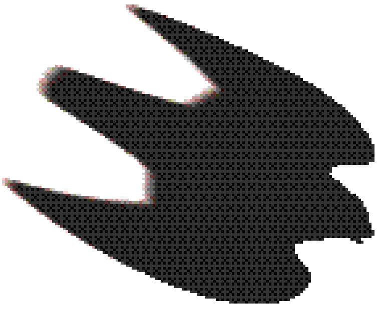
Draft for public hearing

Swedish Society for Nature Conservation | Foundations concerning criteria for BRA MILJÖVAL

Fragrances
2000



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1 INTRODUCTION

On behalf of The Swedish society for Nature Conservation, Norwegian Institute for Water Research (NIVA), has evaluated data for fragrance compounds in cleaning and cleansing products as a background document for criteria for Good Environmental Choice ("bra miljöval"). Cleaning and cleansing products include both household detergents like laundry, dishwashing and cleaning agents and "cosmetic products" like soaps, shampoos, conditioners, lotions, and so on.

2 REPORT BASICS

2.1. Selection of chemicals

The selection of chemicals for this document should have been based on information from producers of cleaning and cleansing products, producers of fragrances and their professional and industrial bodies. The industry has not reported any chemical names or CAS-numbers of fragrance substances used in cleaning and cleansing products, due to complex formulations or confidentiality. Due to lack of data from the industry, chemical names or CAS-numbers are found from internet and other literature. For example are fragrance substances used for allergy testing and musk compounds discussed in this report. We expect that, at least, some of these substances are relevant for use in cleaning and cleansing products.

2.2. Collection of data

Data were collected from the producers of cleaning and cleansing products, producers of fragrances, their professional and industrial bodies (International Fragrance Association (IFRA)) and authorities. In addition handbooks, internet, databases and papers published in scientific journals were used.. A list of literature used for ecotoxicity data search is given in Appendix 1. Other references used are listed in the reference list.

First we contacted producers of cleaning and cleansing products and their fragrance suppliers. None of the fragrance supplier wanted to answer us directly, but referred to their professional body IFRA. Even if our questions were specific, the information given by IFRA were general. No CAS numbers or ecotoxicity test data were given. The data we have found in literature must be used with caution. Safe conclusions and ranking is difficult to make due to lack of data and unsafe data, but we have tried to summarise from the informations that are given in this report.

Both test data and QSAR estimates are included if such data has been available. In most cases, the quality of the data could not be evaluated and in some cases only data of supposedly low quality were available.

The last years, musk compounds have been much in focus as fragrance ingredients and more data have been available for musk compounds than for other fragrance substances. This fact may be conspicuous in this report, but some of the data relevant for musk compounds may also be relevant for other fragrance substances.

3 FRAGRANCES IN CLEANING AND CLEANSING PRODUCTS

Fragrance and extracts are used in many cleaning and cleansing products like soap, creams, lotions and oils, toiletries, bath preparations, detergents for dishwashing, laundry and washing machine and rinse aid.

Fragrances are not used for their cleaning effect, but some fragrances and herb and spice extracts used as fragrances might have antimicrobial effect. In addition preserving agents added to the fragrance compounds might have antimicrobial effect.

In detergents fragrances are added to give the product a pleasant odour during use and to impart a pleasing scent to clothes after they have been washed, dried and ironed. They camouflage unpleasant odour of other ingredients in the products and of dirt in the washing water. They contribute nothing to the detergency of the formulation, but they do provide aesthetic appeal. In fact, many consumers apparently associate the pleasant fragrance with cleanliness and may even judge performance to some degree by this association.

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. These substantive properties relate to their poor water solubility, the relatively low volatility and to their high solubility in organic solvents and tissues (OSPAR, 1999).

A complete list of fragrance substances with CAS-numbers is not available because many of the fragrance substances are often unspecified compounds, which widely vary and often change. There have been much confidentiality regarding fragrances. Producers and fragrance organisations have used mysticism as a concept. Since the potential problems regarding these substances have been suggested, the authorities, consumers, and others have urged the industry to present more data for these substances.

The producers of cleaning and cleansing products claim that the fragrance compositions are confidential and not accessible for them. The International Fragrance Association (IFRA) informs that the fragrances contain a large number of compounds. Which fragrance mixes that are used in different fragrance variants is unknown for the producers of cleaning and cleansing products, but they suppose that the differences are small. As literature regarding fragrance compounds they recommend Monografene, published in F. Cosmet. Toxicol. Vol 11, pp 95-115, pp 855-876, pp 1011-1081. This literature has not been available during this project.

In a paper by Goronszy (1992) on treatment of wastewater from fragrance manufacturing further information on the composition of fragrances is presented. Fragrances contain 22 percent fragrance oils together with alcohol, dye solutions, water and propylene glycol with extenders, fixers and stabilizers. Various base fragrance oils are formulated to generate specific olfactory effects in fragrance. Fragrances or perfumes consist of a combination of numerous ingredients comprising single materials, complex reaction mixtures, basic odour components natural basically botanical or animal derived compounds. The actual formulae of fragrance compounds used by the industry are often patented. It is not uncommon to have some 250 identifiable compounds in a fragrance formulation. Many of these compounds are highly complex organics.

Fragrances are extremely complex mixtures of chemicals and many include phenylpropanals, cyclohexane derivates, tertiary alcohols, alkoxy-alkyl phenols, norborny derivatives, allylic alcohols, tricyclododecane derivatives, heterocyclic compounds, polycyclic

Diels – Alder adducts, α,β-dialkyl conjugated aliphatic nitriles, norsequiterpene derivatives, chain terpene alcohols, cycloalkylated aromatic nitriles, α-methylstyrene dimers or terpine dimers.

Typical fragrance compounds include octadienes, hexyloxyacetonitriles, cyclopentane derivatives, α-oxo (oxo) sulfides, aliphatic dibasic acid diesters, 3-(10-undecenyloxy) propionitrile, tricyclodecane-methylol derivatives, 2-methyl-2-alkyl-alkanoic esters, trimethylcyclonexylethyl ethers, cyanoethylidene-bicyclo-heptenes, crotonyl-trimethyl cyclohexanes, nonanols, nonenols, α-oxo (oxo) mercaptanes, safranic acid esters and maltyl-2-methyl alkenoates (Goronszy 1992). Examples of some of these compounds, which are commonly used in the industry, are summarized in **Table 1.**

Table 1. Examples of compounds and fragrances used in industry (from Goronszy 1992)

Compound	Fragrance
3-(4-tert-butyl-phenyl)-butanol-1	used for flower oil such as lavender, lily of the valley, linden, iris, lily, lilac, cyclamen
3-(4-hydroxy-4 methylcyclohexyl)-butanol	mild floral odour of lilac or muguet
1-hydroxy-3 methoxyphenyl)-1-butene	soft, flowery-sweet and hard mossy leather
2-cyclopropyl-4-isopropyl-2, 5,5-trimethyl-1,3 dioxane	jasmine fragrance
2-n-pentyl-3-(2-oxopropyl)-1-cyclopentanone	magnolia
methyl-1-ethynylcyclohexyl carbonate	fruity, herbal complex odor distinctive of dill
β-phellandrena (1-methylene-4-isopropyl-2-cyclohexene	peppery, minty, refreshing, slightly citrusy odour
3-methylthio-2, 6 dimethyl-4-heptanone	sweet, slightly floral and woody aroma with fruity and berry nuances

A list of fragrance used in allergy testing may serve as a indication of types of fragrances that may be included in cleaning and cleansing products (See **Table 2**) We have not obtained any information on which of these compounds, if any, that are used in cleaning and cleansing products.

Table 2. Data for the fragrance mix used in T.R.U.E. TEST ® (Allergen Patch Test) (Truetest.2000)

Concentration	0.43 mg/cm^2	
Allergen component per patch:	Geraniol	0.070 mg
	Cinnamaldehyde	0.034 mg
	Hydroxycitronellal	0.054 mg
	Cinnamyl alcohol	0.054 mg
	Eugenol	0.034 mg
	Isoeugenol	0.015 mg
	α-amylcinnamaldehyde	0.015 mg
	Oak moss	0.070 mg
Vehicle:	Hydroxypropyl cellulose, β-cyclodextrin	

Synonyms and/or components:	**Synonyms:** cologne, toilet water, fragrance, masking or unscented perfume or fragrance, aroma chemicals, essential oils of plants and animals. **Individual fragrance allergens:** Cinnamic alcohol, Cinnamic aldehyde, Oak moss absolute, α-amylcinnamic alcohol, Anisyl alcohol Benzyl alcohol, Benzyl salicylate, Coumarin, Sandalwood oil, Musk ambrette, Wood tars
Other substances to which the patient may react:	Balsam of Peru, Ethylene bassylate (Musk T^{TM}), Cloves, Cinnamon, Cassia oil, Citronella candles
Occurrence:	Fragrances, toiletries, scented household products, flavorings, food, industrial products

Further examples for fragrance compounds are given in **Table 3**. Some of these compounds are included on the panels for T.R.U.E. TEST ® (Allergen Patch Test).

Table 3. Some examples for fragrance compounds

Fragrance compound	Reference
Geraniol	Truetest (2000)
Cinnamaldehyde	Truetest (2000)
Hydroxycitronellal	Truetest (2000)
Cinnamyl alcohol	Truetest (2000)
Eugenol	Truetest (2000)
Isoeugenol	Truetest (2000)
α-amylcinnamaldehyde	Truetest (2000)
Oak moss	Truetest (2000)
Benzylalcohol	Tænk (1999)
Benzyl salicylate	Tænk (1999)
Cinnamal	Tænk (1999)
Citral	Tænk (1999)
Amylcinnamal	Tænk (1999)
Coumarin	Tænk (1999)
Hydroxymethylpentylcyclohexene carboxaldehyde	Tænk (1999)

From the fragrance names given in **Table 2** and **Table 3** we have found the respective CAS numbers. This made it easier to seach for human and ecotoxicity data in literature. The CAS numbers found are given in **Table 4**. None of the CAS numbers in **Table 4** are classified as dangerous for the environment in EU (Annex 1 Directive 67/548 EC, including 24 ATP).

Table 4. CAS numbers for fragrance compounds given in **Table 2** and **Table 3**. Sorted alphabetic by names.

Fragrance compound	CAS number	Sum formula
α-amylcinnamaldehyde	122-40-7	$C_{14}H_{18}O$
α-amylcinnamic alcohol	101-85-9	$C_{14}H_{20}O$
Anisyl alcohol	1331-81-3	$C_8H_{10}O_2$
Benzyl salicylate	118-58-1	$C_{14}H_{12}O_3$
Benzylalcohol	100-51-6	C_7H_8O
Cinnamaldehyde = Cinnamic aldehyde = Cinnamal	104-55-2	C_9H_8O
Cinnamon brown	8052-76-4	
Cinnamon oil	8015-91-6	
Cinnamyl alcohol = Cinnamic alcohol	104-54-1	$C_9H_{10}O$
Citral	5392-40-5	$C_{10}H_{16}O$
Coumarin	91-64-5	$C_9H_6O_2$
Eugenol	97-53-0	$C_{10}H_{12}O_2$
Geraniol	106-24-1	$C_{10}H_{18}O$
Hydroxycitronellal	107-75-5	$C_{10}H_{20}O_2$
Isoeugenol	97-54-1	$C_{10}H_{12}O_2$
Oak moss resin	9000-50-4	
Sandalwood oil	8006-87-9	

There has been special attention regarding musks, and data for these compounds are more easily accessible. Artificial musks may be of different types as nitromusks, macrocyclic musks and polycyclic musks. **Natural musk** is obtained from the musk glands of the male musk deer (*Moscus moschiferu*), and the Louisiana musk-rat. The fragrance compounds of natural musk are mainly muscone (a macrocyclic ketone) and muscopyridine (a macrocyclic pyridine). Natural musk is expensive and available only in limited amounts. The musk deer belongs to an endangered species. Therefore, **synthetic musks** are widely used since decades as cheaper fragrances and aroma compounds in perfumes and colognes, creams, lotions and body oils, bath preparations, in pre- and aftershaves, toiletries and other cosmetics, in soaps, washing powders and other detergents, and on textiles. (OSPAR, 1997).

Examples of synthetic musks are shown in **Table 5**. **Musk Xylene** is produced in large amounts as an inexpensive substitute for natural musk. **Musk Ketone** is a fixateur for "flowery compositions" and very stable in cosmetics, soaps, and detergents (Römpp, 1997). **AHTN** and **HHCB** are used in fragrances for cosmetics and detergents (Plassche and Balk, 1997).

Table 5. Examples for Type, Name, CAS-No. and Sum formula of some (artificial) musks (OSPAR, 1999).

