Review and evaluation of environmental emission scenarios for fragrance materials during compounding of perfume oils and formulation of consumer products

Research Institute for Fragrance Materials

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A COMPANY OF

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SUMMARY

The Environmental Task Force of IFRA, the International Fragrance Association, recognised the need to undertake a study to better describe the operational conditions and environmental exposure scenarios during the formulation of fragrance preparations and their incorporation into household and personal care products. Therefore RIFM initiated a study that aimed to deliver an evidence-based Emission Scenario Document using qualitative and quantitative information on the operational conditions, environmental exposure scenarios and emission factors. The project is limited to emissions to wastewater. The emissions to other compartments are not considered relevant compared to those going to wastewater.

In this study the existing exposure scenarios for the compounding and formulation stages of fragrance ingredients were reviewed. Information on operating conditions and practices within participating companies was obtained by means of an inquiry sent to RIFM members and clients.

Following the results of this study, the recommended scenario for the compounding and formulation of fragrance ingredients is summarized in the table below.

Table: Recommended emission scenario

Variable/Parameter		Unit	Symbol		S/D/O/P[1)]
Input					
Annual tonnage of final product		[Ton/yr]	TONNAGEproduct		S
Average annual use rate of fragrance oil		[kg/y/site]	TONNAGEoil		S
Number of emission days of aroma chemical		[d/y]	Temission	250	S/D
Faction of aroma chemical in fragrance oil			Fsubst_oil		S
Fraction of fragrance oil in final product		[-]	Foil		S
Fraction of tonnage released to wastewater		[-]	Fwastewater		
Compounding	Large+Medium/ Small			0.002/ 0.005	D
Soap	Large/ Small			0.0005/ 0.001	D
Granular Detergents	Large/ Small			0.001/ 0.002	D
Liquid conditioners, cleaners, Shampoo, Shower gel -	Large/ Small			0.001/ 0.002	D
Creams, lotions				0.01	D
Fine fragrances (if not cleaned with alcohol)				0.015	D

Output			
Faction of aroma chemical in final product		Fsubst_prod	O
Release to wastewater during life-cycle stager formulation	[kg/d]	$Elocal_{wastewater}$	

Calculations

Fsubst_prod = Fsubst_oil * Foil

1. $Elocal_{wastewater}$ = Fwastewater * Fsubst_prod * TONNAGEproduct * 1000 / Temission

OR

2. $Elocal_{wastewater}$ = Fwastewater * Fsubst_oil * TONNAGEoil * 1000 / Temission

1) **S** data to be Set by the user
D Default, parameter has a standard value but can be changed by the user

The newly derived default values for the emission factors to the wastewater compartment are shaded in the table. The number of emission days for the substance should be considered with care. For ingredients that are not often used, the number of days should be reduced in order not to underestimate the daily emission per event.

This study showed that it is common practice that the waste water is treated in a physical-chemical treatment system before it is discharged into a biological wastewater treatment plant on-site or in a municipal sewage treatment plant.

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1 REVIEW AND EVALUATION OF EMISSION SCENARIOS FOR FRAGRANCE INGREDIENTS

1.1 Introduction

The Environmental Task Force of IFRA, the International Fragrance Association, recognised the need to undertake a study to better describe the operational conditions and environmental exposure scenarios during the formulation of fragrance preparations and their incorporation into household and personal care products. This recognition is a result of the following three key drivers:

1. For an exposure assessment within the EU, exposure scenarios for each life cycle stage of different use categories of chemicals are described within the Technical Guidance Document on Risk Assessment (TGD, EC2003). These exposure scenarios contain parameters such as emission factors to the various environmental compartments during production, formulation and post consumer use. The experience of the fragrance industry in using the default values set out in the TGD is that the emissions factors specific for the formulation stages of a fragrance preparation are most often highly conservative, thus contributing to a high PEC_{local} and potentially leading to false positive identification of a risk to the local environment.

