products, there is 1600 kg of the monomer bisphenol A in polycarbonates of which 160 kg reaches the environment and furthermore there is 20 kg monomer in can linings (ER) of which < 1kg reaches the environment.

4.5 Transboundary emissions

4.5.1 Atmospheric deposition

No data are available on the atmospheric deposition of gaseous or dust emissions in the Netherlands or in the EU. Neither is known in what way and to what extent released emissions are susceptible to wet or dry deposition.

4.5.2 Hydrological transport

Data on emission levels or emissions loads in rivers, entering or leaving the Netherlands, are also not known.

4.6 Evaluation

4.6.1 Basic process and emission data

The emissions from material flows are in many ways only an approximation to the actual amounts involved. They refer to the manufacturing process for the respective substances (production, processing, transport) and to the products sold and those in use.

Only identifiable emissions are addressed, since no indicators are available to estimate emissions for a number of important product groups. This is true in particular for epoxy resins in the case of bisphenol A. No quantifiable information can be given on emissions from the disposal phase of products withdrawn from the production and consumption process, since the empirical foundations are insufficient.

4.6.2 Reliability of emission factors

The emission factors used in this study were derived from process and emission data in the Technical Guidance Document (EU, 1996). Factual information that supports or justifies the assumed or extrapolated values could not be retrieved in these studies. In none of the reports data were given on the actual wastewater amounts e.g. the nominal wastewater production/tonne product.

Furthermore it should be mentioned that models such as EUSES do not account for concentrations that exceed the water solubility. Therefore, the results of the

emission estimation and emission distribution calculations need to be used carefully, and where possible verified/amended by actual data.

4.7 Conclusions and recommendations

From emission computations and emission distribution results the following conclusions can be made with respect to the release of bisphenol A in the Netherlands and the EU:

1. Emissions of bisphenol A may occur during bisphenol A production, production of products using bisphenol A and from products in-use.
2. Emission during bisphenol A production is around 2 tonnes/year to surface waters and 1 tonne to air.
3. The most important emissions during bisphenol A product processing occur during production of phenoplast cast resins (18.5 tonnes to water in Europe), thermal paper production (151 tonnes to water in Europe) and the use of bisphenol A as inhibitor during PVC production (25 tonnes to water in Europe). Total emissions are 2.1 tonnes to air, 199 tonnes to water and 30 tonnes to soil in Europe. The specific emissions for the Netherlands are unknown.
4. Emissions from products in-use are estimated at 160 kg from polycarbonates and <1 kg of epoxy resins used in can lining. Furthermore losses from PVC articles in-use are 20 tonnes to air and 30 tonnes to water.
5. Concerning emissions are the leaches of bisphenol A from baby bottles, cans and flasks to food. In baby bottles in a study an average of 56 ppm is found to leach and in another study a maximum of 20 mg BADGE/kg plastic leached from cans. However these amounts remain below the estimated acceptable daily intake.
6. Quantitative data, on waste disposal methods for materials containing bisphenol A, are lacking.
7. With respect to the representativity of the computed emissions, uncertainty exists about the actual magnitude of the used emission factors and the form in which selected compounds are present in raw and treated wastewater. Practical information e.g. further research is required to verify these matters.

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5 Behaviour in the aquatic environment

5.1 Introduction

The behaviour of organic micropollutants in the aquatic environment is determined by the properties of the compound (solubility, hydrophobicity, volatility,) and by the characteristics of the water system of concern (residence time of the water, sedimentation area, organic matter content, etcetera). These compound and system specific properties determine to what extent a compound will accumulate in organisms.

5.2 Solubility and volatilisation

The water solubility of a compound is a good indication of the extent to which this compound can be transported with water. In general poorly soluble compounds have a high affinity for silt particles in a water system. This is the reason that the compound will settle together with the sediment and suspended particles and thereby the transport along with the water stream will be slowed down. Poorly soluble compounds can also accumulate in organisms more easily. Solubility and vapour pressure further determine together whether a compound will evaporate out of water. The volatility of a compound is characterised by its Henry constant.

5.2.1 Bisphenol A

Bisphenol A has a moderate solubility and a low vapour pressure.

Table 5.1:

Vapour pressure, solubility and volatility parameters of bisphenol A (HSDB, 2000; TemaNord, 1996)

| | Bisphenol A |
|--|-------------|
| Mole weight (g/mole) | 228.29 |
| Solubility (mg/l) | 120-300 |
| Solubility (mol/m ³) | 0.53-1.31 |
| Vapour pressure (10 ⁻⁶ Pa) | 5.3 |
| Henry coefficient ^a (10 ⁻⁶ Pa.m ³ /mol) | 4 –10 |

^a : Quotient of vapour pressure and aqueous solubility

The volatilisation of bisphenol A from surface water to air may be estimated by the Henry's Law constant. This is calculated using EUSES as $4.03 \times 10^{-6} \text{ Pa.m}^3.\text{mol}^{-1}$ at 25 °C for bisphenol A using a vapour pressure of $5.3 \cdot 10^{-6} \text{ Pa}$ at 25 °C and a water solubility of 120 - 300 mg/l at 25 °C (HSDB, 2000; TemaNord, 1996; UK, 2000). This value of Henry's Law constant suggests that volatilisation would be insignificant from all bodies of water (Lyman, et al., 1982). Due to its relatively low vapour pressure and its tendency to adsorb to soil, bisphenol A is not expected to volatilise significantly from wet or dry soil surfaces (HSDB, 2000).

The air-water partitioning coefficient ($K_{\text{air-water}}$) may be derived from the Henry's law constant and is calculated as $1.7 \times 10^{-9} \text{ m}^3/\text{m}^3$ for bisphenol A. Both the Henry's law constant and air-water partitioning coefficient are very low suggesting that volatilisation is unlikely to be a significant removal mechanism for bisphenol A from water systems (UK, 2000).

Bisphenol A is not volatile and is relatively short lived in the atmosphere. Therefore, it is unlikely to enter the atmosphere in large amounts. Removal of bisphenol A by precipitation is therefore likely to be negligible and the resulting rainwater concentration very low. As the lifetime of bisphenol A in the atmosphere is relatively short it is unlikely to be transported a long distance from its point of emission. Any resultant concentrations in soil due to precipitation are therefore likely to be close to the point of emission (UK, 2000).

5.3 Sorption

The extent of sorption of a compound strongly depends on the compound's hydrophobicity and the availability of organic matter in soil, sediment or suspended particles. The hydrophobicity of a compound is characterised by its octanol water partition coefficient (K_{ow}). To what extent the compound will adsorb onto soil, sediment or suspended solids further depends on the organic matter e.g. organic carbon content of these media. The specific affinity of a compound can be directly related to organic carbon content by means of the K_{oc} value. For various media, the organic carbon content is known. Furthermore, detailed measurements have been performed on adsorption of organic compounds onto these media. According to the TGD for risk assessment, partition coefficients of hydrophobic chemicals in organic carbon / water systems (K_{oc}) can be derived from the following equation:

$$\log K_{\text{oc}} = 0.81 * \log K_{\text{ow}} + 0.10 \quad \text{for } 1.0 < \log K_{\text{ow}} < 7.5$$

With a standard fractional organic carbon content of soil, sediment and suspended sediment taken as 2, 5 and 10% respectively, specific adsorption constants (K_p) for soil, sediment and suspended sediment can be calculated directly from the K_{oc} or K_{ow} value.

5.3.1 Adsorption

Furun et al. (1990) studied the treatment of wastewater containing bisphenol A by biological processes, activated carbon adsorption and large pore resin adsorption. The results from the experiments looking at the removal of bisphenol A from wastewater by biological processes are reported in chapter 5.4.3. Static and dynamic adsorption studies were carried out using activated carbon (UK, 2000). In the static adsorption study 500 mg activated carbon was added to 100 ml bisphenol A solution (347.6 mg/l). After shaking for 2 hours the residual bisphenol A concentration was determined and the average adsorption capacity of the activated carbon was calculated as 44.7 mg bisphenol A/g carbon (by weight). The regeneration capacity of the activated carbon using sodium hydroxide was found to be very poor (Furun, et al., 1990 in UK, 2000).

In the dynamic adsorption study activated carbon was packed into an adsorption column and a 100 mg/l bisphenol A solution was pumped through it. The bisphenol A concentration in the effluent was measured every hour. The adsorption capacity of the activated carbon was determined as 50 g bisphenol A /l activated carbon. As with the static experiment the regeneration capacity of the activated carbon using sodium hydroxide was found to be very poor (Furun, et al., 1990 in UK, 2000).

Further adsorption studies were carried out using an adsorption resin. In static adsorption tests carried out on 6 different resins the adsorption capacities were found to be between 7.5 to 21.0 mg bisphenol A /g wet resin. Of the resins tested 2, were found to be just as efficient at adsorbing bisphenol A after regeneration with sodium hydroxide (UK, 2000).

These studies do not allow the adsorption coefficients for other environmental media to be estimated and the TGD methods as implemented in EUSES have to be used (UK, 2000).

The Koc is calculated by Syracuse (SRC, 1988 in CIS Envirofate, 2000) as 293. Dorn et al. (1987) estimated the Koc values between 314 and 1524 suggesting that mobility of bisphenol A in soil would be moderate to extensive (Dorn, et al., 1987; Hansch et al., 1985, Lyman et al., 1982 & Swann, et al., 1983 in HSDB, 2000). In Fransen (1997) the log Koc is 2.5 to 3.2.

Partition coefficients for bisphenol A have been calculated using EUSES using a log Kow of 3.40.

| | | |
|-------------------------|-------------------------------------|--|
| Koc | 715 l/kg | Organic carbon-water partition coefficient |
| Kp _{soil} | 14.3 l/kg | Solids-water partition coefficient in soil |
| Kp _{sed} | 35.8 l/kg | Solids-water partition coefficient in sediment |
| Kp _{susp} | 71.5 l/kg | Solids-water partition coefficient in suspended matter |
| K _{susp-water} | 18.8 m ³ /m ³ | Suspended matter-water partition coefficient |
| K _{soil-water} | 21.7 m ³ /m ³ | Soil-water partition coefficient |
| K _{sed-water} | 18.7 m ³ /m ³ | Sediment-water partition coefficient |

These data indicate that bisphenol A is likely to be moderately adsorbed to solids upon release to the environment (UK, 2000).

5.4 Transformations in freshwater and marine environments

5.4.1 Hydrolysis

No information on the hydrolysis of bisphenol A in water is reported. The physical and chemical properties of bisphenol A suggest that hydrolysis is likely to be negligible (UK, 2000).

Bisphenol A is considered to be resistant to hydrolysis due to the absence of hydrolysable groups (Hedin & Perenius 1993, Hanze 1994 in TemaNord, 1996).

5.4.2 Photolysis

Photolysis is the transformation of a chemical by direct absorption of radiant energy into a new chemical or chemicals different from the precursor (Pedersen et al., 1994). Bisphenol A may be transformed in water by photolysis at wavelengths above 290 nm and most readily under alkaline conditions (Hanze 1994). Additionally, Peltonen et al. (1986a) have reported a photo-decomposition of vaporised bisphenol A, when irradiated by UV-B light, which yields reactive free radicals.

These data indicate that bisphenol A has the potential to photolyze in water, and that this potential is somewhat greater under basic conditions (SRC). These data also indicate that bisphenol A has potential to undergo photolysis in the atmosphere (SRC).

The significance of photolysis as an important degradation process seems low as bisphenol A is expected to bind to organic materials and, therefore, may undergo sedimentation in aquatic systems.

In air, bisphenol A may react with hydroxyl radicals with an estimated half life (T_{1/2}) of 4 hours (Hanze, 1994 in TemaNord, 1996). Photodecomposition products of bisphenol A vapor are phenol, 4-isopropylphenol, and a semiquinone derivative of bisphenol A (Peltonen, 1986). However, bisphenol A is expected to exist almost entirely in the particulate phase in the atmosphere, and reaction with hydroxyl radicals is expected to be much slower in particulate form than in vapor form (SRC).

The rate constant for the reaction of bisphenol A with hydroxyl radicals in the atmosphere are estimated by the AOPWIN program as $80.6 \times 10^{-12} \text{ cm}^3 \cdot \text{Mol}^{-1} \cdot \text{sec}^{-1}$ and by EUSES as 3.48 d^{-1} respectively. From this rate constant the half-life for the reaction of hydroxyl radicals with bisphenol A in the atmosphere is calculated by EUSES as 0.2 days. The fraction of chemical absorbed to aerosol particles is calculated by EUSES as 0.385. Bisphenol A released to the atmosphere is therefore likely to be degraded by reaction with hydroxyl radicals (UK, 2000).

5.4.3 Biodegradation and mineralisation

Half-life in soil is 1-180 days, in air 0.74-7.4 hours, in ground water 2-360 days and in surface water 1-150 days (HEDSET, 1993 in Dutch Health Council, 1999). If released to soil, bisphenol A is expected to have moderate to low mobility. It may biodegrade under aerobic conditions following acclimation. If released to the atmosphere, bisphenol A is expected to exist almost entirely in the particulate phase. Bisphenol A in particulate form may be removed from the atmosphere by dry deposition or photolysis.

Microbial degradation of bisphenol A

Some micro-organisms seem to be able to degrade bisphenol A. Biodegradation studies performed on bisphenol A are summarized in Table 5.3. It appears from this data that a straight forward conclusion concerning the biodegradability of bisphenol A is difficult to make due to conflicting test results. Turner & Watkinson (1986) used the "modified SCAS procedure" to test the biodegradation of bisphenol A and concluded that bisphenol A is "inherently" biodegradable. Wagner (1993) using the "EPA Shake Flask Method" found bisphenol A to be "readily biodegradable" using an unadapted inoculum (TemaNord, 1996).

In natural waters collected adjacent to a bisphenol A chemical plant discharge Dorn et al. (1987) found a greater than 90% degradation of bisphenol A within four days and concluded that the compound is "readily biodegradable". Bisphenol A removal appeared to be rapid once the system had become acclimated. The waters, which already received bisphenol A or were near the bisphenol A effluent outflow, became acclimated first (UK, 2000; TemaNord, 1996).

Contrary to these results, Stone & Watkinson (1983) reported that bisphenol A is "not readily biodegradable". This conclusion was based on the results obtained in the "Closed Bottle Test" and the "Modified Sturm Test", which are standardised OECD screening tests for biodegradability. MITI (1992) found that 0% of the bisphenol A inoculated with activated sludge was degraded after a 14 day period, and concluded that bisphenol A is "not easily biodegradable". In other OECD biodegradation studies of bisphenol A, biodegradation was observed to be very slow (Hanze, 1994 in TemaNord, 1996).

