

**4-(dimethylbutylamino)diphenylamine
(6PPD)**



**OSPAR Commission
2005 (2006 Update)**

The Convention for the Protection of the Marine Environment of the North-East Atlantic (the "OSPAR Convention") was opened for signature at the Ministerial Meeting of the former Oslo and Paris Commissions in Paris on 22 September 1992. The Convention entered into force on 25 March 1998. It has been ratified by Belgium, Denmark, Finland, France, Germany, Iceland, Ireland, Luxembourg, Netherlands, Norway, Portugal, Sweden, Switzerland and the United Kingdom and approved by the European Community and Spain.

La Convention pour la protection du milieu marin de l'Atlantique du Nord-Est, dite Convention OSPAR, a été ouverte à la signature à la réunion ministérielle des anciennes Commissions d'Oslo et de Paris, à Paris le 22 septembre 1992. La Convention est entrée en vigueur le 25 mars 1998. La Convention a été ratifiée par l'Allemagne, la Belgique, le Danemark, la Finlande, la France, l'Irlande, l'Islande, le Luxembourg, la Norvège, les Pays-Bas, le Portugal, le Royaume-Uni de Grande Bretagne et d'Irlande du Nord, la Suède et la Suisse et approuvée par la Communauté européenne et l'Espagne.

© OSPAR Commission, 2005 (updated in 2006). Permission may be granted by the publishers for the report to be wholly or partly reproduced in publications provided that the source of the extract is clearly indicated.

© *Commission OSPAR, 2005 (mise à jour 2006). La reproduction de tout ou partie de ce rapport dans une publication peut être autorisée par l'Editeur, sous réserve que l'origine de l'extrait soit clairement mentionnée.*

ISBN 1-905859-05-8
ISBN 978-1-905859-05-4

Publication Number: 271/2006

contents

Abbreviations	4
Executive Summary/ <i>Récapitulatif</i>	5
Introduction	7
1 Identification of sources of 6PPD and its pathways to the marine environment	7
1.1 Production of 6PPD	7
1.2 Main uses of 6PPD	8
2 Monitoring data, quantification of sources and assessment of the extent of problems	8
2.1 Monitoring data	8
2.1.1 <i>European Rivers (surface water)</i>	8
2.1.2 <i>Ground water</i>	8
2.1.3 <i>Marine waters</i>	8
2.2 Quantification of sources	8
2.2.1 <i>Emissions from manufacturing</i>	8
2.2.2 <i>Emissions from rubber products</i>	9
2.3 Assessment of the extent of the problem	10
2.3.1 <i>Physico-chemical properties</i>	10
2.3.2 <i>Abiotic and biotic degradation</i>	10
2.3.3 <i>Bioaccumulation</i>	14
2.3.4 <i>Acute and chronic ecotoxicity effects</i>	14
2.3.5 <i>Carcinogenicity, mutagenicity or harmful reproductive effects (CMR properties)</i>	16
2.4 Risk to the environment	17
3 Desired reduction	19
4 Review of agreed measures and possible substitutes	19
4.1 Review of agreed national and international measures for the regulation of 6PPD	19
4.2 Choice of substitutes	19
5 Choice for action/measures	20
6 References	20
Annex 1: Physico-chemical properties of 6PPD	22
Annex 2: SIDS Initial Assessment Profile	24
Annex 3: Monitoring strategy for 6PPD	27

ABBREVIATIONS

4-ADPA	4-aminodiphenylamine
6PPD	N-(1,3-dimethylbutyl)-N'-phenyl-1,4-phenylenediamine
BOD	Biological oxygen demand
BUA	Beratergremium für umweltrelevante Altstoffe (Germany)
CMR	Carcinogenic, mutagenic and reproductive toxicity (properties)
COMMPS	Combined monitoring-based and modelling-based priority setting
DPA	Diphenylamine
DPPD	N,N'-diphenyl paraphenylenediamine
EC ₅₀	Effect concentration for 50% of the test organisms
EUSES	European Uniform System for Evaluation of Substances
ICCA	International Council of Chemical Associations
IPPD	N-isopropyl-N'-phenyl-p-phenylenediamine
IUCLID	International Uniform Chemical Information Database
MIBK	Isobutyl ketone
NOAEL	No observed adverse effect level
NOEC	No observed effect concentration
PBN	4-phenylbutylamine
PEC	Predicted environmental concentration(s) for the compartment surface water, sediment, soil, and air
SIAM	SIDS Initial Assessment Meeting
SIAP	SIDS Initial Assessment Profile
SIAR	SIDS Initial Assessment Report
SIDS	Screening of Information Data Sets

EXECUTIVE SUMMARY/RÉCAPITULATIF

6PPD (N-(1,3-dimethylbutyl)-N'-phenyl-1,4-phenylenediamine) (CAS No. 793-24-8) is an aromatic amine which is used in high production volumes as a protective agent (anti-ozonant and anti-oxidant) mainly in the rubber industry. The main area of use is the tyre sector but the chemical is also found in other consumer products, e.g. seals of pressure cookers. 6PPD was added to the OSPAR List of Chemicals for Priority Action in 2002.

Le 6PPD (N-(1,3-diméthylbutyl)-N'-phényl-1,4-phénylènediamine) (N° CAS 793-24-8) est une amine aromatique qui sert d'agent de protection (anti-ozonant et anti-oxydant) dans la production de masse, surtout dans l'industrie du caoutchouc. Le principal domaine d'utilisation est le secteur des pneumatiques, la présence de ce produit chimique étant aussi constatée dans d'autres produits de grande consommation, p.ex. dans les joints des autocuiseurs. Le 6PPD a été inscrit en 2002 sur la Liste OSPAR des produits chimiques devant faire l'objet de mesures prioritaires.

6PPD is manufactured at one facility in Germany with a volume ranging between 10 000 to 25 000 tonnes/year. No other production sites are known in the OSPAR Convention area. The global production in 2001 was estimated as being around 130 000 tonnes/year.

Le 6PPD est fabriqué dans une installation implantée en Allemagne, à raison de 10 000 à 25 000 tonnes par an. Aucun autre site de production n'est connu dans la zone de la Convention OSPAR. En 2001, la production mondiale a été estimée à 130 000 tonnes par an environ.

6PPD can be released to the environment from production and use in the rubber industry, but mainly during use and disposal of rubber products. Emissions from manufacturing into the wastewater may occur during vulcanisation processes, cleaning processes, recycling of used rubber and production of technical rubber articles. From the surface of rubber products, 6PPD might enter the hydrosphere via the rain water and it might evaporate into the atmosphere, although 6PPD has a low volatility. The main entry pathway of 6PPD to the environment is, however, through tyre abrasion. Up to the early 90s, tyres were also deposited in dumps. Since then, recycling and incineration are increasingly applied, thus reducing the possible emissions of 6PPD from deposits. There are no recent data on the amount of rubber deposited in the OSPAR Convention area which would allow to quantify the amounts of 6PPD entering the environment by this pathway.

Le 6PPD peut être libéré dans l'environnement du fait de la fabrication et de son utilisation dans l'industrie du caoutchouc, quoique pour l'essentiel pendant l'utilisation et l'élimination des produits en caoutchouc. Des émissions dans les eaux usées peuvent se produire du fait de la fabrication, ceci pendant les processus de vulcanisation, de nettoyage, de recyclage du caoutchouc usé et pendant la fabrication d'articles techniques en caoutchouc. Depuis la surface des produits en caoutchouc, du 6PPD peut pénétrer dans l'hydrosphère par le biais de l'eau de pluie, et peut s'évaporer dans l'atmosphère, en dépit du fait qu'il ne soit que faiblement volatil. Toutefois, la principale voie de pénétration du 6PPD dans l'environnement est celle de l'abrasion des pneumatiques. Jusqu'au début des années 90, les pneumatiques étaient aussi mis en décharge. Depuis lors, on pratique de plus en plus le recyclage et l'incinération, ce qui réduit les émissions éventuelles de 6PPD provenant des dépôts. L'on ne dispose d'aucune statistique récente sur la quantité de caoutchouc mis en dépôt dans la zone de la Convention OSPAR, statistiques qui permettraient de quantifier le 6PPD qui pénètre dans l'environnement par cette voie.

6PPD is not a PBT substance according to the EU-TGD PBT criteria. It is expected to be rapidly photodegraded in air. In water, 6PPD is not "readily biodegradable", but it is unstable and degrades rapidly by biotic and abiotic processes. No information is available on the stability of 6PPD and its metabolites in sediment but there is indication of a strong tendency of 6PPD to absorb to organic matter. This gives reason to consider 6PPD fulfilling the criterion on persistence. Due to the low stability of 6PPD in aqueous media, a potential for bioaccumulation and geo-accumulation is expected to be low. Acute toxicity is caused by both 6PPD and, at a lower level, by degradation products. Exposure of 6PPD to the environment and transport to the sea is anticipated to be low, and therefore risks to marine organisms are expected to be negligible. Nevertheless, 6PPD is a high production volume chemical. This justifies a continuous attention towards this substance and its metabolites. 6PPD is included in the list of existing substances produced within or imported to the European Community in quantities exceeding 1000 tonnes/year (Council Regulation (EEC) No. 793/93) and is subject to ongoing evaluation by the OECD Existing Chemicals Programme.

Selon les critères PBT du Document d'orientation technique (DOT) de l'Union européenne, le 6PPD n'est pas une substance PBT. Il devrait en effet se photodégrader rapidement dans l'air. Dans l'eau, le 6PPD n'est pas « directement biodégradable » ; toutefois, il est instable et se dégrade rapidement par des processus biotiques et abiotiques. Si l'on ne dispose d'aucun renseignement sur la stabilité du 6PPD et de ses métabolites dans les sédiments, il n'y a aucune indication d'une forte tendance à l'absorption du 6PPD par la matière organique. Ceci donne des raisons de penser que le 6PPD répond au critère de la persistance. Du

fait de la faible stabilité du 6PPD dans les médias aqueux, le potentiel de bioaccumulation et de géo-accumulation devrait être faible. Le 6PPD et, à un moindre degré, les produits de sa dégradation, provoquent une toxicité aiguë. L'exposition du 6PPD à l'environnement et son transport jusqu'à la mer devraient être faibles, et par conséquent, les risques pour les organismes marins devraient être négligeables. Cependant, le 6PPD est un produit chimique fabriqué en gros volumes. Cet état de choses justifie que l'on porte continuellement attention à cette substance et à ses métabolites. Le 6PPD figure sur la liste des substances existantes fabriquées ou importées dans la Communauté européenne à des quantités supérieures à 1000 tonnes/an (Règlement du Conseil (CEE) N° 793/93) et fait l'objet d'une évaluation permanente dans le cadre du Programme OCDE visant les produits chimiques existants.