Type of musk	Name	CAS-No.	Sum formula
Nitromusks	Musk ketone	81-14-1	$C_{14}H_{18}N_2O_5$
	Musk Xylene	81-15-2	$C_{12}H_{15}N_3O_6$
	Musk Ambrette (artificial ambrette)	83-66-9	$C_{12}H_{16}N_2O_5$
	Musk Tibetene	145-39-1	$C_{13}H_{18}N_2O_4$
	Musk Moskene	116-66-5	$C_{14}H_{18}N_2O_4$

Type of musk	Name	CAS-No.	Sum formula
Macrocyclic musks	Musk natural, (natural ambrette)	123-69-3	$C_{16}H_{28}O_2$
	Musk R1	3391-83-1	$C_{15}H_{28}O_3$
	Thibetolide		
	Muscone	541-91-3	$C_{16}H_{30}O$
Polycyclic musks	Musk Moskene	116-66-5	$C_{14}H_{18}N_2O_4$
	Phantolide (AHMI)	15323-35-0	$C_{17}H_{24}O$
	Galaxolide (HHCB)	1222-05-5	$C_{18}H_{26}O$
	Tonalide (AHTN)	406-02-1; 1506-02-1	$C_{18}H_{26}O$
	Versalide (ATTN/AETT), Musk 36A	88-29-9	$C_{18}H_{26}O$
	Celestolide (ADBI)	13171-00-1	$C_{17}H_{24}O$
	Traseolide (AITI)	68140-48-7	$C_{18}H_{26}O$
Unknown	Musk T	105-95-3	$C_{15}H_{26}O_4$
	Cashmeran	33704-61-9	$C_{14}H_{22}O$

Substance name (IUPAC), other chemical and trivial names are given in **Table 6**.

Table 6. Substance name (IUPAC), other chemical and trivial names for (artificial) musks.

Substance	Synonyms
Musk natural	(Z)-Oxacycloheptadec-8-en-2-one; Ambrettolid; Ambrettolide; Musk ambrette; Musk ambrette (natural); **Natural musk ambrette**
Musk Ambrette	Benzene, 1-(1,1-dimethylethyl)-2-methoxy-4-methyl-3,5-dinitro-; 6-t-Butyl-3-methyl-2,4-dinitro-anisole; 6-tert-Butyl-3-methyl-2,4-dinitroanisole; 1-(1,1-Dimethylethyl)-2-methoxy-4-methyl-3,5-dinitrobenzene; 2,6-Dinitro-3-methoxy-4-tert-butyltoluene; **Synthetic musk ambrette**; Artificial musk ambrette
Musk Ketone	4'-tert-Butyl-2',6'-dimethyl-3',5'-dinitroacetopheneone; 1-(4-(1,1-dimethylethyl)-2,6-dimethyl-3,5-dinitrophenyl)-ethanone; 2-Acetyl-5-t-butyl-4,6-dinitroxylene; 1-(4-(1,1-Dimethylethyl)-2,6-dimethyl-3,5-dinitrophenyl)ethanone; **Synthetic musk ketone**; Keton-Moschus (german); Almiscar cetona; Ketonmuskus; Musc cetona; Musc cetone; Muschio chetone
Muscone	3-Methyl-cyclopentadecanone; 3-Methyl-1-cyclopentadecanone; Methylexaltone;

Substance	Synonyms
	Natural musk ketone
Musk Moskene	4,6-Dinitro-1,1,3,3,5-pentamethylindan; 1,1,3,3,5-Pentamethyl-4,6-dinitroindane; 2,3-dihydro-1,1,3,3,5-pentamethyl-4,6-dinitro-1H-Indene; Moskene
Musk Tibetene	1-(1,1-dimethylethyl)-2,6-dinitro-3,4,5-trimethyl-benzene; Benzene, 1-tert-butyl-2,6-dinitro-3,4,5-trimethyl-; 5-tert-Butyl-1,2,3-trimethyl-4,6-dinitrobenzene
Musk Xylene	2,4,6-Trinitro-1,3-dimethyl-5-tert-butylbenzene, 5-tert-Butyl-2,4,6-trinitroxylene; 5-t-Butyl-2,4,6-trinitro-m-xylene; 1-t-butyl-3,5-dimethyl-2,4,6-trinitro-benzene; 1-(1,1-Dimethylethyl)-3,5-dimethyl-2,4,6-trinitrobenzene; 2,4,6-Trinitro-1,3-dimethyl-5-tert-butylbenzene; 2,4,6-Trinitro-3,5-dimethyl-1-tert-butylbenzene; Xylene musk (engl.) Musk xylol; Moschusxylol (german) Ambrette de xyline (french) Muschio xilolo (Italian) Almizole de xileno (spanish)
Musk 36A	7-Acetyl-1,1,4,4-tetramethyl-6-ethyl-tetrahydronaphthalene **ATTN**; 3'-Ethyl-5',6',7',8'-tetrahydro-5',5',8',8'-tetramethyl-2'-acetonaphthone; **Versalide®**
Musk R 1	1,7-Dioxacycloheptadecan-17-one (macrocyclic)
Musk T	1,1'-Undecanedicarboxylic acid, ester with ethylene glycol; Ethylene brassylate; Ethylene undecane dicarboxylate; Tridecanedioic acid, cyclic ethylene ester; **Astratone**; **Emeressence 1150**
Cashmeran	1,2,3,5,6,7-hexahydro-1,1,2,3,3-pentamethyl-4.*H*-inden-4-one
Celestolide®	4-Acetyl-1,1-dimethyl-6-tert.-butyldihydroindene **ADBI**; 6-tert-butyl-1,1-dimethylindan-4-yl methyl ketone; **Crysolide®**
Phantolide®	6-Acetyl-1,1,2,3,3,5-hexamethyldihydroindene **AHDI**
Cashmeran®	6,7-Dihydro-1,1,2,3,3-pentamethyl-4(5H)indanon **DPMI**
Traseolide®	5-Acetyl-1,1,2,6-tetramethyl-3-isopropyl-dihydroinden **ATII**
Galaxolide®	1,3,4,6,7,8-Hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-(g)-2-benzopyran **HHCB** (polycyclic) **Abbalide®** **Pearlide®**
Tonalide®	7-Acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene **AHTN;** 1-(5,6,7,8-tetrahydro-3,5,5,6,8,8-hexamethyl-2-naphthyl)ethan-1-one; **Fixolide®**

Analysis of fragrance in German products is given in **Table 7**. The compounds found were mostly polycyclic musk compounds, sometimes even nitromusk compounds.

Table 7. Analysis of fragrance in German products (Ökotest, 1998-99)

Ökotest Number	Product	Number of tested products	Number containing Musk	Fraction containing Musk
10-99	Foot cream	30	None	0
6-98	Condomes	17	None	0
6-98	Agents for sunburn and insect bite	27	1	4
6-99	Suntan lotion	16	3	19
10-98	Allround detergents	29	3 +3 (traces)	21
2-99	Toys, theatre painting	34	3 +7 (traces)	30
3-98	Cosmetics for allergics	40	13	33
1-99	Foaming products	25	9	36
9-98	Shampoo for kids	39	14	36
9-99	Cosmetic creams	31	12	39
9-99	Shampoo	30	1 +11 (traces)	40
2-99	Incense	7	3	43
11-98	Day creams	27	16	60
2-98	Soap	35	22	63
3-99	Shaving foam	21	14	67
4-98	Deodorant	40	1 +29 (traces)	75
12-98	Fragrance	15	15	100

Herb and spice extracts are used as fragrance ingredients as well. Cloves (*Syzygium aromaticum L*) is used in dishwashing liquid, and has an antimicrobial effect on e.g cloths. Some of these herb and spice extracts might have antimicrobial effect. We suppose that use of these extracts in cleaning and cleansing products is small and an extensive study of these substances is not included in this report.

3.1. Concentrations

The dosage of fragrance in a product depends on the fragrance ingredients and the end products.

The fragrance compound may contain hundreds of fragrance ingredients usually in an organic solvent.

The concentration of a **fragrance compound** in toilet soap may be 1.5 %, in a shampoo 0.5 % and in a detergent 0.15 %.

The amount of fragrances and colorants in powder and liquid laundry detergent formulations is about 1 percent by weight content (Modler, R.F. et al. 1998).

A producer of cleaning and cleansing products states that the concentrations of fragrances are from 0.05 % to 0,5 %. Some special products as WC-blocks and deodorisation agents may contain higher concentrations.

The concentration of a given **fragrance ingredient** in a toilet soap can be between 0.01 and 0.1 % and may only reach 0.4 % in exceptional cases. The concentrations in detergents would be 0.001 - 0.01 % or 0.04 % (IFRA, 2000[1]).

3.2. Production and use volumes

More that 3 000 individual chemicals are utilized in flavor and fragrance (f&f) compositions worldwide. Only a few hundred chemicals are used in quantities above 50 t/y. Synthetic organic chemicals constitute more than 80-90 % (by weight and value) of the raw materials used (Somogyi et al., 1994).

The consumption of some household detergents that may contain fragrances in the Nordic countries is shown in **Table 8**. The total use of textile washing detergents in Denmark was 40 000 tons in 1997.

Table 8. Total annual consumption of selected cleaning and cleansing products in Nordic countries in tons/year. (Source: Criteria documents for Nordic Ecolabelling).

Product category	Finland	Norway	Sweden	Year
Laundry detergents	27000	23000	49000	1993-1994
Hand dishwashing	5500	5500	11300	1995
Machine dishwashing	3004	3247	4930	1995
General cleaners	4300	10000	7900	1997

A recent review of the use of household chemicals in Sweden (Hagenfors 1999) showed similar figures as those shown in **Table 8** and includes also data on toilet cleaners, soap and shampoo, which also may contain fragrances (**Table 9**.)

Table 9. Consumption of household chemicals in Sweden 1996 in tons/year (From Hagenfors 1999).

Product category	Consumption (ton/year)	ton/year, water excluded
Laundry detergents	42500	36900
Hand dishwashing	11000	3600
Machine dishwashing	6900	6600
General cleaners	8900	1600
Toilet cleaners	1600	500
Soap and shampoo	11500	3200
Total	82400	52400

The presence or amounts of fragrances in these products are not known. According to Hagenfors (1999) the total consumption of fragrances in cleaning and cleansing products was 260 tons in 1996. If this amount is included in the products listed in **Table 9**, it gives an average content of 0.32 % fragrances. This appears high, considering that several products contain no fragrances. Inte så högt om det gäller tillsatsen i receptet, inte själva parfymämnesinnehållet i tillsatsen.

Production volumes for some musk substances for some countries or areas throughout the world are given in **Table 10**. The global production of all synthetic musk compounds was 7000 tons in 1988. China had an increase in production of Musk Xylene, Ketone and Ambrette from 856 tons to 942 tons from 1991 to 1992. It is not possible to read any trends for use of fragrances out of these data for production volumes. To make any conclusions for trends more complete time series are necessary.

Currently, Musk xylene, Musk ketone, AHTN and HHCB represent about 95 % of the market in Europe for all nitro musks 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. Facts on trends for a long-term increase or decrease in consumption in Europe are therefore not available. After 1992, the use of Musk xylene, Musk ketone and AHTN has been declining whereas the use of HHCB is now more or less stable. The two most used polycyclic musks are AHTN and HHCB. The nitro musk Musk ambrette and the polycyclic musk AETT (Versalide) are no longer used (OSPAR 1999).

Macrocyclic musks (**ketone** and **lactone**) hold the smallest market share at a production level of 100 tons worldwide (OSPAR, 1997).

The world annual sale of aroma chemicals is estimated at $1.2 billion. Between 1988 and 1992 demand grew by an estimated 4 % annual in volume. China's importance as a source of flavour and fragrance products is steadily increasing (currently ≈ 100 enterprises in China producing more than 800 varieties of aromatic chemicals). Total production volume of aroma chemicals in China reached almost 40 thousand metric tons in 1991. The quality and variety of Chinese products has improved as a result of technology upgrades provided from both original research and joint ventures with a number of leading Western companies (Somogyi et al. 1994).

The worldwide polycyclic musk market has grown from 4,400 metric tons in 1987 to its estimated size of 5,000 to 6,000 metric tons in 1992. It is reported that the polycyclic musk compounds constituted about 60% of the worldwide production volume exceeding the production volume of nitro musk compounds (OSPAR, 1997).

Table 10. Production volumes for some musk substances.