West and Goodwin (1997a) evaluated the ready biodegradability of bisphenol A using the OECD 301F manometric respirometry test. Bisphenol A of 99.7% purity (confirmed by HPLC) was used in the test. The theoretical oxygen demand (ThOD) of bisphenol A was calculated as 2.52 mg O₂/mg. The inoculum used in the

experiment consisted of activated sludge mixed liquor collected from a municipal sewage treatment plant. The experimental details followed the procedures detailed in the OECD 301F test to Good Laboratory Practice (GLP) standards. However, the temperature used in the experiment was 27.1°C, which is 2.1°C above the range of temperatures quoted in the OECD guidelines. Oxygen consumption and CO₂ evolution were measured over 28 days and removal of dissolved organic carbon (DOC) from the biodegradation reactions was determined after 28 days. The rate and extent of bisphenol A mineralisation observed indicate that bisphenol A can be classified as 'readily biodegradable'. Evolution of CO₂ resulting from mineralisation of bisphenol A closely followed biodegradation of the compound as measured from oxygen consumption. Maximum yields of CO₂ ranged from 73.0% to 80.1% of ThCO₂ indicating nearly complete conversion of the added organic carbon to CO₂ (UK, 2000).

West and Goodwin (1997b) repeated the above experiment at a lower temperature of 22.5°C to meet OECD guidelines for this test. Apart from the temperature the experimental conditions were the same as West and Goodwin (1997a). The results of the experiments confirmed the earlier test result that bisphenol A can be classed as 'readily biodegradable' according to the OECD 301F manometric respirometry test (UK, 2000).

Matsui et al. (1988) studied the biodegradability of organic substances in an activated sludge test using inocula from an industrial wastewater treatment plant. The sludge was acclimated for a total of 24 hours before the first samples were taken. The chemical oxygen demand (COD) was determined with KMnO₄ and total organic carbon (TOC) was measured. For bisphenol A the removal was 72% COD and 57% TOC. It is not possible to say from these results whether bisphenol A is readily biodegradable, but the results indicate that bisphenol A is at least inherently biodegradable (UK, 2000).

Furun et al. (1990) studied the treatment of wastewater containing bisphenol A by biological processes, activated carbon adsorption and large pore resin adsorption. The ability of biological wastewater treatment to degrade bisphenol A was tested using the activated sludge treatment process. The activated sludge used in the test was taken from a plant treating petrochemical wastewater. After two weeks exposure the removal rate of bisphenol A was 99.7%. The biological treatment experiment was also conducted on the effluent from a polycarbonate production plant. The acclimation stage of the activated sludge lasted about two months. After a period of adaptation the bisphenol A removal rate from the effluent was 99.4%. The authors noted that actual production wastewater often contains high levels of sodium chloride which can cause the biological treatment to be ineffective (UK, 2000).

Alexander and Batchelder (1975) reported a 5 day biodegradation for bisphenol A of 26% (BOD/ThOD) and a 20 day BOD/ThOD of 70.6% (UK, 2000).

The removal of bisphenol A in a biopond system is reported as greater than 95.5% (DOW, 1984). No indication is given about the main removal mechanism (UK, 2000).

The results of an aerobic biodegradation study on bisphenol A are reported by Mobil Oil Corporation (1993). The initial test concentration of 10 mg carbon/l using the EPA shake flask method with an unacclimated sewage/soil inoculum. In 28 days, 83.6% of the carbon in the study mixture was converted to CO₂. In the control 71.7% of the carbon was converted to CO₂. The study substance met the criteria for readily biodegradable meeting the 10 day test window (UK, 2000).

Industry has recently commissioned a river die-away study looking at the degradation of bisphenol A in shake flask microcosms and respirometer tests. The study has been designed to look at the effect of acclimation of micro-organisms to bisphenol A. Water and sediment samples are collected upstream and downstream from a wastewater treatment plant treating wastewater containing bisphenol A. The effect of sediment on degradation is being studied with sediment added to the samples at 500 mg/l (UK, 2000).

Preliminary results based upon respirometer studies on water and sediment samples from the indicated rivers are available. It should be noted that these are preliminary results based upon visual interpolation of the data. The average half-life for biodegradation is 1.2 ± 0.8 days after the initial lag phase. The average maximum oxygen consumption is $80 \pm 10\%$ and maximum carbon dioxide production is $71 \pm 10\%$. Similar results are found for water only samples and water with sediment samples added. There does not appear to be much difference in the results between upstream and downstream samples (UK, 2000).

Lobos et al. (1992) isolated a gram-negative aerobic bacillus species (strain MV1) from a sludge enrichment obtained from a waste water treatment plant associated with a plastics manufacturing facility. The bacterial strain was able to use bisphenol A as a sole carbon and energy source. 60% of the carbon contained in bisphenol A was mineralised to CO₂, 20% was associated with the bacterial cells and the remaining 20% was converted to soluble organic compounds (Lobos et al. 1992). The main metabolites were identified as 2,2-bis(4-hydroxyphenyl)-1-propanol, 4-hydroxyacetophenone with trace amounts of 4-hydroxybenzoic acid. Formation of metabolites was rapid in the first 8 hours then their concentrations slowly declined. The concentration of 2,2-bis(4-hydroxyphenyl)-1-propanol was found to be proportional to cell growth. The proposed pathways for the degradation of bisphenol A by strain MV1 by the authors are given in Figure 5.1 (UK, 2000).

No information is available of any possible anaerobic degradation (UK, 2000).

The conflicting results obtained concerning the biodegradability of bisphenol A may arise from differences in test method conditions, including differences in the ratio of the number of micro-organisms and the concentration of the test substance (Pedersen et al. 1994). Furthermore, toxic inhibitory effects of the test substance towards micro-organisms may arise when high concentrations of the test substance used, inhibit or limit microbial degradation of the substance. Finally, variability in test result may be due to biological variation of the test systems themselves, for instance differences in number of active degraders in the inocula used (Pedersen et al. 1994 in TemaNord, 1996).

Acclimatisation and redox conditions seem to play a significant role for the biodegradation of bisphenol A. In aerobic aquatic tests (non-acclimated) the half-life of bisphenol A has been reported to lie in the range 24 hours to 6 months, whereas acclimatised aerobic test showed a fast degradation of bisphenol A with a half-life (T_{1/2}) of 2.5 to 4 days. Under anaerobic conditions (non-acclimated) the half life of bisphenol A lay in the range 96 hours to 24 months (Howard et al. 1991, cited-in Hanze 1994 in TemaNord, 1996).

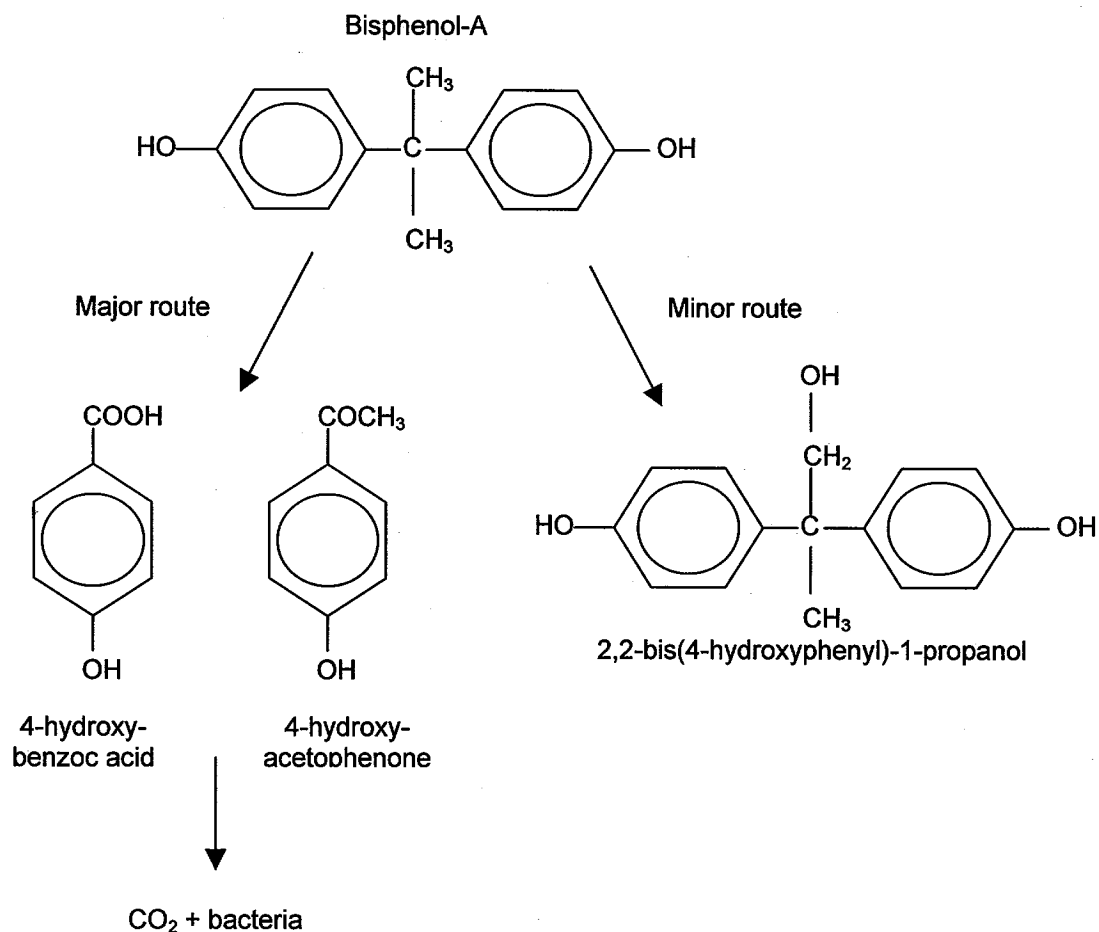


Figure 5.1:
Possible degradation pathways of bisphenol A

Table 5.3:
Biodegradation of bisphenol A (TemaNord,1996; UK,2000; Cis Envirofate,2000)

| Biodegradation in % | Exposure conc. In mg/l | Test conditions/ test type | Conclusion | Reference |
|--|------------------------|---|---------------------------|---|
| BPA consumed none its theoretical O2 demand | 3 | 28 d Closed Bottle Test. 20°C, OECD | Not readily biodegradable | Stone &Watkinson, 1983 (TemaNord, 1996; UK, 2000) |
| 1-2% of the theoretical CO2 demand was evolved | 20 | 28 d Modified Sturm test, aerobic, OECD | Not readily biodegradable | Stone &Watkinson, 1983 (TemaNord, 1996; UK, 2000) |
| 0% degraded during a 2 week period | - | BOD | - | Hanze, 1994 (TemaNord, 1996; UK, 2000) |
| Lag phase of 13-17 d, thereafter a removal in DOC of 87-95%. | 20 | Modified SCAS procedure, 20°C | Inherently biodegradable | Turner & Watkinson, 1986 (TemaNord, 1996; UK, 2000) |
| 83.6% of the carbon in BPA was converted to CO2 | 12.6 | EPA shake Flask method (unacclimated sewage soil inoculum), aerobic, 25°C | Ready biodegradable | Wagner, 1993 (TemaNord, 1996) |

| | | | | |
|--|-------------------|--|--|--|
| 9d: 30-40% degradation 20d: 40-50% degradation | 25, 50, 75 | Mixed bacteria cultures, 37°C | - | Munjko & Hegedic, 1980 (TemaNord, 1996) |
| 9d: 10-20% degradation 20d: 90-100% degradation | 25, 50, 75 | Mixed bacteria cultures, 20°C | - | Munjko & Hegedic, 1980 (TemaNord, 1996) |
| 20d: 60% degradation | 100 | Mixed bacteria cultures, 37°C | - | Munjko & Hegedic, 1980 (TemaNord, 1996) |
| 0-29% degradation within 2 weeks | 100 | MITI test for ready biodegradability | Not ready biodegradable | MITI, 1992 (TemaNord, 1996) |
| - | - | MITI test | No or slow biodegradation in water | Sasaki, 1978 (cis envirofate, 2000) |
| 0-29 %BODT 14 d | 100 ppm | Activated sludge, MITI, aerobic, BOD, 25°C pH 7 | Biodegrades slow | Sasaki, 1978 (cis envirofate, 2000) |
| 0% BODT 14 d | 100 ppm | Activated sludge, Modified MITI, OECD 301C, 302C, aerobic, 25°C, pH 7 | Biodegrades slow with acclimation | Chemicals Inspection and Testing Institute (Japan), 1992 (cis envirofate, 2000) |
| 11 % COD removal at 2 h 43% COD removal at 4 h 72% COD removal at 24 h | 105 ppm | Activated sludge, aerobic, 25°C, inocula from industrial waste- water plant (SCAS), COD, aerated 5 l/min, acclimation assumed to have occurred | Biodegrades fast with acclimation | Matsui, et al., 1975 (cis envirofate, 2000) |
| 0 % degradation at 0 d 0 % degradation at 1 d 30 % degradation at 2 d 59 % degradation at 3 d >99 % degradation at 5 d >99 % degradation at 6 d >99 % degradation at 8 d | 3 ppm | Aerobic, 22-25°C, pH 7.3 - 8.3, reverse phase HPLC, | Biodegrades fast with acclimation in chemical planted treated process sample | Dorn, et al., 1987 (cis envirofate, 2000; TemaNord, 1996) |
| 0 % degradation at 0 d 0 % degradation at 1 d 17 % degradation at 2 d >99 % degradation at 3 d >99 % degradation at 5 d >99 % degradation at 8 d | 3 ppm | Aerobic, 22-25°C, pH 7.3 - 8.3, reverse phase HPLC, | Biodegrades fast with acclimation in water (Patrick's bayou, Texas) | Dorn, et al., 1987 (cis envirofate, 2000; TemaNord, 1996) |
| 0 % degradation at 0 d 0 % degradation at 1 d 3% degradation at 2 d 3 % degradation at 3 d >99 % degradation at 5 d >99 % degradation at 6 d >99 % degradation at 8 d | 3 ppm | Aerobic, 22-25°C, pH 7.3 - 8.3, reverse phase HPLC, | Biodegrades fast with acclimation in water (Houston ship channel, Texas) | Dorn, et al., 1987 (cis envirofate, 2000; TemaNord, 1996) |
| 10% degradation in 5.6 - 6.1d 60% degradation in 9.1 – 11.1 d 84.6% degradation in 28 d (7mg/l) 81.7% degradation in 28 d (25 mg/l) | 7 mg/l 25 mg/l | OECD 301F manometric respirometry test, 28 d, ThOD 2.52 mg O ₂ /mg, act. Sludge, GLP, 27.1C (above the OECD pref. Temp.) | Readily biodegradable | West & Goodwin, 1997a (UK, 2000) |
| 10% degradation in 4.7 - 5.2d 93.1% degradation in 28 d (7mg/l) 81% degradation in 28 d (25 mg/l) | 7 mg/l 25 mg/l | OECD 301F manometric respirometry test, ThOD 2.52 mg O ₂ /mg, act. Sludge, GLP, 22.5C, 28 d | Readily biodegradable | West & Goodwin, 1997b (UK, 2000) |

| | | | | |
|--|----------------------------------|---|--------------------------|---|
| 72% COD removal in 24 h 57% TOC removal in 24 h | 58 mg/l | Act. Sludge from indust. WWTP, 2-3 g/l MLSS in aeration container, air flow 150 ml/min, 25-30 C 24 h acclimatisation | Inherently biodegradable | Matsui, et al., 1988 (UK, 2000) |
| 99.4% removal 99.7% removal after 2 weeks | 100 mg/l 200 mg/l | Act. Sludge, 1 week adaptation (200 mg/l) and 2 months (100 mg/l) | - | Furun, et al., 1990 (UK, 2000) |
| 60% mineralised to CO2 20% associated with bacteria cells 20% remained | - | Bacillus strain MV1 from sludge of WWTP | - | Lobos, et al., 1992 (UK, 2000) |
| 26% BOD/ThOD in 5 d 70.6% BOD/ThOD in 20 d | - | ThOD 2.52 mg O2/mg; COD 2.31 mg O2/mg; BOD 0.66 mg O2/mg (5d); 1.42 mg O2/mg (9d); 1.78 mg O2/mg(20d) | - | Alexander & Batchelder, 1975 (UK, 2000) |
| 95.5% removal | | Biopond system | | Dow (UK, 2000) |
| 83.6% degradation in 28 d | - | EPA shake flask method, unacclimated sewage/soil inoculum; control 71.7% C degraded in 28 d | Readily biodegradable | Mobil Oil Corporation, 1993 (UK, 2000) |
| Average lag -phase 3.4 days Average biodegr. half life 1.2 d Average max. O2 consumption 80% Max. CO2 production 71% Rivers: Rhine Krefeld; Ohio at Vernon; Westerschelde; Ware Massachusetts; Monte Sanyo Bayou Louisiana; Mississippi. | 50 µg/l 500 µg/l 5000 µg/l | River die-away study, shake flask microcosms + respirometer tests; water + sediment upstream and downstream of WWTP | - | UK, 2000 |

In summary, factors which influence the biodegradability of bisphenol A seem to be the microbial composition of the receiving environment and the prevailing redox conditions. In media where bisphenol A has not previously be introduced (non-acclimated/non-adapted), the degradation rate may turn out to be very slow. On the contrary, in acclimated media a complete mineralisation of bisphenol A may quickly occur. Anaerobic conditions seem to retard the biodegradation of the compound (TemaNord, 1996).

