

Hazardous Substances Series

Musk xylene and other musks



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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.

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Executive summary

Musk ingredients are substances with a typical musky scent, used by the fragrance industry in wide range of consumer products. Synthetic musks are generally divided into three groups of substances with similar properties but different chemical structures: nitromusks, polycyclic musks and macrocyclic musks. The main nitromusks are musk xylene and musk ketone. The main polycyclic musks are HHCB and AHTN. This background document also covers some macrocyclic because these substances have to be considered as possible substitutes for musk xylene. The group musk xylene and other musks was added to the OSPAR List of Chemicals for Priority Action in 1998. This document is a revision of the OSPAR Background Document on Musk Xylene and other Musks published in 2000.

Nitromusks are not produced in Europe and production in Europe of AHTN and HHCB is concentrated at one (inland) plant in the EU for each substance. There are significant imports and exports of synthetic musks to and from the convention area both as pure substances and in finished products. Point source releases from the formulation of products are negligible in relation to the overall diffuse release to the marine environment due to the widespread dispersive use of consumer products containing these substances. Currently, musk ketone, musk xylene, HHCB and AHTN represent about 95% of the market in Europe for all nitromusks and polycyclic musks.

Musk xylene and musk ketone and the two main polycyclic musks (AHTN and HHCB) have been included in priority lists under the EC existing substances regulation (ESR). Since publication of the first background document a risk assessment for musk xylene has been finalised, and risk assessments are currently being prepared for the other musks. The marine risk assessment described in this document draws on this on-going work. It is also clear that negative publicity has led to a reduction in the use of polycyclic musks and musk xylene in certain products, particularly in northern Europe. Representatives of the nitromusks and polycyclic musks have been detected in environmental samples and human milk and tissue, however downward trends in concentrations of some synthetic musks in some environmental media have been reported.

Musk xylene is considered a candidate PBT substance. A test on degradability in the marine environment is currently being carried out under the ESR process. Although this work is on-going, the initial conclusion of the marine risk assessment is that the risks both from industrial use of musk xylene and consumer uses are low. The other synthetic musks do not meet one or more of the PBT criteria and the marine risk assessment indicates that musk ketone and the polycyclic musks appear to pose low risks for the marine environment. However further investigations on the long-term toxicity and environmental fate of polycyclic musks are being carried out. The macrocyclic musks appear to have a more favourable environmental profile but this needs further confirmation before they can be recommended as substitutes.

Although there is a need to await the collection of further relevant information before finalising conclusion on the choice for actions, the following actions are already thought to be justified: to promote the substitution of Musk xylene with substitutes with a more favourable environmental profile; to urge the International Fragrance Association (IFRA) to fulfil its reporting commitment on the use volumes of the various musk fragrance ingredients; to encourage Contracting Parties, industry associations and individual companies to study and assess possible substitutes and to promote their use when the risk profile is favourable; to discourage the use or promotion of polycyclic musks as replacements for musk xylene; to re-evaluate the risks posed by the consumer use of musk xylene and the polycyclic musks when further information has been collected in the ongoing research programmes. If PBT-status of musk xylene is confirmed within the European Union, OSPAR should recommend the EU to take into consideration the need to take controlling actions on musk xylene leading to the cessation of marketing and use and invite Contracting Parties that are not EU Members to implement similar measures.

Récapitulatif

Les ingrédients musqués sont des substances dont émane un parfum musqué caractéristique, utilisés par l'industrie des parfums dans un vaste éventail de produits de grande consommation. Les muscs synthétiques sont en général divisés en trois groupes de substances présentant des propriétés analogues, mais des structures chimiques différentes. Ce sont les nitromuscs, les muscs polycycliques et les muscs macrocycliques. Les principaux nitromuscs sont le xylène musqué et le cétone musqué. Les principaux muscs polycycliques sont le HHCB et le AHTN. Le présent document de fond porte aussi sur certains muscs macrocycliques, car ces substances doivent être considérées comme des substituts éventuels du xylène musqué. Le groupe des xylènes musqués et autres muscs a été ajouté en 1998 à la liste OSPAR des produits chimiques devant faire l'objet de mesures prioritaires. Le présent document constitue une nouvelle version du document de fond OSPAR sur le xylène musqué et autres muscs, publié en 2000.

Aucun nitromusc n'est fabriqué en Europe, et la fabrication, en Europe, du AHTN et du HHCB est concentrée à une seule installation (enclavée) dans l'Union européenne, les deux substances y étant fabriquées. Les importations et les exportations de muscs synthétiques vers et au départ de la zone de la Convention, que ce soit sous forme de substances pures ou dans des produits finis, sont importantes. Les émissions de source ponctuelle dues à la formulation des produits sont négligeables par rapport aux émissions générales diffuse dans le milieu marin, ceci en raison de l'utilisation très répandue et dispersive des produits de grande consommation qui contiennent ces substances. A l'heure actuelle, le cétone musqué, le xylène musqué, le HHCB et l'AHTN représentent environ 95% du marché européen de l'ensemble des nitromuscs et des muscs polycycliques.

Le xylène musqué, le cétone musqué et les deux principaux muscs polycycliques (AHTN et HHCB) ont été inscrits sur les listes prioritaires en vertu du règlement communautaire européen relatif aux substances existantes (ESR). Depuis la publication du premier document de fond, une évaluation des risques suscités par le xylène musqué a été réalisée, et des évaluations des risques sont en cours pour les autres muscs. L'évaluation des risques pour le milieu marin, dont il est fait état dans le présent document, profite des travaux ainsi en cours. Il est également clair que la publicité négative a abouti à une baisse de la consommation des muscs polycycliques et du xylène musqué dans certains produits, en particulier en Europe du nord. Des représentants des nitromuscs et des muscs polycycliques ont été décelés dans des échantillons prélevés dans l'environnement, ainsi que dans le lait et les tissus humains, quoique l'on ait signalé des tendances à la baisse des teneurs de certains muscs synthétiques dans certains médias environnementaux.

Le xylène musqué est considéré comme une substance PBT candidate. Un test de dégradabilité dans le milieu marin est effectué à l'heure actuelle dans le contexte du processus ESR. Bien que ces travaux soient en cours, la conclusion initiale de l'évaluation des risques dans le milieu marin est que les risques suscités tant par l'usage industriel du xylène musqué que par ses utilisations par les consommateurs sont faibles. Les autres muscs synthétiques ne répondent pas à un ou plusieurs des critères PBT, et l'évaluation des risques pour le milieu marin indique que le cétone musqué et les muscs polycycliques semblent ne présenter que de faibles risques pour le milieu marin. Toutefois, l'on poursuit l'étude de la toxicité sur le long terme et du devenir environnemental des muscs polycycliques. Les muscs macrocycliques paraissent avoir un profil environnemental plus favorable, ce point devant être confirmé avant qu'on ne puisse les recommander comme substances de substitution.

Bien qu'il faille attendre que l'on ait recueilli de nouveaux renseignements pertinents avant d'aboutir à une conclusion finale sur le choix des actions, les actions suivantes sont d'ores et déjà considérées comme justifiées : favoriser le remplacement du xylène musqué par des substances de substitution présentant un profil environnemental plus favorable ; presser l'Association Internationale des Parfums de remplir l'engagement qu'elle a contracté de notifier les volumes de la consommation des divers ingrédients musqués dans les parfums ; encourager les Parties contractantes, les fédérations de l'industrie et les entreprises individuelles à étudier et à évaluer des substituts possibles, ainsi qu'à favoriser leur utilisation lorsque le profil de risque est favorable ; décourager l'utilisation ou la promotion des muscs polycycliques comme remplacements du xylène musqué ; réévaluer les risques présentés par l'utilisation, par les consommateurs, du xylène musqué et des muscs polycycliques lorsque de nouveaux renseignements auront été recueillis grâce aux programmes de recherche en cours. Si le statut PBT du xylène musqué est confirmé dans l'Union européenne, il conviendrait qu'OSPAR recommande à l'Union européenne d'étudier la nécessité de prendre des mesures de lutte visant le xylène musqué, mesures aboutissant à la cessation de sa commercialisation et de son utilisation, et qu'elle invite les Parties contractantes qui ne sont pas des membres de l'Union européenne à appliquer des mesures analogues.

Introduction

Musk ingredients are substances with a typical musky scent, which determines largely the odour of a product. They are important for the fragrance industry and are widely used in cosmetics, detergents, fabric softeners, cleaning products and other household products.

The synthetic musks are generally divided into three groups of substances with similar substantive properties but otherwise completely different chemical structure: nitromusks, polycyclic musks and macrocyclic musks. Musk xylene, which was identified at OSPAR/MMC 1998 for priority action belongs to the group of nitromusks. Three other nitromusks belong to this group: musk ketone, muskene and musk tibetene. Products of more commercial interest are the polycyclic musks (HHCB, ADBI, AHTN, AITI and AHMI). Some macrocyclic musks (e.g. cyclopentadecanolide, ethylenebrassyilat) are also included in this review because these substances have to be considered as possible substitutes for musk xylene. AHTN and HHCB represent about 95% of the market.

Due to their dispersive use and the relatively low rate of degradation, representatives of the nitromusks and polycyclic musk ingredients have been detected in environmental samples and human milk and tissue. These findings have prompted activities in different countries and national and international fora, resulting in the compilation and assessment of the data on musk ingredients in several review articles and reports. At the request of the Ministry of Environment, Space Planning and Housing (VROM), the Dutch National Institute of Public Health and the Environment (RIVM) carried out an environmental risk assessment for the European usage of musk xylene and musk ketone (RIVM, 1996) and of the two most used polycyclic musks AHTN and HHCB (RIVM, 1997). Refined versions of these assessments were published later (Tas *et al.*, 1997; Balk and Ford, 1999a,b). As these four substances were listed as Priority Substances, more extensive risk assessments were performed within the scope of the Existing Substances Regulation.

The papers mentioned above, including the risk assessment reports and some specific papers on the environmental occurrence were the basis for the revision of the first OSPAR Background Document. Existing data compilations and assessments have been supplemented by information made available by the International Fragrance Association (IFRA), and by other easily accessible data. Additional and partially unpublished monitoring data have also been included. Results from existing assessments based on internationally accepted rules were not re-evaluated and taken on board unchanged in this background document, unless new information and findings differed considerably from the data already assessed.

1. Identification of the Sources of Musks and their Pathways to the Marine Environment

1.1 Characterisation of musks

Nitromusks and polycyclic musks are low-cost fragrance ingredients with a musky odour. Musks are important ingredients for the fragrance industry, not only because of their typical and unique smell which determines the odour of a product to a great extent. In addition, some of them have a positive effect on the quality of a fragrance. They make it more balanced and longer lasting because of their ability to bind fragrances to fabrics and to the skin, so-called substantive properties. They are used in most fragrances for detergents, cleaning agents and cosmetic products.

The group of macrocyclic musks are macrocyclic ketones or lactones having approximately 15 carbons in their ring structures. The group includes artificial as well as nature-identical members. They are not only found in animals (musk deer: muscone) but also in plants. In contrast to the nitromusks, the macrocyclic musks are more expensive.

Nitromusks and polycyclic musks are important ingredients for the fragrance industry, not only because of their typical and unique smell which determines the odour of a product to a great extent. In addition, some of them have a positive effect on the quality of a fragrance. They make it more balanced and longer lasting because of their ability to bind fragrances to fabrics and to the skin. Macrocyclic musks may have different odour profiles and other stability behaviour.

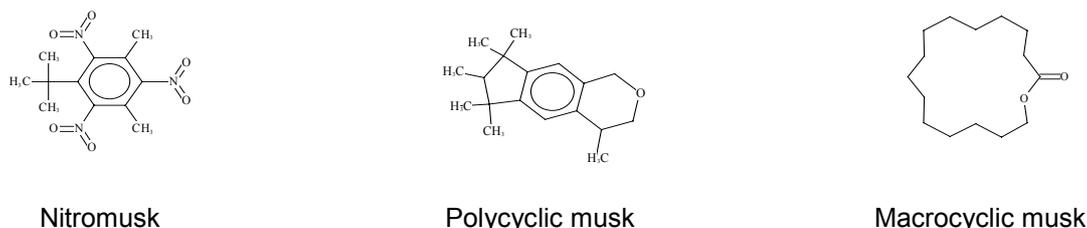


Figure 1. Examples of a nitromusk, a polycyclic musk and a macrocylic musk

The general characteristics of the three groups of musks (see figure 1) are their substantive properties that relate to the lipophilic character and the relatively low volatility. The lipophilic character is reflected in the relatively high log Kow values from 4,3 to 6 and low solubility in water. This property implies a high solubility in organic solvents and tissues and adsorption to organic matter. Whereas in the past chemical stability, i.e. resistance to degradation, was a highly desired property, current requirements are for a fragrance to be stable enough not to change during a consumer product's life time, but biodegradable enough to disappear swiftly once the product has been used (Huber the Nose, 2003). This is where the nitromusks and the polycyclic musks with their lower biodegradation rates differ from the macrocylic musks. The chemical identity, physical chemical properties of the substances are included in Appendix 1.

In standard tests for biodegradation, musk xylene, musk ketone, AHTN, HHCB, ADBI and AHMI were not readily degradable. For AITI no data are available. For musk ketone and musk xylene transformation of the nitro-group was observed and aminometabolites were detected in sewage treatment plants and in fish (Gatermann et al. 2002). For AHTN, HHCB and AHMI the ability to degrade has been shown, for example in soil studies, in a microcosm and in biotransformation studies. Simulation tests and measurements in sewage treatment plants have shown that elimination is caused not only by adsorption to sludge but also by biotransformation and some mineralisation. The decrease in the concentration of the parent compounds coincides with an increase of transformation products. These are more polar metabolites including for example HHCB-lactone and hydroxy acid. The DT50 in an activated sludge system ranged from 12 to 24 hours for AHTN and from 33 to 69 hours for HHCB, whereas the DT50 in river water ranged from 33 to 43 hours for HHCB. In a microcosm test containing river sediment incubated with HHCB, significant amounts of polar metabolites were found and only 4% of the initial HHCB concentration remained. The estimated DT50 was 79 days (Haskoning 2003a,b). Evidence of degradation has also been shown for musk xylene, musk ketone, AHTN and HHCB in fish bioaccumulation studies (EC 2003a,b, Haskoning a,b).