Country/ Area	Year	Tons	Substance	Reference
Global	1988	7000	All synth. Musk compounds, incl.:	Gatermann et al, 1998 and Dragoco, 1998
		4300	Non-nitro benzenoids (61%) [Polycyclic musks]	
		2450	Nitro benzenoids (35%)	
		≈250	Macrocyclic musks (3-4 %)	
	1996	>5000	Polycyclic musks (estimated) (85% of synth. musk prod.)	Rebmann et al, 1998
		700	Nitromusks (12% of synth. musk prod.)	Rebmann et al, 1998
		≈250	Macrocyclic musks (3-4 % of synth. musk prod.)	Rebmann et al, 1998
	?	1000	Musk Xylene	FDA,1998
EU	?	500	Musk Xylene (*consumption*, estimated)	Schlatter and Hunyady, 1993
Europe	1995	585	AHTN	Plassche and Balk, 1997
	1995	1482	HHCB	Plassche and Balk, 1997
USA	1997	≈122	Artificial musks (*imports for consumption*) (customs value $0.5M; 96% from China, 4% from Switzerland)	Internet ita. doc.gov

Country/ Area	Year	Tons	Substance	Reference
China	1990	856	Musk Xylene, Ketone and Ambrette	
	1991	942	Musk Xylene, Ketone and Ambrette	Quinghua, 1993

Estimated use volumes of **Nitromusks** in Europe are given in **Table 11**.

Table 11. Estimated use volumes of **Nitromusks** in Europe (tons). Estimated by Research Institute for Fragrance Materials (RIFM) (OSPAR, 1999).

Year	Musk Xylene	Musk Ketone	Moskene	Musk tibetene
1992	174	124		
1995	110	61	5	0.8
1998	86	40		

Estimated use volumes of **polycyclic musks** in Europe are given in **Table 12**.

Table 12. Estimated use volumes of **polycyclic musks** in Europe (tons). Estimated by the International Fragrance Association (IFRA) (OSPAR, 1999).

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Year	HHCB	AHTN	ADBI	AHMI	AITI
1992	2400	885			
1995	1482	585	34	50	40
1998	1473	385	18	19	2

The total amounts of Muskxylenes used in Norway in 1998 were ≈ 40 kg (Benestad 1999).

In 1996, the worldwide flavor and fragrance business, including sales of compounded flavor and fragrance compositions and essential oils, was valued at an estimated $10 billion, representing a 7.5% compounded yearly growth since 1992. Production of aroma chemicals, calculated from unaudited estimates of supply/demand by major geographic region, accounted for $1.7 billion of the total value.

Although overcapacity is known to exist for some products, the estimated production of aroma chemicals appears to be only in slight excess of consumption. The current demand for aroma chemicals is estimated to be approximately in balance with the supply.

In 1996, the United States and Western Europe together accounted for approximately 70% of the value of all aroma chemicals and more than 90% of the value of musk chemicals consumed in flavor and fragrance compositions. These high ratios also characterize the estimated consumption of aroma chemicals for 1996.

Steady growth in demand for "natural," albeit more expensive, aroma chemicals has contributed to the expansion of individual compounds, some of which have grown at rates significantly higher than the average - for example, hexyl cinnamaldehyde, phenethyl alcohol, p-tert-alpha-methyl-cinnamaldehyde and certain polycyclic musks. On occasion, above-average growth rates have resulted from rapid fluctuations in unit price caused by random temporary dislocations in the supply/demand situation and by the relative strength of major currencies against the dollar. The latter effect can be magnified as international flavor and fragrance companies typically concentrate their aroma chemical procurement and production practices in those areas with the weakest currencies.

There are three types of companies (Somogyi et al., 1994):

Traditional flavour and fragrance houses

They produce aroma chemicals as needed for their own compounding and also sell them to the merchant market (e.g. IFF, Givaudan).

Large chemical companies

They manufacture certain aroma chemicals by upgrading small portions of their large-scale chemical production of flavour and fragrance specifications (e.g. Eastman Chemicals, Akzo Chemicals, Dow Chemical).

Small to medium-sized custom synthesis houses and chemical producers with specialised technical know-how

They manufacture selected high-unit-value aroma chemical specialities (e.g. Tastemaker, Penta International Corporation).

3.3. Alternatives

Since customers and the flavour and fragrance industries detected problems regarding human health and the environment related to some of the flavour and fragrance compounds used, a search for substitutes/alternatives have been intensified. Some examples are given here (OSPAR, 1997).

The alternative to fragrances might be "no fragrance". Many consumers have been increasingly objecting to strong fragrances, and some claim their health is adversely affected by them. Thus, some products are offered in an unscented version in addition to the regular type containing fragrances (e.g., Procter & Gamble Co.'s Tide® laundry powder) (Modler, R.F. et al. 1998). However, soaps, detergents etc. without fragrance are not well accepted by consumers according to International Fragrance Association (IFRA). Wet clothes, which have been washed with a detergent without fragrance, have an unpleasant odour. Consumers associate the smell of fragranced fabric with cleanliness and an efficient washing process (IFRA, 2000[1]).

Within the musk family of fragrances synthetic musks have replaced the natural musk, mainly for economic reasons. Among the synthetic musk's, the trend is to replace the nitrocyclic musks with macrocyclic and polycyclic musks. This is due to the superior fragrance qualities of the newer materials and to the concerns about potential toxicity of the nitro musk (OSPAR, 1997).

Some companies try to find alternatives for main uses of fragrances. Some examples are given in **Table 13**.

Table 13. Alternatives for main uses of fragrances for some companies

Country	Company	Alternatives
Japan	Soda Aromatic Co. Japan	The company has announced that it will increase its capacity for the mainstream synthetic fragrance **macrocyclic musk** by 100 %, to attract customers of its competitors by cashing in on issues such as the negative effects of **polycyclic musk** and **nitromusk** on humans. The twofold expansion, which will cost Soda Aromatic several hundred million yen, covers the macrocyclic musk production facility at the firm's Noda factory in Chiba Pref. (Japan Chemical Week, 1998)
Japan	Japan Energy	The company is close to completing capacity expan-

Country	Company	Alternatives
	Corp. (JE)	sion of **brassylic acid** from 180 to 500 t/y at its Funakawa oil refinery and will try to expand the market for use as a material for fragrance in cosmetics and toiletry goods. Brassylic acid is made into **ethylene brassylate** having a chemical structure resembling that of **natural musk** and featuring a high level of biodegradability. JE's production method features higher purity and lower costs as it uses modified yeast in fermentation of n-paraffin hydrocarbon into brassylic acid. JE began commercial production in 1985 at a 100 t/m rate and has supplied the chemical to cosmetic and toiletry goods makers as synthetic musk material. Synthetic musk is available in nitro musk, polycyclic musk and macrocyclic musk; use of **nitro musk** is limited because of phototoxicity, and **polycyclic musk** may face limited use in the future as it is not biodegradable. Brassylic acid that belongs to **macrocyclic musk** is expected to find an increasing market as a replacement for polycyclic musk, according to observers (Japan Chemical Week, 1998-6).
	Creanova Spezialchemie GmbH	Has developed a petrochemical-based process for synthesising **brassylic acid** and its derivatives, which until now has been produced biochemically or from natural sources. One derivative, **ethylene brassylate**, is used as a musk ingredient in many fragrances. The company has been producing **macrocyclic musk** components, which in contrast to **nitrocyclic** and **polycyclic** substances**, present no health hazards and are biodegradable**. The one disadvantage was that up to this point, brassylic acid was relatively expensive as a raw material and available only in limited quantities. A balance has been reached between the economic and environmental concerns, and the production-ready process seems poised to revolutionise not only the cosmetic and household product industries, but also the production of pharmaceutical products and additional fragrances.

3.4. Trends

A review of cleaning products by the Swedish Chemicals Inspectorate (KEMI 1994) indicates that there was an increase in consumption of fragrances in from 170 tons in 1988 to 250 tons in 1992, and the observation was explained as a result of influence from Central Europe where cleaning and cleansing products tend to be more perfumed. In 1996, the amount was 260 tons (Hagenfors 1999), which may be an indication that the consumption of fragrances in cleaning products no longer increases. This is also expressed by producers for the Scandinavian market

For musk compounds the trends seem to go the following way:

Nitro musk → Polycyclic musk (Galaxolide and Tonalide) → Macrocyclic musk (Brassylic

acid)

It seems to be a trend that the polycyclic musk compounds are used as alternatives to the nitro musks. This is due to the superior fragrance qualities of the newer materials and to the concerns about potential toxicity of the nitro musk (OSPAR, 1997).

Polycyclic musk may face limited use in the future as it is not biodegradable. Brassylic acid that belongs to **macrocyclic musk** is expected to find an increasing market as a replacement for polycyclic musk, according to observers (Japan Chemical Week, 1998-6).

More companies will try to produce **macrocyclic musk** components (as Brassylic acid), which in contrast to **nitrocyclic** and **polycyclic** substances, present no health hazards and are biodegradable.

The rate of production of **nitromusk** compounds decreased annually by about 5 % between 1983 and 1987. This recession led to a simultaneous 5 % increase in the annual production of **polycyclic musk** compounds. This development can be explained by the persistence, bioaccumulation potential and toxicological fears about the nitromusk compounds. The commercial importance of nitromusks has continued to decrease.

The worldwide polycyclic musk market has grown from 4,400 metric tons in 1987 to its estimated size of 5,000 to 6,000 metric tons in 1992 (OSPAR, 1997). The use of polycyclic musks in Europe has decreased from 1992 to 1998 (**Table 12**).

The German Industrieverband Koerperpflege und Waschmittel eV (the body-care and detergents association) recommended its members from 1994 onwards to refrain from the use of **Musk Xylene** in household products, detergents and cleansing products. **Nitromusk** compounds are hardly produced any more in Europe, and at present, they are only still in production in relatively large quantities in China (800-900 tons/y).

The renunciation of the use of **nitromusks** has led to the use of substitutes, mainly **polycyclic musks**. **Galaxolide** and **Tonalide** are the principal substitutes used. The importance of **polycyclic musks** as fragrances was expected to increase because they can be used as substitutes for **nitro musks**. The use volumes for Europe reported in **Table 12**, however, do not confirm this concern.

Due to the actions already taken, and the general concern about the environmental fate and toxicity of nitro musks, their importance as fragrances is decreasing. As can be seen from Chapter 3.2 Production and use volumes, the use of **Musk Xylene** has decreased by about 50 % (from 174 tons in 1992 to 86 tons in 1998) in the last six years. For **Musk Ketone** the decrease is even more important during the same period.

Within the fragrance industry, extensive programs of safety testing of fragrance materials, both natural and synthetic started in the late 1960s and have continued and expanded ever since. Their most significant impact at the consumer level has been the reversal of the trend towards even more diffusive, pervasive and long-lasting fragrances which had started in the 1970s and had gained additional force in the '80s (Dragoco, 1997). A weekness of the programs is that environmental evaluations of the fragrance materials have not been performed.

The authorities might be steering the trends by introducing regulations for e.g. import, production, use, limits for spill and concentration levels in products. In addition legalizing the substitution duty, introduction of environmental taxes, agreements with the industry or economic life, official support for development of environment-friendly products, intensivation of their control, improvement of knowledge and improvement of information to industry and consumers may be important for steering the trends.

A producer of cleaning and cleansing products informs that the fragrance is the ingredient in a product that may be the one that is most often changed. The single fragrance has, due to this, a relative short lifetime. It is the consumers that control the demand and use of the different fragrances. Due to increasing demands for products without fragrances, the producer believes that the consumption of fragrances has decreased the last years. Increasing use of microfibre cloths and mops will also contribute to a decrease in use of fragrance containing cleaning agents.

A producer of cleaning and cleansing products was asked if they had any policy for use of natural contra synthetic fragrances. They answered that most of the fragrances probably were mixes of both natural and synthetic compounds, and a selection between natural contra synthetic fragrances rarely was an option. The same producer informed that due to the health and environmental harmful properties of musk compounds, they have demanded their suppliers years ago that the fragrances should not contain such substances. They were not aware if other fragrance compounds have musk-like harmful properties.

A population growth and a growth in one- person household will generally increase the consumption of detergents. The last years there has been both a population growth and a growth in one- person household. One- person household has problems to fill up a full washing machine and wash more often with half-filled machines. Accessibility to a washing machine within the single household also increases the washing frequency.

There have been changes in washing pattern the last years. The numbers of hours used for cleaning the house are reduced and a decrease in consumption of allround detergents is expected due to this factor. The numbers of showers and bathing are more frequent, particularly in households including young people. The consumption of shampoos, hair conditioners etc. is probably increased due to this factor.

For more information about trends also look to Chapter 3.2 Production and use volumes.

3.5. Differences between countries.

No extensive survey of differences between countries in use of fragrances has been performed, but some information on this matter has been obtained. There is probably a tendency to prefer less strongly fragranced products in the Nordic countries as compared to other European countries.

According to IFRA no geographical differences should be expected for the release pattern for musk ingredients into domestic waste water within Europe, unless a country has taken specific measures to phase out a certain substance (OSPAR, 1999).

In Germany and Switzerland voluntary actions to phase out Musk Xylene in detergents and cleaning agents have been successful. This is demonstrated by recent monitoring data. Musk Xylene could be detected only in one of 30 surface water samples taken in 1996 at different sites in the Berlin area and in sewage sludge, Musk Xylene was detected only in one of 12 treatment plants sampled at different locations in Switzerland (OSPAR, 1999).