Because adapted/re-exposed inocula/media have been used in most of the tests yielding results indicating "inherent biodegradability" or "ready biodegradability", which is not "allowed" in ready biodegradability tests (Petersen et al., 1994), the conclusions on biodegradability presented here are based on tests using unadapted inocula.

Based on these tests, it may be concluded that bisphenol A is not readily biodegradable (TemaNord, 1996).

5.5 Bioconcentration

Bioconcentration is the process in which micro contaminants are taken up by organisms. The contaminant is concentrated to higher internal concentrations in case it is not metabolised by the organism as compared to the case that it is metabolised. Bioconcentration is considered to be a partition process between water and organisms and comparable with for example sorption and octanol-water partitioning. Bioconcentration of compounds in aquatic organisms can occur through uptake of compounds directly from the water (bioaccumulation) or

through food (biomagnification). Bioaccumulation can be measured in different ways. Organisms can be exposed to water with contaminants until equilibrium is attained (internal contents do not increase anymore). The bioconcentration factor (BCF) can be calculated from the ratio between the content in organisms and water: $BCF = C_{organism} / C_{water}$. The BCF can be expressed on lipid basis as well as on fresh weight basis.

According to commonly used guidelines for the classification of the environmental hazard of chemicals within the EU, a chemical with a log Pow value > 3 and/or a BCF value of ≥ 100 is considered to have a bioaccumulative potential (Pedersen et al. 1994 in TemaNord, 1996).

Only sparse information concerning the bioaccumulation of bisphenol A in biota has been published. The US EPA (1984) estimated bioconcentration factors of bisphenol A from 15 to 366 using a model of Veith et al. (1979) and log Kow data (3.32, 3.84, 2.2 to 3.4) obtained by Korenman & Goreklov (1971), Lyman et al. (1982) and Eadsforth (1983), respectively (in TemaNord, 1996).

Kawasaki, 1980 reported a log BCF of 1-2 for fish in a MITI test (CIS envirofate, 2000).

In another study the measured BCF in fish is between 5 and 68 (Staples, 1998). This means hardly any bioaccumulation. Biomagnification up the food chain is not expected to be significant because of metabolism and excretion in mammals (Staples, 1995).

BCF of 42 and 196 were estimated for bisphenol A based on a water solubility of 120 mg/l at 25°C and a log Kow of 3.32, respectively (Dorn, et al., 1987 en Hansch, et al., 1985 in HSDB, 2000). These BCF value indicate that bisphenol A probably will not bioaccumulate significantly in aquatic organisms.

Table 5.4:
BCF values for bisphenol A

| BCF | Estimated/ Experimental | Reference |
|-------------|-------------------------|--|
| 15 – 366 | Estimated | US EPA, 1984 |
| 10 – 100 | Experimental, fish | Kawasaki, 1980 |
| 5 – 68 | Experimental, fish | Staples, 1998 |
| 42 – 196 | Estimated | Dorn, 1997; Hansch, 1985 in HSDB, 2000 |
| < 20 – 67.7 | Experimental, fish | MITI, 1977 |
| 5.1 – 13.3 | Experimental, fish | MITI, 1977 |

Bioconcentration factors for bisphenol A have been measured by MITI (1977). Bioconcentration factors were determined for carp (*Cyprinus carpio*) exposed to bisphenol A concentrations of 150 µg/l and 15 µg/l in a flow through system. The carp were exposed to bisphenol A for six weeks. At the 150 µg/l exposure concentration bioconcentration factors of 5.1 to 13.3 were measured over the 6 week exposure period. At the 15 µg/l exposure concentration bioconcentration factors of <20 to 67.7 were measured over the 6 week exposure period. Bisphenol A was judged to have a low bioaccumulation potential. This study was conducted to MITI guidelines. The length of the test appears to have been sufficient to allow a steady state between the concentration of bisphenol A in fish and water to be achieved. The test is considered valid for the determination of the bioconcentration factor of bisphenol A in fish (UK, 2000; TemaNord, 1996).

A bioconcentration factor for fish can also be calculated from the log Kow. For bisphenol A a log Kow of 3.4 is taken as the most representative value. This gives a calculated BCF for fish of 155, assuming no metabolism in the organism (UK, 2000).

The measured bioconcentration factors in fish suggests that bisphenol A has a moderate potential for bioaccumulation in aquatic species, in agreement with the moderate potential indicated by the log Kow value.

5.5.1 Prediction of the environmental distribution of bisphenol A

Bisphenol A may, upon discharge to the environment, distribute between the air, water, soils, sediments and biota compartments.

Henry's Law constant describes the extent of partitioning of a chemical substance between a solution and the above air. Eisenreich et al. (1981) reported that substances with a Henry's Law constant between 10^{-6} and 10^{-8} tend to partition predominately into water, whereas chemicals with a constant in the range 10^{-3} to 10^{-5} tend to distribute equally between liquid and gas phases. Based on the moderately high water solubility (120 mg/l at 25C), the very low vapour pressure (5.32×10^{-6} Pa at 25C) and the low Henry's Law constant of 1.0×10^{-6} to 1.0×10^{-5} Pa m³ mol⁻¹ of bisphenol A (see Table 2.1 in chapter 2) it is concluded that bisphenol A may have a tendency to partition into water and that the rate of evaporation from soil and water will be low.

On the basis of the Koc of 293 to 1,524 and the moderately high log Kow value of bisphenol A it is concluded that this chemical has a moderate potential for absorption to organic materials.

In a fugacity calculation (level 1) using the "ESTHER" manual (Ken-d 4/89) the environmental distribution of bisphenol A has been estimated to be: 32% in sediments, 43% in water, 24% in soil and 3.5×10^{-5} in air (Hanze, 1994 in TemaNord, 1996).

Transport in air

Based on the low vapour pressure of bisphenol A at room temperature, evaporation to and transportation in air is expected to be minimal. However, at elevated temperatures the vapour pressure of bisphenol A rises which will result in an increased volatility of the compound. In work place air, elevated concentrations of bisphenol A have been detected in several occasions.

Bisphenol A is expected to exist almost entirely in the particulate phase in the atmosphere. Loss from the atmosphere may occur by dry deposition or photolysis (Hedin & Pererüus, 1993; Hanze, 1994 in TemaNord, 1996).

Transport in soil

If released to soil, the moderate affinity of bisphenol A for organic materials (based on log Kow, and Koc values) indicates that mobility in soil is expected to be relatively low (TemaNord, 1996).

Based upon aqueous biodegradation tests (Dorn, et al., 1987; Matsui, et al., 1975 in HSDB, 2000), bisphenol A may biodegrade under aerobic conditions following acclimation. This compound is not expected to undergo chemical hydrolysis or volatilize significantly from soil surfaces (SRC).

Transport in water

Transportation of bisphenol A in the aquatic environment is considered to be the predominant pathway, for distributing the compound between environmental

compartments. In the receiving water bisphenol A is expected to moderately partition into particulate matter, sediments and biota considering the log P_{ow} , and K_{ow} values of the compound (see table 2.2.). Therefore, it is expected that bisphenol A will have a low to moderate mobility in terrestrial soils and when entering aquatic environments will moderately tend to partition into the sediment, dissolved organic matter and biota (TemaNord, 1996).

If released to acclimated water, biodegradation would be the dominant fate process (half-life less than or equal to 4 days). In nonacclimated waters, bisphenol A biodegrades, it may adsorb extensively to suspended solids and sediments, or it may photolyze (Dorn, et al., 1987 in HSDB, 2000). This compound is not expected to bioaccumulate significantly in aquatic organisms, volatilize, or undergo chemical hydrolysis (SRC).

5.6 Distribution in water systems

The behaviour of a substance and its distribution in the environment is primarily governed by properties such as solubility in water, volatility and biodegradability. To what extent these properties are favoured or hindered, depends further on the environmental conditions. The influence of environmental circumstances on the substance's behaviour can be simulated through modelling of the relevant mass transfer processes. Two modelling programmes, EPIWIN from the Syracuse Research Corporation and EUSES from the EU, have been used to compute the volatilisation from surface water and the substance distribution over air, water and sewage sludge during wastewater treatment.

With the EPIWIN estimation program it is possible to estimate environmental properties from the compound's chemical structure (chemical bond estimation method). Computed values are subsequently used to calculate basic emission distributions between water, air and soil, or the (a)biotic degradation in water and atmosphere. For compounds without experimental data for relevant environmental properties, this estimation method can provide a first indication of the required properties and behaviour in the environment. However, calibrations computations for compounds with reliable data show that sometimes computed values for K_{ow} , K_{oc} and Henry's Law coefficient significantly differ from experimental values and that accordingly, emission distributions will deviate substantially from results obtained with experimental data.

For the selected compounds, the environmental behaviour in lakes, rivers and wastewater treatment plants was quantified. Furthermore, a theoretical half-life value was computed for atmospheric photolysis in order to obtain an indication of the persistence of compound after it is released into the atmosphere. Basic conditions for volatilisation from river and lake are given in table 5.11.

Table 5.11:
Basic parameters for volatilisation (EPIWIN)

| | River | Lake |
|------------------------------|-------|------|
| Water depth (m) | 1 | 1 |
| Wind velocity (m/s) | 3 | 0.5 |
| Water current velocity (m/s) | 1 | 0.05 |

For computation of the emission distribution during wastewater treatment, an activated sludge plant was chosen with a regular set-up consisting of primary sedimentation, aeration and secondary sedimentation. Under these conditions, the biodegradability of the selected compounds was assumed to be negligible.

The modelling results are summarised in table 5.12. From the volatilisation results for river and lake, it shows that compounds, with low Henry's Law coefficients are hardly removed from surface waters.

Table 5.12:
Results of EPIWIN estimation programmes for environmental distribution of bisphenol A

| Property | Bisphenol A |
|--|--------------------|
| Log Kow (measured) | 3.4 |
| Solubility | 120 |
| Vapour pressure (measured) (mm Hg) | 4×10^{-8} |
| Volatilisation half-life from river | 1512 y |
| Volatilisation half-life from lake | 10990 y |
| Half-life for reaction with hydroxyl radicals ^c | 1.6 h |

H: Henry's law constant, WWTP: Wastewater Treatment Plant, TGD: Technical Guidance Document

^c: Calculated from OH reaction rate constant estimated by the method of Atkinson and assuming a OH radical concentration of 1.5×10^6 molecules/cm³ and 12 hours sunlight/day

5.7 Conclusions and recommendations

With respect to the environmental properties and behaviour in the aquatic systems the following conclusions can be drawn for the selected compound:

1. The log K_{ow} value varies from 2.2 to 3.4 and the solubility is moderately high. As a result of these characteristics bisphenol A is moderately soluble in water, which will be the primary pathway for distribution and in water has a tendency to moderately bind to particulate matter, sediments and biota. The rate of evaporation from soil and water will be low. The log Kow indicates a moderate bioaccumulative potential. Based on experimental data the BCF varies from 1 to 196, which also indicates a low potential to bioaccumulate in aquatic species.
2. Bisphenol A is not susceptible to hydrolysis but has a potential to photolyse in water if not bound to organic matters (particulate phase) in water.
3. Results from a number of biodegradation studies are reported for bisphenol A. In the OECD 301F manometric respirometry test bisphenol A meets the criteria for ready biodegradability. However in the OECD 301D closed bottle test and OECD 301B modified Sturm test no biodegradation was observed. In a modified SCAS procedure bisphenol A met the criteria for inherently biodegradable substances, although this test can not give any indication of the potential for bisphenol A to undergo ready biodegradation. From biodegradation tests bisphenol A is found to be not readily biodegradable, but to be inherently biodegradable.
4. Measured levels of bisphenol A before and after wastewater treatment at chemical plant and major users of bisphenol A suggest a high level of removal. It is not possible to say if this is via adsorption to sludge or biodegradation, although based upon its chemical properties biodegradation is likely to be the major removal mechanism. From this biodegradation studies reported

bisphenol A would be appear to be readily biodegradable, possibly with a short period of adaptation.

5.8 References

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6 Occurrence in the aquatic environment

6.1 Analytical techniques

Belfroid et al. (1999) reported a procedure for the analysis of hormones and bisphenol A in here study on oestrogen active substances. Special care was taken on the use of Bisphenol A free sampling bottles. Samples should be collected in glass sampling bottles with a teflon stopper. All bottles have to be rinsed with HPLC water and dried for 10 hours at 250 °C and pre-treated with a dimethyl dichlorosilane (DMDCS) sollution. Hereafter they are rinsed with successively with toluene and methanol (for residue analysis).

Pre-treatment with DMDCS is meant to fill in so-called active sites in the glass that may bind hormones. As BPA may occur in (plastic) tools, use of plastic has to be minimised as much as possible.