The bioconcentration of musk xylene and musk ketone was determined in well-conducted studies using radio-labelled material (Tas *et al.*, 1997). For musk xylene a bioconcentration factor (BCF) of 1600 was reported based on radio-labelled residue in fish. An important fraction of the residue was more polar than the parent, so the BCF based on parent material will be lower. Other bioconcentration studies are available that showed a number of uncertainties, with BCF ranging from 60 to 5000 (EC 2003a). In spite of the absence of proper documentation, the uncertainties and the unexplained high variability within tests, the Risk Assessment Report for musk xylene, based on a 'weight of evidence' approach, proposes a value of 4400 l/kg to be used.

The bioaccumulation study for musk ketone showed the formation of three polar metabolites. For musk ketone the BCF of 1380 was based on total radio-labelled material including parent material and metabolites. During the accumulation phase between 70 and 100% of the excreted radioactivity may consist of these polar metabolites. The elimination half-life was estimated at 2,2-2,6 days (Tas *et al.* 1997). Hence the uptake of musk ketone is highly reversible.

BCF values for the polycyclic musks are 600 for AHTN and 624 to 1584 for HHCB (Balk and Ford 1999a, Butte and Ewald 1999). Polar metabolites were observed that were rapidly excreted from the fish. The elimination half-lives were between 1 and 3 days. Bioaccumulation ratios under natural conditions are below the BCFs determined in the laboratory (Haskoning 2003a,b).

The high log Kow of the macrocylic musks suggests a high bioaccumulation potential. However, based on the stated ready degradability of these molecules it is expected that they will be biotransformed easily and thus would not accumulate to a great extent.

1.2 Sources of musk xylene and other musks and pathways to the marine environment

Musk fragrance ingredients are used in most fragrance mixtures for detergents, fabric softeners, fabric conditioners, cleaning agents, air fresheners and other household products and in cosmetic products such

as soaps, shampoos and perfumes. Musk xylene is primarily used in detergents and soaps. The principal use of musk ketone is in cosmetics. Many fragrance oils or compounds contain musks; when present, at a concentration of 2-4%. The final concentration of fragrances in detergents and soaps ranges from 0,2 to 1%, in cosmetic products higher levels may be present.

The fragrance ingredients used in washing and cleaning agents and in soaps and shower products are discharged after use via domestic waste water to the sewer and subsequently to a sewage treatment plant. There some part will be removed by adsorption to sludge and biodegradation. The remaining fraction will be discharged with the effluent into the freshwater environment. In the waterways leading to sea, the concentrations will be lowered by dilution, adsorption to organic matter and biodegradation. A smaller fraction will be left on the surface where it was applied and will eventually evaporate or be washed of at a later time.

Other uses are not known. Releases into the environment due to other uses can therefore be excluded.

Nitromusks are not produced in Europe. Formulation (compounding of fragrance mixture) is a possible point source, but does not contribute significantly to the overall diffuse release to the marine environment due to the use of consumer products containing these substances. The production in Europe of AHTN and HHCB is concentrated at one (inland) plant in the EU for each substance.

2. Quantification of Sources

For AHTN as well as for HHCB the production volume is reported to be between 1000 and 5000 tonnes per year. A significant part of the production of AHTN and HHCB is exported as the 'pure substance' outside the EU and also a part of the formulated products (cosmetics as well as detergents and cleaning agents) will be exported. Industry sources estimate that 20 to 30% of their total production is exported as finished fragrance mixture or in consumer products, whereas import volumes are expected to be far below the export volumes.

Data on the consumption of musks fragrance ingredients in Europe have been estimated by the Research Institute for Fragrance Materials (RIFM) for 1992, 1995, 1998 and by the International Fragrance Association (IFRA) for 2000. These data relate to the volumes used in fragrance compounding, i.e. the preparation of mixtures that are used by the formulators of consumer products anywhere. It was not possible to obtain the volumes in consumer products actually sold in Europe. The results are presented in Table 1.

No data are available for the use of macrocyclic musks in Europe. The production was stated to be 3 to 4% of the world production of synthetic musks (Rebmann et al. 1998).

Table 1. European use volume in tonnes (RIFM, IFRA)

	1992	1995	1998	2000
<i>Nitromusks</i>				
Musk xylene	174	110	86	67
Musk ketone	124	61	40	35
Musk moskene		5		¹⁾
Musk tibetene		0,8		¹⁾
<i>Polycyclic musks</i>				
HHCB	2400	1482	1473	1427
AHTN	885	585	385	358
ADBI		34	18	14,9
AHMI		50	19	2,2
AITI		40	2	13,2
<i>Macrocyclic musks</i>				
.....				

¹⁾ no longer included in survey due to their listing in Annex II of the European Cosmetics Directive (IFRA 2002)

Currently, musk ketone, musk xylene, HHCB and AHTN represent about 95% of the market in Europe for all nitromusks and polycyclic musks. No reliable data seem to be available for the time before 1992. Data that have been published vary considerably and are often difficult to interpret. After 1992, an overall decline was observed, whereas between 1995 and 2000 the use of AHTN and HHCB seemed to be more or less stable.

Yet a downward trend is observed in recent environmental concentrations as compared to earlier reports. Due to negative publicity, European-wide brands abstained from polycyclic musks containing fragrances in detergents and cosmetics. This trend was followed by producers of locally marketed products in Northern European countries, whereas in other parts of Europe locally operating producers followed this trend to a lesser extent. However, this trend is not (yet) visible in the reported use volumes for all of Europe. With the use volumes kept at a stable level, for arithmetic reasons, a decreased use volume in the Northern region would imply an *increased* use in the Southern region. In the draft Risk Assessment Report the 'worst case' scenario assumes no use in the Northern region thus the total volume is used in the Southern European countries. An analysis of the consumption of detergents and cosmetics in the EU countries showed that the difference between North and South is a factor of 1,25 at the most (HERA 2002, COLIPA 2001). The combination of the replacement of the materials with the 'cultural' differences leads to a 'worst case' scenario that equals the standard regional scenario of the TGD (using 10% of the European volume) and a 'reasonable estimate' scenario for Northern Europe that is lower by a factor of 5 to 7 (Haskoning 2003a,b). It should be kept in mind, however, that the assumptions underlying the 'worst case' scenario are extreme, i.e. the total volume is consumed only in Southern Europe.

The use of fragrance oils per product category in the EU was summarised by Somogyi et al. (1995), see figure 2. Thus the share of the fragrance ingredients used in products that are discharged to the sewer is estimated at 77%.

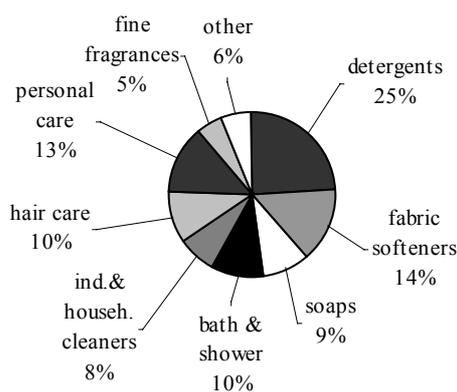


Figure 2. The use of fragrance oils in the European Union.

[figure taken from Balk et al. 2001, ACS Symposium Series 791, p. 171]

As a worst case for the aquatic environment the risk assessment assumed that 100% of the musks used in compounding in Europe is used in consumer products in Europe, and that this 100% is released into the waste water and that no substance remains on the fabric, skin or surfaces or has evaporated.

3. Monitoring data on Discharges, Emissions and Losses

3.1 Aquatic inputs to the marine environment

No data are available on loads of musk xylene and other musks fragrance ingredients entering the OSPAR Convention Waters and the Greater North Sea. As stated above, it is assumed that 100% of the volume used in compounding finds its way to the sewerage, thus to the aquatic environment. Tentative mass balance calculations, however, failed to confirm this. Only a fraction of the reported use volumes could be accounted for in the influents. Apparently the use volume in consumer products or/and the assumption of 100% to wastewater is a conservative approach. With the reported 90 to 95% removal in an STP and ongoing removal from the water phase during its way to the sea, the fraction entering the marine environment will be very low (less than 0,5% of the use volume for HHCB).

3.2 Atmospheric inputs

No data are available on regional atmospheric inputs of musk xylene or other musks but considering the low vapour pressure (see Appendix 1) and the tendency to adsorb to soils and sediments it can be expected that atmospheric concentrations will be extremely low.

In the RARs for AHTN and HHCB, the local emission to air from the production site and the 5 largest compounding sites was estimated based on site-specific data and assumptions. The estimated emission was <69 kg per year for AHTN and <205 kg for HHCB (Haskoning 2003a,b). This is 0,01 – 0,02 % of the reported use volumes.

In a recent study by TNO for Greenpeace, rainwater samples (actually deposition) were taken on 47 locations in The Netherlands, on 2 locations in Germany and 1 in Belgium. Musk xylene was not detected in any of the samples (<2 ng/l). Musk ambrette was detected in 36% of the samples, with a maximum level of 14 ng/l. Musk ketone was found in 4% of the samples, with a maximum of 3,4 ng/l. Musk tibetene was found only once, at 10 ng/l.

HHCB was found in almost all samples with concentrations ranging from 7 to 25 ng/l. AHTN was found in almost all samples; concentrations ranged from < 2 to 19 ng/l. ADBI, AHMI and AITI were detected in 0 to 4% of the samples (maxima < 2 to 4,5 ng/l) (Peters 2003). Using the prediction by EUSES of the total deposition flux for HHCB in an area with 700 mm of rainfall gives a concentration of 8 ng/l in rainwater, thus falling right in the observed range.

With 700 mm of rain per year and an average concentration of 10 ng/l rainwater, 280 kg would precipitate per year in a region of 200 * 200 km² as defined by the EU TGD (EC 2003c).

Musk xylene and musk ketone were shown to be rapidly photodegradable under laboratory conditions. Outdoor rates were lower (Butte et al. 1999). The predicted half-lives in the atmosphere (with $0,5 * 10^6 \text{ cm}^{-3}$ and a photoperiod of 24h) is 19 and 12,5 days for musk xylene and musk ketone (AOPWin programme, SRC). Experiments for HHCB and some similar structures showed that the rate constants for the gas phase reactions were accurately predicted by the AOPWin programme (Ashmann et al. 2001). With half-lives of 10 and 20 hours for HHCB and AHTN, respectively, polycyclic musks released to the atmosphere are likely to be degraded rapidly by reaction with hydroxyl radicals. With this short lifetime in the atmosphere, these substances are unlikely to be transported over a long distance from its point of emission and therefore concentrations due to atmospheric washout by precipitation from the atmosphere are likely to be greatest near the point of emission. This is illustrated by the contour plot for AHTN that showed slightly increased concentrations downwind of the production plant.

3.3 Concentrations in the marine environment (and other waters)

A compilation of measured concentrations of the various musk fragrance ingredients in various environmental compartments was given in Annex 1 of OSPAR (2000). Data from studies carried out in the marine environment as well as studies carried out recently in the freshwater environment will be summarised here.

3.3.1 Water, suspended matter and sediment

Samples were taken in the North Sea, in the German Bight, in 1993, 10 m below the water surface. For 15 of the 33 both musk xylene and musk ketone were at or below the detection limit (0,03 and 0,02 ng/l). Musk ketone was not detected in 23 of the 33 samples. Musk ketone was found in concentrations up to 0,08 ng/l (90th-percentile: 0,05 ng/l) and musk xylene up to 0,17 ng/l (90th-percentile: 0,12 ng/l) (Gatermann et al., 1995). In the same area samples were taken from a depth of 5 m at 7 stations in 1990 and 1995 to determine the concentrations of AHTN and HHCB. The concentrations of HHCB were 0,26 ng/l (median value) and those of AHTN 0,2 ng/l (median value). Maximum concentrations encountered at sea were 2,6 and 4,8 ng/l for AHTN and HHCB, respectively. Decreasing values (0,09 ng/l) towards the northern and north-western stations in the German Bight illustrate the increasing dilution in marine waters. The sharp drop of concentrations in the mouth of the estuary may be attributed to sedimentation processes in this zone (Bester et al. 1998). No other musk ingredients have been reported. Results from samples taken after 1995 are not available.

More data are available for the freshwater catchment areas. The concentrations are highly variable, with higher concentrations clearly related to samples in close proximity to STP discharge points. Data were available from Germany, Switzerland and The Netherlands (OSPAR 2000). For musk ketone the median and 90th-percentile of the combination of over 200 samples were < 0,005 and 0,04 µg/l. The concentrations for Musk xylene were even lower than for musk ketone, with the median below the detection limit (Balk et al. 2001). The amino-metabolites of musk xylene and musk ketone were also detected in surface waters, mostly

in levels of the same order of magnitude as the parent substance. Some extremely high concentrations of both nitromusks and polycyclic musks were observed in surface waters in Berlin where a high proportion of the flow consists of sewage treatment effluents (data from 1996-1997, Heberer et al. 1999, Fromme et al. 2001a).