The actions recommended in this Background Document are: Contracting Parties to consider to improve the exposure assessment for 6PPD and its metabolites in order to clarify whether the wide-spread release of 6PPD, mainly from tyres, on the one hand, and the rapid degradation in the environment on the other hand, may lead to a significant load to the marine environment; in support of this, Contracting Parties to develop a monitoring strategy which includes 6PPD and its metabolites; when undertaking further work on the exposure assessment, Contracting Parties to co-ordinate their work with ongoing activities in the OECD framework; to invite Contracting Parties to check that the operation of plants manufacturing or formulating 6PPD is regulated according to the principles of best available technology and that any releases are eliminated or minimised to the greatest possible extent; OSPAR 2010 to re-examine what action is needed; to communicate this Background Document to the European Commission and to other appropriate international organisations which deal with hazardous substances.

Les actions recommandées dans le présent document de fond sont les suivantes : les Parties contractantes considéreront comment améliorer l'évaluation de l'exposition au 6PPD et à ses métabolites, de manière à clarifier la question de savoir si les émissions très répandues de 6PPD, surtout du fait des pneumatiques d'une part, et d'autre part sa dégradation rapide dans l'environnement, peuvent aboutir à une charge significative dans le milieu marin ; à l'appui de ce qui précède, les Parties contractantes élaboreront une stratégie de surveillance englobant le 6PPD et ses métabolites ; en entreprenant les nouveaux travaux d'évaluation de l'exposition, les Parties contractantes coordonneront leurs travaux avec les activités en cours dans le cadre de l'OCDE ; inviter les Parties contractantes à s'assurer que l'exploitation des installations de fabrication ou de formulation du 6PPD est réglementée selon les principes de la meilleure technologie disponible et que toutes les émissions sont éliminées ou minimisées dans toute la mesure du possible ; il conviendrait qu'OSPAR 2010 revoie les mesures qui s'imposeront ; communiquer le présent document de fond à la Commission européenne ainsi qu'aux autres organisations internationales compétentes traitant des substances dangereuses.

A monitoring strategy for 6PPD is annexed to this background document.

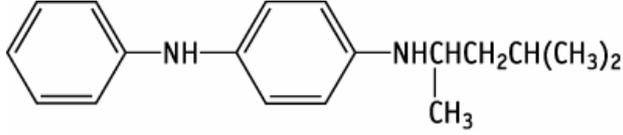
Une stratégie de surveillance relative au 6PPD est annexée à ce document de fond.

INTRODUCTION

4-(dimethylbutylamino)diphenylamine (6PPD) is an aromatic amine and is used in high production volumes as a protective agent (anti-ozonant and antioxidant) in the rubber industry. The main area of application is the tyre sector. As such, the main entry pathway of 6PPD to the environment is through tyre abrasion.

The chemical identity of 6PPD is presented in Table 1; further information on the physico-chemical properties is given in Annex 1.

Table 1: Chemical identity of 6PPD

6PPD CAS-No. 793-24-8 EINECS-No. 212-344-0	
<u>Synonyms:</u> N-(1,3-dimethylbutyl)-N'-phenyl-1,4-phenylenediamine (IUPAC) 4-(dimethylbutylamino)diphenylamine	
<u>Trade names (examples):</u> Santoflex 13, Vulkanox 4020	

6PPD is subject to the OECD Existing Chemicals Programme (Investigation of High Production Volume Chemicals, HPVC) by an initiative of the International Council of Chemical Associations (ICCA). In this context, a Screening of Information Data Sets (SIDS) on the basis of an IUCLID Dataset was undertaken, and a SIDS Initial Assessment Report (SIAR) was prepared for the 18th SIDS Initial Assessment Meeting (Paris, April 20 - 23, 2004). The final SIAR (2005) and the SIDS Initial Assessment Profile (SIAP; see Annex 2) are available at UNEP Chemicals (www.chem.unep.ch/irptc/sids/OECDsids/sidspub.html). A report of the Beratergremium für umweltrelevante Altstoffe (BUA Stoffbericht Nr. 208, 1997) has also contributed to the SIAR.

Information in this Background Document is essentially based on the SIAR (2005), the BUA report (1997) and the supporting IUCLID Datasets. Information from other sources is explicitly indicated. References to studies which are contained in the IUCLID Dataset are not itemised in this Background Document.

1 IDENTIFICATION OF SOURCES OF 6PPD AND ITS PATHWAYS TO THE MARINE ENVIRONMENT

1.1 Production of 6PPD

In Germany, 6PPD is manufactured in an industrial scale only at the Bayer AG Brunsbüttel plant with a manufacturing volume in the range of 10 000 – 25 000 tonnes/year. In a continuously working closed system 4-aminodiphenylamine (4-ADPA) is reacted with an excess of methyl isobutyl ketone (MIBK) to a Schiff's base. This base is then hydrogenated catalytically. The excess of MIBK is separated off. The hydrogenation by-products are purged with steam. Impurities are removed by distillation under reduced pressure yielding 6PPD with a purity of > 98%.

The total 6PPD production volume of Bayer at the Brunsbüttel site is processed onsite into pellets or sold as a liquid product.

No other production sites for 6PPD are known in the OSPAR Convention area. There are no data available on the global production of 6PPD. However, the global production capacity of 4-aminodiphenylamine (4-ADPA) was about 140 000 tonnes in 1995 (OECD SIDS Report 4-Aminodiphenylamine, CAS 101-54-2). 4-ADPA is nearly exclusively used for the manufacturing of anti-ozonants for the rubber industry. The total anti-ozonants production in 1995 amounted to 117 000 tonnes by approximately 20 producers in 1995, with most of the production in Northern America (44%), Western Europe (30%), SE-Asia including Japan (15%), E-Europe (7%), S-America (3%), South Africa (2%). It is estimated that about 90% of 4-ADPA are used for the manufacturing of 6PPD.

In Japan, 6PPD is produced by two companies with a total annual production volume of about 10 000 tonnes in 2002. Use patterns and production method of 6PPD in Japan are similar to those in Germany.

Bayer AG estimates the worldwide market volume of PPDs (mostly 6PPD and IPPD: N-isopropyl-N'-phenyl-p-phenylenediamine; cf. OECD SIDS Report, CAS 101-72-4) to be 140 000 tonnes/year in 2001. Assuming that 90% of the PPDs are 6PPD, the estimated total production of 6PPD was about 130 000 tonnes/year in 2001.

1.2 Main uses of 6PPD

6PPD is used as rubber antidegradant which reacts as an anti-ozonant and antioxidant (Abele et al. 1977). 6PPD plays an essential role for protecting rubber against ageing (e.g. in vehicle tyres and seals on pressure cookers). In Japan, in Germany, and on a global scale, the main area of application of 6PPD is the rubber sector, with the majority of the manufacturing volume going into tyres (BUA 1996). In the rubber industry 6PPD applications include the use in pneumatic tyre components, solid tyres, transmission belts, hoses, cables, automotive mounts, bushings and general mechanical products that are exposed to continuous and intermittent dynamic operating conditions and require protection from ozonation. 6PPD provides antioxidant and anti-ozonant properties with high temperature, fatigue and flex resistance for natural and synthetic rubber compounds under both static and dynamic operating conditions. 6PPD also gives rubber protection against catalytic degradation by copper and other heavy metals.

6PPD is an industrial product only, but the chemical is present in consumer products as well.

2 MONITORING DATA, QUANTIFICATION OF SOURCES AND ASSESSMENT OF THE EXTENT OF PROBLEMS

2.1 Monitoring data

2.1.1 European Rivers (surface water)

Within the Water Framework Directive 2000/60/EC, the European Commission has set up a legal framework for the prioritisation of substances potentially hazardous for the aquatic environment. A combined monitoring-based and modelling-based priority setting (COMMPS) was applied in the selection process of the proposed priority substances. In this context, monitoring data from many European rivers were collected, weighted and aggregated (see Chapter 3.3 of the COMMPS-Report; available under:

http://europa.eu.int/comm/environment/water/water-dangersub/commps_report.pdf).

6PPD was not evaluated or prioritised in the COMMPS procedure. Consequently, there are no monitoring data for surface water available to be reported here.

No environmental monitoring data on 6PPD are available in Germany (Bundesministerium für Umwelt, Naturschutz und Reaktorsicherheit 2001; update by Umweltbundesamt 2003). No monitoring data have been reported by other OSPAR Contracting Parties.

2.1.2 Ground water

6PPD is a substance with a high log P_{OW} (4,7). Therefore leaching to ground water is not to be expected. Monitoring data for ground water are not available.

2.1.3 Marine waters

Due to the high K_{oc} of 6PPD (69 700 l/kg), the substance has the tendency to dissipate rapidly from the water phase and to bind to organic matter (suspended matter and sediment). Although presently not available, eventual future monitoring in the marine environment should therefore take the sediment phase into account. Due to the rapid photodegradation of 6PPD in air, a transport to marine waters via this medium may be excluded.

Discharges from the production site in Brunsbüttel on the River Elbe near the German Bight are considered to be low (about 0,73 kg/a in 2002; cf. Section 2.2.1).

2.2 Quantification of sources

Releases of 6PPD into the environment may occur from production, from use in the rubber industry and during use and disposal of rubber products.

2.2.1 Emissions from manufacturing

Information on exposure from manufacturing of the chemical is available for the Bayer Polymers production plant at Brunsbüttel, Germany.

The production plant is a closed system in which 6PPD is manufactured from 4-aminodiphenylamine (4-ADPA), which is synthesised from aniline and p-chloronitrobenzene in the same plant. 6PPD is sold in a liquid or pastillated form as an antidegradant.

The manufacturing and the filling of 6PPD are executed in a closed system (e.g. transport via pipings and railcars, sampling without dead volume, gas-shuttle pipe for filling processes). Cleaning of the reactors takes place only in the case of maintenance.

The exhausts from manufacturing of 6PPD are connected to thermal exhaust purification plants. For the trochisation area there is an additional filter for particulates. Important physical and chemical parameters of the exhaust gases are continuously monitored. Thus, during normal operation practically no 6PPD (< 25 kg/a) is emitted into the atmosphere.

Waste from the manufacturing and processing of 6PPD is incinerated in an incinerator for hazardous wastes.