6.1.1 Watery matrices

Sampling water is filtered immediatly in the laboratory over 0.45 µm and 1.2 µm glass filters and extracted with a SDB-XC disk. Substances on the disk are eluted with methanol, concentrated and dissolved in purified hexane (using a combination of C18 and NH₂ columns). The extract is dissolved in eluens (methanol/water 65/35) and purified using a High Liquid Performance Chromatography (HPLC). The bisphenol A containing fraction is collected and condense-dried. Extracts are silylated with SIL A reagents, washed in water and dried over sodiumsulphate. Detection is performed with GC-MS.

Typical recoveries of bisphenol A using established methods are in the range of 80% (SD= 29%). Detection limits were in surfaces waters 3.1-19 ng/l, in effluent and influent of an WTP <10 ng/l and in sewerage sludge 15-124 ng/l (Belfroid et al., 1999). Detection limit is strongly influenced by contamination of the samples. Normally 1 litre or a few grams of sludge are sufficient for detection. It appeared that 10 days storage at 4°C had no significant effect on the BPA concentration in the sample.

Influents can also be analysed for BPA in the residue after filtration. The filters including the remaining matrix is freeze-dried and shaken with DCM for 30 minutes. The sample is concentrated and treated and analysed as described above.

6.1.2 Non-watery matrices

BPA analysis in suspended solids, sediment, sewage and activated sludge and/or biota may use an accelerated solvent extractor (ASE) with dichloromethane /acetone (50/50) as solvent. Before extraction the samples are freeze-dried. The ASE technique extracts samples for 20 minutes at high pressure (200 psi) and 100°C using the solvent. The further procedure for treatment and analysis is the same as described above (Belfroid et al., 1999).

Table 6.1:
Analytical methods for Bisphenol A

| Sample | Extraction and clean-up | Separation and detection | Limit of Determination | Ref |
|---------------------------|--|--------------------------|------------------------|-----------------------|
| surface water | Extraction hexane/HPLC/SIL A | GC MS/MS | 3.1-19 ng/l | Belfroid et al., 1999 |
| Effluent | Extraction hexane/HPLC/SIL A | GC MS/MS | <10 ng/l | Belfroid et al., 1999 |
| Influent | Extraction hexane/HPLC/SIL A | GC MS/MS | <10 ng/l | Belfroid et al., 1999 |
| Sewerage | Extraction hexane/HPLC/SIL A | GC MS/MS | 15-124 ng/l | Belfroid et al., 1999 |
| Influent residue | Freeze-dried, ASE technique with dichloromethane /acetone (50/50) | GC MS/MS | | Belfroid et al., 1999 |
| Suspended solids sediment | extract freeze-dried powdered sample solvent dichloromethane /acetone (50/50) ASE extraction procedure | GC MS/MS | | Belfroid et al., 1999 |
| Fish | Freeze-dried, ASE technique with dichloromethane /acetone (50/50) | GC MS/MS | | Belfroid et al., 1999 |

6.2 Measurements in freshwater systems

In 1997 in the Netherlands BPA was analysed in several matrices of surface and sewerage water (Belfroid et al., 1999).

In a 1997 study of measured concentrations of bisphenol A in the U.S., receiving waters upstream and downstream of four of five bisphenol A manufacturing sites and two processing sites had no detectable bisphenol A at a detection limit (quantification with confirmation) of 1 µg/l. The fifth manufacturing site had bisphenol A concentrations ranging from 2 to 8 µg/l upstream and from 7 to 8 µg/l downstream. This facility's discharge makes up a large percentage of the receiving water flow during dry conditions, when samples were collected. Some bisphenol A was apparently present in the discharged effluent and likely flowed back into the area where the upstream samples were collected (Staples, 1998).

Table 6.2:
Levels of bisphenol A in water in different water systems in the Netherlands

| Location | Comments | Level (ng/l) | Reference |
|---|---|-------------------------------|-----------------------|
| Rhine, Lobith, 1997 | Two dates: 27/8 and 11/11 resp. SS 65 and 18 mg/l resp. | 28 - <19 | Belfroid et al., 1999 |
| Meuse, Eysden, 1997 | Three dates: 26/8, 5/11 and 9/12. | 37, 65, 160 | Belfroid et al., 1999 |
| Nieuwe waterweg, Maassluis, 1997 | Two dates: 20/8 and 3/11 | 34, 38 | Belfroid et al., 1999 |
| Haringvlietsluizen, 1997 | 5/11 replicates | <18 and 21 | Belfroid et al., 1999 |
| Nieuwe waterweg, Beneluxtunnel, 1997 | One date: 2/10 | 40 | Belfroid et al., 1999 |
| House hold sewerage water, Oostergemeente, 1997 | Two dates: 8/10, 18/12 | 260, 490+26 ¹ | Belfroid et al., 1999 |
| House hold sewerage sludge, Oostergemeente, 1997 | One date: 8/10 | 46 | Belfroid et al., 1999 |
| WTP influent, Amsterdam-Westerpoort, 1997 | Two dates: 15/10, 1/12 | 250, 690+32 ¹ | Belfroid et al., 1999 |
| WTP effluent, Amsterdam-Westerpoort, 1997 | Two dates: 15/10, 1/12 | 33, 130 | Belfroid et al., 1999 |
| WTP sludge (primary and excess) Amsterdam-Westerpoort, 1997 | One date: 1/12 | <124 | Belfroid et al., 1999 |
| WTP influent, Kralingseveer, 1997 | Two dates: 1/10, 3/12 | 240, 1000 | Belfroid et al., 1999 |
| WTP effluent, Kralingseveer, 1997 | Two dates: 1/10, 3/12 | 33, 320 | Belfroid et al., 1999 |
| WTP sludge (primary and excess) Kralingseveer, 1997 | One date: 3/12 | 210 | Belfroid et al., 1999 |
| WTP influent, Eindhoven, 1997 | Two dates: 30/9, 4/12 | (330, 360) ² , 570 | Belfroid et al., 1999 |
| WTP effluent, Eindhoven, 1997 | Two dates: 30/9, 4/12 | 70, 370 | Belfroid et al., 1999 |
| WTP sludge (primary and excess) Eindhoven, 1997 | One date: 4/12 | 270 | Belfroid et al., 1999 |
| ASTP influent, location A, 1997 | Two dates: 14/10, 2/12 | 480, >2000+30 ¹ | Belfroid et al., 1999 |
| ASTP effluent, location A, 1997 | Two dates: 14/10, 2/12 | 46, 22 | Belfroid et al., 1999 |
| ASTP sludge (primary and excess), location A, 1997 | One date: 2/12 | <15 | Belfroid et al., 1999 |
| ASTP influent, location B, 1997 | Two dates: 16/10,16/12 | 700, >2000 | Belfroid et al., 1999 |
| ASTP effluent, location B, 1997 | Two dates: 16/10,16/12 | 100, 22 | Belfroid et al., 1999 |
| Industrial wastewater, sewerage water, location C, 1997 | Two dates: 9/10,10/12 | 540, 480 | Belfroid et al., 1999 |
| Industrial wastewater, sludge, location C, 1997 | One date: 10/12 | 22 | Belfroid et al., 1999 |
| Industrial wastewater, sewerage water, location D, 1997 | Two dates: 2/10,9/12 | 420, 540 | Belfroid et al., 1999 |
| Industrial wastewater, sludge, location D, 1997 | One date: 9/12 | 120 | Belfroid et al., 1999 |

1: content in filtrate (watery fraction) + content in residue (solid matrix)

2: replicates samples were treated with β -glucuronidase

Concentrations bisphenol A in industrial and urban waste water are in the same range (300 to 700 ng/l). However at two industrial location (A and B) the bisphenol A concentration was > 2000 ng/l. Whereas in at other sampling date concentrations were comparable with the 'normal' range. Efficiency of removal is considerate, resulting in concentrations in the effluent of 20 to 400 ng/l. The bisphenol A content in the residue of wastewater was less than 5% in three samples. Bisphenol A concentrations in sewerage/wastewater sludge was high ranging between <116 to 7000 ng/l (15 to 270 ng/g dry matter).

In Japan during the period 1974 to 1978 in river surface waters in the Tokyo, Japan area concentrations bisphenol A of 60 to 1900 ng/l were measured (Howard, 1989; Matsumoto, 1982 in HSDB, 2000).

6.2.1 Sediment

In sampled sediments and suspended solids of rivers and river-deltas the concentrations BPA remained below detection limit (0.05-0.25 µg/kg dry matter) (Belfroid et al., 1999).

6.2.2 Organisms

No data were found on concentrations of bisphenol A in organisms.

6.2.3 Groundwater

In 1996 in Spain, in spring water no bisphenol A was detected (Del Olmo, 1997). Furthermore no data were found on concentrations of bisphenol A in groundwater.

6.2.4 Rainwater

For bisphenol A no measurement data were available with respect to the presence in rainwater.

6.3 Measurements in marine systems

6.3.1 Surface water

Concentrations in the marine Delta of the Netherlands were generally 1 order of a magnitude lower than concentrations in fresh water river waters and varied from 3.5 to 23 ng/l.

Table 6.3:

Levels bisphenol A in marine waters

| Location | Comments | Level (ng/l) | Reference |
|--------------------------------|-----------------|--------------|-----------------------|
| Noordzeekanaal, Ijmuiden, 1997 | One date: 1/10 | 9.9 | Belfroid et al., 1999 |
| Zeehavenkanaal, Delfzijl, 1997 | One date: 14/10 | 23 | Belfroid et al., 1999 |
| Westerschelde, Hansweert, 1997 | One date: 23/9 | 4.3 | Belfroid et al., 1999 |
| Westerschelde, Terneuzen, 1997 | One date: 24/9 | 3.5 | Belfroid et al., 1999 |
| Kanaal Gent, Terneuzen, 1997 | One date: 24/9 | 3.8 | Belfroid et al., 1999 |
| Oosterschelde, Oesterput, 1997 | One date: 13/10 | 3.7 | Belfroid et al., 1999 |

In 1996 in Spain, in marine surface water no bisphenol A was detected (De Olmo, 1997).

6.3.2 Sediment

No data were found on concentrations of bisphenol A in marine sediment.

6.3.3 Organisms

No data were found on concentrations of bisphenol A in marine organisms.

6.4 Occurrence in human tissues

No data were found on concentrations of bisphenol A in human tissue.

6.5 Conclusions

The following conclusions can be made with respect to the occurrence of bisphenol A.

1. In the Netherlands concentrations of 21 to 40 ng/l have been found in fresh waters and of 3.5 to 23 ng/l in marine waters. In Japan concentrations of 60 to 1900 ng/l have been measured in surface water in 1974-1978.
2. The concentrations in industrial and urban wastewater are in the range of 300 to 700 ng/l but for two locations, where the concentration reached the 2 mg/l.
3. Bisphenol A concentration in sewerage and wastewater sludge ranged from <116 to 7000 ng/l (15-270 ng/g dry matter).
4. In sediments concentrations were below the detection limit of 0.05 - 0.25 µg/kg dry matter.
5. There are no data on concentrations in other environmental compartments. Additional measurements for these environmental compartments as well as in food, are recommended.

In addition to the lack of environmental relevant data, can be mentioned that currently an extensive EU risk assessment is being completed. In this risk assessment, the environmental aspects of the use and the risks of bisphenol A are discussed in greater detail. It is recommended to await the final conclusions of these assessments.

6.6 References

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7 Toxicity in the aquatic environment

7.1 Mechanism of toxicity

The direct estrogenic substances may act in at least 3 different ways. At first they may bind to the estrogen receptor, in which case the mechanism of action is identical to 17 β -oestradiol. The second mechanism is based on stimulation of the endogenous production of 17 β -oestradiol. A third mechanism could be the diminishing of 17 β -oestradiol degradation. Furthermore there are substances that may bind to the estrogen receptor but do not cause an estrogenic effect in organisms. These substances are anti-estrogenic, because they prevent the binding of endogenous oestradiol and thereby cause endocrine disruption. There are also substances that influence the hormone regulation in an indirect way, e.g. because they influence the metabolism or the excretion of 17 β -oestradiol (RIKZ, 1996).

Bisphenol A is anti-estrogenic through the inhibition of 17 β -oestradiol induced transcription (62, 54 mg/kg bw) and estrogenic through prolactine production (67, 4-45 μ g/dag) and in vitro Yeast ER assay (75, 5000-15000 less potent than E2) (Dutch Health Council, 1999).

7.1.1 Metabolism

No information has been found concerning the metabolic conversion of bisphenol A in aquatic and terrestrial invertebrates or vertebrates.

In mammals (rats) bisphenol A metabolism occurs through a partial conversion into phenols, increasing their urinary content in a free and bound form. Bisphenol A is passed unaltered and in the form of glucuronids from the body in the urine and faeces (Knaak et al. 1966 cited in Sheftel, 1995).

When administered as a single dose by gavage to male CFE rats, 28% of the 14C-labeled bisphenol A was excreted in the urine (primarily as the glucosamide) and 56% in the faeces (20% as free bisphenol A, 20% as a hydroxylated bisphenol A, and the rest as an unidentified conjugate). No carbon-labeled residues were detected in animals killed after 8 days (DHHS/NTP, 1982 in HSDB, 2000).

7.2 Toxic effects in the aquatic environment

7.2.1 General

This paragraph describes the data on toxicity retrieved from the literature. Toxic effects for species in the aquatic environment are distinguished into acute and chronic effects. Furthermore a distinction is made between (pelagic) water organisms and ((epi) bentic) sediment organisms. It is not possible to base this distinction on the larger taxonomic groups. Within every group there are representatives of a typical bentic and a typical pelagic way of living. Even within one species there can be a shift of one compartment to the other during the development from larvae to adult. The placing of a taxonomic group under pelagic or bentic organisms is therefore arbitrary.

In this report the available toxicity data are presented per group of species. The retrieved toxicity data are not evaluated except for the lowest values used for the derivation of iMPCs. However, when available, the test methodology used is reflected, which gives an indication about the quality of the data.

The level of toxicity of bisphenol A is classified according to the classification system in Annex 2.1.

7.2.2 Toxic effects in freshwater aquatic environment

General

In this report the Daphnids, are incorporated with the pelagic freshwater environment. The other freshwater crustaceans and insect larvae are incorporated with the benthical environment. Algae, bacteria, protozoa and fish are incorporated with the pelagic environment. Data from tests with sediment with several organisms are also incorporated with the benthical environment.

The decision whether a test is acute or chronic depends on the generation time of the specific species (group) and in principal chronic tests should enclose more than 1 generation. In this report the toxicity tests on insects, crustaceans and molluscs with a testing time of 96 h and less, are regarded as acute. The other tests are regarded as chronic. For algae, bacteria and protozoa the EC₅₀ values at 96 h and less are regarded as acute and the NOEC values at 96 h as chronic. For fish the data are regarded per test. Tests on early life stages (ELS) are regarded as chronic. In table 7.2 all retrieved acute and chronic toxicity data of bisphenol A for freshwater organisms are presented. Table 7.1 gives an overview of the level of toxicity. In this table the data from crustaceans of pelagic and bentic environments are combined.