The results of more recent monitoring activities are summarised in Table 2 and Table 3. In the UK concentrations were determined in the Aire Basin in 2000 (Sabaliunas et al. 2001). In Hessen, in Germany an extensive monitoring programme was carried out in the catchment of the River Main. Surface water samples were taken on 20 sites in rivers in 1999 and 2000. From 1996 to 2000, concentrations in suspended matter were analysed once per year in 17 samples from rivers. The concentrations for musk ketone, AHTN and HHCB clearly show a downward trend. The other nitromusks and polycyclic musks were included in the programme but they were always below the detection limits. Samples were also taken of suspended matter from 12 brooks with a high effluent input. In some of these brooks also sediment samples were analysed. The same downward trend was observed. The highest level of the minor polycyclic musks in the sediment (1999) was 0,033 mg/kg, whereas in the suspended solids it was up to 0,160 mg/kg, roughly a factor of 20 or more below the levels of AHTN and HHCB (HLUG 2001).

A comparison was made of the concentrations of AHTN and HHCB found in surface water samples taken before 1995 (n=96) and after 1996 (n=122 for AHTN and n=152 for HHCB). The 90th-percentile concentrations decreased from 0,20 to 0,14 µg/l for AHTN and from 0,50 to 0,26 µg/l for HHCB (Haskoning 2003a,b).

Table 2. Concentrations in surface water reported after OSPAR (2000)

Location	Year	Subst.	Concentration (µg/l)	Reference
<i>Surface water</i>				
UK, Yorkshire, Aire Basin	2000	MX	0,002 (upstream of STP)	Sabaliunas et al. 2001
			0,007 (downstream) – 0,003 (3,5 km downstream)	
		MK	0,002 (upstream of STP)	
			0,024 (downstream) – 0,017 (3,5 km downstream)	
Germany, Hessen	1999 – 2000	MX	all samples < 0,02	HLUG 2001
		MK	80% of samples < 0,02, max 0,04	
		AHTN	median 0,05, 90th-perc. 0,17	
		HHCB	median 0,15, 90th-perc. 0,46	
Germany, Main	1998	HHCB	median 0,10, 90th-perc. 0,20	Klasmeier et al. 2001

Table 3. Concentrations in suspended matter and sediment reported after OSPAR (2000)

Location	Year	Subst.	Concentration (mg/kg)	Reference
<i>Suspended matter</i>				
Germany, Hessen	1994-2000	MX	max. decreasing from 0,014 to 0,06	HLUG 2001
		MK	max. decreasing from 0,454 to 0,056, median from 0,150 to 0,008	
	1996-2000	AHTN	median decreasing from 0,29 to 0,11, max. from 0,85 to 0,26	
		HHCB	median decreasing from 0,27 to 0,15, max. from 1,13 to 0,39	
	1996-2000	AHTN	in contaminated brooks, ranges 0,54-12,7 in 1996 to 0,6 – 0,97 in 2000	
	1996-2000	HHCB	in contaminated brooks, ranges 0,9-13,7 in 1996 to 0,7 – 1,1 in 2000	

Location	Year	Subst.	Concentration (mg/kg)	Reference
<i>Sediment</i>				
Germany, Hessen	1995-1999	MK	in contaminated brooks (downward) 0,033 – 0,007	
	1996-1999	AHTN	in contaminated brooks (downward) 4,8 – 0,7	
		HHCB	in contaminated brooks (downward) 4,9 – 0,6	
Germany, Berlin	1996-1997	AHTN	median low: 0,2; moderate: 0,24; high: 0,93, 90-perc. 2,21	Fromme et al. 2001
		HHCB	median low: <dl; moderate: 0,23; high: 0,91, 90-perc. 1,90	

3.3.2 Sewage treatment plants

The downward trend in time in surface waters is related to the downward trend observed in (total) effluent and sludge concentrations, see Table 4 and Table 5. Since OSPAR (2000) samples of influent and effluent were analysed from Austria, Switzerland, Germany, The Netherlands and UK. In Hessen, Germany, concentrations on sludge were monitored in 9 STPs from 1994 to 2000, and effluents were analysed in 1999 and 2000. The effluent concentrations in Hessen in the year 2000 were below the detection limit (< 0,02 µg/l) for musk xylene. This is below the median of 0,12 µg/l reported by Eschke et al (1995) by a factor of 6 at least. For musk ketone, AHTN and HHCB the decrease is a factor of 10, 5 and 2, respectively.

In Wien, Austria, samples were taken on 4 consecutive days in 1999. Musk ketone was detected in the influent as well as in the effluent of a pilot plant, musk xylene only in the influent. The other nitromusks were not detectable (Hohenblum et al. 2000). Samples taken in Switzerland in 1997 from three STP effluents showed only musk ketone to be detectable, whereas the other nitromusks were below the detection limit. For the polycyclic musks study the effluents of 6 STP were analysed. Again the concentrations of the minor polycyclic musks ADBI, AHMI and AITI were below AHTN and HHCB by a factor of circa 20 (Noser et al. 1999). As compared to those data, the results of the samples taken 5 years later by Brändli et al. (2002) had decreased by a factor of 3 or more.

Samples taken in six STPs in the UK were analysed for nitromusks and polycyclic musks. Musk ambrette, musk moskene, musk tibetene were not detected in the influents. The minor musks ADBI, AHMI and AITI were detected only occasionally (Kanda et al. 2003). Samples of three STPs in the UK were also analysed by Simonich et al. (2002). Musk xylene was detected in a more narrow range in the influents, the maximum being lower by an order of magnitude. The levels of Musk ketone, AHTN and HHCB reported by Simonich et al. (2002) were at the same levels as with Kanda et al. (2003). Overall the data suggest that the use in the UK is higher than on the mainland of N-Europe.

Simonich et al. (2002) also reported on the concentrations in two STPs in The Netherlands. The effluent levels of musk xylene and musk ketone were below or at the detection levels. The effluent concentrations of AHTN and HHCB correspond nicely with those reported by Artola (2002).

For the first time data were reported for Southern Europe. García-Jones et al. (2002) reported recent effluent concentrations from Spain that were at the same low level as for Northern European countries.

Table 4. Concentrations in influents and effluents of sewage treatment plants reported after OSPAR (2000)

Location	Year	Substance	Concentration (µg/l)		Reference
			Influent	Effluent	
<i>Influent/effluent</i>			<i>Influent</i>	<i>Effluent</i>	
Germany, Hessen	1999-2000	MX		< 0,02	HLUG 2001
		MK		median 0,07, 90-perc. 0,09	
		AHTN		median 0,4, 90-perc. 0,6	
		HHCB		median 1,1, 90-perc. 1,6	
Austria	1999	MX	0,023 – 0,037	< 0,01	Hohenblum et al. 2000
		MK	0,049 – 0,069	0,038 – 0,053	
Switzerland	1997	MX		< 0,025	Noser et al. 1999
		MK		0,1 – 0,15	
		AHTN		1,4 – 2,4	
		HHCB		1,9 – 3,4	
		ADBI		0,055 – 0,14	
		AHMI		0,09 – 0,12	
		AITI		0,03 – 0,06	
Switzerland	2002	AHTN	mean 1,5, max. 1,5	mean 0,2, max. 0,3	Brändli et al. 2002
		HHCB	mean 4,5, max. 6,9	mean 0,8, max. 1,1	
The Netherlands	2001	AHTN	median 1,3, max. 1,8	median 0,7, max. 1,2	Artola 2002
		HHCB	median 3,4, max. 4,3	median 1,6, max. 2,2	
UK	1999-2000	MX	0,2 – 0,5	0,01 – 0,17	Simonich et al. 2002 and (*) pers. comm.
		MK	0,4 – 2,5	0,04 – 0,2	
		AHTN	3,7 – 13,2	0,6 – 2,7	
		HHCB	9,1 – 17,6	1 – 4,6	
The Netherlands	1999	MX	0,1	0,01	
		MK	0,63 – 0,8	< d.l. (*)	
		AHTN	2,4 – 3,9	1,2	
		HHCB	3,2 – 5,9	1	
UK	2001	MX	< 0,01 – 4,7	< 0,01 - 0,65	Kanda et al. 2003
		MK	< 0,01 – 2,0	< 0,01 – 0,71	
		AHTN	2,2 – 8,1	0,46 – 2,7	
		HHCB	7,8 – 19,2	1,3 – 6,4	
		ADBI	< 0,01 – 0,44	< 0,01 – 0,09	
		AHMI	< 0,01 – 0,10	< 0,01 – 0,05	
		AITI	< 0,01 – 2,9	< 0,01 – 0,79	
Spain	200X	AHTN		0,15	García-Jares et al. 2002
		HHCB		0,5	
		ADBI		0,01	
		AHMI		0,006	
		AITI		0,015	
		Ambrettolide		not detected	

Concentrations in activated or wasted sludge (with or without digestion) are given in Table 5. Long-year series are available from Hessen, Germany, showing that the concentrations are steadily decreasing over the years. However, where initially musk ketone was observed in sludge from 2 out of 9 STPs, in 1999 and 2000 it was detected in 8 and 5 of the 9 STPs, respectively. The polycyclic musks were detected in all samples.

Concentrations in Berlin (1997) seemed to be in the same range as for Hessen (Heberer et al. 2002). Concentrations found recently in sludge in the UK show a wide variety but they tend to be higher than on the European mainland, as for the effluents.

Table 5. Concentrations in wasted sludge of sewage treatment plants reported after OSPAR (2000)

Location	Year	Subst.	Concentration (mg/kg)	Reference
<i>Sludge</i>				
UK	200X	AHTN	median 4, range 0,12 – 16	Stevens et al. 2002
		HHCB	median 26, range 1,9 – 81	
		ADBI	median 0,035, range 0,01 – 0,26	
		AHMI	median 0,39, range 0,03 – 1,1	
		AITI	median 0,45, range 0,044 – 1,1	
Germany, Hessen	1994-2000	MX	< 0,01	HLUG 2001
		MK	median 0,54 decreasing to 0,144	
	1996 - 2000	AHTN	median 15,0, range 12,0 – 20,1 decreasing to median 4,2, range 2,9 – 6,1	
		HHCB	median 17,1, range 11,9 – 21,6 decreasing to median 6,7, range 4,3 – 8,6	
	1999-2000	ADBI	median 0,19 – 0,16	
		AHMI	median 0,49 – 0,32	
AITI		median 0,69 – 0,51		
Germany, Berlin	1997	AHTN	up to 5,1	Heberer et al. 2002
		HHCB	up to 11,4	

The generally observed decrease in time of the concentrations in the environmental compartments is illustrated in figure 3 with data from Hessen, in Germany. The concentrations in sludge and suspended matter decreased by a factor of 3 to 4 for AHTN and 2 to 3 for HHCB (note the logarithmic scale). Concentrations in sludge are directly reflecting the decreasing input of AHTN and HHCB to the sewer systems over the years. It is remarkable that not only the concentrations in suspended solids and surface water follow the downward trend but this trend was also directly observed in the sediment (Haskoning 2003a,b, based on data of HLUG 2001). The data summarised above show that this decrease is also observed, but not documented as completely, in other regions of North-western Europe.

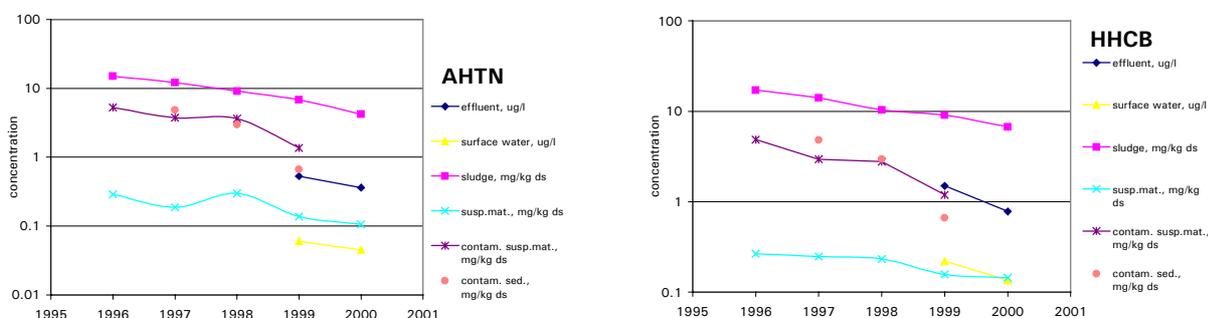


Figure 3. Trend in the median concentrations of AHTN and HHCB in various environmental compartments, Hessen, Germany (Haskoning 2003a,b, based on data from HLUG 2001) (Note: Logarithmic scale)

3.3.4 Aquatic biota

For the 4 main musk ingredients many data are available, and many were already summarised in OSPAR (2000). Concentrations in fish are reported from areas with high effluent input and from more remote regions in freshwater systems as well as from the North Sea and from the Norwegian Coast. By far the highest concentrations of AHTN and HHCB were observed in the areas classified as 'high effluent input areas' (virtually no dilution) in Berlin, Germany. These levels are of the order of magnitude of those found in fish reared in effluent ponds by Eschke et al. (1995) and Rimkus (1999). The overall median of 396 fish in Germany (including Berlin), The Netherlands, and Italy is at the level of the detection limit for some studies (< 0,02 mg/kg fw). In view of the extreme conditions in some surface waters in Berlin, the data set was analysed separately. The 90th-percentile for fish from Berlin was 0,57 mg/kg for AHTN and 1,5 mg/kg for HHCB. For the other regions, the 90th-percentile was 0,1 mg/kg for both substances.

In the Czech Republic, fish were sampled from three rivers, each year between 1997 and 2000. Almost 800 samples of five species were analysed. Concentrations were expressed based on lipid contents only (Hajslova, pers. comm. 2001). The concentrations seem to be at the same level as those for fish in the low/medium effluent input area in Berlin. The time trend observed from various compartments in Northern Europe is not detected in this extensive series of samples taken outside of the EU. Table 6 shows the range of the median concentrations per species and per river system. The 90th-percentile in the table is the highest 90th-percentile of the three rivers.