At the Bayer Polymers Brunsbüttel plant, wastewater with significant organic load is separated from wastewater with minor load and incinerated by vapour-phase oxidation. Wastewater with minor load is lead to the Bayer industrial wastewater treatment plant. Its concentrated sewage sludge is incinerated by vapour-phase oxidation.

In 2002, about 0,73 kg/a 6PPD entered the biological wastewater treatment plant at the Bayer Brunsbüttel site. In the influent, the determination limit was 0,1 mg/l, and the maximum 6PPD concentration was 0,24 mg/l. In its effluent 6PPD was not detectable by 250 measurements with a determination limit of 10 µg/l.

Taking into account the detection limit (10 µg/l), a dilution with other wastewater and cooling water with a factor of 40 in the receiving water course, and the default dilution factor of 100 for emission into the sea (EC 2003), for the receiving Elbe estuary a

Predicted Environmental Concentration (PEC_{sea water}) of less than 0,0025 µg/l

is calculated. The effluent of the Brunsbüttel Bayer plant passes into the Elbe which is a tidal water at that site a few kilometres upstream of the German Bight. However, this worst case estimate does not take into account the additional dilution due to strong tidal water exchange in the North Sea. The Technical Guidance Document (EC 2003) mentions a dilution factor of more than 500 for the North Sea, 200 m away from the discharge point (see Chapter 4.2.4.2 of TGD).

Other production sites are not known in the OSPAR Convention area. Therefore, this PEC may be used as a specific PEC for production. While releases of the anti-ozonants into the atmosphere are expected to be low based on their low volatility, emissions into the wastewater may occur during vulcanisation processes, cleaning processes, recycling of used rubber and production of technical rubber articles. However, (BUA 1996) considers the quantification of these releases in order to estimate a generic PEC_{water} from production sites as not possible based on the available information.

2.2.2 Emissions from rubber products

Emissions from rubber products were evaluated in the context of the draft SIAR (2004) and based on the situation for Germany (BUA 1997). Although emission pathways will probably not be very different in other European countries, there is presently no basis for a quantitative assessment like in Germany. Literature refereed below (indicated in *italics*) is taken from the above mentioned sources and not listed in the reference list (Chapter 6).

Rubber antioxidants are employed in the manufacture of tyres (more than half of the antioxidants), and of other rubber articles like conveyor belts, spring parts, sealings, packings, drive-belts, hoses, cables, and gaskets. Depending on the conditions of the vulcanisation, up to 20% (*Lorenz et al. 1985*) or even up to 45% (*Kempermann et al. 1987*) of the antioxidants can be bound to the polymer matrix. These bound antioxidants - in general - are not extractable with water or organic solvents. The predominant sink of 6PPD is the reaction with ozone, which is the chemical base of the anti-cracking effect of 6PPD (*Lorenz et al. 1985*, *Kempermann et al. 1987*, *Baumann and Ismeier 1998*).

During the use of rubber articles, 6PPD can be introduced into the environment by two pathways:

- 6PPD can migrate to the surface of rubber products (*John et al. 1984*). However, BUA (1996) considered the diversity of rubber articles, in general, too large to make a generic estimate of this process, except for tyres (see below). In consequence, no data are available for the extent of the successive reactions: From the surface, 6PPD might enter the hydrosphere via the rain water and it might evaporate into the atmosphere. It might also (anew) be bound to the rubber matrix. Since 6PPD is a reactive anti-ozonant and antioxidant, 6PPD which reaches the surface of rubber products will be rapidly degraded by ozone, or other photooxidants (*Lattimer et al. 1982, Layer and Lattimer 1990*). Since potential degradation products (e.g. 4-hydroxydiphenylamine and N-phenylbenzoquinoneimine) also react with ozone, it is not clear what degradation products are formed and released. The eluates of freshly prepared tyre rubber particles, but not the run-off from roads, contained 6PPD and IPPD (*Baumann and Ismeier 1998*). Gaseous emissions of 6PPD from tyres could not be detected under laboratory conditions. The release of volatile rubber components from tyres during use was examined by GC/FID (*Dannis 1975*, cited according to *BUA 1996*). During tyre use no emissions of volatile rubber components (including 6PPD) could be detected.
- From the wear of rubber products. In general, new tyres for passenger vehicles contain up to 1% of IPPD and 6PPD, lorry tyres up to 2% (*Baumann and Ismeier 1998*). In 2000, the amount of rubber debris from the normal wear of tyres was calculated to be 65 000 tonnes/year. This calculation is in good agreement with previous estimates of 65 000 – 80 000 tonnes/year in Western Germany in 1989 (*Bundesministerium für Verkehr 1989*).

As a worst case for new tyres, rubber particulates containing up to 800 tonnes/year 6PPD were released in Germany in the year 2000. Since the chemical base of the anti-cracking effect of 6PPD is the reaction of 6PPD with ozone, with the age of the tyres the PPD content decreases sharply (*John et al. 1984*) to about 0,1% (*Baumann and Ismeier 1998*). Thus, it is more likely that the amount of 6PPD in tyre abrasion particles is less than 100 tonnes/year.

Also after their use rubber articles might be a source of environmental 6PPD. The amount of rubber wastes in Germany is estimated to be 1 million tonnes, of which 55% are used tyres. For 1993, the fate of 91% of the used tyres was traced. Only 2% of tyres were landfilled in 1993. On the other hand, most other used rubber products were deposited after use, in 1990 about 370 000 tonnes/year (*Löffler 1998*). Assuming the 6PPD content to be 0,8%, about 3000 tonnes 6PPD were transferred to dumps in 1990 in Germany. Since 1993, the landfilling of wastes containing more than a limited amount of organics is prohibited (e.g. 3% TOC in household wastes, TA Siedlungsabfall 1993) in Germany. The amount of rubber products deposited was decreased considerably due to increased

- recycling of used rubber e.g. in road or sports ground covers, as insulation material, by pyrolysis;
- thermic recycling e.g. as a fuel in cement production;
- waste incineration.

Unfortunately there are no recent data for the amount of rubber deposited in Germany or other European countries.

2.3 Assessment of the extent of the problem

Test results and assessments presented in this section are based on the draft SIDS Initial Assessment Report (2004, revised 2005) and based on the BUA-Report (1997) and the IUCLID Dataset (rev. 1994). The sources for data are not indicated individually, but may be found in the IUCLID Dataset.

2.3.1 Physico-chemical properties

Representative physico-chemical data of 6PPD are presented in Annex 1.

2.3.2 Abiotic and biotic degradation

PHOTODEGRADATION IN AIR

6PPD entering into the atmosphere is expected to be photodegraded rapidly by OH-radicals. The calculated half-life of 6PPD in air due to indirect photodegradation is $t_{1/2\text{air}} = 1 \text{ h}$ (24 h-day; $0,5 \cdot 10^{-6} \text{ OH}\cdot/\text{cm}^3$). Since 6PPD absorbs UV-B radiation at 291 nm and 350 nm, it is expected that 6PPD will undergo direct photolysis due to absorbance of environmental UV light.

STABILITY IN WATER (ABIOTIC DEGRADATION)

Several studies (1979, 1981) indicate that 6PPD undergoes abiotic degradation in water. The reaction is dependent on the presence of oxygen and heavy metals, pH-value, temperature, and irradiation. Further impression on the degradability of 6PPD can be gained by bridging to the similar substances 4-ADPA (4-aminodiphenylamine) and IPPD (N-isopropyl-N'-phenyl-p-phenylenediamine).

4-aminodiphenylamine (4-ADPA) has a structure similar to that of 6PPD, except that the alkyl group is missing. 4-ADPA undergoes abiotic degradation. A recent study designed similarly to OECD TG 111 examined the influence of oxygen, heavy metals, and light on the rate of 4-ADPA degradation. Under anaerobic conditions, degradation was very slow and no degradation rate was determined (half-life > 50 h). Under aerobic conditions, half-life periods of 4-ADPA were 22 and 26 h at 50 °C in presence or absence of radiation, respectively. In the presence of nutrient medium containing traces of ions of heavy metals such as Mn, Co, Cu, Mo, and Zn, the half-life period was decreased to 7 h at the same temperature. 4-hydroxydiphenylamine was identified as an intermediate of 4-ADPA degradation. In a GLP study according to OECD TG 111 4-ADPA half-lives at 50 °C were 80 h at pH 4, 57 h at pH 7, and 5 h at pH 9.

The 6PPD-analogous substance, N-isopropyl-N'-phenyl-p-phenylenediamine (IPPD) which contains an isopropyl group instead of the 1,3-dimethylbutyl group, was oxidised nearly completely (99%) within 24 h in deionised water under aerobic conditions. N-phenylbenzoquinone imine was the major degradation product. It may be an oxidation product of 4-hydroxydiphenylamine, which was identified as a by-product of hydrolysis.

With 6PPD similar results were obtained in a study (1979) on the degradation of several rubber chemicals in aerated water. Within 25 h, 60% of the initial 1 mg/l 6PPD solution were degraded yielding a half-life period of less than 1 day at 24 °C. A later study (1981) on the biodegradation of 6PPD also examined the stability of 6PPD in aqueous test solutions under aerobic conditions. The half-lives of 6PPD were 6,8 h in sterile and deionised water, and 3,9 h in sterile Mississippi river water containing traces of heavy metals.

In the cold, 6PPD is reported (1992) to be stable for at least 4 weeks in aqueous solutions at pH 2, but will be degraded at neutral or basic pH within a few hours.

Degradation of 6PPD in buffered aerobic solution and environmental water was recently examined in a study (Bayer Industry Services 2003) similar to OECD TG 111. 6PPD degradation in aerobic solutions is dependent on the temperature and on heavy metals. In buffered aerobic solution at 50 °C the half-life of 6PPD is 5 h, which is increased to about 14 h at 26 °C. To simulate environmental conditions, 6PPD was dissolved in algae nutrient medium containing traces of ions of heavy metals such as Mn, Co, Cu, Mo, and Zn. Compared to buffered aerobic solution, in algae medium the half-life period was significantly decreased to 8 h at 26 °C. 4-hydroxydiphenylamine was identified as the major aromatic intermediate of 6PPD degradation under all conditions. From the time course of 4-hydroxydiphenylamine formation and degradation at 50 °C, it is apparent that 4-hydroxydiphenylamine is not stable in aerobic media.

Reports on stability of 6PPD and its analogues in water are compiled in Table 2.