Table 7.1:

Overview of the toxicity data on bisphenol A in the freshwater environment classified according to the classification system in Annex 2.1

0 = very slightly toxic; * = slightly toxic; ** = moderately toxic; *** = very toxic

| Chemical | CAS no | Bacteria | | Algae | | Crustaceans | | Fish | | Amphibians | |
|-------------|---------|----------|---------|-------|---------|-------------|---------|-------|---------|------------|------------------|
| | | Acute | Chronic | Acute | Chronic | Acute | Chronic | Acute | Chronic | Acute | Chronic |
| Bisphenol A | 80-05-7 | * | - | ** | 0 | ** | 0 | ** | * | 0 | *** ^a |

Effects on sex-ratio

Bisphenol A

The table 7.2a and b show that there are toxicity data available for almost all of the relevant organism groups for bisphenol A. It appears that bisphenol A is acutely moderately toxic to algae, crustaceans and fish, slightly toxic to bacteria and very slightly toxic to amphibians. Chronically bisphenol A is slightly toxic to fish and very slightly toxic to algae and crustaceans. To amphibians bisphenol A is chronically very toxic. However this is based on an endocrine disrupting effect: skewed sex-ratios. There is only 1 study on the toxicity to sediment organisms, which indicates the same toxicity as for water organisms. The toxicity values are almost all below the level of water solubility, which is 120-300 mg/l.

Table 7.2.a:

Retrieved acute effect concentration (LC₅₀ and/or EC₅₀) (mg/l) of bisphenol A for groups of species from the freshwater aquatic environment

| Class | Conc. (mg/l) | Testing time | Effect type | Organism | Method | Literature (source) |
|-------|--------------|--------------|-------------|----------|--------|---------------------|
|-------|--------------|--------------|-------------|----------|--------|---------------------|

| | | | | | | |
|-------------|--------------|------------|--|---------------------------|--|--|
| Bacteria | 35 | - | EC10 respiration decrease | Pseudomonas | Modified test cond. (48°C and low nutrient conditions) | Pilz, 1990 (TemaNord, 1996) |
| Bacteria | 54.5 | - | IC50 growth inhibition | Pseudomonas fluorescens | OECD | Stone & Watkinson, 1983 (TemaNord, 1996; UK, 2000) |
| Bacteria | 90 | - | EC10 respiration decrease | Pseudomonas | Standard conditions (25°C, sodium glutamate as C) | Pilz, 1990 (TemaNord, 1996) |
| Bacteria | 320 >=320 | 18h 18h | LOEC inhibition of growth NOEC inhibition of growth | Pseudomonas putida | 25°C, GLP | Fabig, 1988 (TemaNord, 1996) Dow, 1988 (UK, 2000) |
| Algae | 2.5 | 96h | EC50 reduction in cell count | Selenastrum capricornutum | 24°C, constant illumination of 3000 lux, nom.conc. | Stephenson, 1983 (TemaNord, 1996; UK, 2000) |
| Algae | 2.73 | 96h | EC50 reduction in cell count (growth) | Selenastrum capricornutum | Static | Alexander, et al., 1985, 1988 (TemaNord, 1996 ; AQUIRE) |
| Algae | 3.10 | 96h | EC50 reduction in total cell volume (pop. growth) | Selenastrum capricornutum | Static | Alexander, et al., 1985, 1988 (TemaNord, 1996 ; AQUIRE) |
| Crustaceans | 3.9 | 48h | EC50 Immobility | Daphnia magna | Static, 20°C, pH 8.3-8.4, nom.conc | Stephenson, 1983 (TemaNord, 1996; UK, 2000) |
| Crustaceans | 4.11 | 48h | NOEC | Daphnia magna | - | ECETOC, 1993 (TemaNord, 1996) |
| Crustaceans | <=6.97 | - | NOEC | Daphnia magna | Static, 20°C, pH 8.0-8.3 | Alexander, et al., 1985b, 1988 (TemaNord, 1996) |
| Crustaceans | 10 | 24h | EC50 Immobility | Daphnia magna | Static, 20°C, pH 8.3-8.4, 19.8-20.4°C | Stephenson, 1983 (TemaNord, 1996; UK, 2000) |
| Crustaceans | 10.2 | 48h | EC50 | Daphnia magna | Static, 20°C, pH 8.0-8.3, 19.8-20.4°C, ASTM E35.21, meas.conc. | Alexander, et al., 1985b, 1988 (TemaNord, 1996; AQUIRE; UK, 2000) |
| Crustaceans | 15.5 | 24h | EC50 | Daphnia magna | Static, 20°C, pH 8.0-8.3, ASTM E35.21, meas.conc. | Alexander, et al., 1985b, 1988 (TemaNord, 1996; AQUIRE; UK, 2000) |
| Fish | >0.64 | - | NOEC survival, weight, length, vitellogenin 32 d posthatch | Pimephales promelas | Range finder study for a full fish life cycle study | Caunter, et al., 1999 (UK, 2000) |
| Fish | 3-5 | 96h | LC50 | Salmo gairdneri | Static, 15°C, at 10 mg/l all died within 24 h. pH 8.4 | Fish & Reiff, 1979 (TemaNord, 1996) |
| Fish | 4.6 | 96h | LC50 | Pimephales promelas | Flow-through, 16.1-17.9°C, pH 7-8.1, ASTM E35.21, nom.conc. | Alexander, et al., 1985c, 1988 (TemaNord, 1996 ; AQUIRE; UK, 2000) |
| Fish | 4.7 | 96h | LC50 | Pimephales promelas | Static, 17-17.5°C, pH 7.6-8 | Alexander, et al., 1985c, 1988 (TemaNord, 1996; AQUIRE; UK, 2000) |
| Fish | 5 | 48 h | LC0 / NOEC | Salmo gairdneri | Renewal, 16-21.5°C | Lysak & Marcinek, 1972 (TemaNord, 1996; AQUIRE; UK, 2000) |
| Fish | 7 | 24 h | LC100 | Salmo gairdneri | Renewal, 16-21.5°C | Lysak & Marcinek, 1972 (TemaNord, 1996; AQUIRE; UK, 2000) |
| Fish | 3.64 11.0 | - | NOEC LOEC | Onchorhynchus mykiss | OECD juvenile growth test, measured conc., | Bayer AG, 1999b (UK, 2000) |

| | | | | | | |
|-----------|--------------------------------|------|---|-----------------------------|----------------------------------|-----------------------------|
| Fish | 3.2 10.15 | 14 d | NOEC LOEC | Brachydanio rerio | Semistatic, OECD 204, meas.conc. | Bayer AG, 1999a (UK, 2000) |
| Fish | 15 | 48h | LC50 | Oryzias latipes | Static | MITI, 1992 (TemaNord, 1996) |
| Fish | 1 µM (~228 µg/l) | 96 h | LOEC Induction of vitellogenin-mRNA | Salmo gairdneri hepatocytes | - | Islinger, et al., 1999 |
| Fish | <50 µM (~11.4 mg/l) | - | LOEC Induction of vitellogenin synthesis | Cyprinus carpio hepatocytes | In vitro | Smeets, et al., 1999 |
| Amphibian | 30198 µM (~ 6,900 mg/l) | - | IC50 binding affinity to ER | Xenopus laevis Liver cells | - | Lutz, et al., 1999 |

Table 7.2.b:
Retrieved chronic effect concentration (NOEC) (mg/l) of bisphenol A for groups of species from the freshwater aquatic environment

| Class | Substance | Conc. (mg/l) | Testing time | Effect type | Organism | Method | Literature (source) |
|-----------------------|---------------|--------------------------|--------------|---|---------------------------|--|--|
| Waterorganisms | | | | | | | |
| Algae | | 1.17 | - | NOEC | Selenastrum capricornutum | - | ECETOC, 1993 (TemaNord, 1996) |
| Algae | | >1.99 | 96h | LOEC inhibition | Selenastrum capricornutum | - | Alexander , et al., 1985a, 1988 (TemaNord, 1996) |
| Mollusc | | <0.001 | 5 m | LOEC induction superfemales | Marisa cornuarietis | renewal, tap water, 22 C | Oehlmann, et al. , 2000 |
| Mollusc | | <0.001 | 12 m | LOEC induction superfemales | Marisa cornuarietis | renewal, tap water, 22 C, life cycle test | Oehlmann, et al. , 2000 |
| Crustacean | | >= 3.16 | - | NOEC moulting behaviour | Daphnia magna | | Caspers, 1998 (UK, 2000) |
| Crustacean | 99.94% purity | >=3.146 (meas) | 21 d | NOEC reproduction | Daphnia magna | Semistatic, 20°C, PH 7.7-8.1, OECD 202, GLP | Caspers, 1998 in Cefic, 1999 and Bayer AG, 1996 (UK, 2000) |
| Fish | | 0.4 2 | 115 – 145 d | NOEC Sex ratio LOEC Sex ratio skewed towards females, reduced growth | Medaka F0-generation | Life cycle study; 115 d post hatch to 145 d post hatch | Yokota, et al., 1999 in Cefic, 1999 |
| Fish | | 0.64 | 32 d | NOEC Growth, weight, survival, vitellogenin concentration | Pimephales promelas | Early life stage test | CEFIC, in prep in CEFIC, 1999 |

| | | | | | | | |
|---------------------------|------------|--------------------------------|-------------|---|-------------------------|---|-------------------------------------|
| Fish | | 2 | 115 – 145 d | NOEC Percentage hatch, time to hatch, survival | Medaka F0-generation | Life cycle study; 115 d post hatch to 145 d post hatch | Yokota, et al., 1999 in Cefic, 1999 |
| Amphibian | | 0.0023 0.023 | 12 w | NOEC Sex-ratio LOEC Sex-ratio skewed towards females | Xenopus laevis | Renewal 3 times/week | Kloas, et al., 1999 in Cefic, 1999 |
| Sediment organisms | | | | | | | |
| Crustacean | 98% purity | 1.6 1.3 | 10 d | LC50 EC50 total adverse effects | Corophium volutator | Artificial sediment OECD 1984, with acetone 1.4 and 1.1 mg/l resp.in interstitial water | Whale, et al., 1999 (UK, 2000) |
| Crustacean | 98% purity | 60 mg/kg dw 36 mg/kg dw | 10 d | LC50 EC50 total adverse effects | Corophium volutator | Artificial sediment OECD 1984, with acetone 46 and 31 mg/kg dw resp.in sediment | Whale, et al., 1999 (UK, 2000) |

Overview of the toxicity data for fresh water organisms

In table 7.3 an overview is given of the lowest retrieved acute and chronic effect concentrations. The concentrations are reflected in **mg/l**.

Table 7.3:

Overview of the lowest retrieved acute effect concentrations (L(E)C₅₀) (in mg/l) and the lowest retrieved chronic effect concentrations (NOEC) (in mg/l) of bisphenol A in the freshwater environment

| Effect concentrations | Lowest retrieved acute effect concentrations L(E)C ₅₀ | Lowest retrieved chronic effect concentrations NOEC |
|---------------------------|--|---|
| Water organisms | | |
| Bacteria | 54.5 | - |
| Algae | 2.5 | 1.17 |
| Crustaceans | 3.9 | = 3.146 |
| Fish | 4.6 | 0.64 |
| Amphibians | 6,900 | 0.0023* |
| Sediment organisms | | |

| | | |
|-------------|---|-------|
| Crustaceans | - | 1.6** |
|-------------|---|-------|

* based on sex-ratio effects

** based on LC50

Table 7.2 and 7.3 show that most data are available for almost all organism groups but that data are not very abundant.

Effects observed in the environment

No data on bisphenol A are retrieved on effects observed in the environment.

7.2.3 Comparing exposure concentrations to environmental criteria

Until now no environmental criteria are set for bisphenol A. Therefore a comparison with exposure concentrations can not be made.

7.2.4 Toxic effects in marine aquatic environment

General

In table 7.4 the retrieved acute and chronic toxicity data of bisphenol A for marine organisms are reproduced. In this report the toxicity tests on crustaceans and molluscs with a testing time of 96 h and less, are regarded as acute. The other tests are regarded as chronic. For algae the EC₅₀ values at 96 h are regarded as acute and the NOEC values at 96 h as chronic. For fish the data are regarded per test. Tests on early life stages (ELS) are regarded as chronic. No distinction is made between water and sediment organisms.

Table 7.4 gives an overview of the level of toxicity.

Table 7.4:

Overview of the toxicity data on bisphenol A in the marine environment classified according to the classification system in Annex 2.1

0 = very slightly toxic; * = slightly toxic; ** = moderately toxic; *** = very toxic

| Chemical | CAS no | Bacteria | | Algae | | Crustaceans | | Fish | |
|-------------|---------|----------|---------|-------|---------|-------------|------------------|-------|---------|
| | | Acute | Chronic | Acute | Chronic | Acute | Chronic | Acute | Chronic |
| Bisphenol A | 80-05-7 | - | - | ** | - | ** | *** ^a | ** | - |

a. based on a EC10

Bisphenol A

The table 7.5a and b shows the toxicity data of bisphenol A for marine organisms. Bisphenol is acutely moderately toxic to algae, crustaceans and fish. There are only 2 data available on chronic toxicity data on bisphenol A, 1 on larval development and 1 on an endocrine effect. These data indicate a moderate toxicity to crustaceans and very toxic to molluscs. Toxicity data are well below the limit of water solubility (120-300 mg/l).