4 RAW MATERIALS AND PRODUCTION

4.1. Introduction

A lifecycle analysis includes evaluation of production of raw materials, manufacturing, use and waste disposal. Each of the phases includes material and energy use, global, regional and local environmental stress and health influence. Global environmental stress includes two effects - greenhouse effect and degradation of the ozone layer. Regional environmental stress includes acidification, production of ozone near the ground and water pollution from nutrient salt loads and less degradable substances. Local stress includes landscape changes, as well as air, water, soil and ground water pollution and dust, noise and smell problems.

The limited information available on the composition, properties and amounts of fragrances used in cleaning and cleansing products does not allow any life-cycle approach in evaluation of environmental impact. Because of the use pattern of most cleaning and cleansing products, they tend to end up in the sewerage systems. Therefore the dominating environmental effects of the components of such products are generally associated with disposal of the washing water effluent. In addition, the fragrance compounds together with production chemicals are released to the wastewater at manufacturing of fragrances. Chemicals introduced into the municipal wastewater streams may, if degradation processes do not efficiently remove them, enter the environment via the effluent from the wastewater system or be incorporated in the sludge.

4.2. Raw materials

Fragrance raw material may be of natural (citrus oils, mint oils, pine oils etc.) or of synthetic (petrochemical) origin (IFRA, 2000[1]).

Large volume, natural raw materials used as fragrance in detergents are produced by agricultural methods, which involves the use of pesticides and fertilizers. Specific insecticides and fungicides are authorized for certain essential oil crops and their residues in the final product are limited. Certain low volume, high price materials, used specially in fine fragrances, are collected from wild plants (IFRA, 2000[1]).

The energy consumption for raw materials is mainly associated with the destillation process.

Hazardous chemicals might be used as reagents. The listed chemicals are not used as fragrance ingredients. If used as reagents, they will only be used inside closed reactors and not reach the environment (IFRA, 2000[1]).

Musk Xylene is synthesized from m-xylen by alkylation with isobuten, giving 1-tert.- butyl-3,5-dimethylbenzene, followed by nitration with HNO_3/H_2SO_4. The substances involved are known as human health hazards.

4.3. Production

Flavour and fragrances are either produced by synthesis or isolated from microbial, plant or animal sources.

The residues of the distillation of hydrocarbons and other organic molecules containing C, H and O can be burned and with that, the waste problems of the refinement reduced (IFRA, 2000[1]). Substances of environmental concern, as halogene compounds might be used. Very few halogenated fragrance ingredients are used in perfumery. Examples are bromostyrene and trichlorometyl phenyl carbinyl acetate.

To avoid environmental problems with the production process, the fragrance manufacturers have invested in sewage treatment plants for the factories and in equipment to avoid odour emissions during manufacturing and compounding. Emissions from fragrance production are now much lower than previously. No increase of sewage and odour emissions is expected to occur in the future (IFRA, 2000[1]).

Carrier solvents are needed for the uniform distribution of concentrated fragrance compounds in consumer products. Aqueous ethanol is the vehicle for applications of perfumes, eau de toilette, etc. Other solvents used in fragrances are e.g. diethylene glycol, propylene glycol, diethyl phthalate and iso-propanol (IFRA, 2000[2]). The producers of cleaning and cleansing products are in general not informed about what solvents that is used in the fragrance compound.

Goronszy (1992) describes the waste water from a fragrance producing factory. The majority of the total hydraulic load derives from washdown operations of the compounding vessels and cleaning of the production lines. Washwaters are essentially deionized water and alcohol mixtures combined with cleaning agents. Operation of the production line results in the addition of quantities of alkyl dimetylbenzyl ammonium chloride, a complex organic phosphate ester, a sulphonated aliphatic polyester and a nonylphenolethoxilate $(C_2H_4O)_{15}C_{15}H_{24}O$. In addition alcohol is used in formulation and cleaning operation. This results in a wastewater with a high organic load. The combined fragrance manufacturing waste stream was characterized by an initial COD (Chemical Oxygen Demand) of around 23000 mg/L.

Conventional biological treatment of the wastewater did not meet the requirements and indicated presence of toxic compounds. The toxicity was interpreted as deriving from a component in the wastewater or from an intermediate formed during the degradation reaction. Addition of a readily degradable alcohol-based co-substrate improved the performance of the biological treatment plant. Satisfactory removal of residual COD to meet the discharge specification was obtained in bench tests using catalyzed chemical oxidants following biological treatment (Goronszy 1992). This study shows that manufacturing of fragrances may produce wastewaters with a high content of organic compounds including components that are toxic and not readily degradable. Such wastewaters will usually require specifically designed treatment facilities.

Procter & Gamble in USA have carried out another study of the degradation of fragrance compounds in wastewater treatment plant. This has only been available as an abstract of a conference presentation (Simonich et al. 1999). Therefore the details on specific compounds are not known, but some general information is given. The physical-chemical properties (octanol-water partitioning and Henry's Law Constant) of the group of fragrance materials varied over several orders of magnitude. Fragrance material removal during activated sludge and trickling filter sewage treatment was measured. Removal after primary settling ranged from 32-67% while measured final removal ranged from 80 to greater than 99% depending on the physical-chemical properties and biodegradability's of the fragrance compounds.

4.4. By-products , impurities and additives

Data for parameters as by-products, impurities, disposal, degradation and ecotoxicity is specific for each ingredient. Since thousands of different fragrance ingredients are used, it is difficult to make a summary for these parameters.

There are none clorine or organometal content in artificial musks.

As anti-oxidants in fragrances, BHT (2,6-di-tert-butylhydroxytoluene, CAS 128-37-0) and Benzophenone (Diphenylmethanone, CAS 119-61-9) may be used. None of these CAS numbers are included in the Norwegian "Stoffliste" (Norwegian Pollution Control Authority, 1998). Data for the substances indicate that they are classified as dangerous for the environment (EnviChem 1.0). BHT is expected to be allergenic. BHT is included on the Swedish OBSERVATION (OBS) list, with danger for the environment as selection criteria (Internet, kemi.se).

The use of anti-oxidants is recommended for certain essential oils to prevent the formation of sensitizing oxidation products. This use is considered good manufacturing practice. In addition to BHT, BHA is most often used (IFRA, 2000[2]). A producer of cleaning and cleansing products informs that in general they are not informed if or to what extent the fragrances contain anti-oxidants.

4.5. Waste disposal

Disposal of cleaning and cleansing products will mainly occur to the municipal wastewater. The materials are discharged to the sewer and find their way to a sewage treatment plant. There, some part will be removed by adsorption to sludge and biodegradation. The remaining fraction in the effluent will be discharged in the freshwater environment. In the waterways leading to sea the concentrations will be lowered by dilution, adsorption to organic matter and biodegradation (OSPAR, 1999).

All musk ingredients are used in fragrances for products such as cosmetics, detergents, fabric softeners, household cleaning products etc. A large amount used for these purposes will therefore be released into domestic waste water. According to IFRA no geographical differences should be expected for the release pattern for musk ingredients into domestic waste water within Europe, unless a country has taken specific measures to phase out a certain substance (OSPAR, 1999). As a worst case for the aquatic environment it can therefore be assumed that 100% of the musks used in Europe is released into the waste water and that no substance remains on the fabric, skin or surfaces or has evaporated (OSPAR, 1999). Estimated use volumes of musks in Europe are given in Chapter 3.2. An equivalent comparison can be done for other types of ingredients in fragrances.
Nitro musks are not produced in Europe. Formulation is a possible point source, but probably does not contribute significantly to the overall release of these substances to the marine environment (OSPAR, 1999).

Monitoring in sewerage systems and in the environment has demonstrated that musk compounds are present in municipal wastewater and to some extent enters the receiving waters.

Musk xylene and other musk ingredients are lipophilic, poorly degradable and have a tendency to bioaccumulate. There have been discussions if they should be considered as Persistent Organic Pollutants POPs (OSPAR, 1999). Half-lives and degradation data are given in Chapter 5.1.

Some data for environmental concentrations of musks can be found in the literature. Nitromusks were first found in the environment in 1981. Musk substances are found in rivers, sewage waste water, fish, human milk and fat samples.

Some data for environmental concentrations of musks are given in **Table 14**. The high levels found in Europe compared to Japan correspond to the differences in use amounts between Europe and Asia.

The level of different musk compounds in water presented in literature (Bester et al., 1998, Eschke et al, 1994[1], Eschke et al, 1994[2], 1995, Gatermann, 1998, Paxeus, 1996, Yamagishi et al., 1981, Yamagishi et al., 1983), were in the range from 0.09 ng/L (HHCB in North Sea) (Bester et al., 1998) to 6000 ng/L HHCB and 5000 ng/L Musk Ketone in Swedish sewage waste water (Paxeus, 1996). High levels were found in Europe compared to Japan. River, Tama, Japan had a level of average 4.1 ng/L water for Musk xylene and 9.9 ng/L water for Musk ketone. Corresponding level for river Ruhr, Germany were 10 ng/L and 30 ng/L. Sewage effluents in Japan had a level of average 32 ng/L water for Musk xylene and 270 ng/L water for Musk ketone. Corresponding level for sewage effluents in Germany were up to 310 ng/L and up to 1300 ng/L.

Table 14. Some data for environmental concentrations of musks

Musk compound	**Place**	**Material**	**Concentration**
HHCB	North Sea	Water	0.09 ng/L
HHCB	Sweden	Sewage waste water	6000 ng/L
Musk Ketone	Sweden	Sewage waste water	5000 ng/L
Musk Xylene	Japan	River water	4.1 ng/L
Musk Xylene	Japan	Sewage effluent	32 ng/L
Musk Ketone	Japan, Tama	River water	9.9 ng/L
Musk Ketone	Japan	Sewage effluent	270 ng/L
HHCB	Germany	Sewage effluent	Average 1090 ng/L
Musk Xylene	Germany, Ruhr	River water	10 ng/L
Musk xylene	Germany (25 STP)	Sewage influent	90-1700 ng/l
Musk Xylene	Germany (25 STP)	Sewage effluent	Average 120 ng/L
Musk Xylene	Germany, Hamburg	Sewage influent	150 ng/l
Musk Xylene	Germany, Hamburg	Sewage effluent	10 ng/l
Musk Ketone	Germany, Ruhr	River water	30 ng/L
Musk Ketone	Germany (25 STP)	Sewage influent	570-2400
Musk Ketone	Germany (25 STP)	Sewage effluent	Average 630 ng/l
Musk Ketone	Germany, Hamburg	Sewage influent	550 ng/l
Musk Ketone	Germany, Hamburg	Sewage effluent	6 ng/l

The different investigations of musks in sewage water in Germany (Eschke et al. 1994) and Gatermann et al. (1998) indicate that the concentrations in effluents from sewage treatment plants may have been lower in the later study, which was carried out after the voluntary agrement on reduced use of musks in 1994. However, Gatermanns study included only one site (Hamburg), and gives no indication on the effectiveness of the agreement. The musk HHCB showed a trend towards higher concentrations in 1995 compared to 1990 at some stations in estuarine and marine waters (North Sea). Nitromusks (mainly Musk xylene and ketone) are found regularly in fish from German rivers (Rimkus, 1996[1], 1997[1]), e.g. up to 1.8 mg/kg fat tissue of Musk xylene in German trout (Hahn, 1993).

4.6. Energy consumption

No details on the energy consumption involved in production of fragrances were available. Fragrance ingredients are often refined by distillation. The energy needed for the distillation of essential oils can be obtained from burning of the exhausted plant material. The energy consumption during the production is unknown according to IFRA (IFRA, 2000[1]).

5 INHERENT PROPERTIES

5.1. Degradation

Some fragrances and herb and spice extracts used as fragrances might have antimicrobial effect. In addition preserving agents added to the fragrance compounds might have antimicrobial effect. Toxic effects on bacteria may reduce the potential for biodegradation in sewage treatment plants as shown e.g. by Goronszy (1992). The complex nature of many of the fragrance compounds also suggests that many of them may not be readily biodegradable although information on this subject is scarce.

A search for degradation data for fragrance compounds given in **Table 2** and **Table 3** has been made. The result is shown in **Table 15**. A list of literature used for data search is given in Appendix 1.

Most of the fragrance compounds listed in **Table 15** for which information is available show that they are readily biodegradable. However for several compounds no information could be found. It should be noted that it is not known to which extent these fragrances are used in cleaning and cleansing products.

A study performed in USA has shown a removal of 80-99% of fragrance materials in sewage treatment plants (Simonich et al. 1999), but it is not known to which extent the removal was caused by adsorption to the sludge rather than biodegradation. Note that also the non-readily degradable musk xylenes and musk ketones may be removed more than 90% in treatment plants (Gatermann et al. 1998)

Table 15. Degradation data for some fragrance compounds.