Table 2: Stability of 6PPD in water

Parameter	Method	Result
Stability of 4-ADPA in water	Aqueous test solutions under aerobic or anaerobic conditions, similar to OECD TG 111	4-ADPA abiotic degradation dependent on oxygen, heavy metals, and light. Estimated half-lives at 50 °C: distilled water, anaerobic, darkness > 50 h; distilled water, aerobic, darkness 26 h; distilled water, aerobic, light 22 h; nutrient medium containing traces of heavy metals such as Mn, Co, Cu, Mo, and Zn, aerobic, light 7 h 4-hydroxydiphenylamine identified as degradation intermediate.
Stability of 4-ADPA in water	OECD TG 111	4-ADPA half-lives: 80 h at pH 4 57 h at pH 7 5 h at pH 9
Stability of IPPD in water	Deionised water under aerobic conditions.	IPPD degraded 99% within 24 h; N-phenylbenzoquinoneimine and 4-hydroxydiphenylamine identified as degradation intermediates.
Stability of 6PPD in water	Aerated water	6PPD half-life less than 1 d.
Stability of 6PPD in water	Sterile and deionised water/ Sterile Mississippi river water.	6PPD half-lives were 6,8 h in sterile and deionised water, and 3,9 h in sterile Mississippi river water containing traces of heavy metals.
Stability of 6PPD in water	Aqueous solutions	6PPD stable for weeks at pH 2 in the cold, but degraded within a few hours at neutral or basic pH.
Degradation of 6PPD in pure and environmental water	Aqueous test solutions under aerobic conditions, test design similar to OECD TG 111	In buffered aerobic solution at 50 °C the half-life of 6PPD is about 5 h, at 26 °C it is 14 h. In the presence of traces of heavy metals such as Mn, Co, Cu, Mo, and Zn, the half-life decreased significantly. 4-hydroxydiphenylamine was the major aromatic intermediate of 6PPD degradation.

BIODEGRADATION IN WATER

6PPD is not "readily biodegradable" but it is degraded rapidly in the environment by biotic and abiotic processes.

In an OECD TG 301C test on ready biodegradability (1994), based on BOD, only ca. 2% of 6PPD was mineralised. However, based on HPLC, ca. 92% of 6PPD was removed within 28 d indicating that 6PPD was transformed. About 2/3 of the theoretical amounts of the transformation products 4-hydroxydiphenylamine, phenylbenzoquinoneimine, and 97% of the 1,3-dimethylbutylamine were recovered. Although the 2-ring intermediates were degraded further, neither aniline nor p-benzoquinone, were recovered in significant quantities. This observation is consistent with the results of the study on abiotic degradation of 6PPD and 4-hydroxydiphenylamine.

In another respirometer test (1984) according to OECD TG 301C, 13 – 40 % of 6PPD were mineralised within 28 d. The difference between the results of 2 replicates was explained with the poor solubility of 6PPD.

In an insufficiently described shake flask test (1979) comparable to an US EPA 40 CFR method, measuring biodegradation from CO₂ release, only part of 6PPD (7%) was completely degraded after 32 d. However, primary degradation was also checked with aerated water, and a rapid 6PPD decline (60% primary degradation in 25 h) of a 1 mg/l solution was observed. It is not excluded that abiotic degradation occurred during these tests.

The primary biodegradation of 6PPD was studied using Mississippi river water under aerobic conditions (1981). Controls of this biodegradation study were made with sterile and with deionised water. During 2 h, the concentration of 6PPD decreased by 57% in the active river water, by 30% in the sterile river water, and by 12% in the deionised water, indicating that both biotic and abiotic degradation occurred. After 22 h, when the experiment was finished, 97% of 6PPD had disappeared from the active river water, 96% from the sterile river water, and 88% from the deionised water. The estimated half-lives due to primary transformation are 2,9 h in biologically active river water, 3,9 h in sterile river water, and 6,8 h in sterile deionised water. Apparently, both biotic and abiotic degradation occurred leading to the rapid removal of 6PPD under aerobic conditions.

Data on biodegradation tests in the aquatic compartment are summarised in Table 3.

Table 3: Biodegradation of 6PPD; both biotic and abiotic degradation are observed in these tests

Inoculum	Procedure	Result
Activated sludge, non-adapted	OECD TG 301C	Biodegradation within 28 d BOD ca. 2%; 6PPD removal (HPLC) ca. 92%; degradation products identified p-hydroxy-diphenylamine, phenylbenzoquinone imine, 1,3-dimethylbutylamine aniline, p-benzoquinone
non adapted mixed microbial inoculum	Modified MITI I test according to OECD TG 301C	13 - 40 % mineralisation within 28 d, 10 d window was not fulfilled
Activated sludge, adapted	shake flask test comparable to an US EPA 40 CFR	7% mineralisation
Mississippi river water (= biologically active river water); controls with sterile river water and with deionised water	River die-away assay	During 2 h (22 h), the concentration of 6PPD decreased by 57% (97%) in the active river water, by 30% (96%) in the sterile river water, and by 12% (88%) in the deionised water. The estimated half-lives are 2,9 h in active river water, 3,9 h in sterile river water, and 6,8 h in sterile deionised water.

In 2002, about 0,73 kg/a 6PPD entered the biological wastewater treatment plant at the Bayer 6PPD manufacturing site in Brunsbüttel. In the influent, the determination limit was 0,1 mg/l, and the maximum 6PPD concentration was 0,24 mg/l. In its effluent 6PPD was not detectable by 250 measurements with a determination limit of 10 µg/l. It can be concluded from these data that the elimination of the Brunsbüttel industrial wastewater treatment plant exceeds at least 96%. This removal cannot be transferred to other wastewater treatment plants due to different wastewater composition and adaptation processes.

Data on biodegradation in sediment are not available. However, due to the high K_{oc} of 6PPD (69 700), sediments act as a sink for this substance. Calculations with ELPOS (Environmental Long-Range Transport and Persistence of Organic Substances, USF, University of Osnabrück, Germany, 2002) considering water solubility and adsorption, resulted in travel distances in water of 6 km. Until further evidence on the biodegradability in sediment is provided, 6PPD should be considered as persistent in sediments.

VOLATILISATION FROM WATER

Taking into account the water solubility (1 mg/l) and vapour pressure ($6,85 \times 10^{-3}$ Pa), a Henry's Law Constant was estimated to be $7,43 \times 10^{-4}$ [-] at 25 °C. This indicates a moderate potential for volatilisation from surface waters according to the scheme of Thomas (1990).

STABILITY IN SOIL

In the IUCLID Dataset, there are no data available on the stability of 6PPD in soil or removal from soil surfaces by evaporation.

Taking into account the photodegradability of 6PPD, substance reaching the soil surface as dust or by run-off from roads might be degraded there.

There is no test result available on geoaccumulation. Binding to soil organic matter has been calculated with $K_{oc} = 69\,700$. For 4-hydroxydiphenylamine a K_{oc} of 3056 was calculated (EPIWIN). According to Litz (1990) 6PPD and its degradation product 4-hydroxydiphenylamine can be regarded as a substance with geoaccumulation properties in their unprotonated forms. Since both substances are amines, it is expected that their pK_a values are in the range of 9 - 12 (expert judgement). Thus, these compounds are likely to be protonated at environmental pH and their geo-accumulation potential appears to be decreased.

CONCLUSIONS FOR DEGRADATION

6PPD is not stable in water under environmental conditions. The hydrolytic half-life is less than 1 day under aerobic conditions. The major degradation products are 4-hydroxydiphenylamine, N-phenyl-p-benzoquinone monoimine and 1,3-dimethylbutylamine.

6PPD is not "readily biodegradable". In an OECD TG 301C test on ready biodegradability, based on BOD, only ca. 2% of 6PPD was mineralised. However, based on HPLC, ca. 92% of 6PPD was removed within 28 d indicating that 6PPD was transformed. In another respirometer test according to OECD TG 301C, 13 - 40 % of 6PPD were degraded within 28 d. In a River die-away test in Mississippi River water 6PPD was quantitatively removed (97% within 22 h). The estimated half-lives are 2,9 h in biologically active river water, 3,9 h in sterile river water, and 6,8 h in sterile deionised water, indicating that both biotic and abiotic degradation occurred.

The measured Henry's law constant of $7,43 \cdot 10^{-4}$ indicates that the compound has a moderate potential for volatilisation from surface waters. In the atmosphere rapid photodegradation takes place by reaction with photochemically produced OH radicals. The half-life in air is calculated to be 1 hour. On lighted surfaces and in the air, 6PPD will undergo direct photolysis due to absorbance of environmental UV light.

No information is available on stability in sediment and soil, but a strong tendency of 6PPD to adsorb to sediment can be assumed from the high K_{oc} . Considering a short travel distance in rivers (ELPOS calculations: 6 km), and that resuspended 6PPD might be exposed to hydrolysis and photodegradation, it is unlikely that 6PPD bound to sediment will be transported to the marine environment to a large degree.

As a conclusion, 6PPD will not undergo biodegradation to an extensive degree, but hydrolysis and photodegradation are the major means of transformation (i.e. $t_{1/2, \text{freshwater}} < 40$ d). However, persistence in sediment and soil may be anticipated, even if the amounts of 6PPD which may reach these compartments are low, due to the previous abiotic degradation. The fate of the degradation products 4-hydroxydiphenylamine, N-phenyl-p-benzoquinone monoimine and 1,3-dimethylbutylamine was not fully elucidated. These metabolites have a lower tendency for adsorbance and biodegradation appears to be possible. This gives reason to the statement that, as long as no further evidence on the biodegradability of 6PPD in sediment and soil as well as on the fate of the metabolites is provided, the criterion on persistence should be considered fulfilled.

2.3.3 Bioaccumulation

Due to the low stability of 6PPD in aqueous media, a bioaccumulation and geo-accumulation potential is not expected, although QSAR calculations indicate some accumulation potential. The calculated $\log P_{ow}$ value ($\log P_{ow} = 4,68$) and a calculated BCF ($BCF = 801$, calculated with BCFWIN v2.15), indicate that - if 6PPD was stable - there is a moderate potential for bioaccumulation in aquatic organisms.

Bioaccumulation test results are available with some degradation products. Measured bioconcentration factors in *Cyprinus carpio* are in the range of $< 1,2 - 23$ for the degradation product N-phenyl-p-benzoquinone monoimine (concentration during incubation 6,83 $\mu\text{g/l}$ or 0,683 $\mu\text{g/l}$), and in the range of $< 1,7 - 17$ for 1,3-dimethylbutylamine (concentration during incubation 0,2 mg/l or 0,02 mg/l). For 4-hydroxydiphenylamine a BCF of 30 (BCFWIN v2.15) was calculated. These data indicate that there is no potential for bioaccumulation of these metabolites.