Table 7.5.a:

Retrieved acute effect concentration (LC₅₀ and/or EC₅₀) (mg/l) of bisphenol A for groups of species from the marine aquatic environment

| Class | Conc. (mg/l) | Testing time | Effect type | Organism | Method | Literature (source) |
|-------|--------------|--------------|-------------|----------|--------|---------------------|
|-------|--------------|--------------|-------------|----------|--------|---------------------|

| | | | | | | |
|-------------|-------------|------|---|-----------------------|--|---|
| Algae | 1 | 96h | EC50 reduction in cell count (growth) | Skeletonema costatum | 20°C, art. seawater, 28‰ | Surprenant, 1985c (TemaNord, 1996) Springborn Bionomics, 1985 + Alexander, 1988 (UK, 2000) |
| Algae | 1.8 | 96h | EC50 Chlorophyll content | Skeletonema costatum | 20°C, art. seawater, 28‰ | Springborn Bionomics, 1985 + Alexander, 1988 (UK, 2000) |
| Crustaceans | 0.51 | 96h | NOEC | Mysidopsis bahia | Flowthrough, 20‰, 24-25° C, pH 7.5-8.1 | Surprenant, 1985b (TemaNord, 1996; UK, 2000) |
| Crustaceans | 1.1 | 96h | LC50 | Mysidopsis bahia | Flowthrough, 20‰, 24-25° C. meas.conc., pH 7.5-8.1 | Surprenant, 1985b (TemaNord, 1996) Alexander, 1988 (UK, 2000) |
| Crustaceans | 1.6 | 48h | LC50 | Mysidopsis bahia | Flowthrough, 20‰, 24-25° C, meas.conc., pH 7.5-8.1 | Surprenant, 1985b (TemaNord, 1996) Alexander, 1988 (UK, 2000) |
| Crustaceans | 3.4 | 48 h | LC50 | Acartia tonsa | Static, nom.conc., Red sea commercial salt mixture, 20°C, 18‰, | Kusk, et al., 1999 (UK, 2000) |
| Crustaceans | 4.2 | 48 h | LC50 | Acartia tonsa | Static, nom.conc., Synthetic medium, 20°C, 18‰, | Kusk, et al., 1999 (UK, 2000) |
| Crustaceans | 5 | 48 h | LC50 | Acartia tonsa | Static, nom.conc., 18‰ natural seawater, 20°C | Kusk, et al., 1999 (UK, 2000) |
| Fish | 0.46 1.8 | 96 h | EC10 malformed embryo's EC100 Malformed embryo's | Brachydanio rerio | | Knorz, et al., 1999 (CEFIC, 1999) |
| Fish | 7.5 | 96h | LC50 | Cyprinodon variegatus | Flowthrough, 26.6°C, meas.conc. | Emmitte, 1978 (TemaNord, 1996; UK, 2000) |
| Fish | 9.4 | 96h | LC50 | Menidia menidia | Flowthrough, 22-23°C, 20-21‰, pH 7.9-8.3, meas.conc. | Surprenant, 1985a (TemaNord, 1996) Alexander, et al., 1988 (AQUIRE) Springborn Bionomics, 1985 (UK, 2000) |
| Fish | 15 | 48h | LC50 | Oryzias latipes | - | MITI, 1977 (UK, 2000) |

Table 7.5.b:
Retrieved chronic effect concentration (NOEC) (mg/l) of bisphenol A for groups of species from the marine aquatic environment

| Class | Conc. (mg/l) | Testing time | Effect type | Organism | Method | Literature (source) |
|---------|--------------|--------------|--|-------------------|---------------------|------------------------|
| Mollusc | <0.001 | 3 m | LOEC enlarged accessory pallial sex glands + enhanced oocyte production; reduced penis and prostate gland length | Nucellus lapillus | renewal, 35 ‰, 14 C | Oehlmann, et al., 2000 |

| | | | | | | |
|-------------|------|-----|---|---------------|--------------------------------------|-----------------------------------|
| Crustaceans | 0.10 | 5 d | EC10 Larval development rate EC50 | Acartia tonsa | Renewal (3 d), early life stage test | Andersen, et al., 2000 (UK, 2000) |
| | 0.55 | | | | | |

Overview of toxicity data for marine organisms

In the Tables 7.6 an overview is given of the lowest retrieved acute and chronic effect concentrations. The concentrations are reflected in **mg/l**.

Table 7.6:

Overview of the lowest retrieved acute effect concentrations (L(E)C₅₀) (in mg/l) and the lowest retrieved chronic effect concentrations (NOEC) (in mg/l) of bisphenol A in the marine environment

| Effect concentrations | Lowest retrieved acute effect concentrations L(E)C ₅₀ | Lowest retrieved chronic effect concentrations NOEC |
|------------------------|--|---|
| Water organisms | | |
| Bacteria | - | - |
| Algae | 1 | - |
| Crustaceans | 1.1 | 0.1* |
| Fish | 7.5 | - |
| Amphibians | - | - |

* based on EC10

From table 7.6 it is clear that toxicity data on bisphenol A for the marine environment are scarce. From the available data it seems that these substances are moderately toxic to marine organisms.

7.3 Standards and derivation of iMPCs

In MilBoWa (1999) harmonized standards are derived for several environmental compartments for a number of chemicals. The purpose of MilBoWa (1999) is to create a system of limit- and target values for soil and surface water.

A limit value is a quality level that minimally should be achieved or maintained. A target value is a quality level at which no adverse effects are to be expected. The limit value is based upon the "maximal permissible concentration" (MPC), the target value on the "negligible concentration" (NC). At time it could be possible that different MPCs were operative for the same substance because there were also MPCs derived in the framework of the admission of plant protection products and biocides. In 1999 (Kalf, et al., 1999) the procedure for the derivation of MPCs for admission policy of plant protection products and biocides and the setting of environmental quality standards are harmonised.

As a starting-point it is formulated that a MPC is comparable to the concentration at which at least 95% of the species in the ecosystem will be protected (method of Van Straalen and Denneman (1989), modified to the model of Aldenberg and Slob (1991; 1993). There is also formulated that the negligible risk level is comparable to 1% of the MPC.

For the bisphenol A there are no standards derived yet.

For the derivation of MPCs directly from ecotoxicological endpoints two different methods are used: the refined effect assessment method and the preliminary effect assessment method. Because long term chronic data are preferred above short term acute data the aim is to apply the refined effect assessment method. However application of this method is based on data availability: at least four NOEC values are needed for four different taxonomic groups of organisms. If these data are not

available the preliminary effect assessment method is applied. In this case in principle the TGD is applied. In figure 7.1 the direct method for MPC derivation is presented.

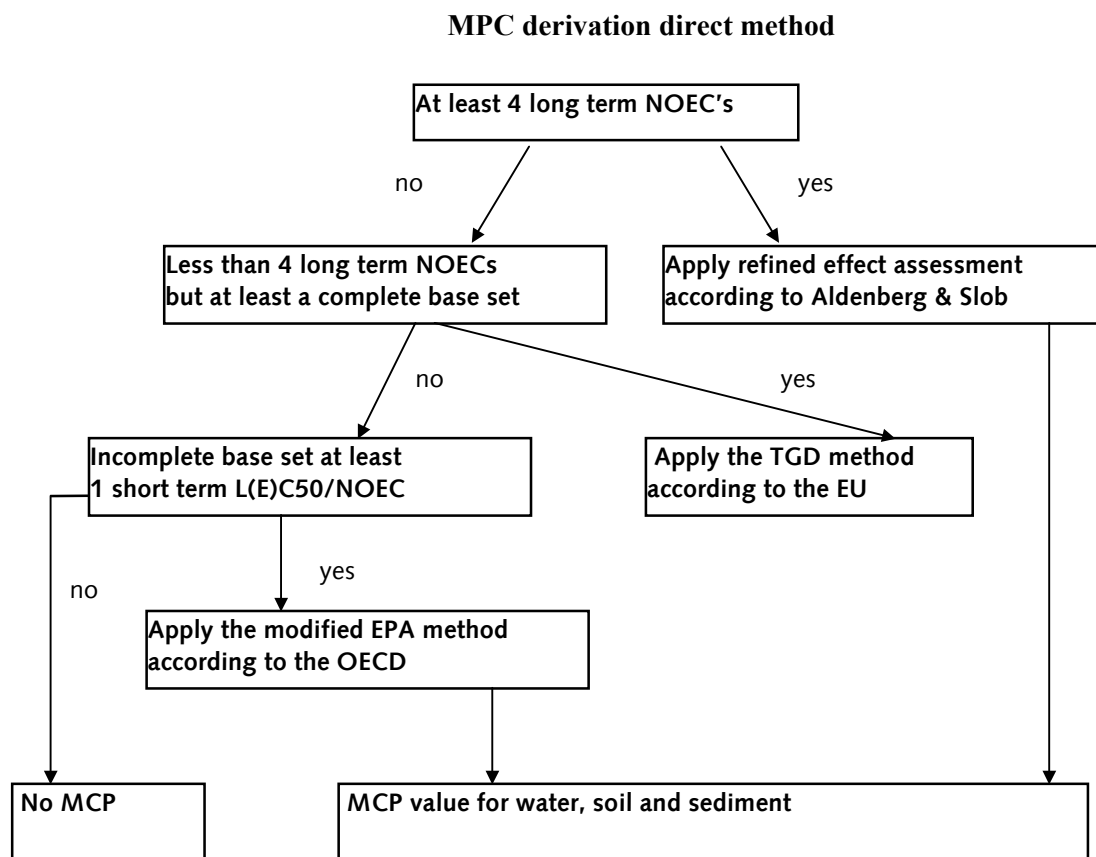


Fig. 7.1:
Scheme for the derivation of the MPC: direct method

The aim of the environmental quality standards is that the MPC is set at a level that protects all species in an ecosystem. However, in order to be able to use extrapolation methods like the one of Aldenberg & Slob, a 95% protection level is chosen as a sort of cut-off value.

The 95% protection level can be defined for an individual substance if there are NOEC values for at least four different groups of species (e.g. fish, mollusc, crustacean and algae) available. The method of Aldenberg & Slob assumes that the NOECs used for estimating distribution, fit the log-logistic distribution.

If there are not enough data to apply the method of Aldenberg & Slob, the preliminary effect assessment method is used. In principle the assessment factors of the ECB (1998), laid down in the Technical Guidance Documents (TGD), are used. The application of the TGD assessment factors is presented in table 7.7.

Table 7.7:

Assessment factors for aquatic toxicity data following EU/TGD (ECB, 1996) according to EUSES (EC, 1996)

| | |
|---|---|
| Available valid data | Assessment factor to be applied to the lowest L(E)C50 or long-term NOEC |
| At least one short-term L(E)C50 from each of 3 trophic levels of the base-set (fish, Daphnia and algae) | 1000 ^a |
| One long-term NOEC (either fish or Daphnia) | 100 ^b |

| | |
|--|-------------------------------------|
| Two long-term NOECs from species representing two trophic levels (fish and/or Daphnia and/or algae) | 100 ^b 50 ^c |
| Long-term NOECs from at least 3 species (normally fish, Daphnia and algae) representing three trophic levels | 50 ^c 10 ^d |
| Field data or model ecosystems | Reviewed on a case by case basis |

- Base set= 3 L(E)C50 values from acute aquatic toxicity tests, carried out with 3 organisms each representing a different trophic level (algae, Daphnia and fish).
 - NOEC should be from long term test and L(E)C50 from short test.
- a. Except for substances with intermittent release under no circumstances should a factor lower than 100 be used in deriving a iMPCwater from short-term toxicity data.
 - b. An assessment factor of 100 applies to a single long-term NOEC (fish or Daphnia) if this NOEC was generated for the trophic level showing the lowest L(E)C50 in short-term tests.
An assessment factor of 100 applies also to the lowest of two long-term NOECs covering two trophic levels when such NOECs have not been generated from that showing the lowest L(E)C50 of short-term tests.
 - c. An assessment factor of 50 applies to the lowest of two NOECs covering two trophic levels when such NOECs have been generated covering that level showing the lowest L(E)C50 in the short-term tests. It also applies to the lowest of 3 NOECs covering three trophic levels when such NOECs have not been generated from that level showing the lowest L(E)C50 in the short-term tests.
 - d. An assessment factor of 10 will normally only be applied when long-term toxicity NOECs are available from at least three species across three trophic levels (e.g. fish, Daphnia, and algae or a non-standard organism instead of a standard organism). The PNECwater should be calculated from the lowest available NOEC. This is only sufficient, however, if the species tested can be considered to represent one of the more sensitive groups. This is particularly important if the substance does not have the potential to bioaccumulate. If it is not possible to make this judgement, then an assessment factor of 50 should be applied to take into account any interspecies variation in sensitivity.
 - e. For compounds with a high log Kow no short term toxicity may be found. Also, even in long term tests this may be the case or steady state may still not have been reached. For tests with fish for non-polar narcosis the latter can be substantiated by the use of long-term QSARs. It can be considered to use a higher assessment factor in such cases where steady state seems not to have been reached.
 - f. For substances for which no toxicity is observed in short term tests a long term test has to be carried out if the log Kow > 3 (or BCF > 100) and if PEClocal/regional is > 1/100th of the water solubility. The NOEC from this test can then be used with an assessment factor of 100. If in addition another NOEC from an algae test of the base set is determined, an assessment factor of 50 is applied.

There are two exceptions to the use of the TGD method:

1. Only when long term NOECs on three trophic levels are available, a comparison with data from the (complete) base set is no longer demanded.
2. It is inferred that for more hydrophobic compounds, short term toxicity data may not be representative, since the time span of an acute test may be too short to reach a toxic internal level. In those cases, base set completeness is not demanded and an assessment factor of 100 may be applied to a chronic test, which should not be an algae test if this is the only chronic test available.

If the base set is incomplete, the TGD method cannot be applied, arbitrary safety factors are used (the modified EPA-method (OECD, 1992)): a factor 10 and/or 1000 will be applied to the NOEC and/or L(E)C50, respectively, to derive the

MPC. It should be stressed here that this exception may only be used if the TGD can not be applied.

In table 7.8 the safety factors of the modified EPA method, dependent on the number of available toxicity data, are presented.

The calculated MTR in this report will be defined as "indicative MPC" (iMPC). In contradiction to the limit and target values the derived iMPCs have only a technical status and no political value. They are not legally set and may change as soon as more toxicity data become available and/or an MTR is derived by the INS-project.

Table 7.8:
Safety factors for the derivation of iMPCs in surface water (modified EPA method)

| Available toxicity data | Safety factor |
|---|---------------|
| Lowest acute L(E)C ₅₀ or QSAR estimation for acute toxicity | 1000 |
| Lowest acute L(E)C ₅₀ or QSAR estimation for acute toxicity for at least algae, crustaceans and fish | 100 |
| Lowest NOEC or QSAR estimation for chronic toxicity | 10* |
| Lowest NOEC or QSAR estimation for chronic toxicity for at least algae, crustaceans and fish | 10 |

* this value will be compared with the value based on acute L(E)C₅₀ values. The lowest value will be selected

Based on the retrieved toxicity data the iMPCs are derived using the procedure described by Kalf (1999). For the derivation of the iMPCs the fresh and salt water toxicity data are combined just as the data concerning pelagic and benthic organisms (based on the assumption that benthic organisms are exposed through the same medium as the pelagic organisms). Biomagnification is not included in this calculation. The toxicity data used for the derivation of the iMPC are reflected in Annex 2.2. The iMPC is 0.064 mg/l in water and 22.9 mg/kg in sediment.

The iMPCs for sediment are calculated using the equilibrium partition (EP) method (see Slooff, 1992; Beek, 1993; Kalf, 1999).

$$MPC_{sed} = MPC_{water} \times K_p$$

The equilibrium partition coefficient is calculated with the K_{oc} (see chapter 5) using the following formula:

$$K_p = K_{oc} \times f_{oc} \text{ (l.kg}^{-1}\text{)}$$

In the calculation the standard soil is assumed to contain 5% organic carbon.

As no limit value is derived for bisphenol A there is no comparison possible with the iMPC. However a comparison with the concentrations in the environment can be made. Bisphenol A is found in water, sewage water and in- and effluents in the Netherlands. In table 7.9 the measured concentrations from chapter 6.2 and 6.3 are summarized. Data are available on bisphenol A and are compared with the derived iMPC. The iMPC of bisphenol A in water is 0.064 mg/l and in sediment 22.9 mg/kg. Bisphenol A concentrations in the Netherlands range from 21 to 40 ng/l in fresh water and from 3.5 to 23 ng/l in marine water. The concentrations in

industrial and urban wastewater are in the range of 300 to 700 ng/l but for two locations, where the concentration reached the 2 mg/l. Bisphenol A concentration in sewerage and wastewater sludge ranged from <116 to 7000 ng/l (15-270 ng/g dry matter). In sediments concentrations were below the detection limit of 0.05 - 0.25 µg/kg dry matter. This means that in the Netherlands the concentrations in water, wastewater and sediment do not exceed iMPC except for the two locations where the concentration reached 2 mg/l. Furthermore in Japan concentrations of 60 to 1900 ng/l have been measured in surface water in 1974-1978. This means also that the iMPC is not exceeded. However, the concentrations in surface water in Japan and in sewerage and wastewater sludge in the Netherlands are close to the iMPC (1/3 x iMPC).