Fragrance compound	CAS number	Degradation data	Reference
α-amylcinnamaldehyde	122-40-7	Not readily biodegradable (51 %)	MITI (1992)
α-amylcinnamic alcohol	101-85-9	No data	
Anisyl alcohol	1331-81-3	No data	
Benzyl salicylate	118-58-1	No data	
Benzylalcohol	100-51-6	Readily biodegradable (Mod. MITI 301C method) Inherent biodegradable (92 %) QSAR calculated 98.78 % degradation	Envichem + MITI (1992) Envichem QSAR

Fragrance compound	CAS number	Degradation data	Reference
Cinnamaldehyde = Cinnamic aldehyde = Cinnamal	104-55-2	Readily biodegradable QSAR calculated 100 % degradation	IUCLID QSAR
Cinnamon **brown**	8052-76-4	No data	
Cinnamon **oil**	8015-91-6	No data	
Cinnamyl alcohol = Cinnamic alcohol	104-54-1	Readily biodegradable Readily biodegradable (91 %) QSAR calculated 98.24 % degradation	IUCLID MITI (1992) QSAR
Citral	5392-40-5	Readily biodegradable Readily biodegradable (94 %) QSAR calculated 99.97 % degradation	IUCLID MITI (1992) QSAR
Coumarin	91-64-5	Readily biodegradable Readily biodegradable (100 %) Inherent biodegradable (100 %) QSAR calculated 99.34 % degradation	Envichem MITI (1992) Envichem QSAR
Eugenol	97-53-0	QSAR calculated 98.8 % degradation	QSAR
Geraniol	106-24-1	Readily biodegradable QSAR calculated 87 % degradation	IUCLID QSAR
Hydroxycitronellal	107-75-5	QSAR calculated 99.76 % degradation	QSAR
Isoeugenol	97-54-1	QSAR calculated 97.88 % degradation	QSAR
Oak moss **resin**	9000-50-4	No data	
Sandalwood oil	8006-87-9	No data	

Among the synthetic musk compounds, nitromusks and polycyclic musks have the lowest potential for biodegradation. Indeed, several biodegradation tests performed with the four nitro musks (Musk xylene, Musk ketone, Musk moskene and Musk tibetene) demonstrate that these chemicals do not mineralise under standard test conditions. Macrocyclic musks, which have a structure more similar to naturally occurring musks, seem to be biodegraded much easier, with less potential of causing long-lasting effects in the environment. Ethylene brassylate, which is produced from brassylic acid, has a chemical structure resembling that of natural musk and featuring a high level of biodegradability (Japan Chemical Week 1998).

Degradation data for some musk compounds are given in **Table 16**.

Table 16. Degradation data for some musk compounds (OSPAR, 1999)

Type of musk	Degradation data
Nitromusks	
Musk ketone	Not inherently biodegradable (MITI II)
Musk xylene	Not readily biodegradable (MITI I)
Musk tibetene	Not inherently biodegradable (MITI II)
Musk moskene	Not inherently biodegradable (MITI II)
Polycyclic musks	

Type of musk	Degradation data
HHCB	Not readily biodegradable (mod. Sturm test)
AHTN	Not inherently biodegradable (MITI II) (<1% biodegradation after 28 days) Low mineralisation (ISO 10708)
ADBI	Not inherently biodegradable (MITI II) (<1% biodegradation after 28 days)
AITI	No data available
AHMI	Low mineralisation (ISO 10708)

Recently, the biotransformation of HHCB was examined under realistic conditions in activated sludge. It was found that HHCB is biotransformed during wastewater treatment with an estimated half-life of approximately 35 hours to 2 polar metabolites that have substantially lower Pow values than the parent (measured values: 5.9 for HHCB, 2.0-3.0 for metabolite 1, ca. 0 for metabolite 2). No volatilisation of HHCB was observed (OSPAR, 1999, Annex 3).Data from a sewage treatment plant in Germany indicate that the level of Musk xylene and Musk ketone are reduced with respectively 93 % and 99 % during the treatment process. The level of the metabolites 4-amino-metabolite and 2-amino-metabolite increased from "not detectable" in the influent to 34 ng/L and 250 ng/L respectively in the effluent.

The decrease in the concentration of the parent compounds and the increase of the amino derivatives suggest that, besides adsorption to sludge, the transformation of the nitromusks is an important process in the treatment plant (OSPAR, 1999).

Data for river water and sewage treatment plant in Germany are given in **Table 17**.

Table 17. Data for river water and sewage treatment plant in Germany (Gatermann et al., 1998)

Elbe river, Germany, 1995:	River water	Sewage treatment plant (conc. in ng/L) Influent	 Effluent
Musk Xylene		150	10
4-amino-metabolite	1-9	n.d.	34
Musk Ketone		550	6
2-amino-metabolite	7	n.d.	250

In a recent study, degradation products of nitro musks were analysed in digested sewage sludge from Swiss treatment plants. 4-Amino Musk xylene was detected in 6 of 12 samples and 2-Amino Musk ketone in 1 of 12 samples. Degradation products of Musk xylene have also been detected in sediments of river Elbe, Germany (OSPAR, 1999).

Polycyclic musks-possible substitutes for musk xylene- have a similar hazard profile to nitro musks. HHCB and AHTN have been detected in many samples of wastewater, surface water, sewage sludge, suspended matter, sediments and biota at levels exceeding those of Musk xylene. The ubiquitous presence of these substances in the aquatic environment may be explained by the continuous input of these chemicals through sewage treatment plant effluent discharges into the aquatic environment and the low degradation rates. The concentrations detected so far seem to be at a safe level and the formation of toxic metabolites has not been reported. The risk of causing adverse effects, therefore, is lower for polycyclic musks than for nitro musks and immediate action is not considered necessary by OSPAR (1999).

The photodegradation half-lives for the nitro musks (Musk xylene, Musk ketone, Musk moskene and Musk tibetene) are in the range of 2.0-8.2 minutes. The half-life of AHTN under similar conditions was determined to be 1.25 minutes (OSPAR, 1999).

5.2. Ecotoxicity

No data regarding ecotoxicity has been accessible from the producers of cleaning and cleansing products or the fragrance producers. Producers of cleaning and cleansing products claims that toxicity data rarely are given in data they got from the fragrance producers.

We have made some search in literature for exotoxicity data for fragrance compounds given in **Table 2** and **Table 3**. These exotoxicity data are given in **Table 18**. A list of literature used for data search is given in Appendix 1.

Table 18. Ecotoxicity data for some fragrance compounds. Acute toxicity data are expressed as LC_{50} or EC_{50} values, Chronic toxicity as NOEC.

Fragrance compound	CAS number	Ecotoxicity data	Reference
α-amylcinnamaldehyde	122-40-7	Acute QSAR calculated: Fish: 2 mg/L Daphnia: 0.7 mg/L Algae: 0.6 mg/L	QSAR
α-amylcinnamic alcohol	101-85-9	No data	
Anisyl alcohol	1331-81-3	No data	
Benzyl salicylate	118-58-1	No data	
Benzylalcohol	100-51-6	Acute: Fish: 10 mg/L Daphnia: 55 mg/L Daphnia: 400 mg/L Algae: 336 mg/L Algae: 2600 mg/L Algae: 100 mg/L Chronic: Fish: 63 mg/L Daphnia: 20 mg/L Acute QSAR calculated: Fish: 530 mg/L Daphnia: 490 mg/L Algae: 530 mg/L Chronic QSAR calculated: Fish: 58 mg/L	 IUCLID+Aquire IUCLID Nordbas2 IUCLID Nordbas2 Aquire IUCLID IUCLID QSAR QSAR
Cinnamaldehyde = Cinnamic aldehyde = Cinnamal	104-55-2	Acute QSAR calculated: Fish: 150 mg/L Daphnia: 120 mg/L Algae: 120 mg/L	QSAR
Cinnamon brown	8052-76-4	No data	
Cinnamon oil	8015-91-6	No data	
Cinnamyl alcohol = Cinnamic alcohol	104-54-1	Acute QSAR calculated: Fish: 150 mg/L Daphnia: 110 mg/L Algae: 110 mg/L	QSAR

Fragrance compound	CAS number	Ecotoxicity data	Reference
Citral	5392-40-5	Acute:	
		Fish: 4.6 mg/L	IUCLID
		Daphnia: 7 mg/L	IUCLID
		Algae: 16 mg/L	IUCLID
		Chronic:	
		Fish: 2.0 mg/L	IUCLID
		Daphnia: 1.1 mg/L	IUCLID
		Acute QSAR calculated:	QSAR
		Fish: 7 mg/L	
		Daphnia: 4 mg/L	
		Algae: 3 mg/L	
Coumarin	91-64-5	Acute:	
		Fish: 8.3 mg/L	Aquire
		Acute QSAR calculated:	QSAR
		Fish: 310 mg/L	
		Daphnia: 260 mg/L	
		Algae: 270 mg/L	
		Chronic QSAR calculated:	QSAR
		Fish: 32 mg/L	
Eugenol	97-53-0	Acute:	
		Fish: 24 mg/L	Aquire
		Acute QSAR calculated:	QSAR
		Fish: 32 mg/L	
		Daphnia: 20 mg/L	
		Algae: 18 mg/L	
		Chronic QSAR calculated:	QSAR
		Fish: 3 mg/L	
Geraniol	106-24-1	Acute QSAR calculated:	QSAR
		Fish: 7 mg/L	
		Daphnia: 4 mg/L	
		Algae: 3 mg/L	
		Chronic QSAR calculated:	QSAR
		Fish: 0.6 mg/L	
Hydroxycitronellal	107-75-5	Acute QSAR calculated:	QSAR
		Fish: 110 mg/L	
		Daphnia: 80 mg/L	
		Algae: 79 mg/L	
		Chronic QSAR calculated:	QSAR
		Fish: 11 mg/L	
Isoeugenol	97-54-1	Acute QSAR calculated:	QSAR
		Fish: 37 mg/L	
		Daphnia: 24 mg/L	
		Algae: 22 mg/L	
		Chronic QSAR calculated:	QSAR
		Fish: 3 mg/L	

Fragrance compound	CAS number	Ecotoxicity data	Reference
Oak moss resin	9000-50-4	No data	
Sandalwood oil	8006-87-9	No data	

Several studies concerning the aquatic toxicity of the nitro musk ingredients are available. The most reliable studies are summarised in **Table 19**. The lowest reported NOEC values, which have been used for the risk assessment, are: 0.063 mg/L (fish) for Musk Ketone and 0.056 mg/L (Daphnia) for Musk Xylene (OSPAR, 1999).

Table 19. Aquatic toxicity of nitro musks (OSPAR, 1999)

Nitro musks	Bacteria	Algae	Crustacean	Fish
Moskene	*Vibrio fischeri* EC$_{50}$ 30 min. > 0.037 mg/L	*Scenedesmus subspicatus*, EC$_{50}$ 72h > 0.046 mg/L (no effect at water solubility)	*Daphnia magna*, EC$_{50}$ 48h > 0.046 mg/L (no effect at water solubility)	
Musk Tibetene	*Vibrio fischeri* EC$_{50}$ 30 min. > 0.042 mg/L	*Scenedesmus subspicatus*, EC$_{50}$ 72h > 0.052 mg/L (no effect at water solubility)	*Daphnia magna*, EC$_{50}$ 48h > 0.052 mg/L (no effect at water solubility)	
Musk Ketone	*Vibrio fischeri* EC$_{50}$ 30 min. > 0.34 mg/L	*Selenastrum capricornutum*, E_rC_{50} 72h = 0.244 mg/L *Scenedesmus subspicatus*, EC$_{50}$ 72h > 0.46 mg/L (no effect at water solubility)	*Daphnia magna*, EC$_{50}$ 48h > 0.46 mg/L (no effect at water solubility) *Daphnia magna*, EC$_{50}$ 21d (reproduction) = 0.169-0.338 mg/L	*Oncorhynchus mykiss*, NOEC 21 d. = 0.063 mg/L
Musk Xylene	*Vibrio fischeri* EC$_5$0 30 min. > 0.12 mg/L	*Selenastrum capricornutum*, NOEC 5d. > 5.6 mg/L *Scenedesmus subspicatus*, EC$_{50}$ 72h > 0.15 mg/L (no effect at water solubility)	*Daphnia magna*, NOEC 48h. = 0.32 mg/L *Daphnia magna*, NOEC 21d (reproduction) = 0.056 mg/L	*Bluegill sunfish*, LC50 96h = 1.2 mg/L *Brachydanio rerio*, LC$_{50}$ 14d. = 0.4 mg/L

The aquatic toxicity for the polycyclic musks is summarised in **Table 20**. The lowest reported NOEC values which have been used for the risk assessment are 0.068 mg/L (fish) for HHCB and 0.035 mg/L (fish) for AHTN (OSPAR, 1999).