2. Under the auspices of the OECD Environmental Exposure Assessment Task Force, the US EPA has developed a draft Emission Scenario Document for "The blending of fine and functional fragrance oils into commercial and consumer products – emission scenario document for estimating occupational exposures and releases". This Emission Scenario Document (ESD) includes conservative, screening level estimates of release and environmental exposure, and, as with the default values within the TGD, may contribute to a higher PEC_{local} and a false positive identification of a risk to the local environment.

3. The REACH regulations in the EU require Chemical Safety Assessments (CSA) to be conducted for all chemicals manufactured and imported within the EU at greater than 10 tonnes per annum. These CSA are intended to document the risks throughout the entire life cycle of a substance. Without more realistic and evidence based information on environmental exposures, particularly within the formulation steps, existing default values (e.g. from the TGD or the OECD) will need to be used within fragrance material CSA. This may result in the derivation of overly conservative PEC_{local} and an inaccurate assessment of environmental risks leading to unnecessary and costly risk management measures being implemented within the supply chain.

Therefore RIFM, on behalf of the IFRA Environmental Task Force, initiated a study that aimed to deliver an evidence based Emission Scenario Document using qualitative and quantitative information on the operational conditions, environmental exposure scenarios and emission factors within the life-cycle stages "formulation 1" (formulation of the fragrance preparation) and "formulation 2" (incorporation of the fragrance into a household or personal care product) (see Figure 1). Within the fragrance industry the formulation 1 and 2 stages are known as 'compounding' and 'formulation', respectively.

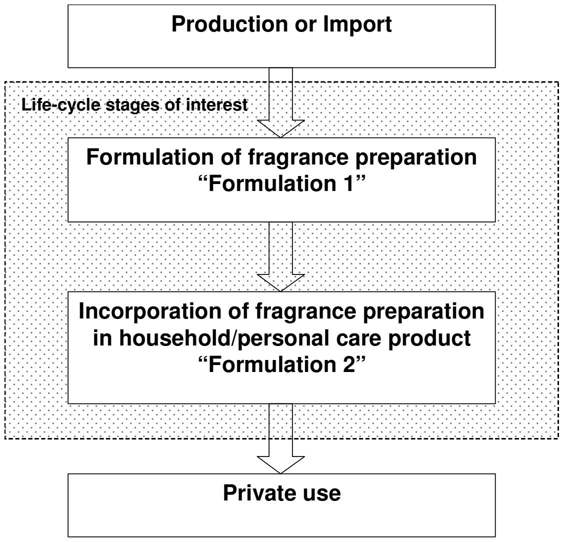

Figure 1 Life cycle stages for a substance used as fragrance ingredient (formulation 1: 'compounding', formulation 2: 'formulation')

The objectives of intended study were to:
1. Review the existing exposure scenario data for wastewater and waste relevant for the compounding and formulation stages of fragrance ingredients.
2. Review of operating conditions/practices within participating companies to derive evidence-based, quantitative environmental exposure scenarios.
3. Develop a tiered approach to the use of exposure scenarios within fragrance component risk assessments that could be used for example, for the risk assessment within REACH.

For the review various literature resources are available. In addition, information was supplied by the participating companies through IFRA or RIFM.

For pragmatic reasons, this current project is limited to emissions to water and soil/waste. The emissions to air are not considered relevant compared to those going to waste and effluent.

1.2 Available scenarios and sources

For fragrance ingredients a number of scenarios for emissions to wastewater and waste are examined for the life-cycle stages compounding and formulation. The scenarios for the use of fragrance ingredients in cosmetics and personal care products are based on the following resources:
- EU-TGD (EC 2003a).
- OECD draft emission scenario document (US-EPA 2006).
- Site specific information obtained during site visits in the EU (2001).
- Risk Assessment Reports (RAR) on the polycyclic musks HHCB and AHTN (2008).
- EFFA SPORT exercise (EFFA 2005).

The various documents focus on different steps in the life cycle stages of the fragrance ingredients, as shown in Table 1. The life stages relevant for this project are shaded in the table.