Table 7.9:
Concentration ranges in fresh and marine surface water, wastewater and wastewater sludge in ng/l on several locations based on data from chapter 6.2. and 6.3

| Location | Fresh / Marine | Surface water In ng/l | Wastewater In ng/l | Wastewater sludge In ng/l | Effluent In ng/l | Sediment Mg/kg dry matter |
|------------------|----------------|--------------------------|--|--|---------------------|------------------------------|
| Netherlands 1997 | Fresh | 21-40 ^a | 300-700 ng/l ^a max 2 mg/l ^a | <116-7000 ^a (~15-270 ng/g dry matter) ^a | 20-400 ^a | <0.05-0.25 (dl) |
| Netherlands 1997 | Marine | 3.5-23 ^b | - | - | - | - |
| Japan 1974-1978 | - | 60-1900 | - | - | - | - |
| USA | Fresh | <1000-8000 | - | - | - | - |

a. based on table 6.2

b. based on table 6.3 dl = detection limit

7.4 Human toxicity

General effects

Bisphenol A is listed as an endocrine disrupter (Colborn, 1993).

A recent study showed that exposing pregnant mice to bisphenol A, caused their male offspring to have enlarged prostate glands. In humans, enlarged prostate glands may predispose individuals to prostate cancer in later life. The effect in mice occurred at doses close to those to which humans are exposed through eating canned vegetables, which can be contaminated with bisphenol A from the lining of food cans (Nagel, et al., 1997 in Greenpeace, 1997).

In 1993 Krishnan (Krishnan, et al.) showed that bisphenol A binds to the estrogen receptor. In 1995 Brotons (Brotons, et al.) showed that bisphenol is also estrogenic in E-screen tests. Furthermore they showed that in water which has been in contact with polycarbonate sealing material, bisphenol is found in concentrations that cause estrogenic activity in E-screen tests (RIKZ 1996).

The affinity of bisphenol A for the estrogen receptor is 2000 times lower than that of oestradiol. The biological activity in an in vitro MCF-7 test was 5000 times less than that of oestradiol (Krishnan, et al., 1993; Lan et al., 1976).

Bisphenol A has been implicated as weakly estrogenic in vitro (Routledge, et al., 1996) and in MCF-7 rat cells (Krishnan, et al., 1993) and in vivo (vom Saal, et al., 1997) in mice (UK, 1998).

No epidemiological data, relevant to the carcinogenicity of bisphenol-diglycidyl-ether, were available. There is limited evidence in experimental animals for the

carcinogenicity of bisphenol A-diglycidyl-ether. Bisphenol-A-diglycidyl-ether is not classifiable as to its carcinogenicity to humans (IARC, 1999).

Table 7.10: Acute toxicity data on mammalian organism

| Dose/Effect | Mode/Specie | Concentration | Source |
|-------------|---------------|--------------------------|-----------------------|
| SEV | eye / rabbit | 20 mg/24h | Sax, 1989 |
| LD50 | Ipr / mouse | 150 mg/kg | Sax, 1989/ HSDB, 2000 |
| LC50 | Ihl / rat | 200 ppm | HSDB, 2000 |
| MLD | skin / rabbit | 250 mg | Sax, 1989/ HSDB, 2000 |
| SEV | Eye / rabbit | 250 µg/24 h | HSDB, 2000 |
| MLD | Skin / rabbit | 500 mg/ 24 h | HSDB, 2000 |
| TDL0 | Ipr / rat | 1275 mg/kg (1-15d preg) | GR, 1999/ HSDB, 2000 |
| TDL0 | Ipr / rat | 1875 mg/kg (1-15d preg) | GR, 1999/ HSDB, 2000 |
| LD50 | Oral / rabbit | 2230 mg/kg | Sax, 1989/ HSDB, 2000 |
| LD50 | Oral/ mouse | 2500 mg/kg | Sax, 1989/ HSDB, 2000 |
| LD50 | skin / rabbit | 3000 mg/kg | Sax, 1989/ HSDB, 2000 |
| LD50 | oral / rat | 3250mg/kg | Sax, 1989/ HSDB, 2000 |
| LD50 | Oral/ rat | 4040 mg/kg | Sax, 1989 |
| LD50 | oral / mammal | 6500 mg/kg | Sax, 1989/ HSDB, 2000 |
| TDL0 rep | oral / mouse | 7500 mg/kg (6-15d preg) | Sax, 1989/ HSDB, 2000 |
| TDL0 rep | Oral / rat | 10000 mg/kg (6-15d preg) | Sax, 1989/ HSDB, 2000 |
| TDL0 | Oral / mouse | 12500 mg/kg (6-15d preg) | GR, 1999/ HSDB, 2000 |
| TDL0 | Oral / rat | 15000 mg/kg (6-15d preg) | GR, 1999/ HSDB, 2000 |

SEV = severe effects, MLD = mild effects, Ihl = inhalation, Ipr = intraperitoneal
 From table 7.10 it follows that bisphenol A is slightly toxic by the intraperitoneal route, eyes and skin. However bisphenol A is very slightly toxic by ingestion. Bisphenol A is furthermore an experimental teratogen (Sax, 1989).

Bisphenol A is estrogenic in the in-vitro E-screen (Krishnan, et al., 1993 in WWF-OSPAR). It stimulates cell proliferation and induces expression of estrogen responsive genes (Ben and Steinmetz, 1998 in WWF-OSPAR). In-vivo, bisphenol A increase prolactin release and stimulates uterine, vaginal and mammary growth and differentiation. A dose of 2 ng/g body weight (2 ppb), permanently increased the size of prepubertal glands and reduced the epididymes, in male rats exposed in-utero on gestation days 11-17 (vom Saal, et al., 1998 in WWF-OSPAR).

The acute toxicity of bisphenol A is relatively low. At 1-3 hr after ingestion, animals exhibited a certain atony which can go as far as deep sleep. Profuse diarrhea occurs with most rats. Bisphenol A has also diuretic action. It is about 5 times that of urea. It also has marked estrogenic action (LeFaux, 1968 in HSDB, 2000).

In subacute toxicity studies no abnormal symptoms have been revealed but marked reduction in rate of increase in body weight in treated animals, whether male or female was observed. 1% Bisphenol A in food for 8 weeks caused a marked drop in growth (LeFaux, 1968 in HSDB, 2000).

Bisphenol A was evaluated for developmental toxicity in CD rats and CD-1 mice dosed daily by gastric intubation on gestational days 6 through 15. In rats, maternal weight gain during gestation, weight gain corrected for gravid uterine weight, and weight gain during treatment were significantly reduced at all bisphenol A doses. Gravid uterine weight and average fetal body weight per litter were not affected by bisphenol A. No increase in percentage resorptions per litter or percentage fetuses malformed per litter was detected.

In mice, maternal mortality occurred at all bisphenol A doses, reaching 18% at the high dose, which also produced a significant decrease in maternal body weight gain during gestation and treatment. Weight gain corrected for gravid uterine

weight was not affected by bisphenol A. Reductions in gravid uterine weight and average fetal body weight were observed with the 1250 mg/kg dose of bisphenol A. Relative maternal liver weight was increased at all doses of bisphenol A. There was a significant increase in the percentage of resorptions per litter with 1250 mg bisphenol A/kg/day.

Bisphenol A treatment at maternally toxic dose levels during organogenesis produced fetal toxicity in mice but not in rats and did not alter fetal morphologic development in either species (Morrissey, et al., 1987 in HSDB, 2000).

A carcinogenesis bioassay of bisphenol A was conducted by feeding diets for 103 weeks containing 1,000 or 2,000 ppm bisphenol A to groups of 50 F344 rats of either sex, 1,000 or 5,000 ppm to groups of 50 male B6C3F1 mice, 5,000 or 10,000 ppm to groups of 50 female B6C3F1 mice. Groups of 50 rats and 50 mice of either sex served as controls. Under the conditions of this bioassay, there was no evidence that bisphenol A was carcinogenic for F344 rats or B6C3F1 mice of either sex (DHHS/NTP, 1982).

Exposure routes in the aquatic environment.

Contamination of the aquatic environment (surface water and sediment) can pose a threat to public health. The hazards can be caused by direct and/or indirect contact with the contaminants.

In principle, uptake of contaminants by humans can take place by ingestion (oral), dermal contact (via the skin) and inhalation (via the lungs).

The most probable routes of human exposure to bisphenol A are inhalation and dermal contact of workers involved in the manufacture, use, transport or packaging of this compound or use of epoxy powder paint (Peltonen, 1986). Furthermore the exposure through the leaching of bisphenol A from flasks and cans into food, may be important route of exposure.

Human health risk assessment evaluation with exposure to sediment

BKH (1991) has conducted a study into the human health risks of recreants potentially exposed to contaminants in sediment. Because children are seen as the most vulnerable group, recreating children are used as a starting point for the derivation of a human-toxicologic based advisory value (HTBA-value) for contaminations in sediment.

Above this value adverse health effects may be expected. In Annex 2.3 the human health assessment evaluation-method is described. The calculated HTBA-value for bisphenol A is 247 mg/kg. The HTBA-value is based on the ADI-value (Acceptable Daily Intake) from the literature and the K_{ow} -value. There is no official ADI or TDI value in the Netherlands. In EPA (1997) a maximum acceptable dose of 0.05 mg/kg bw/day is given. This value is used as an indicative ADI-value to calculate the HTBA-value.

The derived HTBA-values only have an indicative value, because the risk assessment method contains uncertainties. These uncertainties concern in the exposure model, which is based on a number of assumptions, as well as the ADI-values, that contain intrinsic uncertainties. Because dissociation is not adjusted for, it is possible that the HTBA values might be underestimated. When the HTBA-values are exceeded, the actual risk must be assessed. This means that the actual exposure on the particular location must be defined so that the human health risks can be estimated.

Table 7.11:

Humane toxicologic based advisory value (HTBA-value) for bisphenol A

| Substance | Log K _{ow} | ADI (µg/kg/day) | HTBA-waarde (mg/kg dw) |
|-------------|---------------------|-----------------|------------------------|
| Bisphenol A | 2.2 - 3.84 | 50 | 247 |

Comparing with exposure concentrations in sediment and water

The measured concentrations in sediment are given in chapter 6 and are summarized in table 7.9. There are concentrations measured in Dutch surface water. These vary between 3.5 and 40 ng/l. For bisphenol A, the concentrations in sediment are below the detection limit of 0.05 – 0.25 µg/kg dry matter. This means the indicative HTBA-value is not exceeded.

It should be noted that the derivation of the HTBA-value uses a worst case approach.

The derivation of HTBA-values should be done with official ADI values and measured log K_{ow} values as soon as these values are available.

7.5 Conclusions and recommendations

7.5.1 Mode of action

The direct estrogenic substances may act in at least 3 different ways: binding to the estrogen receptor; stimulating the endogenous production of 17β-oestradiol; and diminishing of 17β-oestradiol degradation. Furthermore there are anti-estrogenic substances that prevent the binding of endogenous oestradiol and thereby cause endocrine disruption.

Bisphenol is as well anti-estrogenic (inhibition transcription) as estrogenic (prolactine production, in vitro Yeast assay).

Metabolism in aquatic organisms is unknown. In mammals (rats) bisphenol A metabolism occurs through a partial conversion into phenols, increasing their urinary content in a free and bound form. Bisphenol A is passed unaltered and in the form of glucuronids from the body, in the urine and faeces.

7.5.2 Toxicity in freshwater and marine environment

Bisphenol A is acutely moderately toxic to freshwater and marine algae, fish and crustaceans. Based on chronic tests bisphenol A is very slightly to slightly toxic in freshwater and moderately toxic in marine water. Based on 1 chronic study with endocrine effects (skewed sex-ratio) with an amphibian, bisphenol A is very toxic.

7.5.3 Limit values and indicative MTRs

There are no limit values derived for bisphenol A.

All measured concentrations are considerable lower than the calculated HTBA value of 247 mg/kg and lower than the calculated iMPCs of 0.064 mg/l and 22.9 mg/kg for resp. surface water and sediment.

7.5.4 Humane toxicity

The most probable routes of human exposure to bisphenol A are inhalation and dermal contact of workers involved in the manufacture, use, transport or packaging of this compound or use of epoxy powder paint. Furthermore the exposure through the leaching of bisphenol A from flasks and cans into food, may be important route of exposure.

Bisphenol A is slightly toxic to mammals by the intraperitoneal route, eyes and skin. However bisphenol A is very slightly toxic to mammals by ingestion. Bisphenol A is furthermore an experimental teratogen but not proven to be a carcinogen. Bisphenol A is furthermore estrogenic in the in-vitro E-screen, stimulates cell proliferation and induces expression of estrogen responsive genes. In-vivo, bisphenol A increase prolactin release and stimulates uterine, vaginal and mammary growth and differentiation.

7.5.5 Recommendations

For evaluation of the aquatic toxicity of bisphenol A, a limited amount of data was available. Considering the large emission estimates to surface water, their high tendency to spread in aquatic systems and the fact that bisphenol A is moderately toxic to aquatic organisms, it is recommended to generate new toxicity data. Especially in the area of endocrine disrupting effects more research should be done because the effect concentrations may be a factor 100-1000 lower. Further research into concentrations in food are also considered important in relation to the leaching of bisphenol A from baby bottles, flasks and cans.

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8 Policy overview

8.1 National environmental policy

8.1.1 Netherlands

In the National Environmental Policy Plan (NMP, 1989) and the more recently published National Environmental Policy Plan-3 (NMP-3, 1997) the general environmental policy is described.

In the year 2010 the environmental targets and target values must be reached. Concerning the reverse of the risks caused by high concentrations of chemicals, specific policy targets have been set in the National Environmental Policy Plan of 1989. These targets imply the aim to not exceed the Maximum Permissible Concentrations (MPCs) and the Negligible Concentrations (NCs) in 2010, by means of prevention and reconstruction. These values are guidelines but not legally binding. When the environmental quality standards are set, other aspects, such as political and technical feasibility, are also taken into account. Target values are either set at the NC or at the background value. The derivation of MPCs and NCs is explained in chapter 7.3.

In the report on integral standardisation on substances (INS, 1997) environmental quality standards have been derived. For bisphenol A no specific quality standards, MPCs or NCs have been set.

The current water policy is reflected in the Fourth Note on Watermanagement (1997). In this note the targets and headlines of the policy for the national water management are given.

8.1.2 Other country specific policy

Norway

Bisphenol A is not regulated in Norway. Because the chemical may cause both environmental and health effects, waste containing larger amounts of bisphenol A has to be considered special waste and treated as prescribed in the special waste treatment regulations (TemaNord, 1996).