In Norway a total of 10 pooled Atlantic cod liver samples (*Gadus morhua*) was collected from harbours, fjords and the open coast, winter 1997/1998. The samples were collected in recipients for industrial and municipal wastewater, in the vicinity of densely populated areas. Fifteen fish samples were taken from two inner harbours in 1999. Concentrations were estimated in liver and filet and expressed on the basis of the lipid content. With the lipid contents given in the paper the figures were recalculated to freshwater concentrations. Musk xylene and musk ketone were detected in half of the samples (Atlantic cod samples taken from the Oslo fjord), whereas AHTN was detected in two-thirds of the samples and HHCB in 90%. HHCB-lactone was detected at variable concentrations, sometimes up to the same level as the parent HHCB. AITI was also detected, at a level of a factor of circa 5 to 10 below the levels of AHTN (Kallenborn et al. 2002). The concentrations in liver are above those in filet by an order of magnitude or more.

The concentrations of musk xylene, musk ketone, AHTN, HHCB and HHCB-lactone and AITI were determined in Canadian and Arctic samples of Ringed Seal blubber, Arctic Char, Blue Mussels and Lake Trout. The values for AHTN were not reliable due to matrix co-elution problems. The concentrations of musk xylene, musk ketone and AITI were below the limit of detection except in Lake Trout. The concentration of AHTN in the Char, Blue Mussels and Trout seemed to be elevated as compared to the background, whereas the concentration in the Ringed Seal was at the background level. The concentrations of HHCB and HHCB-lactone in Trout seemed to be elevated, but the concentrations in Char, Mussels and in Ringed Seal blubber were at/below the background level. The HHCB-lactone level was higher than HHCB by a factor of 2 (Hühnerfuss et al. 2002). There is no indication for biomagnification.

Table 6. Concentrations in fish reported after OSPAR (2000)

Location	Year	Subst.	Concentration	Reference
Czech Republic (mg/kg lipids) (789 fish)	1997 - 2000	MX	Chub: median 0,03 – 0,53 90-perc. 0,68 Bream: median 0,08 – 0,83 90-perc. 1,8 Barbel: median 0,06 – 1,88 90-perc. 2,3 Perch: median 0,11 – 0,52 90-perc. 0,55 Trout: median 0,08 – 1,74 90-perc. 2,0	Hajslova et al. 1998, Hajslova 2002
		MK	Chub: median 0,03 – 0,23 90-perc. 0,24 Bream: median 0,06 – 0,32 90-perc. 0,74 Barbel: median 0,05 – 0,58 90-perc. 0,86 Perch: median 0,09 – 0,26 90-perc. 0,33 Trout: median 0,06 – 0,22 90-perc. 0,28	
		AHTN	Chub: median 0,6 – 2,4 90-perc. 2,9 Bream: median 0,9 – 3,5 90-perc. 9,5 Barbel: median 0,5 – 11,4 90-perc. 14,3 Perch: median 0,4 – 3,7 90-perc. 3,8 Trout: median 0,3 – 3,1 90-perc. 3,4	
		HHCB	Chub: median 0,4 – 2,7 90-perc. 3,4 Bream: median 1,2 – 8,4 90-perc. 9,3 Barbel: median 0,3 – 10,8 90-perc. 12,6 Perch: median 0,4 – 5,8 90-perc. 9,5 Trout: median 0,3 – 2,2 90-perc. 2,8	
		ADBI	Chub: median 0,02 – 0,11 90-perc. 0,12 Bream: median 0,02 – 0 11 90-perc. 0,21 Barbel: median 0,01 – 0,10 90-perc. 0,11 Perch: median 0,04 – 0,28 90-perc. 0,37 Trout: median 0,03 – 0,11 90-perc. 0,15	
		AHMI	Chub: median 0,04 – 0,22 90-perc. 0,26 Bream: median 0,07 – 0,30 90-perc. 1,08 Barbel: median 0,14 – 0,41 90-perc. 0,51 Perch: median 0,08 – 2,36 90-perc. 0,54 Trout: median 0,06 – 0,20 90-perc. 0,24	
		AITI	Chub: median 0,02 – 0,12 90-perc. 0,12 Bream: median 0,04 – 0,11 90-perc. 0,50 Barbel: median 0,04 – 0,11 90-perc. 0,24 Perch: median 0,04 – 0,29 90-perc. 0,36 Trout: median 0,04 – 0,07 90-perc. 0,13	
Germany, Berlin (mg/kg fresh weight) (165 fish)	1996- 1997	AHTN	Eel: median: low < dl; mod. 0,032; high 0,668 Perch: median: low/mod. < dl; high 0,047 Common bream: low/mod. < dl; high 0,324 Roach: median: low/mod. < dl; high 0,064 Pike: median: < dl; high 0,05 Pike perch: low/mod. < dl; high 0,037 Maximum 0,362	Fromme et al. 2001b
Germany, Berlin (mg/kg fresh weight) (165 fish) (cont.)		HHCB	Eel: median: low 0,050; mod. 0,077; high 1,47 Perch: median: low/mod. < dl; high 0,20 Common bream: low/mod. 0,04; high 1,57 Roach: median: low/mod. < dl; high 0,17 Pike: median: < dl; high 0,37 Pike perch: low/mod. < dl; high 0,19 Maximum 384	

Location	Year	Subst.	Concentration	Reference
Norway, coast high effluent input areas (mg/kg fresh weight) (25 fish)	1997- 1998	MX	9 of 18 samples < dl Cod liver from Oslo Fjord mean 0,019, max 0,034	Kallenborn et al. 2002
		MK	9 of 16 samples < dl Cod liver from Oslo Fjord mean 0,010, max 0,015	
		AHTN	Thornback ray filet: 0,0008 Haddock filet: mean 0,001, max 0,002 Atlantic cod filet: mean 0,002, max 0,003 Saithe filet: 0,002 Thornback ray liver: 0,001 Haddock liver: mean 0,016, max 0,023 Atlantic cod liver mean 0,035, max 0,133 Saithe liver: 0,0004	
		HHCB	Thornback ray filet: 0,0006 Haddock filet: mean 0,0016, max 0,002 Atlantic cod filet: mean 0,007, max 0,008 Saithe filet: 0,005 Thornback ray liver: 0,008 Haddock liver: mean 0,162, max 0,25 Atlantic cod liver mean 0,098, max 0,53 Saithe liver: 0,003	
		AITI	Thornback ray filet: 0,0001 Haddock filet: mean 0,0002, max 0,0003 Atlantic cod filet: mean 0,0002, max 0,0005 Saithe filet: 0,0003 Thornback ray liver: 0,0008 Haddock liver: mean 0,0094, max 0,173 Atlantic cod liver mean 0,0028, max 0,0087 Saithe liver: 0,0004	

4. Assessment of the extent of the problem

4.1 Introduction

In order to assess the extent of the problem, the marine risk assessment was carried out based on the EU Technical Guidance Document (EC 2003c). This involved two steps. Firstly, the preparation of a PBT assessment to ascertain whether a substance is so hazardous that measures should be developed solely on the basis of the information available on sources and pathways to the marine environment. This was followed by the risk assessment approach where the predicted environmental concentrations were compared with the predicted no effect concentrations to give PEC/PNEC ratios. The details of the marine risk assessment are given in Appendix 2 of this document. The marine risk assessment draws heavily on data and information in the RARs for musk xylene and musk ketone (EC 2003a,b) and the draft RARs for AHTN and HHCB, which will be published in due course when they have been finalised.¹ It is clear that the marine risk assessment would be improved with the provision of more specific information.

4.2 PBT Assessment

The classification of musk xylene and other musks against the EC Technical Guidance Document draft PBT criteria is presented in Appendix 2. The results are summarised in Table 7. AHTN and HHCB were evaluated by the ECB in the TM Subgroup on identification of PBT and vPvB substances.

¹ Current estimates are that it will take at least another year to complete the necessary investigations on exposure and effects and finalise the RARs for AHTN and HHCB.

Table 7. Evaluation of the PBT criteria

Substance	Evaluation P	Evaluation B	Evaluation T
Musk xylene	P or VP ¹⁾	B	T
Musk ketone	P or VP	not B	no decision yet on CMR status
AHTN	Potentially P	not B	not T
HHCB	Potentially P	not B	not T
Macrocyclic musks	not P		no data

¹⁾ A degradation study in the marine environment is in preparation

Musk xylene is considered as a PBT candidate substance. Following the decision of the Technical Meeting, and according to Commission Regulation (EC) No. 67/548 a test on the degradability in the marine environment will be carried out. For the time being it is taken into account that degradability within a reasonable time span might be proven, so a marine risk assessment for musk xylene is still included in the next section.

The other substances musk ketone, AHTN and HHCB do not meet one or more of the PBT-criteria of the EU Technical Guidance Document (see also Appendix 3). It is anticipated that, by analogy, ADBI, AHMI and AITI are also not fulfilling the criteria for the selection as a PBT-candidate substance. In view of their ready biodegradability, the macrocyclic musks are no PBT candidate substances.

4.3 PEC/PNEC ratios for the local marine risk assessment

The PEC/PNEC ratios for the marine risk assessment are given below in Table 8. The PEC/PNEC ratios are for the local environment. For details of the derivation of the PECs and PNECs, see Appendix 2.

Table 8. Estimated PEC/PNEC ratios for musk xylene and other musks for the marine risk assessment for consumer use

Formulation	local PEC/PNEC seawater	PEC/PNEC predator	PEC/PNEC top-predator
Musk xylene			
TGD ('worst case' 10% regional use)	0,87	0,5	0,5
Musk ketone			
TGD ('worst case' 10% regional use)	0,11	0,2	0,07
AHTN			
'Worst case' 10% regional use	0,04	0,006	0,003
'Typical case' N-Europe	0,02	0,002	0,001
HHCB			
'Worst case' 10% regional use	0,06	0,014	0,008
'Typical case' N-Europe	0,02	0,004	0,005

Table 9. Estimated PEC/PNEC ratios for musk xylene and other musks for the marine risk assessment for industrial use

Formulation	local PEC/PNEC seawater	PEC/PNEC predator	PEC/PNEC top-predator
Musk xylene			
End Product Formulator	0,25	0,20	0,33
Musk ketone			
End Product Formulator	0,03	0,06	0,05
AHTN			
Medium/large Compounder	0,91	0,10	0,022
Small Compounder	0,18	0,02	0,01
Large End Product Formulator	0,42	0,05	0,01
Small End Product Formulator	0,17	0,02	0,01
HHCB			
Medium/large Compounder	0,54	0,09	0,02
Small Compounder	0,14	0,03	0,01
Large End Product Formulator	0,20	0,04	0,01
Small End Product Formulator	0,37	0,06	0,02

4.4 Conclusion of the Risk Assessment for the Marine Compartment

For musk xylene the risk assessment shows that the PEC/PNEC ratios for industrial use (compounding and formulation) as well for consumer use are all below 1. The risk assessment is based on conservative scenarios and assumption and no use is made of the much lower measured concentrations to refine the estimation. However, with the low risk ratios there is no need for further refinement.

For the potential substitutes musk ketone, AHTN and HHCB the PEC/PNEC ratios are also below 1. Even with the generic emission scenario assuming that industrial effluents are not treated in a municipal biological STP but discharged directly into the marine environment, the local PEC/PNEC ratios indicate a low risk.

The most relevant emission scenario is the scenario for use in consumer products. The consumer use of AHTN and HHCB gives PEC/PNEC ratios below 0,1 for marine water organisms and at or below 0,01 for predators and top predators. It is concluded that the risk for food chain effects in the marine environment (secondary poisoning) is very low.

The risks for sediment organisms could not be assessed as no empirical data are available on concentrations in marine sediments nor on the toxicity to sediment organisms. Recently industry initiated a programme to generate sediment concentrations and sediment toxicity data for AHTN and HHCB in the freshwater environment. The results might help to evaluate the risks of these substances for the marine sediment system.

In the EU Risk Assessment Report musk xylene was classified as a PBT-candidate according to the EU Technical Guidance Document. A programme is in development to study the degradation in the marine environment. The concentrations in current environmental samples already show a decrease to below the present detection levels without any regulatory measures in place.

5. Achieving The Desired Reductions

5.1 OSPAR targets

The OSPAR Strategy with regard to Hazardous Substances sets out that the OSPAR objective with regard to hazardous substances is *"to prevent pollution of the maritime area by continuing to reduce discharges, emissions and losses of hazardous substances, with the ultimate aim of achieving concentrations in the marine environment near background values for naturally occurring substances and close to zero for man-made synthetic substances."*

The timeframe given in the Strategy states that *"every endeavour will be made to move towards the target of cessation of discharges, emissions and losses of hazardous substances of concern by the year 2020."*

At OSPAR 2002, OSPAR adopted guidance on the role of marine risk assessment, which gives, in particular, advice on the urgency of taking measures based on particular PEC/PNEC ratios (Reference number 2002-19). Switzerland has attempted to apply this guidance and reached the following conclusions.

Based on the data currently available, musk xylene is considered as a PBT-candidate substance according to the EC Technical Guidance Document. If the planned degradation study will confirm its persistence, the substance will be of very high concern. In that case the marine risk assessment is used to identify appropriate measures to be taken as an urgent priority (identifying the sources of musk xylene and its pathways to the marine environment) with the target of immediate cessation of emission. However, if the degradation study shows that musk xylene does not meet the PBT-criteria for persistence, it will be considered as an other priority substance covered by OSPAR's strategy on Hazardous Substances according to the criteria of OSPAR Agreement 2001-1. For such chemicals Background Documents should determine the most appropriate measures and the urgency of these measures.