Table 20. Aquatic toxicity of polycyclic musks (OSPAR, 1999)

Polycyclic musk	Algae	Crustacean	Fish
AITI		*Daphnia magna*, EC_{50} 48h. = 0.42 mg/L	
AHMI	*Selenastrum capricornutum*, E_bC_{50} 72h. = 0.081 mg/L E_rC_{50} 72h. = 0.2 mg/L NOEC (growth rate) = 0.044 mg/L	*Daphnia magna*, EC_{50} 48h. = 0.33 mg/L	*Brachydanio rerio*, NOEC 96h. = 0.9 mg/L
HHCB	*Pseudokirchneriella subcapitata*, E_bC_{50} 72 h = 0.723 mg/L	*Daphnia magna*, NOEC 21d. = 0.111 mg/L	*Lepomis macrochirus,* NOEC 21d. = 0.182 mg/L *Pimephales promelas*, NOEC 36d. = 0.068 mg/L
AHTN	*Pseudokirchneriella subcapitata*, E_bC_{50} 72 h = 0.468 mg/L	*Daphnia magna*, NOEC 21d. = 0.196 mg/L	*Lepomis macrochirus,* LC50 21d. = 0.314 mg/L *Pimephales promelas*, NOEC 36d. = 0.035 mg/L

The musk compounds are designed to mimic natural musk flavour, which is a pheromone in many species. It can be assumed that these substances, if entering the environment in comparably high concentrations, might have confusing or bewildering effects on animals, thus influencing the regulation of the endocrine and reproductive system. This is highly hypothetical as each organism produces highly species-specific pheromones that only to a small extent is reproduced in the artificial produced musks.

5.3. Risk assessment

Risk assessments of chemicals involve the comparison of measured or estimated environmental exposure concentrations (PEC) with the known or predicted no effect concentration (PNEC). When the assessment shows a ratio PEC/PNEC<1, the risk of harm to the environment is expected to be insignificant. Estimation of PEC for different environmental compartments is usually based on various discharge scenarios and models for dissipation and partitioning. PNEC may be estimated from sets of toxicity tests, covering acute and chronic effects on various organisms. The uncertainty involved in these estimates is accounted for by use of appropriate uncertainty factors.

The risk assessment approach may be useful also as a basis for ecolabelling. When ranking of components is based on inherent properties only, too much emphasis may be put on minor ingredients in the products, which contribute little to the total environmental effect of the product. Properly undertaken risk assessments provide a basis for focussing on the components that pose the most significant risk. On the other hand, risk assessment is, of course, much more resource demanding than ranking based on inherent properties. For persistant organic chemicals there is a need for caution even when risks assesments indicate little risk. This is because such compounds will persist long in the environment with the potential of causing effects that could not be forseen. Furthermore, it may be argued that contamination of the environment with xenobiotic compounds should be avoided even if no detrimental effects are expected.

A wide-ranging risk assessment was carried out for Musk xylene and Musk ketone by National Institute of Public Health and Environmental Protection (RIVM), The Netherlands, according to EU Technical Guidance Document for the Risk Assessment of New and Existing Substances (Tas et al., 1997). The PEC/PNEC ratios for aquatic organisms and sediment organisms have been found to be <1 for both Musk xylene and Musk ketone. For Musk xylene, the PEC/PNEC ratio for the soil compartment was just above one. However this value was associated with a rather high uncertainty. High assessment factors have been used to determine the PNEC. In addition, the PEC has been calculated assuming ten yearly applications of sludge to agricultural land and nitro musk content of about 20 mg/kg. Recent data on concentrations in digested sludge indicate levels below this value and sometimes below the detection limits, indicating that the estimated concentrations in sludge and also in soil were overestimated by a factor in the range of 20 to 1'000. This implies that the risk quotient for soil organisms for both Musk xylene and Musk ketone is well below 1 (OSPAR, 1999).

This preliminary assessment needs to be refined by taking into account the presence of degradation products in the environment. This is, however, not possible for the time being. The acute toxicity of 4-amino musk xylene (1-tert-butyl-3,5-dimethyl-4-amino-2,6-dinitrobenzene) and 2-amino musk xylene (1-tert-butyl-3,5-dimethyl-2-amino-2,6-dinitrobenzene) on *Daphnia magna* has recently been determined (Behechti et al., 1998). The toxicity of 4-amino musk xylene was reported to be about three orders of magnitude higher than the parent compound. Sponsored by RIFM the acute test with *Daphnia magna* was repeated under four different test conditions (Putt, 1999). The results of Behechti et al. could not be reproduced. The new study indicates that the toxicity of 4-amino musk xylene is in the same order as reported for the parent compound. A comprehensive evaluation and comparison of the two Daphnia tests and eventually additional toxicity tests with *Daphnia magna* and other aquatic species are needed to draw reliable conclusions on the aquatic toxicity of the metabolites.

In February 1999, a report "Marine occurrence and toxicity of nitro musks" prepared by the Netherlands, has presented to the OSPAR Working group SIME. In this report provisional Ecotoxicological Assessment Criteria (EACs) were estimated. Environmental concentrations below EAC are considered as safe levels. The following EACs have been derived for Musk xylene and Musk ketone:

EACs for Musk xylene:	for water	0.01-0.1 µg/L
	for sediment	5-50 mg/kg
	for mussel	0.5-5 mg/kg
	for fish	0.5-5 mg/kg
EACs for Musk ketone:	for water	0.05-0.5 µg/L
	for sediment	1-10 mg/kg
	for mussel	0.1-1 mg/kg
	for fish	0.1-1 mg/kg

The concentrations of Musk xylene in the marine environment are lower than EACs. The authors concluded that the concentrations of Musk xylene and Musk ketone in the maritime environment appear to be at a safe level (lower than EACs). For the assessment of environmental concentrations however, a better understanding of the risk an extremely toxic metabolite of Musk xylene may pose to marine organisms is necessary. For Musk moskene, Musk tibetene and Musk ambrette it was not possible to assess the concentrations by means of EACs due to lack of sufficient toxicity data (OSPAR, 1999).

The risk associated with the use of Musk moskene and Musk tibetene are concidered to be negligible due to the similar properties but considerably smaller use volume of these compounds.

A similar risk assessment has been performed for the musk compounds HHCB and AHTN by RIVM in 1997. The PEC/PNEC ratios for aquatic organisms and for sediment organisms were clearly less than 1 (OSPAR, 1999). Again the compartment of concern was the soil compartment where PEC/PNEC ratio has been calculated to be greater than 1 for HHCB and close to 1 for AHTN. However, these calculations assume absence of any biodegradation in soil during 120 years, whereas soil degradation data for HHCB show 60% disappearance within one year. Recent soil studies show half-lives of 3 months or less. A refined assessment based on more realistic but still conservative assumptions are now available. Taking a very conservative half-life of 6 months in soil, risk quotients are in the order of 0.1 for the soil compartment. Since the preparation of the initial assessment reports for Musk xylene, Musk ketone, AHTN and HHCB some additional monitoring data have become available. They confirm the overall conclusion that PEC/PNEC ratios are below 1 (OSPAR, 1999).

A preliminary risk assessment was also performed for the "minor" polycyclic musks ADBI, AHMI and AITI by HASKONING on behalf of RIFM. A draft assessment report was made available in June 1998 but has not yet been officially published. As expected the outcome of the assessment demonstrated a low risk for aquatic organisms and sediment organisms (similar properties to other polycyclic musks, smaller use volume) (OSPAR, 1999).

Both the PEC/PNEC approach and the method for derivation of Ecotoxicological Assessment Criteria (EACs) do not indicate a risk for secondary poisoning for musk compounds. Using calculated PECs, the PEC/PNEC ratio for Musk xylene is 0.01. Using monitoring data, this figure drops to 0.0008, and the provisional EAC_{biota} is also below concentrations found in marine and freshwater species. However, all these figures are very uncertain. Toxicity studies using predators present in the environment such as fish-eating birds are not available and it is uncertain whether the toxicity of metabolites and the risk they pose to predators is adequately reflected in these assessments. As a consequence the level of Musk xylene in the North Sea and the OSPAR catchment area cannot be considered as safe. More data are needed to refine the assessment (toxicity of metabolites for additional species; toxicity for marine predators; levels of Musk xylene in predatory mammals). As a precautionary measure discharges, losses and emissions of Musk xylene should be reduced further (OSPAR, 1999).

5.4. Human toxicity

5.4.1 Introduction

No data regarding human toxicity has been accessible from the producers of cleaning and cleansing products or the fragrance producers. Producers of cleaning and cleansing products claims that toxicity data rarely are given in data they got from the fragrance producers. The fragrance products are however evaluated for classification and most of the fragrances are not classified, a few are classified as inflammable, a few as irritating and a few as harmful.

The main source of none-occupational exposure to fragrances and extracts is resorption of these compounds through the skin from cosmetics and freshly washed textiles. Intake from food (mainly fish) plays a minor role (Rimkus, 1996[1], 1997[1], OSPAR 1999).

The problems with fragrances and extracts regarding human health have been related to allergic reactions and lately, possibility for hormone effects by biocides in the fragrances.

Among the musk compounds negative effects on humans have been reported for polycyclic musk and nitromusk. Musk Ambrette caused testicular atrophy in rats and some metabolites of Musk xylene might be carcinogenic, but generally, the acute toxicity of musk compounds is low. Macrocyclic musk components, in contrast to the nitro- and polycyclic musks, appear to present no health hazards and are in addition biodegradable.

Nitromusk compounds have been found in human adipose and human milk samples. The ranking concentrations were as follows: Musk xylene > Musk ketone > Musk ambrette/moskene (Rimkus, 1996[1], 1997[1]). The dermal sorption of these lipophilic compounds from cosmetics and detergents is discussed as a possible contamination route (Rimkus, 1996[2]). Use of nitro musk is limited because of phototoxicity.

For Musk Xylene a "virtual safe dose (VSD) of 3 ng/kg body weight for humans has been derived from experimental mutagenicity data in mice; infants are exposed to 440 ng/kg body weight (calculated average daily intake through female milk), which equals to 150 times the VSD amount (Rimkus, 1996[1], 1997[1]).

The allergic and potentially hormone aspects of fragrances and extracts might be a problem during the hole life-cycle of fragrances and extracts including handling of raw material, production, use and waste disposal. Because workers are protected through working environment legislation and are often more aware of using protective equipment, the focus should be on the consumers.

The allergic reactions of fragrances and extracts are mainly related to allergic reactions by contact, but some people are sensitive even for smell and might get breathing problems. Only few molecules are enough to induce such reactions. In addition to sensitive persons fragrances and extracts are well known as a problem for new-born and kids. Special attentions should be taken for products that might cause problems for these groups. Not only soaps, shampoos, lotions and other products in direct dermal contact are well known as a problem for these peoples, but even clothes washed with detergents or rinsed with rinse aid containing fragrances and extracts may cause severe problems. In addition use of products containing fragrances and extracts might induce sensitivity or allergy over time by persons without such problems. Next, sensitivity for one substance often lead to sensitivity for a large number of substances with following problems for these people and their surroundings.

Fragrances might be a problem for the indoor climate. After cleaning a room, both the cleaners and people using the room will be exposed to the volatile compounds, like fragrances. They might cause headache and respiratory irritation.

More and more products on the market e.g. soap, dishwashing detergents and toothpaste contain anti-microbial agents. Some of these may cause allergy and there might be a risk that these biocides have an influence on the hormones. The effects will be dose dependent. The anti-microbial compounds are biologically active substances and therefore may damage living cells. They may be poorly biodegradable and many products containing them will, due to this reason, not fulfil the ecolabelling criteria. In products containing anti-microbial compounds, these might occur in the fragrances. Because anti-microbial compounds may occur in the fragrances the potential problems of such chemicals are mentioned here. A more detailed evaluation of anti-microbial compounds or biocids, as separate components in products, should be done separately.

The producers consider that natural fragrances and ethereal oils with antibacterial effects are without problems. This claim is not examined. Results ofl ong-term tests have not been available.

5.4.2 Acute toxicity

Generally, the acute toxicity of musk compounds is low (Rimkus, 1996[1], 1997[1]).