The National Foodstuff Inspection has regulations setting maximum limits for food additives. A limit for bisphenol A in foodstuffs has been set in 1995 (TemaNord, 1996).

Furthermore, bisphenol A is included in the "control package" concerning chemicals with estrogen-like effects being prepared-by SFT (TemaNord, 1996).

Some manufacturers in Norway have already phased out bisphenol A in their production due to occupational health considerations (irritation effects of bisphenol A) (TemaNord, 1996)

Denmark

In Denmark, bisphenol A is mainly regulated by the Ministry of Health. As a consequence of the documented estrogenic effects of bisphenol A, the Danish Foodstuff Agency has asked the EU Commission to re-evaluate bisphenol A and other substances with estrogen-like effects used in materials which may come into contact with food (Miljostyrelsen 1995 in TemaNord, 1996).

Furthermore, the Danish Health Agency has started investigating the health implications of bisphenol A in lacquers used in dentistry (Miljostyrelsen 1995 in TemaNord, 1996).

Sweden

Bisphenol A is not regulated in Sweden. A minor part of the total Swedish bisphenol A consumption goes to PVC. Proposals on how to minimise the risks with PVC additives, including bisphenol A, will be presented by the Swedish Chemicals Inspectorate in June 1996 (TemaNord, 1996).

Finland

The use and import of bisphenol A, like phthalates and nonylphenol ethoxylates, is not presently regulated in Finland (TemaNord, 1996).

8.2 European Commission

Bisphenol A is referred to in Commission directive 90/128/EEC relating to plastics materials and article intended to come into contact with foodstuffs and in Council directive 67/548/EEC concerning the classification, packaging and labelling of dangerous substances.

In recognition of the ability of bisphenol A to migrate from food contact materials into food, Specific Migration Limits (SMLs) have been set for the protection of the consumer. The EU legislation relating to the SML for bisphenol A into food is 3 mg bisphenol A per kg food (3 ppm). This migration limit is slightly lower in Japan with a maximum of 2.5 ppm. There is no SML in the US as instead calculations are conducted on a daily intake basis (UK, 2000).

Bisphenol is also on the priority lists of the EC Council regulation 793/93/EEC. At the moment an risk assessment on bisphenol A is prepared by the UK.

8.3 International policy

It is listed by EPA, the Centers for Disease Control & Prevention and the World Wildlife Fund as endocrine modifying chemical.

8.3.1 OSPAR

Bisphenol A is on the list (a) of attention chemicals of OSPAR as a candidate substance (OSPAR, 1997).

8.4 Policy on emissions

8.4.1 Emission limits

There is no national legislation in the European Commission that inspect bisphenol A in the atmospheric emissions, fluid discharges and waste (European Commission, 1996).

In the Netherlands The Dutch Health Council has advised on an advisory value of 5 mg/m³ in air (8h TWA) (Van Raaij, 2000).

8.5 References

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Annex 1: Abbreviation list

| | |
|----------|---|
| ADI | Acceptable daily intake |
| AOPWIN | Aerobic oxidation programme |
| APME | Association of Plastics Manufacturers in Europe |
| ASE | Accelerated solvent extractor |
| ASTP | Activated sludge treatment plant |
| BADGE | Bisphenol A diglycidyl ether |
| BCF | Bioconcentration factor |
| BOD | Biological Oxygen Demand |
| BPA | Bisphenol A |
| BUA | Umwelt Bundes Amt |
| CAS | Chemical Abstract Services |
| CD | Compact discs |
| COD | Chemical Oxygen Demand |
| DGD | Decision guidance document |
| DGXI | Directorate general 11 |
| DIFFCHEM | Working group of OSPAR on Diffuse sources of chemicals |
| DMDCS | Dimethyl dichloro silane |
| DOC | Dissolved Oxygen Content |
| E&E | Electrical and electronic |
| E2 | 17beta-oestradiol |
| EC | European Commission |
| EC10 | Effect concentration with 10% effect |
| EC100 | Effect concentration with 100% effect |
| EC50 | Effect concentration with 50% effect |
| ECD | Electron capture detector |
| ECNI | Electron capture negative ionisation |
| EHC | Environmental Health Criteria |
| ELS | Early life stage |
| EP | Equilibrium partition coefficient |
| EPA | Environmental Protection Agency |
| EpR | Epoxy resin |
| ER | Estrogen receptor |
| EU | European Union |
| FAO | Food and agriculture organisation of the UN |
| Foc | Fraction organic matter in soil |
| GC | Gas chromatography |
| GC/MS | Gas chromatography/ Mass Spectrometry |
| GLP | Good laboratory practice |
| HPLC | High performance liquid chromatography |
| HRGC | High resolution GC |
| HRMS | High resolution MS |
| HTBA | Human toxicologic based advisory value |
| IC50 | Inhibition concentration |
| iMPC | Indicative Maximum Permissible Concentration |
| IMTR | Indicative MTR |
| IP | Intraperitoneal |
| IPCS | International Program for Chemical Safety (a WHO program) |
| ISO | International Standards Organisation |
| IUCLID | International uniform chemical information database |
| KEMI | Swedish national chemicals inspectorate |
| Koc | Organic carbon content |
| Kom | organic matter content |
| Kow | Octanol water partitioning coefficient |
| Kp | Equilibrium partition coefficient |
| LC100 | Effect concentration with 100% mortality |
| LC50 | Effect concentration with 50% mortality |
| LD50 | Effect dosis with 50% effect |
| LOEC | Lowest observed effect concentration |

| | |
|-------------------|--|
| MLD | Mild effects |
| MLSS | Mixed liquor suspended solids |
| MPC | Maximum Permissible Concentrations |
| MS | Mass spectrography |
| MTR | Maximal tolerable risk |
| NAA | Neutron activation analysis |
| NC | Negligible concentration |
| NMP | National Environmental Policy Plan |
| NOEC | No observed effect concentration |
| NR | Negligible risk |
| OECD | Organisation for Economic Cooperation and Development |
| OSPAR | Convention for the Protection of the Marine Environment of the North-East Atlantic |
| PC | Polycarbonates |
| PEC | Predicted effluent concentration |
| PIC | Prior informed consent |
| PNEC | Predicted no effect concentration |
| POP | Persistent organic pollutants |
| Preg | Pregnant |
| PVC | Polyvinyl chloride |
| QSAR | Quantitative structure analysis r |
| REP | Reproduction |
| RIVM | National institute for human health and environment |
| SCAS | Semi-continuous activated sludge |
| SD | Standard deviation |
| SEV | Severe effects |
| SIM | Selection ion monitoring |
| SMLs | Specific Migration Limits |
| TDI | Tolerable daily intake |
| TDL0 | Lowest toxic dos |
| TGD | Technical Guidance Document |
| ThCO ₂ | Theoretical CO ₂ production |
| ThOD | Theoretical oxygen demand |
| TOC | Total Organic Carbon |
| UN | United Nations |
| UN-ECE | United Nations Environmental Commission for Europe |
| UNEP | United Nations Environment Programme |
| UPE | Unsaturated polyesters |
| VIC | Voluntary Industry Commitment |
| VROM | Ministry of spatial planning and environment |
| WHO | World Health Organisation |
| WTP | Wastewater treatment plant |
| WWTP | Wastewater treatment plant |

Annex 2: Background information on aquatic toxicity

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Annex 2.1: Used classification systems for aquatic toxicity

Toxicity to algae (96-h, EC₅₀), crustaceans (48-h, LC₅₀) and fish (96-h, LC₅₀):

Class E(L)C₅₀ (mg/l)

| | | | |
|---------------------|----|-------|-----|
| very toxic | | < 1 | |
| Moderately toxic | 1 | - | 10 |
| slightly toxic | 10 | - | 100 |
| very slightly toxic | | > 100 | |

Toxicity to aquatic organisms: chronic tests:

Class NOEC (mg/l)

| | | | |
|---------------------|------|--------|-----|
| very toxic | | < 0.01 | |
| Moderately toxic | 0.01 | - | 0.1 |
| slightly toxic | 0.1 | - | 1 |
| very slightly toxic | | > 1 | |

Toxicity to birds: acute oral LD₅₀ (mg/kg body weight)

Class LD₅₀ (mg/kg)

| | | | |
|---------------------|----|-------|-----|
| very toxic | | < 5 | |
| Moderately toxic | 5 | - | 50 |
| slightly toxic | 50 | - | 500 |
| very slightly toxic | | > 500 | |

Annex 2.2: Overview of the toxicity data per group of organisms (freshwater and marine) used for the derivation of iMTRs in surface water

Table 1:
Acute toxicity data (mg/l)^a

| Substance | Taxonomic group | L(E)C50 (mg/l) | EPA Safety factor |
|-------------|-----------------|--------------------|-------------------|
| Bisphenol A | Bacteria | 54.5 | - |
| | Algae | 1 | - |
| | Crustaceans | 1.1 | - |
| | Fish | 4.6 | - |
| | Amphibian | 6,900 ^b | - |

- a. QSAR calculations using the equations given for non-polar narcosis in Appendix II of Chapter 4 in the Technical Guidance Document have not been used because of the high log Kow which makes the QSAR unreliable.
- b. Based on an endocrine effect: inhibition of ER binding affinity. Therefore this value may not be used to calculate the iMPC.

Table 2:
Chronic toxicity data (mg/l)^a

| Substance | Taxonomic group | NOEC (mg/l) | EPA Safety factor |
|-------------|-----------------|---------------------|-------------------|
| Bisphenol A | Algae | 1.17 | - |
| | Crustaceans | = 3.146 | - |
| | Fish | 0.64 ^c | 10 |
| | Amphibian | 0.0023 ^b | - |

- a. QSAR calculations using the equations given for non-polar narcosis in Appendix II of Chapter 4 in the Technical Guidance Document have not been used because of the high log Kow which makes the QSAR unreliable.
- b. Based on an endocrine effect: skewed sex-ratio. Therefore this value may not be used to calculate the iMPC.
- c. Article could not be checked (not available).

Annex 2.3: Human health risk assessment evaluation method

Human health risk may occur by direct contact of recreating people with contaminants in the aquatic environment (water, sediment). Playing children (1.5 - 4.5 years old with a body weight of 14 kg) are seen as the most vulnerable groups based on age-bound factors. The relevant exposure routes are through oral intake and dermal contact. The intake (in mg/day) can be calculated for the separate exposure routes for 1 day of playing at the waterside in a worst-case scenario (for a detailed description see BKH, 1991):

Oral intake through sediment

The oral intake through sediment is:

$$I_{o, sed} = S_1 * 10^{-6} * \text{level B}$$

in which:

| | |
|--------------|---|
| $I_{o, sed}$ | daily oral intake of contaminants via sediment (mg/kg bw) |
| S_1 | sediment intake in mg dw/day (1020 mg dw/day) |
| 10^{-6} | conversion factor for units in the given dimensions |
| B | level of contamination in soil material in mg/kg dw |

Oral intake through suspended matter

The oral intake through suspended matter is:

$$I_{o, susp} = I * S_2 * 2 * 10^{-9} * \text{level B}$$

| | |
|---------------|---|
| $I_{o, susp}$ | daily oral intake of contaminants via suspended matter (mg/kg bw) |
| I | intake surface water (50 ml/day) |
| S_2 | concentration in suspended matter (300 mg dw/l) |
| 2 | correction factor for higher concentrations in suspended matter |
| 10^{-9} | conversion factor for units in the given dimensions |
| B | level of contamination in soil material in mg/kg dw |

Oral intake through surface water

The oral intake through surface water is:

$$I_{o, wat} = W_i * 10^{-3} * (10^{0.21} / f_{oc} * K_{ow}) * \text{level B}$$

| | |
|--------------|--|
| $I_{o, wat}$ | daily oral intake of contaminants via water (mg/kg bw) |
| W_i | intake of surface water (50 ml/day) |
| 10^{-3} | conversion factor for units in the given dimensions |
| f_{oc} | organic carbon fraction in sediment (0.05) |
| K_{ow} | partition coefficient octanol/water |
| B | level of contamination in soil material in mg/kg dw |

Dermal contact with sediment

The dermal contact with sediment is:

$$I_{d, \text{sed}} = O_{\text{skin}} * B_{b, \text{skin}} * A * M * 10^{-6} * \text{level B}$$

| | |
|----------------------|--|
| $I_{d, \text{sed}}$ | daily dermal intake of contaminants via sediment (mg/kg bw) |
| O_{skin} | surface of skin exposed (2800 cm ²) |
| $B_{b, \text{skin}}$ | area of skin covered with sediment parts (0.5 mg dw/cm ²) |
| A | absorption coefficient (0.12/day) |
| M | matrix effect: the effect of the binding of contaminants to soil particles on body intake (0.15) |
| 10^{-9} | conversion factors for units in the given dimensions |
| B | level of contamination in soil material in mg/kg dw |

Dermal contact with suspended matter

Dermal contact with suspended matter is negligible compared to dermal contact with sediment.

Dermal contact with water

Dermal contact with water is:

$$I_{d, \text{wat}} = O_{\text{skin}} * t * A'' * B_{w, \text{skin}} * 10^{-9} * C_w$$

| | |
|----------------------|---|
| $I_{d, \text{wat}}$ | daily dermal intake of contaminants via water (mg/kg bw) |
| O_{skin} | exposed skin surface (4560 cm ²) |
| t | exposure time (3 hours/day) |
| A'' | absorption coefficient (0.01/hour) |
| $B_{w, \text{skin}}$ | area of skin covered with water (0.5 µg/cm ²) |
| 10^{-9} | conversion factors for units in the given dimensions |
| C_w | concentration in water; this is: |

$$C_w = 2 * (10^{0.21}) / (f_{oc} * K_{ow}) * 10^3 * \text{level B}$$

with:

| | |
|----------|---|
| f_{oc} | organic carbon fraction in sediment (0.05) |
| K_{ow} | partition coefficient octanol/water |
| 10^3 | conversion factor for units in the given dimensions |
| B | level of contamination in soil material in mg/kg dw |

For the calculation of the yearly-averaged daily intake, the daily intake should be multiplied with a factor 30/365; the number of playing days at the water side is estimated at 30 per year.

For the calculation of concentrations of individual contaminants in sediment, the yearly-averaged daily total intake through the above-mentioned exposures routes are compared to a human health guidance value, at which there is a maximal tolerable risk (MTR, ADI). This means the ADI should be multiplied by 14 kg body weight and 0.05 (MTR) to derive the maximum intake per day for a child of 14 kg. In this way HTBA-values may be derived.

In the report of BKH (1991) the level at which there is a maximal tolerable risk (MTR) is linked to the intervention-value-level, an environmental quality level that is established in view of direct measures and at which there is a "serious risk for

human health". For the derivation of the HTBA-values for sediment, above which there is a "serious risk", the total contribution of exposure to sediment is set at a maximum of 5% of the MTR. Using this percentage, it is expected that other sources as well as the contribution of other substances, which comparable effects, are sufficiently encountered for.