The guidance recognises that where the uncertainties are high in the estimation of risk, this should be taken into account by the Contracting Parties when considering the actions necessary to achieve OSPAR's objectives. In this instance, the estimated PEC/PNEC ratios include high assessment factors due to the lack of reliable information on the emission pathways during the industrial life-cycle stages and the lack of long term toxicity information on marine species.

The estimated PEC/PNEC ratios for the scenarios for local industrial compounding and end-product formulation as well as for consumer use of musk xylene are all below 1. For the major contribution to the environment, consumer use, it is recognised that a default approach was used which is highly conservative and that actual environmental concentrations are at or below the detection limits. Thus actual concentrations are below the predictions by some orders of magnitude. Therefore it is concluded that the risk of musk xylene for the marine environment is low.

For musk ketone as well as for the polycyclic musks AHTN and HHCb the PEC/PNEC ratios are also below 1 and generally close to 0,01. Therefore they could be considered substances requiring action by OSPAR before 2020. Also for musk ketone there is a large distance between the actual concentrations and the predictions. Further refinement based on available measured data could reduce the ratios to below 0,01, rendering them substances requiring action by other stakeholders before 2020. (For musk xylene this is relevant only if the PBT-status is not confirmed.)

It is imperative from OSPAR's point of view that appropriate actions, commensurate with the estimated risks, and taking account of the uncertainties in their estimation, should be taken to achieve the 2020 cessation target.

5.2 OSPAR's role in achieving the desired targets

In order to meet the targets specified in the OSPAR objective and timeframe, it will be necessary to:

- assess the need for further reductions from the various sources and the practicability of such reductions;
- review existing regulations and controls in the light of the need for further reductions;
- decide which organisation is responsible and/or best placed for carrying out detailed assessments and/or implementing controls;
- inform the relevant organisation (if OSPAR sees fit) of the OSPAR Ministerial commitments with regard to hazardous substances and the need for action to address OSPAR concerns;
- set up mechanisms for monitoring the compliance with measures adopted in the relevant forum;
- set up mechanisms to monitor inputs to the marine environment and concentrations in the marine environment and biota to check that levels are falling at a satisfactory rate.

It will be possible, through appropriate assessment and monitoring activities, to consolidate the values obtained in Tables 2 to 6 to determine whether musk xylene (and other musks) occurs in the marine environment at significant levels, and to assess whether the levels are falling due to the implementation of agreed actions, and whether values are approaching near to zero concentrations.

It will be of particular importance to take account of possible actions and monitoring requirements for musk xylene (and other musks) in the EU and other international forums.

6. Identification Of Possible Measures

6.1 Review of Existing OSPAR, EU and National Measures

6.1.1 Measures in OSPAR

Following the adoption of the Background Documents for Hazardous Substances Identified for Priority Action in 2000 (OSPAR 02/7/14, Annex 1), a set of five actions was proposed and they were reviewed several times (latest Feb/March 2002). The actions and the progress of actions have been compiled by the Secretariat as document OSPAR 03/6/13 (June 2003).

6.1.2 Ongoing activities within the European Union

The two main nitromusks musk xylene and musk ketone were included in the Third Priority List in the frame of Council Regulation (EEC) No. 793/93 on the evaluation and control of the risks of existing substances.

In the draft final risk assessment report for musk xylene all aquatic PEC/PNEC ratios are reported to be below 1. For fish eating predators the PEC/PNEC ratios were found to be slightly above 1 based on calculated PECs, but they were overruled by monitoring data. The conclusion for musk xylene was that there is need for further information and/or testing. The conclusion was reached because the substance is considered a PBT candidate chemical. It was decided that a study on its persistency in the marine environment is to be carried out within 18 month after the publication of this decision in the Commission Regulation. In its comments, the CSTEE supported the conclusion with regard to the PBT assessment. In disagreement with the rapporteur the CSTEE suggests that the risk for secondary poisoning should be further considered, taking into account that all calculated PEC/PNEC are above 1, that discharges with no STP are still frequent and that most of the measured concentrations are from countries that already have restricted the use of musk xylene.

The conclusion for musk ketone in the draft final risk assessment report was that there is at present no need for further information and/or testing and no need for risk reduction measures beyond those, which are being applied already. In its comments again the CSTEE disagreed partially with these conclusions.

Following the adoption of the reports on musk xylene and musk ketone by the Technical Meeting within the EU, a SIAR (SIDS initial risk assessment report) is prepared for both substances within the context of the OECD HPV Chemicals Programme, which will be published by the IPCS in due time.

The two main representatives of the polycyclic musks, AHTN and HHCB were included in the Fourth Priority List of the same Regulation. Following discussion of the Draft Risk Assessment Reports between the 'Rapporteur' and the lead companies of the producers in April 2003, a research programme has been agreed to generate monitoring data from specific regions as well as sediment toxicity data. The results will become available in 2004 and will need to be incorporated in the risk assessment reports before they can be brought into the TM for discussion and agreement.

In 2002 the European Chemicals Bureau ECB was commissioned to identify potential PBT substances among the European HPVC and the EU Priority lists from the Existing Substances Regulation. AHTN and HHCB were among the 93 substances identified in this screening exercise. During the TM PBT subgroup meeting in Arona, Italy on 12 - 14 March, 2003 the substances were discussed and both AHTN and HHCB were de-listed from the list of potential PBT/vPvB substances.

In July 1995, the use of musk ambrette was included in the 'list of products cosmetics must not contain' (Annex 2 of Directive 95/34/EEC; 18th amendment of the Cosmetic Directive 76/768/EEC). The same action was taken in 1998 for musk tibetene and moskene (Directive 98/62/EC of 3 September 1998) and for AETT in 2000 (Directive 2000/11/EC of 10 March 2000). Limit concentrations were also introduced for other nitromusks in several cosmetic products. On 1 March 2000 (amendment of 31 January 2000) musk tibetene and moskene were also included in Annex 2 as, due to their low use volumes, industry did not generate the requested information.

6.1.3 National initiatives within some Contracting Parties

In Germany (1993) and in Switzerland (1994), the industry associations responsible for detergents recommended to their member companies not to use musk xylene any more in washing and cleaning agents. So far, no Contracting Party of the OSPAR Convention has taken legally binding measures to restrict the use of musk xylene or other musks in such products.

6.2 Alternatives

One of the guiding principles of the OSPAR Strategy on Hazardous Substances is the principle of substitution (the substitution of hazardous substances by preferably non-hazardous substances where such alternatives are available).

A request was addressed to the manufacturers of consumer products to reduce the amount of these musks in all consumer products that are discharged with wastewater to the lowest level needed for technical reasons. In practice this would involve substitution of these musk fragrance ingredients by other fragrance ingredients with a more favourable environmental profile. It is clear that this process is actually taking place as due to the negative publicity on musks, European wide brands abstained from polycyclic musks containing fragrances in their detergents and cosmetics. Thus the reduction of the use of these substances currently proceeds as an autonomous process without any regulatory pressure.

Substitution of nitromusk and polycyclic musk fragrance ingredients by another substance requires consideration of the following:

- that the substitute is less harmful and poses a lower risk;
- the performance as a base for other fragrance ingredients as well as in the fragrance compositions;
- the price differential between these substances and the musk fragrance ingredients;
- the efficacy of substitutes and the volumes required.

Macrocyclic musks are potential substitutes, but differ technically from the other musks and are less economic. The physicochemical data for the macrocyclic musks indicate that they seem to have a more favourable environmental profile. These substances would need to be investigated further from an environmental point of view to see if they actually pose a lower risk.

On the other hand, the fact that polycyclic musks free consumer products are marketed already shows that substitution has already taken place somehow. Since fragrance compounds are such complex mixtures, replacement of nitromusks or polycyclic musks may be achieved by a variety of ways, including a change of brand-specific odours.

7. Choice for Actions

7.1 Introduction

When considered in the light of the guidance on the role of risk assessment, the results from the marine risk assessment indicate that there should be no concern over the industrial use of musk xylene, musk ketone, AHTN and HHCB, even if trade effluents were locally discharged into the marine environment without proper treatment.

Contrary to the point releases related to the industrial use, the use in consumer products causes a more diffuse emission pattern, probably covering the whole OSPAR Convention area. The risk ratios for the various consumer use scenarios also indicate that there is no reason for concern. This should be taken into account in the evaluation of the substances and the consideration of measures.

Currently, in the context of the risk assessment for the EU Existing Chemicals Regulation, several research activities have been started, including:

- a study on the persistence of musk xylene in the marine environment related to its status as PBT-candidate;
- an extensive monitoring programme to analyse the contents of AHTN and HHCB in samples of:
 - sludge and effluents from 6 STPs each, in Italy and Spain, and 2 STPs in Greece;
 - sludge and effluents from 3 STPs in Berlin;
 - sediments in the Berlin area;
- a study on the long-term toxicity of AHTN and HHCB for three freshwater-sediment species.

The information obtained from these activities is expected to increase the understanding of the environmental behaviour and effects of the musks in general, thereby enabling a further reduction of the uncertainties still included in the marine assessment. It also aims to establish whether there is a difference in use between the northern and the southern regions (which was postulated in one of the use scenarios for private use).

A proper evaluation of the appropriate choices for action can only be made when all relevant information has been collected on the PBT-characterisation for musk xylene and the risk assessment reports for the polycyclic musks AHTN and HHCB within the EU-ESR have been finalised and, if necessary, the relevant risk-reduction scenarios have been developed. Assessment will be required of possible additional measures, examining options against key criteria such as effectiveness, practicability and economic impact. In particular, there needs to be a better understanding of the risks posed by the various substitutes which are available to replace the nitromusks and polycyclic musks. However, the following actions are already thought to be justified.

7.2 Action under OSPAR

Musk xylene is on the OSPAR List of Chemicals for Priority Action. The assessment reviewed in this document leads to the conclusion that the substance has been identified as a PBT-candidate based on the criteria in the EC Technical Guidance Document and that actions have to be taken either immediately or before 2020 at the latest.

The contribution of (industrial) point sources to the emission to the marine environment is considered to be negligible as compared to the diffuse contribution caused by its use in consumer products. Therefore the only option is the substitution of musk xylene in consumer products that are discharged to waste water by another fragrance ingredient to supply the musk odour or by another odour characteristic.

It is observed that in practice the phasing-out process has already started some years ago. OSPAR should continue to promote this process and to contribute to the substitution of musk xylene with substitutes with a more favourable environmental profile by:

- urging the International Fragrance Association (IFRA) to fulfil its reporting commitment on the use volumes of the various musk fragrance ingredients, with a view to ensuring that the volumes used will not increase in future;
- inviting Contracting Parties to negotiate voluntary agreements in their contacts with national associations for detergents industries, to adhere to the AISE Code, to abstain from using persistent ingredients in detergent products and to replace musk xylene by more readily degradable alternatives;
- encouraging Contracting Parties, industry associations and individual companies to study and assess possible substitutes and to promote their use when the risk profile is favourable.

Polycyclic musks should not be promoted as suitable substitutes for nitromusks because, although not actually considered to be PBT-substances according to the criteria of the EC technical guidance document², they have unfavourable characteristics. OSPAR should discourage industry using them, or promoting them as replacements for musk xylene.

Macrocyclic musks appear to have a favourable profile, and to be acceptable alternatives for the time being. But this would need to be confirmed on the basis of results of field studies before they can be recommended as environmentally acceptable substitutes.

OSPAR should re-evaluate the risks posed by the consumer use of musk xylene and the polycyclic musks when further information has been collected in the ongoing research programmes, and any associated measures which might be justified should be addressed through the background document review process.

In case the PBT-status of musk xylene is confirmed within the European Union, OSPAR should recommend the EU to take into consideration the need to take controlling actions on musk xylene leading to the cessation of marketing and use. OSPAR also invites Contracting Parties that are not EU Members to implement similar measures.

² The Risk Assessment Report in the context of the EC Existing Chemicals Regulation is not yet finalised.

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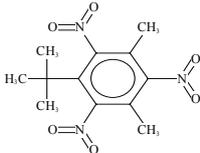
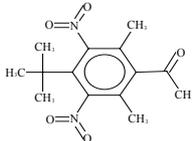
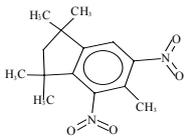
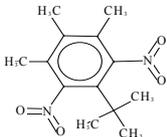
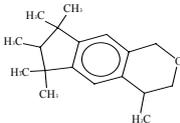
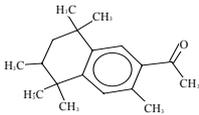
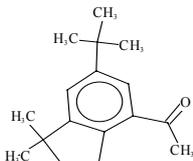
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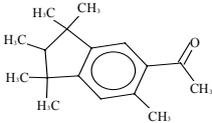
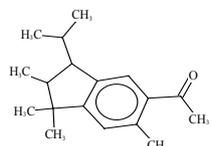
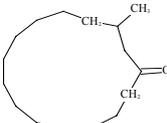
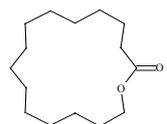
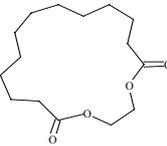
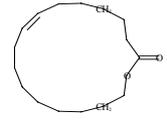
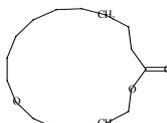
Appendix 1: Identification and summary of physical-chemical data for musk included in this OSPAR Background Document

1. Identification

NM: nitromusk; PCM: polycyclic musk; MCM: macrocyclic musk

Sources: RAR for NM (EC 2003a,b), draft RAR for PCM (Haskoning 2003a,b), OSPAR (2000), for MCM: NIVA (2000), Huber the Nose (2003) and SRC EPI Suite estimation programme.