Some oral, dermal and inhalation data are given below:

Musk natural (for comparative reasons)
T/E unlistd orl-rat LD50: 339 mg/kg (Gekkan, 1980)
T/E unlistd orl-mus LDLo: 1600 mg/kg (Archives of Env. Contam. and Tox., 1985)

Musk Ambrette
J26-R21 orl-rat LD50: 339 mg/kg (Food and Cosmetics Toxicology, 1963-81[1])
Multiple dose toxicity data:
F18-Q30-U01 orl-rat TDLo: 10500 mg/kg/20W-I (Toxicol. and Applied Pharmacology,1967)
A06-B04-C18 orl-rat TDLo: 6300 mg/kg/12W-C (Toxicol. and Applied Pharmacology,1984)
B04-C18-Z73 skn-rat TDLo: 6750 mg/kg/90D-I (Food and Chemical Toxicology, 1990[1])

Musk Ketone
T/E unlistd unr-rat LD50: 10 gm/kg (Bulletin of Environm. Contam. and Toxicology, 1981[1])
T/E unlistd unr-rbt LD50: 10 gm/kg (Bulletin of Environm. Contam. and Toxicology, 1981[1])

Musk Moskene
T/E unlistd orl-rat LD50: >5 gm/kg (Food and Cosmetics Toxicology, 1963-81[2])
T/E unlistd skn-rbt LD50: >5 gm/kg (Food and Cosmetics Toxicology, 1963-81[2])

Musk Xylene
T/E unlistd orl-rat LD50: >10 gm/kg (Bulletin of Environm. Contam. and Toxicology, 1981[1])
T/E unlistd orl-mus LD50: >4 gm/kg (Food and Chemical Toxicology, 1990[2])
T/E unlistd skn-rbt LD50: >15 gm/kg (Bulletin of Envir. Contam. and Toxicology, 1981[2])
Multiple dose toxicity data:
F11-K06-Z01 orl-mus TDLo: 5040 mg/kg/14D-C (Eisei, 1990)
Z01 orl-mus TDLo: 21420 mg/kg/17W-C (Eisei, 1990)

5.4.3 Chronic toxicity

Reproductive toxicity

Musk Ambrette caused testicular atrophy in male rats (Rimkus 1996[1], 1997[1]).

Carcinogenity

Human carcinogens are not used as fragrance ingredients according to IFRA (IFRA, 2000[1]). However, some metabolites of Musk xylene might be carcinogenics, but this is yet not proved (Rimkus 1996[1], 1997[1]).

Musk Xylene: tumorigenic effects: V01-L60-N60 orl-mus TDLo: 36 gm/kg/80W-C (Food and Chemical Toxicology, 1990[3])
Some metabolites might be carcinogenics (not proved).

Genotoxicity/mutagenicity

Musk Ambrette:
mmo-sat 2 µmol/plate (+S9) (Food and Chemical Toxicology, 1983[1])
mmo-sat 100 µg/plate (-S9) (Food and Chemical Toxicology, 1986)
sln-dmg-orl 10 mmol/L (Food and Chemical Toxicology, 1983[2])

The synthetic **polycyclic musk flavor** compounds **Galaxolide, Tonalide, Celestolide, Phantolide, Cashmeran,** and **Trasolide** revealed no significant increase in the frequency of micronuclei in human lymphocytes nor in the human hepatoma cell line Hep G2 (Internet, swan.ac.uk).

Irritation

Musk Ambrette: airborne contact, hyperpigmentation, photoallergy, persistent light reaction; irritation data: skn-rbt 500 mg/24 H MOD (Food and Cosmetics Toxicol., 1975[1])
Musk Ketone: "Weak contact sensibilizator" (Rimkus 1996[1], 1997[1]).
Musk Moskene: Irritation data: skn-rbt 500 mg/24H MOD (Food and Cosmetics Toxicol., 1979)
Musk Tibetene: Irritation data: eye-rbt 100 mg/24 H MLD (Food and Cosmetics Toxicol., 1975[2]).
Musk Xylene: Photoallergy, "weak contact sensibilizator" (Rimkus 1996[1], 1997[1]). Irritation data: skn-hmn 5 mg/48H MLD (Food and Cosmetics Toxicol., 1975[3]).
Musk T: irritation data: skn-rbt 500 mg/24H MOD (Food and Cosmetics Toxicol., 1975[4]).

Neurotoxicity

Musk Ambrette: "Various tests and clinical experience have demonstrated that musk ambrette may cause photocontact **sensitization**, i.e. **allergic reactions** of the skin on exposure to musk ambrette and sunlight. Other studies have indicated that musk ambrette may also cause **neurotoxic** effects. The International Fragrance Association has recommended that musk ambrette should not be used in products applied to the skin, particularly those products used on skin that is customarily also exposed to sunlight" (Internet, vm.cfsan.fda.gov).

Musk Ambrette can cause central and peripherical nervous system damage characterized by degeneration of myelin and selected distal axons and extreme sensitivity to sunlight, in exposed laboratory animals (Internet, thebookstore.com).

Developmental toxicity of synthetic musk fragrances (**Musk Xylene, Galaxolide, Tonalide**) in the rat: Neurobehavioral processes, immune system, neuroendocrine regulation and cytochrome P450 enzyme expression (Internet, unizh.ch).

For **Musk Ambrette** and **ATTN (Versalide**) neurotoxic effects in rats have been shown (Rimkus 1996[1], 1997[1]).

Endocrine potential

Not proved (Rimkus 1996[1], 1997[1])

Metabolites

For **Musk Xylene** in rats, aromatic amines have been found as metabolites (Rimkus 1996[1], 1997[1]).

5.5. Bioaccumulation

Certain fragrance ingredients have been found at very low levels in human fat and milk as well as fish. These materials are slowly excreted and an equilibrium is reached between amounts continuously absorbed through the skin and the amounts eliminated (IFRA, 2000[1]).

We have made some search in literature for bioaccumulation data for fragrance compounds given in **Table 2** and **Table 3**. No bioconcentration studies have been performed with these compounds, but values for octanol water partitioning (Pow) are available or can be calculated using QSAR models. These data are given in **Table 21**. Compounds with Log Pow less than 3 may be regarded as having a low potential of bioaccumulation. A list of literature used for data search is given in Appendix 1.

Most of the fragrances listed in **Table 21** have a low potential for bioaccumulation. Only α-amylcinnamaldehyde, citral and geraniol have Pow values that indicate a moderate potential for bioaccumulation.

Table 21. Bioaccumulation data for some fragrance compounds.

Fragrance compound	CAS number	Bioaccumulation data	Reference
α-amylcinnamaldehyde	122-40-7	Log Pow 4.33 (calculated)	QSAR
α-amylcinnamic alcohol	101-85-9	No data	
Anisyl alcohol	1331-81-3	No data	
Benzyl salicylate	118-58-1	No data	
Benzylalcohol	100-51-6	Log Pow 0.95 - 1.15 Log Pow 1.1 Log Pow 1.08 (calculated)	Nordbas2 IUCLID QSAR
Cinnamaldehyde = Cinnamic aldehyde = Cinnamal	104-55-2	Log Pow 1.88 Log Pow 1.82 (calculated)	Verschueren QSAR
Cinnamon **brown**	8052-76-4	No data	
Cinnamon **oil**	8015-91-6	No data	
Cinnamyl alcohol = Cinnamic alcohol	104-54-1	Log Pow 1.95 Log Pow 1.84 (calculated)	Envichem QSAR
Citral	5392-40-5	Log Pow 2.76 Log Pow 3.45 (calculated)	IUCLID QSAR
Coumarin	91-64-5	Log Pow 1.39 Log Pow 1.51 (calculated)	Envichem QSAR
Eugenol	97-53-0	Log Pow 2.73 (calculated)	QSAR
Geraniol	106-24-1	Log Pow 3.47 (calculated)	QSAR

Fragrance compound	CAS number	Bioaccumulation data	Reference
Hydroxycitronellal	107-75-5	Log Pow 2.11 (calculated)	QSAR
Isoeugenol	97-54-1	Log Pow 2.65 (calculated)	QSAR
Oak moss **resin**	9000-50-4	No data	
Sandalwood oil	8006-87-9	No data	

Musk compounds are known to accumulate in biological tissues. Musk xylene and Musk ketone have high Log Pow and bioconcentration factors (BCF). The elimination rate constant has been found to be 0.27-0.47 d^{-1}, which gives a recalculated elimination half-life of 2.2-2.6 days for Musk ketone in fish. Hence it seems that the uptake of Musk ketone was highly reversible. For Musk xylene no studies with investigations of metabolites and/or determination of elimination rates are available. Estimated elimination half-lives of 1-2 days were reported for AHTN and 2-3 days for HHCB (OSPAR, 1999).

In general Log Pow of nitromusks are high. Nitro- and polycyclic musk compounds are persistent and show high bioconcentration in the aquatic environment. However, biomagnification in food-chains does not occur. Some data for Log Pow and BCF are given in **Table 22**. As in freshwater and sediment samples, amino metabolites of Musk xylene and Musk ketone have also been detected in biota samples as fish and mussels (OSPAR, 1999).

Table 22. Log Pow and BCF data for some musk compounds. BCFs (Bioconcentration Factors) are based on total wet weight (ww) or lipid weight of fish.
Vad innebär w.w och lipid?

Substance	Log Pow	BCF		Reference
Musk Xylene	4.9 (calculated)	3600	Fish	Kuhlmann et al, 1997
		4100	Fish	Yamagashi, 1981,83
		4200-5100	Rainbow trouts (w.w)	Butte et al., 1997
		115,000-122,000	Rainbow trouts (lipid)	Butte et al., 1997
		1440-6740	Carp (w.w)	MITI, 1992
		42,400-198,200	Carp (lipid)	Geyer, 1994
		3800	Different species (w.w)	Rimkus et al., 1997[2]
		79,200	Different species (lipid)	Rimkus et al., 1997[2]
		1600	Bluegill sunfish, whole fish, wet weight	Tas et al. (1997)
	2.97 (calculated)			OSPAR, 1997
	4.4 (measured)			OSPAR, 1997
	4.9 (measured)			OSPAR, 1999
	4.45 (calculated)			OSPAR, 1999
	3.7 (calculated)			OSPAR, 1999
	5.2 (measured)			MITI, 1992
Musk Ketone		1100	Fish	Yamagashi, 1981,83
		760	Different species (w.w)	

Substance	Log Pow	BCF		Reference
		15,800	Different species (lipid)	
	4.3 (measured)			OSPAR, 1999
	3.8 (calculated)			OSPAR, 1999
	4.3 (calculated)			OSPAR, 1999
	3.46 (calculated)			OSPAR, 1997
	3.8 (measured)			OSPAR, 1997
		1380	Rainbow trout, whole fish, wet weight	Tas et al. (1997)
HHCB (Musk) Galaxolide®	Significantly higher Log Pow value than for Musk xylene and Musk ketone			Rimkus, 1996[1], 1997[1]
	5.9 (measured)	1624	BCF based on total radioactivity	OSPAR, 1999
	6.3 (calculated)	1584	BCF based on actual concentration of the parent compound	OSPAR, 1999
AHTN (Musk) Tonalide®	Significantly higher Log Pow value than for Musk xylene and Musk ketone			Rimkus, 1996[1], 1997[1]
	5.7 (measured)	1320	BCF based on total radioactivity	OSPAR, 1999
	6.4 (calculated)	597	BCF based on actual concentration of the parent compound	OSPAR, 1999
Musk Ambrette	3.78 (calculated)			OSPAR, 1997
	4.0 (measured)			OSPAR, 1997
Musk Moskene	4.43 (calculated)			OSPAR, 1997
	4.4 (measured)			OSPAR, 1997
	5.3 (measured)			OSPAR, 1999
Musk Tibetene	5.15 (calculated)			OSPAR, 1997
	5.0 (measured)			OSPAR, 1999
	4.3 (measured)			OSPAR, 1997

6 CHOICE OF ACTION/MEASURES

Due to their use in consumer products (laundry detergents, cleaning agents, fabric softeners, cosmetics etc.) fragrance compounds, including musk ingredients are discharged into the domestic wastewater. Technical measures for emission control are not practicable. The quantities released into the environment are directly correlated with the use figures. OSPAR (1999) has given some possible measures and recommended actions to reduce the emissions of musk compounds into the environment. Some of these items are relevant for other fragrance compounds as well.

Possible measures and recommended actions to reduce the emissions into the environment are:

- As a precautionary measure nitro musks, should not be added to consumer products which are discharged with waste water and which are consumed in large quantities such as detergents and household cleaning agents.

- The presence of nitro musks should be indicated on the label of the consumer products.

- The content of all nitro musks and polycyclic musks in consumer products that are discharged with wastewater should be reduced to the lowest level needed.

- The quantities of nitro musks and polycyclic musks used in Europe should be monitored and reported regularly.

- The concentrations of nitro musks and polycyclic musks should be measured by analysis in selected samples of the aquatic compartment and reported regularly.

- An additional review for actions or measures should be considered if quantities used or concentrations found are increasing during consecutive years.

- In the long term, alternatives with a more favourable hazard profile, e.g. substances for which evidence for inherent primary degradation in standardised tests for inherent biodegradability (> 20 % elimination) is given, should be developed as substitutes for nitro musks and polycyclic musks.

Voluntary agreements with the industry associations haveapperas to be an appropriate tool for the phasing out of Musk xylene in washing and cleaning agents (See section 3.5). As a possible alternative tool, most elements of the recommended actions above could also be integrated into a PARCOM Recommendation or a BEP. If such measures are not successful, the introduction of requirements on the degradability for other components than surfactants into the relevant legislation on detergents and cleaning agents must be envisaged to achieve the long-term goal. Other bodies (EU, OECD) would have to be approached with a view to establishing such a measure.