Table 1 Available environmental emission scenarios

Life-cycle stage	EU-TGD 2003	RAR on polycyclic musks	EFFA SPORT exercise	OECD draft 2006
Production*	Industrial Category IC5/6 generic tables: A1.1/A1# & B1.6/7	two site-specific descriptions		--
Compounding	IC5/6, A2# & B2.1/3	substance-specific: • generic compounding scenario for large/medium sized sites, based on 6 site visits; • generic scenario for small compounders	generalised from RAR	--
Formulation	IC5/6 A2# & B2.1/3	substance-specific generic (and site specific) for L/M based on 1 site visit and 2 enquiries; a-specific generic for small formulators	generalised from RAR	general models from Chemical Engineering Branch, ChemSTEER (EPA)
Private use*	IC5/6 UC9/15	substance-specific approach	generalised	--

* Emission scenarios for this life stage are outside the scope of the current study

Furthermore, the following resources for empirical data on scrap factors and residues for the life-cycle stage compounding were used:

- Letter FMA of September 2006 and data from a large compounder on residues remaining in emptied mixing vessels.
- Data of compounders on releases during the process.

As an action in this project, a questionnaire was prepared and sent out to compounders and formulators to obtain more information for a representation.

1.3 Project Results

The current report first presents a review of the available emission scenarios and emission factors and identifies where conservative default values are used that give room for improvement. The project focused on collecting empirical data on release to wastewater. For obtaining more detailed information a questionnaire was sent to fragrance oil compounder (Formulators 1) and formulators of household and personal care products (Formulators 2). The questionnaire is included in this report as Appendix 1.

Site visits were not included in the activities. Thus the results are based on already available sources as mentioned in section 1.2 and on the information supplied by the response to the inquiry.

The report is intended to be used in response to the invitation of the US-EPA in their draft OECD Emission Scenario Document where they state that approaches used are ''intended to provide conservative, screening-level estimates'' and that resulting ''releases and exposure amounts are likely to be higher, or at least higher than average, as compared to amounts that might actually be occurring in a real world setting.'' In addition it states, ''where specific information is available, it should be used in lieu of the defaults presented, as appropriate''. For this reason the project focused on refining the "conservative screening-level release estimates" presented in the draft OECD Emission Scenario Document.

At the same time the results are also useful in the context of the requirements for REACH for the preparation of higher tier exposure scenarios.

2 AVAILABLE EMISSION SCENARIOS FOR LIFE CYCLE STAGES COMPOUNDING AND FORMULATION

2.1 General emission pathways

For an estimation of the emissions during the compounding and formulation processes, the process steps need to be considered and the sources of environmental release and their pathways to the environment need to be identified. This is done in Figure 2. This scheme is applicable both for compounding and formulation. The aim of emission scenarios is to quantify the flux of material following the arrows to the compartments 'Solid waste' and 'Waste water'.

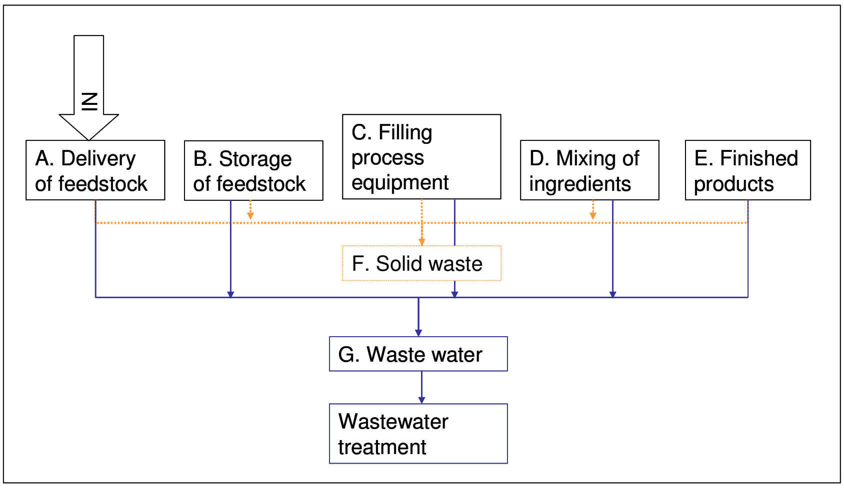

Figure 2 **Emission pathways during compounding or formulation of fragrance ingredients**