Common name	CAS-No	Chemical Formula	Chemical Name
Nitromusks			
Musk xylene	81-15-2		1-tert-Butyl-3,5-dimethyl-2,4,6-trinitrobenzene
Musk ketone	81-14-1		4-tert-Butyl-2,6-dimethyl-3,5-dinitroacetophenone
Moskene	116-66-5		1,1,3,3,5-Pentamethyl-4,6-dinitroindane
Musk tibetene	145-39-1		1-tert-Butyl-3,4,5-trimethyl-2,6-dinitrobenzene
Polycyclic musks			
HHCB Galaxolide □ Abbalide	1222-05-5		1,3,4,6,7,8-Hexamethylcyclopenta[γ]-2-benzopyran
AHTN Tonalide □ Fixolide □ Astralide	1506-02-1 and 21145-77-7		6-Acetyl-1,1,2,4,4,7-hexamethyltetralin
ADB1 Celestolide □ Crysolide	13171-00-1		4-Acetyl-6-tert-butyl-1,1-dimethylindane

Common name	CAS-No	Chemical Formula	Chemical Name
AHMI Phantolide □	15323-35-0		6-Acetyl-1,1,2,3,3,5-hexamethylindane
AITI Traseolide	68140-48-7		5-Acetyl-3-isopropyl-1,1,2,6-tetramethylindane
Macrocyclic musks			
Muscone	541-91-3		3-Methyl-cyclopentadecanone
Cyclopentadecanolide ®	106-02-5		Oxacyclohexadecan-2-one
Exaltolide ®			
Pentalide ®			
Thibetolide ®			
Ethylenbrassylat	105-95-3		1,4-Dioxacycloheptadecane-5,17-dione
Musk T ®			
Astratone ®			
Emeressence 1150			
Musk natural (natural musk ambrette)	123-69-3		Oxacycloheptadec-8-en-2-one
Ambrettolid			
Musk R1	3391-83-1		1,7-Dioxacycloheptadecan-8-one

2. Physical-chemical properties

Nitromusks are poorly soluble in water and have relatively high octanol/water partition coefficients. Measured values for the water solubility reported by Schramm *et al.*, 1996 vary from 0,046 for moskene to 0,46 for musk ketone. For moskene and musk tibetene a somewhat higher value of 2 mg/l has also been reported by a manufacturer (Roche, 1985). For musk ketone and musk xylene the water solubility was also calculated (Isnard & Lambert, 1983). The results are similar to the values determined experimentally. The most reliable measured values for log Kow vary from 4,3 (musk ketone) to 5,3 (moskene). Lower log Kow values have also been reported before: 4,4 for moskene and 4,3 for musk tibetene (Roche, 1985), 3,2 for musk ketone (RIFM data) and 3,4 for musk xylene (Johnson *et al.*, 1984). Calculated values for musk ketone and musk xylene are somewhat lower than those determined experimentally but still of the same order.

The polycyclic musks HHCB and AHTN have slightly higher water solubilities and octanol/water partition coefficients than the nitro musks. Measured log Kow values determined for AHTN and HHCB by HPLC are higher than the ones determined by the slow stirring technique (Artola 2002). For ADBI the Kow was measured but only a calculated value is available for water solubility. For AHMI and AITI no empirical data are available at all.

The macrocyclic musks have predicted log Kow values and water solubilities at the same level as the polycyclic musks. Measured values were not obtained.

Table 10. Water solubilities and log Kow used in the RARs of musk xylene, musk ketone, AHTN and HHCB, and reported for other musks

<i>Common name</i>	S (measured) [mg/l]	S (calculated) [mg/l] ¹⁾	log Kow (measured)	log Kow (calculated) ²⁾
Musk xylene	0,15 (EC 2003a)		4,9 (EC 2003a)	
Musk ketone	0,46 (EC 2003b)		4,3 (EC 2003b)	
Moskene	0,046 (Schramm et al. 1996)		5,3 (Givaudan Roure 1996b)	
Musk tibetene	0,052 (Schramm et al. 1996)		5,0 (Givaudan Roure 1996b)	
HHCB	1,75 (Balk and Ford 1999a)	0,19	5,3 (Artola 2002)	
AHTN	1,25 (Balk and Ford 1999a)	0,36	5,4 (Artola 2002)	
ADBI		0,22	5,4 (Balk 1999)	* 5,4
AHMI		0,9		* 4,9
AITI		0,3		* 5,4
Muscone		0,22; 34 #		5,96
Cyclopentadecanolide		0,15; 37,5 #		6,15
Ethylenbrassylat		1,7; 340 #		4,71
Ambrettolid		0,59; 15,7 #		5,37
Musk R1		1,4; 753 #		4,90

¹⁾ SRC WSKOWIN ²⁾ SRC KOWWIN

* SRC LOGKOW v.1,63 using experimental values adjustment (EVA) based on AHTN data

SRC WaterNT Sol (v.1.01 est) from fragments

Table 11. Vapour pressures used in the RARs of musk xylene, musk ketone, AHTN and HHCB, and reported for other musks

<i>Common name</i>	Vapour pressure (Pa)	Source
Musk xylene	0,00003	EC 2003a
Musk ketone	0,00004	EC 2003b
HHCB	0,0608	Balk and Ford 1999a
AHTN	0,0727	Balk and Ford 1999a
AHMI	0,132	PFW 2003

Table 12. Estimation of the probability of biodegradation according to EPIWIN (SRC)

Common name	Biodegradability results					
	BIOWIN 1	BIOWIN 2	BIOWIN 3	BIOWIN 4	BIOWIN 5	BIOWIN 6
Cut-off criterion		<0,5	< 2,2			< 0,5
Muscone	0,6	0,3	2,6	3,48	0,39	0,36
Cyclopentadecanolide	0,8	0,97	2,8	3,7	0,6	0,79
Ethylenbrassylat	0,96	1,0	2,9	3,9	0,85	0,94
Ambrettolid	0,80	0,97	2,78	3,7	0,57	0,69
Musk R1	0,45	0,50	2,76	3,7	0,57	0,68

Cut-off criterion for the PBT assessment: BIOWin 2 or BIOWin 6 < 0,5 AND BIOWin 3 < 2,2

Appendix 2: Marine Risk Assessment

1. Introduction

This section considers the risks to the marine environment from the production, compounding and use of Musk xylene and other musks. The methodology used is based on the marine risk assessment chapter of the TGD (EC 2003c). The draft RARs for AHTN and HHCB include a marine risk assessment (Haskoning 2003a,b). The marine risk assessments for musk xylene and musk ketone were not included in the RAR (EC 2003a,b) so they are prepared for this OSPAR document in the same way as for AHTN and HHCB. The documents on AHTN and HHCB are still under discussion and new monitoring data (freshwater) are currently collected.

2. Exposure assessment

2.1 Derivation of marine PECs

For the assessment of the exposure in the freshwater environment a local exposure assessment is performed for the production of fragrance ingredients, the compounding of fragrance mixtures, the formulation of consumer products and for the consumer use of the end products (private use scenarios). The production of musk xylene and musks ketone does not take place in Europe, whereas AHTN and HHCB are produced each on one location within Europe, but these sites are not located on the coast. The specific compounding sites considered in the RARs are not located on the coast either, so the marine risk assessment is limited to the generic compounding and formulation scenarios. For the compounding of musk xylene and musk ketone a generic scenario was not included in the RAR.

The methodology outlined in the marine risk assessment guidance essentially assumes that the adsorption/desorption, degradation and accumulation behaviour in the marine environment can, in the absence of specific information for the marine environment, be adequately described by the properties of the substance relevant for the freshwater environment.

For substances used for private or public use, discharge via a biological sewage treatment plant can be assumed, so the effluent concentration from the STP (daily flow 2000 m³) is used as a starting point for the assessment. Therefore the $PEC_{local,seawater}$ (dissolved) is simply derived from $C_{effluent}$ with an dilution factor of 100 and a correction for the sorbed fraction.

For the default assessment trade effluents of industrial sites along the coast are not treated in a municipal biological STP. The dilution factor of effluent in the marine environment is 100 (instead of 10 used in the freshwater environment). This implies that the daily emission from a site is diluted in a marine water flow of $2000 * 100 = 200\ 000\ m^3$.

Most of the characteristics of the coastal environment (regional) are similar to the freshwater compartment apart from the suspended matter concentration. The concentration of suspended matter in the local coastal environment is 15 mg/l and in the regional zone it is set to 5 mg/l (instead of 15 mg/l). By default, the mixing of river water into the coastal sea gives a dilution factor of approximately 10. A suitable distribution model to estimate a regional concentration is not (yet) available, so the simple approach is to use $PEC_{regional,seawater} = 0,1 * PEC_{regional,water}$ for conservative chemicals.

For secondary poisoning, the concentrations in predators and top predators are estimated using the following equations from the TGD:

$$PEC_{Coral,predator} = 0,5 * (PEC_{local,seawater} + PEC_{regional,seawater}) * BCF_{fish} * BMF_1$$

$$PEC_{Coral,top\ predator} = (0,1 * PEC_{local,seawater} + 0,9 * PEC_{regional,seawater}) * BCF_{fish} * BMF_1 * BMF_2$$

BMF_1 and BMF_2 are factors to take potential biomagnification into account. Default values for the BMF are determined by the BDF (fish). For musk ketone, AHTN and HHCB, BMF_1 and BMF_2 equal 1, whereas with the higher BCF of 4400 for musk xylene, both factors will be set at 2. The TGD remarks that the derivation of BMFs is to be considered as preliminary for use in screening purposes, and that where evidence of metabolism exists, the value for BMF may be reduced if proper justification is supplied.

2.2 Marine Exposure Assessment

The results of the calculations are given in Table 13 and Table 14, showing the concentrations in seawater, marine sediment and marine biota. These have been estimated using the methods outlined in the marine risk assessment guidance and the properties for the adsorption and bioaccumulation behaviour the various substances. The range of concentrations given for musk xylene and musk ketone in Table 13 relates to a

default (high) approach and a method based on more specific, realistic information on the 'fraction of the main source'.

The PEC_{local,seawater} from consumer use seem to be considerably higher for musk ketone and musk xylene than for AHTN and HHCB. This is explained by the default approach taken for the nitromusks, whereas in the predictions for AHTN and HHCB concentrations measured in the STP are taken into account. In contrast to the predicted concentrations, measured concentrations show that the actual environmental levels of nitromusks are below those of AHTN and HHCB.

Table 13. Estimated PECs for compounding and formulation

Formulation	Cl _{ocal,seawater} (emission into 200 000 m ³ water per day) [µg/l]	PEC _{regional,seawater} r (PEC _{regional} *0,1) [µg/l]	PEC _{local,seawater} (Cl _{ocal,seawater} + PEC _{regional,seawater}) [µg/l]	Marine PEC _{local,seawater} (eq. part.) [mg/kg dw]	PEC _{coral} predator [mg/kg]	PEC _{coral} top pred. [mg/kg]
Musk xylene						
End product formulator	0,0021 – 0,01 kg/d → 0,01 – 0,05 ⁽²⁾	0,018	0,028 – 0,068	0,019 – 0,045	0,20 – 3,8	0,33 – 0,41
Musk ketone						
End product formulator	0,001 – 0,006 kg/d ^{(1),(2)} → 0,005 – 0,03	0,011	0,016 – 0,041	0,003 – 0,009	0,019 – 0,036	0,016 – 0,019
AHTN						
Medium/large compounder	0,314	0,0036	0,318	0,536	0,096	0,021
Small compounder	0,061	0,0036	0,065	0,110	0,020	0,006
Large end product formulator	0,144	0,0036	0,148	0,250	0,045	0,011
Small end product formulator	0,055	0,0036	0,059	0,100	0,019	0,005
HHCB						
Medium/large compounder	0,35	0,0148	0,365	0,511	0,301	0,079
Small compounder	0,082	0,0148	0,097	0,136	0,088	0,036
Large end product formulator	0,119	0,0148	0,134	0,188	0,118	0,042
Small end product formulator	0,234	0,0148	0,249	0,349	0,209	0,061

⁽¹⁾ The rapporteur adapted the estimation of the emission of musk xylene to more realistic data, but did not apply the adaptation for musk ketone for practical reasons. In this table the adaptation was introduced.

⁽²⁾ No correction for sorbed fraction as the contribution is negligible (~ 1%)

Table 14. Estimated PECs for consumer use

Private Use Scenario for 2000	$C_{local}^{seawater}$ (= $C_{eff1} * 0,01$) [µg/l]	$PEC_{regional}^{seawater}$ (= $0,1 * PEC_{regional}$) [µg/l]	$PEC_{local}^{seawater}$ (= $C_{local}^{seawater} + PEC_{regional}^{seawater}$) [µg/l]	Marine $PEC_{local}^{sediment}$ (eq. part.) [mg/kg dw]	$PEC_{coral}^{predator}$ [mg/kg]	$PEC_{coral}^{toppred.}$ [mg/kg]
Musk xylene						
TGD ('worst case' 10% regional use)	0,078	0,018	0,096	0,064	0,5	0,5
Musk ketone						
TGD ('worst case' 10% regional use)	0,065	0,011	0,076	0,017	0,06	0,02
AHTN						
'Worst case' 10% regional use	0,0115	0,0036	0,0151	0,025	0,006	0,003
'Typical case' N-Europe	0,0064	0,0007	0,0071	0,012	0,002	0,001
HHCB						
'Worst case' 10% regional use	0,027	0,015	0,042	0,06	0,05	0,03
'Typical case' N-Europe	0,012	0,002	0,014	0,02	0,01	0,005

3. Marine effects assessment

3.1 PNEC for marine waters

Two publications are available on marine crustaceans, *Acartia tonsa* and *Nitocra spinipes*, tested on (sub)chronic effects. The results are summarised in Table 15.