The estimated $\log P_{ow}$ of 6PPD (4,68) just exceeds the trigger of 4,5 of the marine PBT assessment. However, the calculated BCF is well below the trigger of 2000. Considering the rapid dissipation from the water phase and the low potential of bioaccumulation of major degradation products, the B-criterion is considered to be not fulfilled.

2.3.4 Acute and chronic ecotoxicity effects

AQUATIC EFFECTS

Due to the instability of the test substance, toxicity is caused both by 6PPD as well as by its degradation products.

Acute toxicity to fish (*Oryzias latipes*) has been tested in accordance with OECD TG 203. All 6PPD concentrations were analysed. A 96 h LC_{50} of 0,028 mg/l (effective concentration) was measured (2001). In

a prolonged toxicity (28 d) study with *Pimephales promelas* a LC₅₀ of 0,15 mg/l (effective concentration) was found for the endpoint mortality (1979). This was the only long-term study available, but the endpoint mortality may not be considered a chronic endpoint.

In a guideline study according to OECD TG 202 with analytical monitoring (2001), a 48 h NOEC of 0,05 mg/l, a 24 h EC₅₀ of 0,4 mg/l, and a 48 h EC₅₀ of 0,23 mg/l were determined for immobilisation of *Daphnia magna*. Acute *Daphnia* toxicity tests were also performed (1978) according to the Methods for Acute Toxicity Tests with Fish, Macroinvertebrates and Amphibians of US-EPA from 1975. In this study a 48 h NOEC of 0,56 mg/l, 24 h LC₅₀ of 1,0 mg/l, and a 48 h LC₅₀ of 0,82 mg/l were obtained (nominal concentrations).

A "degradation toxicity" study with *Daphnia magna* (1984) examined how the toxicity of 6PPD solutions change concurrently with chemical transformation and the occurrence of degradation products. Freshly prepared 6PPD solution exhibited a nominal 48 h NOEC of 0,25 mg/l and a 48 h LC₅₀ of 0,51 mg/l. Stirring for 24 h under aerobic conditions at room temperature, which equals at least 2 half-lives, decreased the toxicity of the test solution (containing 6PPD and degradation products) significantly. The 48 h NOEC of aged 6PPD was larger than 1 mg/l (highest exposure concentration). This detoxification of 6PPD solution is presumably due to oxidation and/or hydrolysis. The transformation and degradation products of 6PPD formed under these conditions are less toxic than 6PPD.

There were two more studies with *Daphnia magna*, one (1978) in a static system yielded an EC₅₀ of 0,82 mg/l (nominal) and the other (2001) in a flow through system yielded an EC₅₀ of 0,23 mg/l (effective).

In a study (1978) according to the Algal Assay Procedure: Bottle Test of the US EPA from 1971 with the green alga *Selenastrum capricornutum*, a 96 h EC₅₀ of 0,6 mg/l (nominal) was obtained.

TOXICITY TO MICRO-ORGANISMS

Regarding the toxicity to micro-organisms, a 3 h oxygen consumption test was performed in accordance to ISO 8192 with activated sludge (1984). An EC₅₀ of 420 mg/l was determined (presumably nominal, original reference not available).

TERRESTRIAL EFFECTS

No test result with plants according to OECD-TG 208 (Terrestrial plant growth test) is known.

CONCLUSIONS FOR ECOTOXICOLOGICAL EFFECTS

A summary of effects on aquatic organisms is given in Table 4.

Table 4: Selected data on the aquatic ecotoxicity of 6PPD

Trophic level	Species/test type	Parameter	Result
Fish	<i>Oryzias latipe</i> flow through	96 h LC ₅₀	0,028 mg/l (effective)
Fish	<i>Pimephales promelas</i> flow through	28 d LC ₅₀	0,15 mg/l (effective)
<i>Daphnia</i>	<i>Daphnia magna</i> flow through	48 h EC ₅₀	0,23 mg/l (effective)
<i>Daphnia</i>	<i>Daphnia magna</i> static	48 h EC ₅₀	0,82 mg/l (nominal)
<i>Daphnia</i>	<i>Daphnia magna</i> static	48 h NOEC of freshly prepared 6PPD solution	0,25 mg/l (nominal)
<i>Daphnia</i>	<i>Daphnia magna</i> static	48 h NOEC of 6PPD degradation products	> 1,0 mg/l (nominal)
Algae	<i>Selenastrum capricornutum</i> static	96 h EC ₅₀ 96 h NOEC	0,6 mg/l ca. 0,2 mg/l (nominal)
Micro-organisms	activated sludge static	3 h EC ₅₀	420 mg/l (presumably nominal)

Considering the lowest LC₅₀ of 0,028 mg/l for *Oryzias latipe* and the toxicity trigger of 0,1 mg/l (100 µg/l) for acute toxicity values (cf. marine Risk Assessment in EC, 2003), the T-criterion is fulfilled for 6PPD.

Metabolites, namely 4-hydroxyphenylenediamine and N-phenyl benzoquinoneimine, were tested with *Daphnia*, and showed a lower toxicity than the parent compound.

2.3.5 Carcinogenicity, mutagenicity or harmful reproductive effects (CMR properties)

An initial assessment of human health hazards of 6PPD (acute and chronic toxicity, irritation, genotoxicity, carcinogenicity and developmental toxicity) came to the following results:

According to the OECD guideline study the acute oral toxicity of 6PPD is moderate (LD₅₀ 500-1000 mg/kg bw).

The acute dermal toxicity of 6PPD is low (LD₅₀ > 3000 mg/kg bw). The skin irritating potential 6PPD is low. 6PPD is slightly irritating to the eye. The substance was found to induce dermal sensitisation in experimental animals and humans. Positive patch-test results in humans partly may be related to para-group cross-sensitisation.

The main targets identified after repeated oral intake of 6PPD by rats are the liver (increase of weight, fatty and vacuolar degeneration) and the blood (anaemia). In studies covering gavage exposure periods ranging from 28 to 48 days a NOAEL of 6 mg/kg bw/day and a LOAEL of 25 mg/kg bw/day can be derived based on salivation and effects on the liver.

From studies with exposure via the feed ranging from 13 weeks to 24 months a NOAEL of 75 mg/kg bw/day and a LOAEL of > 75 mg/kg bw/day can be derived both for male and female rats mainly based on anaemia observed in the 13-week-study at a dose of 2500 ppm (ca. 150 mg/kg bw/day) which is higher than the top dose of 1000 ppm (ca. 75 mg/kg bw/day) tested in the chronic study.

The higher NOAELs and LOAELs in feed studies are plausible taking into account the limited bioavailability of 6PPD when administered without lipophilic vehicle like corn oil used in the gavage studies.

In vitro 6PPD showed no mutagenic activity in bacterial and in mammalian cell test systems and it did not induce unscheduled DNA synthesis in primary rat hepatocytes. 6PPD showed clastogenic activity in CHL cells in vitro. 6PPD showed no clastogenic activity in the cytogenetic assay or the micronucleus test in vivo. Consequently the clastogenic activity reported in an in vitro test was not confirmed in vivo. In view of the

clear negative finding in the in vivo test, there is no longer concern that 6PPD is likely to induce chromosomal aberrations in humans.

The underlying insufficiently documented studies with long-term application of 6PPD gave no indication for a carcinogenic potential of 6PPD in rats.

In rats, up to oral doses of 100 mg/kg bw/day (highest dose tested) no impairment of reproductive performance was observed and there are no indications for teratogenic or developmental effects up to oral doses of 250 mg/kg bw/day (highest dose tested). Exposure during the gestation period demonstrated the absence of a fetotoxic or teratogenic potential and of maternal toxicity in rabbits with doses up to 30 mg/kg bw/day (highest dose tested).

As a conclusion, 6PPD will not present an unacceptable risk to humans with respect to CMR properties.

2.4 Risk to the environment

FATE IN THE ENVIRONMENT (P-CRITERION)

Once in the environment, 6PPD shows transformation by hydrolysis and photodegradation in water, while biodegradation is slow. Both from biotic and abiotic degradation the half-life of 6PPD in freshwater is lower than 40 days. On lighted surfaces and in the air, 6PPD will undergo direct photolysis due to absorbance of environmental UV light. However, persistence in sediment and soil may be anticipated, even if the amounts of 6PPD which may reach these compartments, are low, due to the previous abiotic degradation. The fate of the degradation products 4-hydroxydiphenylamine, N-phenyl-p-benzoquinone monoimine and 1,3-dimethylbutylamine was not fully elucidated. These metabolites have a lower tendency for adsorbance and biodegradation appears to be possible. This gives reason to the statement that, as long as no further evidence on the biodegradability of 6PPD in sediment and soil as well as on the fate of the metabolites is provided, *the criterion on persistence should be considered fulfilled*.

LIABILITY TO BIOACCUMULATE AND TOXICITY (B- AND T-CRITERION)

Based on estimated log P_{ow} (just above 4,5) and calculated BCF (< 2000) of 6PPD, but considering the rapid dissipation from the water phase and the low potential of bioaccumulation of major degradation products, *the B-criterion is considered to be not fulfilled*.

The *T-criterion was fulfilled* for 6PPD on the basis of acute toxicity test results with a value of 0,1 mg/l. Besides that, CMR properties of 6PPD do not present a hazard to humans.

EXPOSURE ASSESSMENT

Since 6PPD is not considered to be a PBT substance in full extent (B-criterion not fulfilled), the marine risk assessment (TGD, EC 2003) provides for a risk characterisation (ratio of exposure and toxicity; PEC/PNEC). The risk characterisation starts with an exposure assessment.

6PPD is a substance which is used inside of matrices (rubber) and may be widely released from these matrices, mainly tyres, by migration and abrasion. Since it is a high production volume, it will enter the environment in considerable amounts. Discharges from production via air and wastewater are considered to be negligible.

Based on estimated production volumes, physico-chemical data (cf. Annex 1) and degradation data, the fate of 6PPD was simulated with EUSES Ver. 2 on regional level, assuming that there is a diffuse release all over Europe from tyre abrasion. For the purposes of EUSES (cf. IUCLID Dataset), 6PPD has the 'industry category' 11 (polymers industry), the 'use category' 49 (stabilisers) and the 'main category for production' 1b (intermediate, stored on-site/continuous production). Emissions to the environment from life-stages other than 'production' are not foreseen for chemicals like 6PPD in EUSES.