2.2 Harmonised presentation of scenarios

In this report, the emission scenarios are presented in text and Tables. In the Tables, the input and output data and calculations are specified, and the lay-out and units are used according to the convention developed in the EU projects on Environmental Emission Scenarios. The input and output data are divided into four groups:

- S data Set: parameter must be present in the input data set for the calculations (no method has been implemented in the system to estimate this parameter; no default value is set, data either to be supplied by the notifier or available in the literature).
- D Default: parameter has a standard value (most defaults can be changed by the user).
- O Output: parameter is the output from another calculation (most output parameters can be overwritten by the user with alternative data).
- P Pick list: parameter values to be chosen from a pick list with values.

2.3 Emission scenarios for compounding of fragrance mixtures (perfumes)

2.3.1 EU Technical Guidance Document

The EU Technical Guidance Document on Risk Assessment contains a simple scenario for the emission during the production of soaps, fabric washing, dish cleaning and surface cleaning products (Use Category UC9) and cosmetics (UC15) for personal/domestic use and use in the public domain, to wastewater during the formulation (Industrial Categories IC5&6, EC 2003a). However, not all EU member states Competent Authorities accept that fragrance ingredients are assigned Use Category 9 and/or 15. Some prefer the more conservative UC36 "odour agents", at least during the compounding stage.

In the approach it is assumed that in comparison to the emission during production, compounding and processing, the majority (>98%) of the release occurs at the use phase and in that stage the fraction of detergent ingredient released to environment = 1.0. However, for major production volumes, the emission during production and formulation may need to be quantified for risk assessment purposes at local scale.

The EU-TGD contains so-called A- and B-tables that enable the calculation of generic release factors in specific industrial categories. In doing so the volume (for compounding) determines whether there are few or many similar production sites in the region (fraction of the main source that is used on a generic site) as well as the number of emission days. The tables relevant for the compounding of fragrance oils are table A2.1 (for UC36), A2# (for UC 9 and 15) and B2.1 (for non-HPV) and B2.3 (for HPV) substances.

Based on this generic approach, the emission scenario during the mixing of fragrance ingredients (compounding) is described in Table 3. It should be realized that TONNAGE in the table refers to the tonnage of the *compound*, the fragrance mixture. The HPVC qualification refers to the fragrance ingredient itself.

Table 2 Emission scenario for compounding of fragrance oils, calculating the release to wastewater (EU-TGD, EC 2003a)

Variable/parameter	Unit	Symbol	Default		S/D/O/P
Input					
Tonnage of the compound	[tonnes.y^{-1}]	TONNAGE			S
Fraction of fragrance ingredient in compound	[-]	Fsubst			S
Fraction of tonnage released to wastewater during compounding	[-]	Fwastewater	UC36: ≥ 1000 t.y^{-1}: 0.003 < 1000 t.y^{-1}: 0.02 [UC9/15: 0.0009]		D
Fraction of tonnage released to waste during compounding		Fwaste	UC36: 0.0001 [UC9/15: 0.0081]		D
Fraction of main source (non-HPVC)	[-]	Fmainsource	< 100 t.y^{-1}: 100-500 t.y^{-1}: 500-1000 t.y^{-1}: ≥ 1000 t.y^{-1}:	1 0.6 0.6 0.4	P