Table 15. Toxicity to marine organisms

Test organism and Reference	Substance	Reported results [mg/l]	Remarks
<i>Nitocra spinipes</i> Breitholz et al. 2002	Musk ketone	96h-LC ₅₀ ≥ 1 7 or 8d-NOEC _{i.d.} = 0,01 NOEC _{rm} = 0,03	I.d.: larval development r.m.: population growth rate concentrations highly variable and not maintained, therefore not used in risk assessment
	AHTN	96h-LC ₅₀ = 1,90 7 or 8d-NOEC _{i.d.} ≥ 0,06 NOEC _{rm} ≥ 0,06	
	HHCB	96h-LC ₅₀ = 0,61 7 or 8d-NOEC _{i.d.} = 0,05 NOEC _{rm} ≥ 0,05	
	ADBI	96h-LC ₅₀ ≥ 2 7 or 8d-NOEC _{i.d.} = 0,1 NOEC _{rm} = 0,04	
<i>Acartia tonsa</i> Wollenberger et al. 2002	Musk ketone	48h-EC ₅₀ = 1,32 5d-NOEC _{juv.surv.} = 0,80 5d-EC _{50 i.d.} = 0,066	juv.surv.: juvenile survival I.d.: larval development no analysis, concentrations not maintained in similar test system, therefore not used in risk assessment
	AHTN	48h-EC ₅₀ = 0,71 5d-NOEC _{juv.surv.} = 0,06 5d-EC _{50 i.d.} = 0,026	

Test organism and Reference	Substance	Reported results [mg/l]	Remarks
	HHCB	48h-EC ₅₀ = 0,47 5d-NOEC _{juv.surv.} = 0,30 5d-EC _{50 l.d.} = 0,059	
	ADBI	48h-EC ₅₀ = 2,50 (>WS) 5d-NOEC _{juv.surv.} = 0,24 5d-EC _{50 l.d.} = 0,16	

In the test with *N. spinipes* concentrations were measured indicating that the concentrations for the polycyclic musks in the water phase of this test system could not be maintained at all and therefore the rapporteur decided that these studies could not be used for the risk assessment reports for AHTN and HHCB. Other comments also dispute the validity of the tests. The reported results suggest that these test organisms are sensitive to the musk fragrance substances. However, this is true only for the parameter larval development rate (which is a ratio measured at one point in time only). The variability in these data is high and the differences in the results between AHTN and HHCB are much more pronounced than observed in other, well performed studies. Therefore it is difficult to judge whether the sensitivity is true or an artefact due to the non-standard parameters used.

Thus, for the risk assessment, the data for freshwater species were used. Toxicity data are available for nitromusks and polycyclic musks (in Annex 2 and 5 of OSPAR 2000). The lowest reported values that have been used for the recent risk assessments are given in Table 16. No data were available for representatives of the macrocyclic musks.

3.2 PNEC for marine sediment

The PNEC_{sediment} for the marine environment is estimated from PNEC_{saltwater} using the equilibrium partitioning method. The results are included in Table 16.

Table 16. Lowest aquatic toxicity data per substance and PNECs derived according to the EU TGD (EC2003c)

Substance	Lowest toxicity test result	Assessment factor	PNEC _{aqua} (µg/l)	PNEC _{sed} mg/kg	Source
Musk xylene	21d-NOEC (reproduction) <i>Daphnia magna</i> 0,056 mg/l	500	0,11	0,025 ww 0,065 dw	EC 2003a
Musk ketone	21d-NOEC (clinical signs) Rainbow trout 0,063 mg/l	100	0,63	0,047 ww 0,122 dw	EC 2003b
AHTN	36d-NOEC e.l.s. fathead minnow and 32d-NOEC e.l.s. zebrafish 0,035 mg/l	100	0,35	0,2	Haskoning 2003a
HHCB	36d-NOEC e.l.s. fathead minnow 0,068 mg/l	100	0,68	0,32	Haskoning 2003b

3.3 PNEC for predators

The PNECs for secondary poisoning is derived in the same manner as for the freshwater environment. The derivation is based on the data presented in Table 17.

Table 17. Hazard description per substance (EC 2003a,b) and PNECoral derived according to the EU TGD (EC2003c)

Substance	Hazard	Assessment factor	PNEC oral (mg/kg food)	Source
Musk xylene	oral NOAEL for peri/post natal toxicity in rats 7,5 mg/kg bw/d E; Xn (carc. cat. 3 by similarity); N R2-40-50/53	150	1	EC 2003a
Musk ketone	oral NOAEL for peri/post natal toxicity in rats 2,5 mg/kg bw/d Xn; N R40 (carcinogen cat. 3 by analogy to MX), R50/53	150	0,3	EC 2003b
AHTN	90d-oral NOAEL in rats 5 mg/kg bw/d or NOEC is 100 mg/kg food 21d-NOAEL reproduction and development in rat 15 mg/kg bw/d or NOEC is 300 mg/kg food Proposed classification: Xn, N; R22, R50/53	90 90 - 300	1,1 3,3 - 1	Haskoning 2003a
HHCB	90d-oral NOAEL in rats 150 mg/kg bw/d or NOEC is 3000 mg/kg food 21d-NOAEL reproduction and development in rat 50 mg/kg bw/d or NOEC is 1000 mg/kg food Proposed classification: N, R50/53	90 90 - 300	33,3 33,3 - 3,3	Haskoning 2003b

4. Risk Characterisation for the Marine Environment

The PEC/PNEC ratios for water and predators/top predators are shown in Table 18 and Table 19. Since both the sediment PNEC and PECs were estimated using equilibrium partitioning, the PEC/PNEC ratios for sediment would not add any new information.

In the consumer use scenario, the PEC/PNEC ratios for musk xylene and musk ketone are below 1 but above 0,01. It should be realised that for both substances, the estimated concentrations PEC (in freshwater that form the basis of this risk assessment) are overestimating the actual concentrations encountered in the freshwater environment by an order of magnitude. This implies that the estimations for the marine environment are over-estimations as well. For AHTN and HHCB the consumer use scenario results in PEC/PNEC ratios below 0,1 or below 0,01.

The local PEC/PNEC ratios for industrial use (compounding and formulation) are below 1 for musk xylene as well as for musk ketone, AHTN and HHCB, even with the generic emission scenario where industrial effluents are discharged directly into the marine environment.

Table 18. Estimated PEC/PNEC ratios for the local marine risk assessment for private use

Private Use Scenario for 2000	PNEC	PEClocal seawater [µg/l]	PEC/PNEC seawater	PECoral predator [mg/kg]	PEC/PNEC predator	PECoral top pred. [mg/kg]	PEC/PNEC top predator
Musk xylene	aq. 0,11 µg/l pred. 1 mg/kg						
TGD ('worst case' 10% regional use)		0,096	0,87	0,5	0,5	0,5	0,5
Musk ketone	aq. 0,63 µg/l pred. 0,3 mg/kg						
TGD ('worst case' 10% regional use)		0,076	0,11	0,06	0,2	0,02	0,07
AHTN	aq. 0,35 µg/l pred. 1 mg/kg						

Private Use Scenario for 2000	PNEC	PEClocal seawater [µg/l]	PEC/PNEC seawater	PECoral predator [mg/kg]	PEC/PNEC predator	PECoral top pred. [mg/kg]	PEC/PNEC top predator
'Worst case' 10% regional use		0,0151	0,04	0,006	0,006	0,003	0,003
'Typical case' N-Europe		0,0071	0,02	0,002	0,002	0,001	0,001
HHCB	aq. 0,68 µg/l pred. 3,3 mg/kg						
'Worst case' 10% regional use		0,042	0,06	0,05	0,014	0,03	0,008
'Typical case' N-Europe		0,014	0,02	0,01	0,004	0,005	0,005

Table 19. Estimated PEC/PNEC ratios for the local marine risk assessment for industrial use

Formulation	PNEC	PEClocal seawater [µg/l]	PEC/PNEC seawater	PECoral predator [mg/kg]	PEC/PNEC predator	PECoral toppred. [mg/kg]	PEC/PNEC top-predator
Musk xylene	aq. 0,11 µg/l pred. 1 mg/kg						
End Product Formulator		0,028 – 0,068	0,25 – 0,62 ¹⁾	0,20 – 3,8	0,20 – 0,38 ¹⁾	0,33 – 0,41	0,33 – 0,4 ¹⁾
Musk ketone	aq. 0,63 µg/l pred. 0,3 mg/kg						
End Product Formulator		0,016 – 0,041	0,03 – 0,07 ¹⁾	0,02 – 0,04	0,06 – 0,12 ¹⁾	0,016 – 0,019	0,05 – 0,06 ¹⁾
AHTN	aq. 0,35 µg/l pred. 1 mg/kg						
Medium/large Compounder		0,318	0,91	0,096	0,10	0,021	0,02
Small Compounder		0,065	0,18	0,020	0,02	0,006	0,01
Large End Product Formulator		0,148	0,42	0,045	0,05	0,011	0,01
Small End Product Formulator		0,059	0,17	0,019	0,02	0,005	0,01
HHCB	aq. 0,68 µg/l pred. 3,3 mg/kg						
Medium/large Compounder		0,365	0,54	0,301	0,09	0,079	0,02
Small Compounder		0,097	0,14	0,088	0,03	0,036	0,01
Large End Product Formulator		0,134	0,20	0,118	0,04	0,042	0,01
Small End Product Formulator		0,249	0,37	0,209	0,06	0,061	0,02

¹⁾ The first value is a 'realistic worst case', the latter is the default calculation of the TGD (related to the 'fraction of the main source').

5. PBT-assessment

The classification of musk xylene and other musks against the EC Technical Guidance Document draft PBT criteria gave the results summarised in Tables 20, 21 and 22.

Table 20. Evaluation of Persistency (Criterion P: DT50 marine water > 60d, DT50 freshwater > 40d, DT50 marine sediment > 180d, DT50 freshwater sediment > 120d)

Substance	Data	Evaluation
Musk xylene	<ul style="list-style-type: none"> . <i>Mineralisation:</i> No ready biodegradation observed . <i>Primary degradation:</i> Biotransformation by reduction of a nitro-group to an amino-metabolite occurs in activated sludge and in fish Photodegradation is observed (with UV, reaction with OH-radicals) <p>¹⁾ A degradation study in the marine environment is in preparation</p>	P or VP ¹⁾
Musk ketone	<ul style="list-style-type: none"> . <i>Mineralisation:</i> No (ready) biodegradation observed . <i>Primary degradation:</i> Biotransformation by reduction of nitro-group to an amino-metabolite occurs in activated sludge and in fish Photodegradation is observed (with UV, reaction with OH-radicals) 	P or VP
AHTN	<ul style="list-style-type: none"> . <i>Mineralisation:</i> No (ready) biodegradation observed (up to 21 % mineralisation in 21 days) . <i>Primary degradation:</i> Evidence for rapid primary biodegradation in soil and activated sludge. DT50 in activated sludge 12 – 24 h. Rapid metabolism in fish and midge larvae. Photodegradation is observed (with UV, reaction with OH-radicals) <p>In view of similar behaviour of AHTN and HHCB, AHTN attracts the same qualification as HHCB</p>	Potentially P
HHCB	<ul style="list-style-type: none"> . <i>Mineralisation:</i> No (ready) biodegradation observed . <i>Primary degradation:</i> In river water DT50 ranges from 33 to 43 hours In freshwater sediment DT50 is 79 d In soil similar degradation rates as in sediment In activated sludge DT50 from 33 to 69 hours. Rapid primary degradation followed by slow mineralisation of the more polar metabolites Rapid metabolism to polar metabolites in fish and in midge larvae. Photodegradation is observed (with UV, reaction with OH-radicals) 	Potentially P
Macrocyclic musks	<p>No data available but considered to be readily biodegradable QSAR predictions do not indicate persistency (see appendix 1)</p>	not P

Table 21. Evaluation of Bioaccumulation Potential (Criterion B: BCF > 2000)

Substance	Data	Evaluation
Musk xylene	measured log Kow range from 3,4 – 4,9 Well documented laboratory study: BCF (¹⁴ C) 1600 Other BCF-values range from 60 to 5000. The RAR proposes 4400 ('weight of evidence' approach)	B
Musk ketone	measured log Kow range from 3,2 – 4,3 BCF (¹⁴ C) 1380 BCF-value in field test is 1100	not B
AHTN	Measured log Kow 5,4 and 5,7 Measured BCF 597, 600 BCF-values in field test 200 – 1790 for eel, 40 – 670 for other fish	not B
HHCB	Measured log Kow 5,3 and 5,9 Measured BCF 1584, 624 BCF-values in field test 150 to 1560 for eel, 50 – 580 for other fish	not B
Macrocyclic musks	No data available	

Table 22. Evaluation of Toxicity (Criterion T: aquatic toxicity < 0,01 mg/l)

Substance	Data	Evaluation
Musk xylene	lowest NOEC 21d-NOEC <i>Daphnia</i> = 0,056 mg/l CMR: R40 (Carc. Cat. 3) was assigned	T
Musk ketone	lowest NOEC 21d-NOEC fish = 0,063 mg/l CMR: All toxicological tests performed on mammals justify: no classification for R25, R28, R45, R46, R48, R60, R61, R62, R63, R64, R68 (Mut.Cat.3). No decision yet on R40 (Carc. Cat.3) There is no evidence of endocrine disrupting potential; not listed in the Comm. Strategy for Endocrine Disruptors (COM(2001)262 final.	not yet decided
AHTN	lowest NOEC 32 and 36 d-NOEC fish e.l.s. = 0,035 mg/l CMR: All toxicological tests performed on mammals justify only classification with R22: no classification for R25, R28, R40 (Carc. Cat.3), R45, R46, R48, R60, R61, R62, R63, R64, R68 (Mut.Cat.3). There is no evidence of endocrine disrupting potential; not listed in the Comm. Strategy for Endocrine Disruptors (COM(2001)262 final.	not T
HHCB	lowest NOEC 36 d-NOEC fish e.l.s. = 0,068 mg/l CMR: All toxicological tests performed on mammals justify: no classification for R25, R28, R40 (Carc. Cat.3), R45, R46, R48, R60, R61, R62, R63, R64, R68 (Mut.Cat.3). There is no evidence of endocrine disrupting potential; not listed in the Comm. Strategy for Endocrine Disruptors (COM(2001)262 final.	not T
Macrocyclic musks	no data available	no data

Musk xylene is considered as a PBT candidate substance. Following the decision of the Technical Meeting, a test on the degradability in the marine environment is in preparation. For the time being it is assumed that degradability within a reasonable time span may still be proven, so a marine risk assessment for musk xylene was also carried.