In order to achieve regional predicted environmental concentrations (PECs), a non-standard approach within EUSES was selected for 6PPD and an additional life-stage (service-life) was introduced. Table 5 shows release fractions for the service life-stage and other input data, besides substance-specific data from Annex 1.

Table 5: Non-standard parameters for exposure assessment of 6PPD with EUSES Ver. 2.0

Parameter	Value	Comment
Production volume EU	39 000 t/a	Assuming 30% of the world production (130 000 t/a in 2001) for Western Europe ^a
Fraction of EU production volume for region	10%	Default from EUSES Ver. 1.0, unlike default of EUSES Ver. 2.0 (100%)
Release fractions for 'service life-stage'		
Fraction of tonnage released to air	0,01	Selection of release fractions is not based on scientific knowledge but set arbitrarily
Fraction of tonnage released to waste water	0,09	
Fraction of tonnage released to surface water	0,4	
Fraction of tonnage released to industrial soil	0,2	
Fraction of tonnage released to agricultural soil	0,3	

^a) An extrapolation of the 6PPD emission to the environment from tyre abrasion (800 t/a in Germany; 2001; cf. § 32) to Europe, based on the ratio of populations (factor 6,17) results in an emission of a little less than 5 000 t/a.

EUSES Ver. 2.0 estimates PECs for all terrestrial aquatic and marine coastal compartments (Table 6). However, it should be kept in mind that this calculation applies to coastal waters and that the PECs are associated with a large degree of uncertainty which originates from an uncertainty in the release to the environment and the distribution there (Table 5, last row), before 6PPD reaches surface water.

Table 6: Predicted environmental concentrations (PECs) for 6PPD (non-standard exposure assessment with EUSES Ver. 2.0)

Regional PEC in	Value	Unit	Comment
Surface water (total)	0,93	µg/l	suspended matter and dissolved
Sediment	1450	µg/kg sed. dw	bound and pore water
Agricultural soil (total)	6,83	µg/kg soil dw	bound and pore water
Natural soil (total)	0,045	µg/kg soil dw	bound and pore water
Industrial soil (total)	95,4	µg/kg soil dw	bound and pore water
Air	0,00033	µg/m ³	
Sea water (total)	0,019	µg/l	suspended matter and dissolved
Sea water sediment (total)	24,3	µg/kg sed. dw	bound and pore water

RISK CHARACTERISATION

The Technical Guidance Document (EC 2003) provides for an assessment factor of 10 000 to toxicity data within the marine risk assessment, if only the standard test data are available. Since there are acute studies from 3 trophic levels, several refined studies for *Daphnia* and a long-term study for fish, a reduced assessment factor of 1000 is applied to determine the PNEC_{aquatic}. Although only freshwater organisms are considered, the variety of test results available justifies the reduction of the assessment factor by one order of magnitude. The lowest effect value was measured during an acute toxicity test to fish (*Oryzias latipes*) with a 96 h LC₅₀ of 0,028 mg/l (effective concentration), resulting in an

PNEC_{aquatic} of 0,028 µg/l

Risk characterisation, using PECs from Table 6 (PEC_{sea water} = 0,019 µg/l), would not indicate a risk for sea water (PEC/PNEC = 0,68 < 1). Uncertainty of the PEC calculations should be kept in mind when evaluating these exposure/toxicity ratios. A more realistic PEC estimate of 0,0024 µg/l, based on emission from tyre abrasion (cf. footnote to Table 5), yields a PEC/PNEC ratio of 0,087. If the basic assessment factor of 10 000 would be used for the PNEC, the ratio is still below 1 (i.e. 0,87).

RISK ASSESSMENT

There are several indications that entry into the marine environment will be very low: 6PPD is not stable in water under environmental conditions; transport in rivers occurs only over short distances (calculated 6 km); degradation is rapid on lighted surfaces and in air; movement directly from soil to the sea is unlikely. On the other hand, there are some knowledge gaps concerning the degradation of 6PPD in soil and the environmental fate and behaviour of the metabolites.

The metabolites of 6PPD, 4-hydroxyphenylenediamine and N-phenyl benzoquinoneimine, need further attention, since less data are available for the metabolites. However, toxicity of the metabolites is lower than with 6PPD, and bioaccumulation is lower too. It only appears that the metabolites are slightly more persistent than the parent compound, but still below the level of concern for the aquatic environment ($t_{1/2} < 40$ d in freshwater).

As a conclusion, exposure of 6PPD to the environment and transport to the sea is anticipated to be low and therefore risks to marine organisms are expected to be negligible.

3 DESIRED REDUCTION

6PPD is not a PBT substance. The risk to the marine environment can be considered low. Nevertheless, 6PPD is a high production volume chemical, and this justifies a continuous attention towards this substance.

Therefore measures and actions by OSPAR should be directed, in general, to avoid a potential future entry of 6PPD into the marine environment. A general quest for a reduction of use of 6PPD, based on a risk to the marine environment, does not seem appropriate.

4 REVIEW OF AGREED MEASURES AND POSSIBLE SUBSTITUTES

4.1 Review of agreed national and international measures for the regulation of 6PPD

OSPAR STRATEGY WITH REGARD TO HAZARDOUS SUBSTANCES

6PPD was selected in the DYNAMEC process early in 2000. At OSPAR 2003, 6PPD was agreed upon as a priority substance and Germany volunteered in the preparation of the draft Background Document for October 2004. The draft Background Document for 6PPD and proposals on action and measures are prepared for decision at OSPAR 2005.

EXISTING SUBSTANCES – COUNCIL REGULATION (EEC) NO. 793/93

6PPD is included in the list of existing substances produced or imported within the European Community in quantities exceeding 1000 tonnes per year (Official Journal EC, L84 of June 4, 1993, p. 1).

OECD EXISTING CHEMICALS PROGRAMME

The inclusion in Council Regulation (EEC) No. 793/93 is the basis for the ongoing evaluation of 6PPD by the OECD Existing Chemicals Programme (www.oecd.org/Environment/Chemical_Safety/Co-operation_on_the_Investigation_of_Existing_Chemicals; cf. § 3-5).

ADMINISTRATIVE RULES CONCERNING SUBSTANCES HAZARDOUS TO WATER

According to German Administrative Rules (Verwaltungsvorschrift wassergefährdende Stoffe GMSMA6, 16, 327, 1996, Appendix 3), 6PPD is classified as "hazardous to water" (Water Hazard Class, WGK 2). The classification forms the basis for water protection requirements for industrial plants in which hazardous substances are handled.

4.2 Choice of substitutes

For its intended uses, 6PPD is a choice among other synthetic rubber antidegradants. However, in comparison to other substances (N,N'-diphenyl paraphenylenediamine, DPPD; diphenylamine, DPA; 4-phenylbutylamine, PBN) it has less effect on processing safety than other alkyl-aryl and dialkyl-p-phenylenediamines, where scorch is a problem. Further, 6PPD is less volatile than other widely used alkyl-aryl and dialkyl-p-phenylenediamines.

5 CHOICE FOR ACTION/MEASURES

The OECD SIAR comes to the following conclusion concerning the environmental risk of 6PPD:

The chemical possesses properties indicating a hazard for the environment. Releases of 6PPD into the environment may occur during manufacturing in the rubber industry from the use of 6PPD as an anti-ozonant, as well as from the utilization of rubber products. Therefore an exposure assessment and, if then indicated, an environmental risk assessment is recommended. This should also include further investigations on nature and properties of degradation products.

The chemical is a candidate for further work.

THE CONCLUSION ON THE AVOIDANCE OF FUTURE RISKS

In order to avoid future risks resulting from production and/or continued use of 6PPD as an anti-ozonant for rubber protection, and considering that 6PPD is produced in large volumes,

- Contracting Parties should consider to improve the exposure assessment for 6PPD and its metabolites, in order to clarify whether the unquestionable wide-spread release of 6PPD, mainly from tyres, on one hand, and the rapid degradation in the environment on the other hand, may lead to a significant load to the marine environment. The metabolites of 6PPD, in specific 4-hydroxyphenylenediamine and N-phenyl-benzoquinoneimine, need further attention, since the data base for these compounds is even less well established as for the parent compound 6PPD;
- Contracting Parties should develop a monitoring strategy which includes parent 6PPD as well as metabolites and which supports the above mentioned improvement of exposure assessment. In specific, the monitoring should clarify the possible pathways and occurrence of 6PPD and metabolites in surface water and coastal waters, as well as in marine sediments, in order to identify areas of intensive emission (e.g. the German Bight). A monitoring strategy should further consider that 6PPD is volatile and rapidly undergoes abiotic degradation in water and air, which might direct the focus of the monitoring to the metabolites, rather than the parent substance;
- Contracting Parties, when undertaking further work for exposure assessment of 6PPD, should co-ordinate their work with ongoing activities in the OECD Existing Chemicals Programme.
- OSPAR should invite Contracting Parties to check that the operation of plants manufacturing or formulating 6PPD is regulated according to the principles of BAT (Best Available Technology) and that any releases are eliminated, or minimised to the greatest possible extent.

To ensure that the information in this Background Document and the conclusions reached by OSPAR are taken into account in the approach of the European Community,

- OSPAR should communicate this Background Document to the European Commission for information.

To ensure that the information in this Background Document can be considered in the context of other international agreements which deal with hazardous substances, and with which Contracting Parties are associated,

- OSPAR should send copies of this Background Document to the appropriate bodies dealing with those agreements and invite Contracting Parties who are parties both to OSPAR and those other agreements to promote action to take account of this Background Document by those other international bodies in a consistent manner. This concerns in specific the OECD Existing Chemicals Programme.

6 REFERENCES

- (BUA) BERATERGEMEINSCHAFT FÜR UMWELTRELEVANTE ALTSTOFFE DER GESELLSCHAFT DEUTSCHER CHEMIKER (1997): BUA Stoffberichte 207 und 208. N-isopropyl-N'-phenyl-1,4-phenyldiamin (IPPD) (Nr. 207). N-(1,3-Dimethylbutyl)-N'-phenyl-1,4-phenyldiamin (6PPD) (Nr. 208). S. Hirzel Wissenschaftl. Verlagsges., 93+78 p.; ISBN 3-7776-0807-6. GDCh-Advisory Committee on Existing Chemicals of Environmental Relevance.
- ABELE, M.; ALBRECHT, K.D., EHOLZER, U.; FRIES, H.; LINGNER, G.-P.; HOFMANN, W. (1977): Kautschuk-Chemikalien und Zuschlagstoffe. In Ullmanns Enzyklopädie der technischen Chemie, 4. Aufl., Weinheim, Verlag Chemie, Bd. 13, 637-670.