Variable/parameter	Unit	Symbol	Default	S/D/O/P
Fraction of main source (HPVC)	[-]	Fmainsource	< 3500 $t.y^{-1}$: 1 3500-10000 $t.y^{-1}$: 0.8 10000-25000 $t.y^{-1}$: 0.7 25000-50000 $t.y^{-1}$: 0.6 ≥ 50000 $t.y^{-1}$: 0.4	P
Output				
Number of emission days	$[d.y^{-1}]$	Temission		
Release during life-cycle stage formulation to wastewater	$[kg.y^{-1}]$	$Elocal_{wastewater}$		
Release during life-cycle stage formulation to waste	$[kg.y^{-1}]$	$Elocal_{waste}$		
Calculations				
Temission (non-HPVC) =				O
for < 100 $t.y^{-1}$ =	2 * Fmainsource * TONNAGE			
for 100-500 $t.y^{-1}$ =	Fmainsource * TONNAGE			
for 500-1000 $t.y^{-1}$ =	0.5 * Fmainsource * TONNAGE			
for ≥ 1000 $t.y^{-1}$ =	300			
Temission (for HPVC) =	300			O
$Elocal_{wastewater}$ = Fwastewater * Fsubst * TONNAGE * 1000 / Temission				
$Elocal_{waste}$ = Fwaste * Fsubst * TONNAGE * 1000 / Temission				

2.3.2 OECD emission scenario document

Under the auspices of the OECD Environmental Exposure Assessment Task Force, the US EPA has recently developed a draft Emission Scenario Document (draft ESD, US-EPA 2006) for "The blending of fine and functional fragrance oils into commercial and consumer products – emission scenario document for estimating occupational exposures and releases".

Thus the OECD draft ESD is directed to the life cycle stage following the compounding stage. No emission scenarios are defined for the compounding stage.

2.3.3 Risk Assessment Reports on polycyclic musks

Within the context of the EU Council Regulation (EEC) 793/93 on the evaluation and control of the risks of 'existing substances', risk assessment reports (RAR) were prepared for the polycyclic musks AHTN and HHCB. For the evaluation of the site-specific risks, six large compounding sites in Europe were visited to collect site-specific information. The results were used not only for the site specific environmental and occupational risk assessment for AHTN and HHCB for the six sites, but also to prepare generic emission scenarios for large and medium sized compounders as well as for small compounders. The findings were reported in draft EU-RAR documents for the polycyclic musks AHTN and HHCB (2008).

The volumes used per site were derived from the visits and from sales data supplied by the producers. In this way the distribution of the use over the large, medium and small sites was generated, see Table 3.

Table 3 **Distribution of the use of polycyclic musks over the sites**

	Large/medium compounders	Small compounders	Directly into Formulation
HHCB	80%	6%	14%
AHTN	70%	10%	20%
Use (visits)	6 very large sites use together 52-72%		
Generic	33 sites use 8% (*5[#]): 1.2% per site 20 sites use 18% (*5[#]): 4.5% per site	0.1% per site	Large: 3.5%-5% Small: 0.4%

[#] to provide for a conservative estimate the average is multiplied by 5

Site-specific emission data were derived for the six compounding sites that were visited and in this way the releases were calculated. The details were reported in confidential site-visit reports and summarized in the RARs for the polycyclic musks AHTN and HHCB. The wastewater receives a physical-chemical treatment on site. Next the treated water is discharged to a biological treatment plant (activated sludge) which is either on the site or a municipal sewage treatment plant. The residues of the treatment plants on site are treated as chemical waste and are collected for incineration or controlled discharge to a landfill.

All solid waste is collected. Used packaging which has been in contact with chemicals are either recycled, collected by waste companies or incinerated. The delivery area as well as the mixing halls are in contained area, so all water is collected in dedicated sewers. This implies that there is no direct emission to the soil. Spills are cleaned with specific sorbing materials or cleaned with water that is collected in dedicated sewers along with the process water. Spilled fragrances may be collected and recycled in the process.