6.1. Regulations

The Cosmetics Directive regulates toilet soap and toothpaste in the EU. The restrictions for fragrance ingredients in Annex 2 and 3 are applicable in all EU Member States. IFRA do not know any coming regulations (IFRA, 2000[1]).

There might be restrictions for use of fragrances. The fragrance industry respects the restrictions given in the IFRA Code and Guidelines according to IFRA (IFRA, 2000[1]).

Some fragrances are strongly allergic, but there are no rules for declaration of such compounds. The fragrances might cause allergic effects in concentrations less than the declaration limit (e.g. < 1 % in the product). Due to this, people are not able to see if the product contains fragrances. This might cause problems for some sensitive people (1-2 % of the population have fragrance allergy) and for using some baby products (Greeninfo, 2000).

Some countries have prohibited use of some selected musk compounds. Other countries have proposed a maximum concentration of some selected musk compounds. Some of the regulations regarding fragrances (musks) are given in **Table 23**.

Table 23. Regulations regarding fragrances (musks) in different countries.

Country/Area	Regulations
Australia	1994: The Australian Customs Service has announced that medicines with endangered species and plants sold in Chinatown in Sydney would be seized in a bid to protect the animals or plants. Under an international agreement, it is illegal to import any medicines containing derivatives from tiger, **musk deer (moschus**), rhinoceros, monkey, elephant, crocodile and bears. Plants include orchids and American ginseng (Australian, 1994).
Denmark	**Musk Xylenes (Moskusxylener)** are listed in the Danish "Prioritylist" (List of undesirable substances) (The Danish Environmental Protection Agency, 1997).
EU	**Musk Xylene** and **Musk Ketone** have been included in the third EU priority list of existing substances (Regulation 143/93). Draft risk assessment assessment reports are not yet available and follow-up actions of the EU risk assessment cannot be expected in the near future. **HHCB** and **AHTN** are substances for which industry has filed full HEDSETs (Harmonised Electronic Data Set) under the Existing Substances Regulation 793/93/EC because they are produced in the EU in excess of 1000 tons per year. For the other musks the produced or imported quantity into the customs territory of the European Union is below 1000 tons per year and regulation 793/93 does not apply at all or only a limited data reporting is required according to the provisions of article 4. Further there are EU regulations for **Musk Moskene** and **Musk Tibetene** (The Scientific Committee on Cosmetology, 1997) and **Musk Ambrette** (EU, 1995). In June 1997, the European Commission DG XXIV Scientific Committee on Food concluded that "**Musk Xylene** is carcinogenic in mice [..] The toxicological data on **Musk Ambrette, Musk Ketone, Musk Tibetene** and **Musk Moskene** are insufficient to allow a reliable eveluation or to provide a basis for the setting of tolerable levels in food. These nitro musk compounds must also be expected to have a high tendency to accumulate. It is therefore the opinion of the Committee that, as a matter of prudence, contamination of food with these compounds should [..] be reduced as much as possible" (Internet, europa.eu.int). Also in June 1997, the European Commission DG XXIV Scientific Committee on Cosmetology classified **Musk Moskene** and **Musk Tibetene** as Class 2a substances ("Substances which must not be used in cosmetic products. Substances may be included in thes group because [..] b) the available data do not justify the assumption that their use in cosmetic products can be considered safe") (**Tibetene** (The Scientific Committee on Cosmetology, 1997).

Country/Area	Regulations
	In July 1995 the use of **Musk ambrette** was banned in the EU by including it in the list of banned components in cosmetics (95/34/EEC;18th amendment of the cosmetic Directive 76/768/EEC). The same action was taken in 1998 for **Musk Tibetene** and **Moskene** (98/62/EC of 3 September 1998) (OSPAR, 1999). In 1995, the European Commision prohibited the use of **Musk Ambrette**: "[..] 4-tert-Butyl-3-methoxy-2,6-dinitrotoluene (Musk Ambrette), is recognized to be a potent photoallergen; [..] on the basis of recent scientific research, use of this substance in cosmetic products poses a risk to human health; whereas it is therefore necessary to prohibit its use [..]"(EU, 1995). In 1987, the EU prohibited the use of **Versalide**: "substance which must not form part of the composition of cosmetic products. The marketing of cosmetic products containing the substance is prohibited" (EU, 1987). The restrictions of the European Cosmetics Directive are only applicable to cosmetic products. The IFRA Guidelines recommend not to use Musk Ambrette and Versalide for fragrance applications in cosmetics as well as in other products (IFRA, 2000[2])
Germany	In Germany (1993), the industry associations responsible for detergents recommended to their member companies not to use **Musk Xylene** any more in washing and cleaning agents (OSPAR, 1999). 1995: German Federal States propose a "guidance value" (Richtwert, not legally binding) of 0.01 mg/kg wet weight of **Musk Xylene** in fish for food (Bundestags, 1995).
International conventions	**Musk Xylene** appears on the OSPAR (Oslo-Paris Commission) List of Chemicals for Priority Action (Annex 2) (Internet, helcom.fi). So far, no action to limit or phase out the use of musk xylene and other musks has been taken by OSPAR (OSPAR, 1999). In June 1981 IFRA in Geneva, Switzerland, recommended in its Code of Practice to limit the use of **Musk ambrette** to 4% in new fragrance compounds. According to the last amendment in July 1994, the Committee recommends that **Musk ambrette** should no longer be used as a fragrance ingredient. The same recommendation was made for **AETT** (1,1,4,4-tetramethyl-7-acetyl-1,2,3,4-tetrahydro-naphtalene) in February 1980 (OSPAR, 1999).
Japan	**Musk Ambrette** is listed at the Japanese National Institute of Health Sciences (NIHS) Division of Medical Devices "List of Allergens" (Internet, dmd.nihs.go.jp).
Norway	**Musk xylenes** are placed on the Norwegian B-list of "the Prioritylist" (List of Chemicals for Priority Action). B-list: The spill will be reduced substantially latest within 2010 (The Norwegian Ministry of the Environment, 1996-1997). Norway have implemented the OSPAR List of Chemicals for Priority Action (Annex 2) for musk xylenes. There are no existing regulations (e.g. for import, use, spill or prohi-

Country/Area	Regulations
	bition) for musk xylenes, other than the normal regulations for labelling of substances according to health- and environment (The Norwegian Ministry of the Environment, 1996-1997).
Sweden	None of the fragrance compounds mentioned with CAS numbers in this report (**Table 4** and **Table 5**) are included in the Swedish Observation (OBS) List. The possible anti-oxidant Benzophenone (Diphenylmethanone, CAS 119-61-9) is not included in the Swedish OBS list, while the anti-oxidant BHT (2,6-di-tert-butylhydroxytoluene, CAS 128-37-0) is included with danger for the environment as selection criteria (Internet, kemi.se).
Switzerland	In 1996, the Swiss Bundesamt für das Gesundheitswesen (Federal Health Agency) proposed a maximum concentration for **nitromusk** compounds in cosmetics (50 to 500 mg/kg for different product types); **Musk Ambrette** should be banned (Mitt.,Gebiete Lebensm.Hyg., 1996). Rimkus (1996[1], 1997[1]) judges this proposed limit value as being 50 times too high when considering the VSD (see human toxicity). There are no limitations for fragrances and extracts. A ban for **Musk Tibetene** and **Moskene** is in preparation (OSPAR, 1999). The use of **Musk Ambrette** in cosmetics was banned in Switzerland (Ordinance on Cosmetic Products, SR 817.042.1; Amendment of 30.January 1998) (OSPAR, 1999). 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. **Musk Ketone, Musk Xylene, HHCB** and **AHTN** met the criteria to be high production volume chemicals in the sense of Art. 3 of EEC Council Regulation No 793/93 on the evaluation and control of the risks of existing substances (OSPAR,1999).

7 RANKING

Due to the scarcity of information on the fragrances and their properties that is available, the basis for ranking these compound from an environmental- or health perspective is indeed very weak. However, some aspects on which factors that ranking could be based are discussed below.

First of all, it has to be considered if any fragrances at all should be allowed in certain cleaning and cleansing products. The main argument for not allowing fragrances would be that they do not contribute to the technical function of the products. In addition, the fact that the actual composition and properties of the fragrances are in general poorly known may justify adoption of a precautionary principle. On the other hand, at least for certain products, the fragrance add a significant qualitative value of the product from the consumers' point of view, and an absolute ban of fragrances in ecolabelled products may exclude products with environmentally sound properties. It should also be recognized that the content of fragrances in most of the cleaning and cleansing products is low, which means that an absolute ban of fragrances may have an insignificant influence on the total environmental profile of the products.

The main problems with fragrances and extracts during their life cycle seem to be related to human health and allergic reactions. Although these effects may not be relevant in the strict environmental sense, they should be considered as a basis for ranking. The confidence on the ecolabelling among the public will definitely be weakened if products containing e.g. strong allergens are labelled as “bra miljöval”.

The potential environmental effects of fragrances in cleaning and cleansing products appears to be primarily associated with discharge of the fragrance compounds and production chemicals in wastewater at the manufacturing sites and leakage of the consumer products to the municipal wastewater. The risk posed by this discharge to the wastewater will depend on the ecotoxicological properties of the specific chemicals, i.e. toxicity, biodegradability and bioaccumulation potential. Among these, biodegradability should be particularly emphasised. This is because readily biodegradable chemicals will be efficiently removed in the sewerage system and in the natural aquatic environment. Because of the low concentrations of fragrances in the cleaning and cleansing products, readily biodegradable fragrances are unlikely to cause environmental effects even if they are moderately toxic. In the ranking according to ecotoxicological properties, chemicals that are both not readily biodegradable and bioaccumulating are less acceptable than those that are not bioaccumulating.

Because biocides might occur in the fragrances the potential problems of biocides should also be addressed. A more detailed evaluation of biocides, as a separate component in products, should be done separately. The biocides are biologically available substances and might cause death of living cells. Some of these biocides cause allergy and there might be a risk that these biocides have an influence on the human hormones. They might be poorly biodegradable due to their toxicity to bacteria and many products containing them will, due to this reason, not fulfil ecolabelling criteria.

Some herb and spice extracts might have antimicrobial effects. It should be evaluated if data for these substances should be available before ecolabelling. Probably problems regarding human health are more relevant than environmental problems for these substances.

In case fragrances of natural origin are included in cleaning and cleansing products these should not be fragrances from endangered species included on the Red List of Endangered Species issued by the International Nature Conservation Union (IUCN). Thousands of species are today included on this lists (IUCN, 2000). It is uncertain if Red List species are used for fragrance production at all or if fragrance organisations as IFRA has excluded use of Red List species. However, it is not expected that fragrances used in cleaning and cleansing products would be made from endangered species, due to expected high prices.

Due to the limited information available on which fragrances that are used in cleaning and cleansing products and the composition and properties of the fragrance compounds in general, it is not possible to propose a ranking list of fragrances as a basis for ecolabelling criteria. However, for the musk family of fragrances a ranking may be suggested as follows:

A: Acceptable in ecolabelled products	
Macrocyclic musks	Biodegradable, no health hazard
B. not acceptable in ecolabelled products	
Nitrocyclic musks (Moskene, Musk tibene, musk ketone, musk xylene)	Not readily biodegradable, toxic
Polycyclic musks (AITI, AHMI, HHCB, AHTN)	Not readily biodegradable, toxic

For fragrances other than musks, documentation of certain properties have to be required in order to allow a ranking as regards potential environmental and health effects. The most important properties in this respect are allergenic effcts and biodegradability. Fragrances are often added to the consumer products as mixtures of active fragrance compounds and solvents. Solvents, which may comprise the major portion of such mixtures, are often readily degradable and therefore, degradation tests of the mixture may indicate that degradation is efficient even if some active ingredients are persistent. To be meaningful, biodegradation tests must therefore be performed on the active fragrance compounds.

Documentation should include:

- Allergen test of active fragance compounds or of the fragrance mixture
- Test of degradability of the active fragrance compounds

Tentative criteria for ranking based on these properties could be:

- Fragrances that are readily biodegradable according to OECD Test Guideline 301 and not allergenic may be included in ecolabelled products
- Fragrances that are inherently (but not readily) biodegradable according to OECD Test Guideline 302 and not allergenic may be considered acceptable but with a limit on amount.
- Fragrances which are allergenic and/or not inherently biodegradable should not be accepted in ecolabelled products.

8 LACK OF DATA

Fragrance substances	Confirmation from industry of which fragrance substances (CAS-numbers) are used in cleaning and cleansing products and data for substances not included in this report.
Antioxidants:	More data regarding substance names, amounts and human- and ecotoxicological data.
Solvents:	More data regarding CAS-numbers, amounts and human- and ecotoxicological data.
Herb and spice extracts:	Finding data had no priority in this report.

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APPENDIX 1

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