- BAUMANN, W.; ISMEIER, N. (1998): Kautschuk und Gummi. 2 Volumes, Daten und Fakten zum Umweltschutz; Berlin, Springer, pp. 272-275; 307-349.
- BUNDESMINISTERIUM FÜR UMWELT, NATURSCHUTZ UND REAKTORSICHERHEIT (2001): Umweltpolitik und Wasserwirtschaft in Deutschland, Teil II, Gewässergüte oberirdischer Binnengewässer. Umweltbundesamt, Berlin, pp. 19, 36.
- BUNDESMINISTERIUM FÜR VERKEHR (1989): Antwort der Bundesregierung auf die kleine Anfrage des Abgeordneten Weiß (München) und der Fraktion Die Grünen. Drucksache 11/3772 (1989).
- EUROPEAN COMMISSION (2003): Technical Guidance Document in support of Commission Directive 93/67/EEC on Risk Assessment for new notified substances, Commission Regulation (EC) 1488/94 on Risk Assessment for existing substances, Directive 98/8/EC of the European Parliament and the Council concerning the placing of biocidal products on the market. Part II, 2nd edition, 328 p., No. EUR 20418 EN/2.
- IUCLID (2000): Dataset for N-(1,3-dimethylbutyl)-N'-phenyl-1,4-phenyldiamine. CAS No. 793-24-8; EINECS No. 212-344-0; created 19-FEB-2000; 40 p.
- LITZ, N. (1990): Schutz vor weiteren anthropogenen Organika-Einträgen. In: Blume, H.-P. (ed.): Handbuch des Bodenschutzes. Bodenökologie und -belastung; Vorbeugende und abwehrende Schutzmaßnahmen. Ecomed-Verlag, Landsberg/Lech, pp. 581.
- THOMAS, R.G. (1990): Volatilization from Water. I: Lyman, W.J.; Reehl, W.F.; Rosenblatt, D.H. (eds.): Handbook of Chemical Property Estimation Methods. Environmental Behaviour of Organic Compounds. MacGraw-Hill Book Company, New York, pp. 15-1 – 15-17.
- UMWELTBUNDESAMT (2003): Wasser – Oberflächengewässer;
http://www.umweltbundesamt.de/wasser/themen/ow_s4_5.htm.

EU-Directives/Regulations quoted

- (EEC) 793/93:** Council Regulation Nr. 793/93 of 23 March 1993 on the evaluation and control of the risks of existing substances.
Official Journal No. L 84 of 05/04/1993, p. 1–75.
- 2000/60/EC:** Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy.
Official Journal No. L 327 of 22/12/2000, p. 1-73.

ANNEX 1: PHYSICO-CHEMICAL PROPERTIES OF 6PPD

Property	Value	Source
Chemical name (IUPAC)	N-(1,3-dimethylbutyl)-N'-phenyl-1,4-phenylenediamine	IUCLID (rev. 1994) SIAR (2005)
CAS-No.	793-24-8	IUCLID (rev. 1994) SIAR (2005)
EEC No. (EINECS)	212-344-0	IUCLID (rev. 1994) SIAR (2005)
Molecular formula	C ₁₈ H ₂₄ N ₂	IUCLID (rev. 1994) SIAR (2005)
Purity of the technical product	> 98% w/w	IUCLID (rev. 1994) SIAR (2005)
Molecular Mass M [g/mol]	268,5	IUCLID (rev. 1994) SIAR (2005)
Physical state of matter at 20 °C	solid	IUCLID (rev. 1994) SIAR (2005)
Colour / odour	brown / no data	IUCLID (rev. 1994) SIAR (2005)
Density [g/cm ³]	0,995 at 50 °C	IUCLID (rev. 1994) SIAR (2005)
Melting point T _m [°C]	45 – 48 °C 50 °C	IUCLID (rev. 1994) Hawley (1977)
Boiling point T _b [°C]	230 °C at 1013 hPa	IUCLID (rev. 1994) EPA 2003
Flash point [°C] Auto flammability [°C]	200 °C 500 °C	IUCLID (rev. 1994) SIAR (2005)
Solubility in water S [g/l]	1 * 10 ⁻³ at 20 °C ca. 1 * 10 ⁻³ at 50 °C	IUCLID (rev. 1994) SIAR (2005)
Solubility in organic solvents	Soluble in acetone, ethyl acetate, methylene chloride	IUCLID (rev. 1994) SIAR (2005)
log P _{ow} [-]	4,68 (calc.) 4,77 (meas., 25 °C)	IUCLID (rev. 1994) SIAR (2005)
Adsorption coefficient log K _{oc} [l/kg]	4,84 (calc.)	IUCLID (rev. 1994) SIAR (2005)
Vapour pressure P [Pa]	6,85 * 10 ⁻³ Pa at 25 °C (calc.)	IUCLID (rev. 1994) SIAR (2005)
Henry's Law constant [-]	7,43 * 10 ⁻⁴ at 25 °C (meas.)	IUCLID (rev. 1994) SIAR (2005)
Volatilisation from water	moderate according to Henry's Law constant of 7,43 * 10 ⁻⁴	IUCLID (rev. 1994) SIAR (2005)
Volatilisation from soil	no data available	IUCLID (rev. 1994) SIAR (2005)
Reactivity with OH-radicals atmospheric half-life [h]	t _{½air} = 1 h (calc.)	IUCLID (rev. 1994) SIAR (2005)
Hydrolysis [%]	93% after 24 h at pH 7 and 25 °C 99% after 7 days at pH 7 and 25 °C (increasing with pH and in the light)	IUCLID (rev. 1994) SIAR (2005)

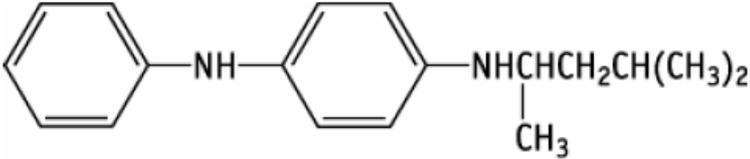
Property	Value	Source
Photodegradation in water half-life [h]	not measurable because of rapid hydrolysis	IUCLID (rev. 1994) SIAR (2005)
Toxicological classif. (EU)	Xi, N (provisional by manufacturer)	IUCLID (rev. 1994)
R-Phrases	R43, R50/R53 (provisional by manufacturer)	IUCLID (rev. 1994)
S-Phrases	S24, S37, S60 (provisional by manufacturer)	IUCLID (rev. 1994)

ANNEX 2: SIDS INITIAL ASSESSMENT PROFILE

SIAM 18, 20-23 April 2004

JP/ICCA

SIDS INITIAL ASSESSMENT PROFILE

CAS No.	793-24-8
Chemical Name	N-(1,3-Dimethylbutyl)-N'-phenyl-1,4-phenylenediamine (6PPD)
Structural Formula	

SUMMARY CONCLUSIONS OF THE SIAR

Human Health

No experimental data are available regarding the toxicokinetic behaviour and metabolism of 6PPD. The appearance of systemic toxicity after oral and dermal exposure shows the principal bioavailability of 6PPD via these routes.

The acute toxicity of 6PPD is moderate after oral administration and low after dermal application. The oral LD₅₀ values in rats were 893 mg/kg bw for females and 1005 mg/kg bw for males. Signs of intoxication were hypoactivity, diarrhea, bradypnea, hypothermia and a prone position accompanied by pathological lesions in digestive organs and respiratory system. The dermal LD₅₀ in rabbits was > 3000 mg/kg bw. Signs of intoxication were reduced food consumption, hypoactivity and lethargy.

The skin irritating potential of 6PPD is low. 6PPD is slightly irritating to the eye. The substance was found to induce dermal sensitization in experimental animals and humans. Positive patch-test results in humans partly may be related to para-group cross-sensitization.

The main targets identified after repeated oral intake of 6PPD by rats are the liver (increase of weight, fatty and vacuolar degeneration) and the blood cells (anemia, lymphocytopenia, and thrombocytopenia). In studies with gavage covering exposure periods ranging from 28 to 48 days a NOAEL of 6 mg/kg bw/day and a LOAEL of 25 mg/kg bw/day can be derived based on a ca. 10 % increase in liver weight in both sexes as well as vacuolar liver degeneration in 2/12 males and salivation in males. From studies with exposure via the feed ranging from 13 weeks to 24 months a NOAEL of 75 mg/kg bw/day and a LOAEL of > 75 mg/kg bw/day can be derived both for male and female rats mainly based on anemia observed in the 13-week-study at a dose of 2500 ppm (ca. 150 mg/kg bw/day) which is higher than the top dose of 1000 ppm (ca. 75 mg/kg bw/day) tested in the chronic study. The higher NOAELs and LOAELs in feed studies are plausible taking into account the limited bioavailability of 6PPD when administered without lipophilic vehicle like corn oil used in the gavage studies.

In vitro 6PPD showed no mutagenic activity in bacterial and in mammalian cell test systems and it did not induce unscheduled DNA synthesis in primary rat hepatocytes. 6PPD showed clastogenic activity in CHL cells *in vitro*. 6PPD showed no clastogenic activity in the cytogenetic assay or the micro-nucleus test *in vivo*. Consequently the clastogenic activity reported in an *in vitro* test was not confirmed *in vivo*. In view of the clear negative finding in the *in vivo* test, there is no longer concern that 6PPD is likely to induce chromosomal aberrations in humans.

The underlying insufficiently documented studies with long-term application of 6PPD via diet gave no indication for a carcinogenic potential of 6PPD in rats.

In rats, up to oral doses of 100 mg/kg bw/day no impairment of reproductive performance was observed and there are no indications for teratogenic or developmental effects up to oral doses of 250 mg/kg bw/day (highest dose tested). Exposure during the gestation period demonstrated the absence of a developmental or teratogenic potential and of maternal toxicity in rabbits for doses up to 30 mg/kg bw/day (highest dose tested).

Environment

6PPD is a brown solid substance with a melting point of 50°C. 6PPD has a calculated boiling point of 370 °C. It is nearly insoluble in water (1 mg/l at 20 °C). The vapour pressure was calculated to be 6.85×10^{-3} Pa at 25 °C. A log K_{ow} value of 4.68 was calculated. The flash point of the substance is 200 °C.