The other substances musk ketone, AHTN and HHCB do not meet one or more of the PBT-criteria of the EU Technical Guidance Document. As a result of the evaluation of the ECB by the TM Subgroup on the identification of PBT and vPvB substances, AHTN and HHCB were deleted from the list, see Appendix 3. It is anticipated that, by analogy, ADBI, AHMI and AITI are also not fulfilling the criteria for the selection as a PBT-candidate substance. In view of their ready biodegradability, the macrocyclic musks are no PBT candidate substances.

6. Marine risk assessment conclusions

Musk xylene was classified as a PBT-candidate according to the EU Technical Guidance Document. A programme is in development to study the degradation in the marine environment. The concentrations in current environmental samples already show a decrease to below the present detection levels without any regulatory measures in place.

For musk xylene the risk assessment shows that the PEC/PNEC ratios for industrial use (compounding and formulation) as well for consumer use are all below 1. The risk assessment is based on conservative scenarios and assumptions and no use is made of the much lower measured concentrations to refine the estimation. However, with the low risk ratios there is no need for further refinement.

For the potential substitutes musk ketone, AHTN and HHCB the PEC/PNEC ratios are also below 1. Even with the generic emission scenario assuming that industrial effluents are not treated in a municipal biological STP but discharged directly into the marine environment, the PEC/PNEC ratios are below 1. Industry is not aware of any compounding, formulation or production site using nitromusks or polycyclic musks that would discharge directly to sea without intermediate (biological) treatment.

The most relevant emission scenario is the scenario for use in consumer products. The consumer use of AHTN and HHCB gives PEC/PNEC ratios below 0,1 for marine water organisms and at or below 0,01 for predators and top predators. It is concluded that the risk for food chain effects in the marine environment (secondary poisoning) is very low.

The risks for sediment organisms could not be assessed as no empirical data are available on environmental concentrations nor on the toxicity to sediment organisms. Recently industry initiated a programme to generate sediment concentrations and sediment toxicity data for AHTN and HHCB in the freshwater environment. The results might help to evaluate the risks of these two substances for the marine sediment system.

Appendix 3: Results of PBT evaluation by ECB for AHTN and HHCB

Copy from Minutes ECB TM subgroup on Identification of PBT and VPVB Substances, Arona March 12-14, 2003

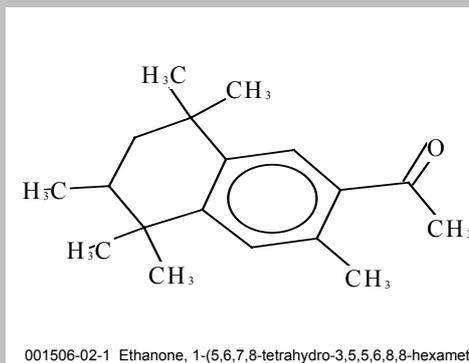
European Chemicals Bureau

PBT Working Group

SUBSTANCE INFORMATION

1-(5,6,7,8-tetrahydro-3,5,5,6,8,8-hexamethyl-2-naphthyl)ethan-1-one

CAS No: 1506-02-1
RAPPORTEUR: NL
SCREENING STUDY: PBT & vPvB



COMMENTS

INDUSTRY CONCLUSION

The substance is not a potential PBT or vPvB. Total score for AHTN is P:B:T = 1: 0: 0 based on both laboratory and environmental measurements reported in the draft RAR. Human Toxicity: No PBT classification warranted; only Xn, R22.

RAPPORTEUR PROPOSAL

The Rapporteur agrees with the conclusion of the industry based on the information and data collected in the draft RAR on AHTN: with P:B:T = 1: 0 : 0.

RAPPORTEUR COMMENTS

Assessment of PBT criteria by the ECB is based on QSARs only. For P-evaluation BIOWIN outputs result in category P1. B-evaluation and T(environment)-evaluation are based on a calculated log Kow and ECOSAR results, respectively. The PBT-screening results for P:B:T in the total score 1: 1: 1.

For P-evaluation no marine, freshwater or sediment data are available. Further supportive evidence for inherent biodegradability is obtained from tests with soil and activated sludge. Moreover, the substance is rapidly metabolised to polar metabolites in fish and midge larvae. Therefore AHTN can be categorised as "potentially persistent" (score P: 1), as stated by the ECB.

For B-evaluation several measured BCF values (under GLP in the laboratory and based on actual measurements in the environment) are available, which are all < 1800 and thus < 2000. It can be concluded that the bioaccumulation criterion is not fulfilled (score B: 0).

For T-evaluation several relevant tests are performed on aquatic species under GLP. The lowest measured long-term NOEC is 0,035 mg/l. Therefore it can be concluded that the criterion for environmental toxicity is not met (score T (env): 0).

Human toxicity: The data that have been submitted following the evaluation of this substance in accordance with the ESR, indicate a need for classification as harmful to humans after oral exposure (Xn, R22). This is not a relevant classification with

respect to PBT. The data do not indicate a further need for classification. Results from carcinogenicity studies are not available, but in absence of genotoxicity, these data do not seem urgently necessary. In addition, the substance has no tumour initiating / promoting activity. Tests for endocrine disrupting activity in mammals in vivo and in mammalian cell systems in vitro did not indicate that this substance is an endocrine disruptor.

**DISCUSSION AT
SUB-GROUP
MEETING**

The working group agreed with the analysis performed by the rapporteur. Substance will be deleted from the list.

CONCLUSION

(Please tick where appropriate)

(Remarks)

- 1. **List of PBT/vPvB**
 - 2. **Further testing needed:**
 - P:
 - B:
 - T:
 - 3. **No PBT/vPvB**
 - 4. **Further discussion necessary**
-

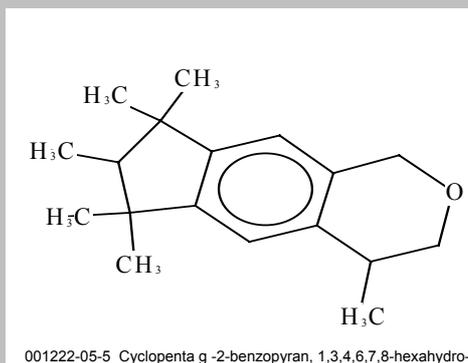
Copy from Minutes ECB TM subgroup on Identification of PBT and VPvB Substances, Arona March 12-14, 2003

European Chemicals Bureau PBT Working Group

SUBSTANCE INFORMATION

1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylindeno[5,6-c]pyran

CAS No: 1222-05-5
RAPPORTEUR: NL
SCREENING STUDY: PBT & vPvB



COMMENTS

INDUSTRY CONCLUSION

The substance is not a potential PBT or vPvB. Total score for HHCB is P:B:T = 1: 0: 0 based on both laboratory and environmental measurements reported in the draft RAR.

No R-phrases for human toxicity applicable.

RAPPORTEUR PROPOSAL

The Rapporteur agrees on the conclusion of the industry based on the data collected in the draft RAR on HHCB: with P:B:T = 1: 0 : 0.

RAPPORTEUR COMMENTS

Assessment of PBT criteria by the ECB is based on QSARs only. For P-evaluation BIOWIN outputs are found to be contradictory, a conservative interpretation resulted in P1. In addition one UK-study is performed and resulted in category P1. B-evaluation and T(environment)-evaluation are based on a calculated log Kow and ECOSAR results, respectively. The PBT-screening results for P:B:T in the total score 2: 1: 1.

For P-evaluation no marine data are available. Experimental derived DT50 values for fresh water are 2 d for water and 79 d for sediment. DT50 values determined in sludge and soil are in the same range. The highest DT50 value is 105 d for sludge amended soil. Moreover, the substance is rapidly metabolised to polar metabolites in fish and midge larvae. Therefore HHCB can be categorised as "potentially persistent" (score P: 1).

For B-evaluation many measured BCF values (under GLP in the laboratory and based on actual measurements in the environment) are available, which are all < 1600 and thus < 2000. It can be concluded that the bioaccumulation criterion is not fulfilled (score B: 0).

For T-evaluation several relevant tests are performed on aquatic species under GLP. The lowest measured long-term NOEC is 0,068 mg/l. Therefore it can be concluded that the criterion for environmental toxicity is not met (score T (env): 0).

With respect to human toxicity endpoints, indeed there seems to be no need for classification, based on the data that have been submitted following the evaluation of this substance in accordance with the ESR. Results from carcinogenicity studies are not available, but in absence of genotoxicity, these data do not seem urgently necessary. Tests for endocrine disrupting activity in mammals in vivo and in mammalian cell systems in vitro did not indicate that this substance is an endocrine disruptor.

**DISCUSSION AT
SUB-GROUP
MEETING**

The working group agreed with the analysis performed by the rapporteur. Substance will be deleted from the list.

CONCLUSION

(Please tick where appropriate)

(Remarks)

- 1. **List of PBT/vPvB**
 - 2. **Further testing needed:**
 - P:
 - B:
 - T:
 - 3. **No PBT/vPvB**
 - 4. **Further discussion necessary**
-

Appendix 4: Monitoring strategy for musk xylene and other musks

As part of the Joint Assessment and Monitoring Programme (*reference number 2003-22*), OSPAR 2004 adopted an Agreement on monitoring strategies for OSPAR Chemicals for Priority Chemicals (*reference number 2004-15*) to implement the following monitoring for tracking progress towards the objectives of the OSPAR Hazardous Substances Strategy (*reference number 2003-21*) with regard to musk xylene and other musks. The Monitoring Strategy for musk xylene and other musks will be updated as and when necessary, and redirected in the light of subsequent experience.

In general, the sources of musk xylene and other musks are well characterised and have been set out in the OSPAR Background Document on musk xylene and other musks.

Musks are used as fragrances in cosmetics, detergents, fabric softeners, cleaning products and other household products. The share of fragrance ingredients used in products that are discharged to the sewer is estimated at 77%. Diffuse discharges to domestic waste water are by far the most important source and can be considered as the only relevant source.

Consumption data are good indicators to track progress with achieving the OSPAR objectives. Regular reporting on quantities produced, sold and used is probably the most efficient and also cheapest monitoring tool. The International Fragrance Association (IFRA) has reported production data regularly. This activity will be continued. Switzerland as the lead country is prepared to collect and compile data provided by individual Contracting Parties and IFRA.

One off surveys in sewage sludge and effluents of selected waste water treatment plants have been performed in a few contracting parties. They are considered to be an appropriate additional tool for source monitoring and for the verification of the consumption data. The HARP-HAZ approach pioneered by Norway and tested out for the 5th North Sea Conference would not be the most appropriate option, because there are no emissions to air and no losses.

Marketing and use restrictions or any voluntary agreement in place in Contracting Parties will reduce the discharges. Evidence from reports on the implementation of such measures will be examined to assess the progress in reducing discharges.

Musk xylene and other musks have not been identified as priority substances under the Water Framework Directive. To date, no co-ordinated environmental monitoring of musk xylene and other musks has taken place in the OSPAR framework. Only limited monitoring has been carried out in Switzerland, Germany and some other Contracting Parties (i.e. OSPAR DIFFCHEM Survey). In general, the concentration of musk xylene and other musks in surface water (fresh and marine) was low and in many cases it was below the limit of detection of the analytical method.

Methodologies for monitoring musk xylene and other musks in the marine environment are generally well understood and the monitoring which has been done shows that detectable concentrations in marine environment are likely to be found at the coast near estuaries. The pathway via atmospheric deposition is not relevant for musks. The limited monitoring that has been carried out shows that concentrations in the marine environment are in general either at or below the detection limit.

Based on this evidence, it would not appear to be sensible to include musks in regular marine monitoring programmes, the OSPAR RID Programme on riverine input or the OSPAR CAMP programme on atmospheric deposition. Information on sources or on pathways near to the source, may provide a better means of checking progress towards the cessation target.

The most appropriate approach to environmental monitoring would be periodic surveys on sediments at specific locations. Such information may be gathered in Contracting Parties for the identification of pressures and impacts as part of the WFD catchment assessments. More regular monitoring in estuarine sediments offer an option for tracking progress on achieving concentrations in the marine environment close to zero, but the resources and infrastructure to carry this out are costly, and it has been decided that this should not be considered for the time being.

MUSK XYLENE AND OTHER MUSKS MONITORING STRATEGY	
<i>Implementation of actions and measures</i>	<ul style="list-style-type: none">• Examination of progress in the implementation of regulations on marketing and/or use or emission and/or discharge which have been agreed, or are endorsed, by the Background Document
<i>Discharges and losses to water</i>	<ul style="list-style-type: none">• The lead country will update information on discharges to water as part of future reviews of the Background Document• A one-off survey in sewage sludge and effluents of selected waste water treatment plants (STPs)
<i>Production/use/sales/figures</i>	<ul style="list-style-type: none">• Collection, with the assistance of industry, of information on quantities produced, sold and used in Europe