6PPD is not stable in water under environmental conditions. The half-life is less than 1 day under aerobic conditions. The major degradation products are 4-hydroxydiphenylamine, N-phenyl-p-benzoquinone monoimine and 1,3-dimethylbutylamine. The favourite target compartments of 6PPD are soil with 95 %, followed by water with 2 %, and sediment with 2 %, according to a Mackay calculation level I. The measured Henry's law constant of $1.84 \text{ Pa}\cdot\text{m}^3\cdot\text{mol}^{-1}$ indicates that the compound has a moderate potential for volatilization from surface waters. In the atmosphere rapid photodegradation takes place by reaction with photochemically produced OH radicals. The half-life is calculated to be 1 hour. On lighted surfaces and in the air, 6PPD will undergo direct photolysis due to absorbance of environmental UV light.

6PPD is not readily biodegradable but it is degraded rapidly in the environment. In an OECD TG 301C test on ready biodegradability, based on BOD, only ca. 2 % of 6PPD was biodegraded. Based on HPLC, ca. 92 % of 6PPD was removed within 28 d indicating that 6PPD was transformed. In another respirometer test according to OECD TG 301C 13 - 40 % of 6PPD were degraded within 28 d. In a River die-away test in Mississippi River water 6PPD was quantitatively removed (97 % within 22 h). The estimated half-lives are 2.9 h in biologically active river water, 3.9 h in sterile river water, and 6.8 h in sterile deionized water.

The calculated log K_{ow} indicates that 6PPD has a potential for bioaccumulation. 6PPD is not stable under certain environmental conditions. Bioaccumulation test results are available with some degradation products. Measured bioconcentration factors in *Cyprinus carpio* are in the range of < 1.2 - 23 for the degradation product N-phenyl-p-benzoquinone monoimine (concentration during incubation 6.83 µg/l or 0.683 µg/l), and in the range of < 1.7 - 17 for 1,3-dimethylbutylamine (concentration during incubation 0.2 mg/l or 0.02 mg/l). For 4-hydroxydiphenylamine a BCF of 30 was calculated. These data indicate that there is no potential for bioaccumulation of these metabolites.

In fish, the lowest acute toxicity was observed in *Oryzias latipes* during a test in accordance with OECD TG 203. A 96 h LC_{50} of 0.028 mg/l (effective concentration) was measured. In daphnids, the lowest effective LC_{50}/EC_{50} was a 48 h EC_{50} of 0.23 mg/l measured with *Daphnia magna* in a Guideline study according to OECD TG 202. In a "degradation toxicity" test with *Daphnia magna*, it was shown that 6PPD solution aged shortly (24 h) lost its toxicity towards *Daphnia magna*. Freshly prepared 6PPD solution exhibited a nominal 48 h NOEC of 0.25 mg/l and a 48 h LC_{50} of 0.51 mg/l. Stirring for 24 h under aerobic conditions at room temperature, decreased the toxicity of the test solution (containing 6PPD and degradation products) significantly. The 48 h NOEC of aged 6PPD was larger than 1 mg/l (highest exposure concentration). In a study according to the Algal Assay Procedure: Bottle Test of the US EPA with the green alga *Selenastrum capricornutum*, a 96 h EC_{50} of 0.6 mg/l (nominal) and a 96 h EC_{10} in the range of 0.2 mg/l were obtained.

It has to be considered that the toxicity observed in the reported studies was caused both by the 6PPD as well as by the degradation products due to the instability of the test substance.

Exposure

The total production of 6PPD is estimated to be about 130,000 t/a in 2001. 6PPD is used as rubber antidegradant which reacts as an excellent antiozonant. The main area of application is the rubber sector, with the majority of the manufacturing volume going into tyres.

SIAM 18, 20-23 April 2004

JP/ICCA

Releases of 6PPD into the environment may occur from production, from use in the rubber industry and during use and disposal of rubber products.

In the Sponsor country, 6PPD is manufactured from 4-aminodiphenylamine (CAS No. 101-54-2) in closed systems. Manufacturing waste is incinerated.

6PPD is lost from rubber articles into the environment, due to tyre abrasion, evaporation from rubber surfaces, and losses from landfilled rubber wastes. There are no environmental monitoring data. Even in the vicinity of new tyres, no 6PPD was detected in the surrounding air.

In the manufacturing plant of the Sponsor company, workplace air sampling of precursors and auxiliaries, which are thought to be indicators of exposure, suggest that the exposure of workers to airborne 6PPD is negligible during manufacturing. In workplace areas of the rubber industry, most workplace concentrations were negligible (peak value of 6.6 mg/m³). In workers of the Sponsor company no adducts with hemoglobin could be detected. 6PPD was found in 15 % of the urine samples (maximum was 1.3 µg/l urine) of 21 workers of the Italian rubber industry. In another study the concentration of 6PPD in urine samples of rubber industry workers was of < 1 to 300 µg/g creatinine (with a peak value of 580 µg/g) in 1982 to 1987.

RECOMMENDATION

The chemical is a candidate for further work

RATIONALE FOR THE RECOMMENDATION AND NATURE OF FURTHER WORK RECOMMENDED

Human Health:

The chemical possesses properties indicating a hazard for human health (skin sensitization, anemia). It is therefore recommended that countries perform an exposure assessment, and, if then indicated, a risk assessment addressing exposure to workers and to humans via the environment.

Environment:

The chemical possesses properties indicating a hazard for the environment. Releases of 6PPD into the environment may occur during manufacturing in the rubber industry from the use of 6PPD as an antiozonant, as well as from the utilization of rubber products. Therefore, an exposure assessment and, if then indicated an environmental risk assessment is recommended. This should also include further investigations on identities and properties of degradation products.

ANNEX 3: MONITORING STRATEGY FOR 6PPD

As part of the Joint Assessment and Monitoring Programme (reference number 2003-22), OSPAR 2005 adopted a revised Agreement on Monitoring Strategies for OSPAR Chemicals for Priority Action (reference number 2004-14) to implement the following monitoring for tracking progress towards the objectives of the OSPAR Hazardous Substances Strategy (reference number 2003-21) with regard to 6PPD. The Monitoring Strategy for 6PPD will be updated as and when necessary, and redirected in the light of subsequent experience.

6PPD (N-(1,3-dimethylbutyl)-N'-phenyl-1,4-phenylenediamine) (CAS No. 793-24-8) is an aromatic amine which is used in high production volumes as a protective agent (anti-ozonant and anti-oxidant) mainly in the rubber industry. The main area of use is the tyre sector but the chemical is also found in other consumer products, e.g. seals of pressure cookers.

6PPD is not a PBT substance according to the EU-TGD PBT criteria. The T-criterion was fulfilled and the criterion on persistence might be considered fulfilled as long as no further evidence on the biodegradability of 6PPD in sediment and soil as well as on the fate of the metabolites is available. Exposure of 6PPD to the environment and transport to the sea is anticipated to be low. 6PPD is not stable in water under environmental conditions; it is not readily biodegradable but is degraded rapidly in the environment.

On lighted surfaces and in the air 6PPD will undergo direct photolysis; movement directly from soil to the sea is unlikely and therefore risks to marine organisms are expected to be negligible. Nevertheless, 6PPD is a high production volume chemical. There are some knowledge gaps concerning the degradation of 6PPD in soil and the environmental fate and behavior of the metabolites. This justifies a further attention towards this substance and its metabolites.

The main entry pathway of 6PPD to the environment is via diffuse sources. 6PPD is used as rubber antidegradant in tyres in rates up to 2%. This means that through rubber abrasion remarkable amounts are released to the environment. The rubber debris will be deposited on roadsides and can be leached out with rainwater. Diffuse emission from disposal of old tyres might be less important because the 6PPD content decreases sharply with the age of the tyres.

Emissions from point sources are of minor importance as there is only one production site of 6PPD in the OSPAR area and this production site is regulated according to the principles of BAT (Best Available Technology).

No environmental monitoring data on 6PPD are available in Germany (Bundesministerium für Umwelt, Naturschutz und Reaktorsicherheit 2001; update by Umweltbundesamt 2003). No monitoring data have been reported by other OSPAR Contracting Parties. 6PPD can be analyzed with a recovery rate of 95% and can be detected sensitively with GC/FID.

6PPD is included in the list of existing substances produced within or imported to the European Community in quantities exceeding 1000 tonnes/year (Council Regulation (EEC) No. 793/93) and is subject to ongoing evaluation by the OECD Existing Chemicals Programme.

In the light of the factors listed above, the monitoring strategy of 6PPD should be as follows:

- a. Contracting Parties to improve the data basis for the exposure assessment for 6PPD and its main degradation products (mainly 4-hydroxydiphenylamine as well as N-phenyl-p-benzoquinone monoamine and 1,3-dimethylbutylamine) in order to clarify whether the unquestionable wide-spread release of 6PPD, mainly from tyres, can lead to a significant load to the marine environment. The main degradation products of 6PPD need further attention regarding their possible PBT-properties and their environmental fate.
- b. Contracting Parties should include parent 6PPD as well as the degradation products (mainly 4-hydroxydiphenylamine) in research projects concerning contamination of splash water and roadside soils from busy streets to investigate the amounts and pathways of the substance and its degradation products from tyre abrasion to the environment.
- c. OSPAR, if undertaking further work for exposure assessment of 6PPD, should coordinate its work with ongoing activities in the OECD Existing Chemicals Programme.

6 PPD (4-(DIMETHYLBUTYLAMINO)DIPHENYLAMINE) MONITORING STRATEGY	
Implementation of actions and measures	<ul style="list-style-type: none"> • Research and screening projects concerning contamination of splash water and roadside soils from busy streets should if appropriate include 6PPD and its main degradation products. • The lead country should update the estimation on the emissions from tyre abrasion.
Concentration in air	<ul style="list-style-type: none"> • No monitoring
Discharges and losses to water	<ul style="list-style-type: none"> • Contracting Parties are invited to submit information on the diffuse emissions of 6PPD from tyre abrasion.
Production/use/sales/figures	<ul style="list-style-type: none"> • The lead country/industry should update the information on the use of 6PPD in tyres. • Contracting Parties are invited to submit information on the use of 6PPD in tyres.
Atmospheric inputs	<ul style="list-style-type: none"> • No monitoring
Riverine inputs	<ul style="list-style-type: none"> • No monitoring
Maritime area:	
Concentrations in sediment	<ul style="list-style-type: none"> • No monitoring
Concentrations in water	<ul style="list-style-type: none"> • No monitoring
Concentration in biota	<ul style="list-style-type: none"> • No monitoring