Table 4 **Generic emission scenario for calculating the release of AHTN and HHCB during compounding**

Variable/parameter	Unit	Symbol	Default	S/D/O/P
Input				
a1. Total tonnage of compounds	[tonnes.y-1]	TONNAGEcomp		S
a2. Fraction of fragrance ingredient X in compound	[-]	Fcomp		S
b. Tonnage of fragrance ingredient X	[tonnes.y-1]	TONNAGEfrag		S
Fraction of tonnage released to wastewater	[-]	Fwastewater	Large/Medium 0.0006 Small 0.002	D
Fraction of tonnage released to soil	[-]	Fwaste *	0	D
Output				
Release to wastewater	$[kg.y^{-1}]$	$Elocal_{wastewater}$		O
Release to waste	$[kg.y^{-1}]$	$Elocal_{waste}$		O

Calculations

a. $Elocal_{wastewater}$ = TONNAGEcomp * Fcomp * Fwastewater

b. $Elocal_{wastewater}$ = TONNAGEfrag * Fwastewater

$Elocal_{waste}$ = 0

* Strictly speaking this is Fsoil

2.3.4 EFFA SPORT

In preparation for REACH (Registration, Evaluation and Authorization of CHemicals) in the EU, industry initiated an exercise called SPORT (Strategic Partnership on REACH Testing) in which the European Flavour & Fragrance Association EFFA participated as well. Within the EFFA SPORT exercise an effort was made to generalize the emission/exposure scenarios developed for the polycyclic musks (see section 2.3.3) and make them applicable for the processes that occur in fragrance compounding and formulation companies throughout Europe.

Based on site visits to 6 companies, a generic scenario was described for the large and medium size compounding facilities. These six companies were responsible for 75 - 85% of the volume used (for PCMs) in all large and medium sized companies, so the generic picture is considered representative. The small size companies have not been visited.

The description of the activities in small size compounding companies is considered to be similar to that for large/medium size compounders. This view is based on the fact that on large sites fragrance oils are produced on batches that vary between 1 and 20,000 kg, so from very small to very large, including automatic as well as manual procedures. In smaller sites the automatic production of large size batches may be absent but the manual handling procedures are the same as in the larger sites.

Size of compounding sites

The environmental emission is expressed as a fraction of the use volume of the site. The size of the sites, expressed as the fraction of the EU use volume, is highly variable. The sites can be ordered according to three categories: large, medium and small. Within each category the data for largest company are used for the emission scenario, thus ensuring a protective approach. When only average figures were known, a ‘realistic worst case’ scenario was generated by multiplication of the average size by a factor of 3.

The following figures were used as a basis:

- 70% of the EU use volume is compounded by large/medium size compounding companies.
- The total number of large and medium size compounders is approximately 40. Among these there are 6 large companies. Together they compound 72% of the EU use volume or on average 72% /6= 12% of the EU use volume each. The largest user uses 25% of the total use volumes.
- The other 34 middle sized companies each compound between 3 and 0.05%.
- Small size compounding companies use circa 10 % of the total use volume. The number of small size companies is approximately 140. The average use volume is 10% /140 = 0.07%. Thus the 'realistic worst case' volume is 3 times 0.07% = 0.2%.

Emission factors

The information collection during the visits to the sites of fragrance compounders was focused on the emissions of polycyclic musks. One may wonder whether the emission factors for these substances would be representative for the whole range of fragrances. The polycyclic musks are characterized by a high log Kow, HHCB has a high viscosity whereas AHTN is a solid/granular, and both have a low vapour pressure. Moreover, they are used frequently and in a high use volume (at least for HHCB). However, all information related to environmental emissions during the mixing process was derived for fragrance compounds (oils) and then interpreted specifically for the polycyclic musks.

The emission of fragrance materials during the mixing process was estimated. In general, small size companies may have higher release rates and possibly the releases occur in fewer working days. These percentages represent the release without any treatment. The releases are not specific for the substances, and hence not influenced by the substance properties. They are based on estimated losses, scrap factors and measurements.

For all large size compounders an on-site waste water treatment is present (physico-chemical and/or biological). It is assumed that the removal of fragrance compounds in on site treatment is 90% ([1]). For medium-sized and small sites the wastewater is not biologically treated on-site but discharged to a municipal STP. Table 5 summarizes the various figures used in the quantification of emissions to sewage derived on the basis of the yearly EU use volume.

Table 5 Typical plant size and release factors in fragrance industry for compounding

Plants	Large	Medium	Small
Number	6	34	140
Average % of EU use volume	12	0.2	0.07
Worst case % of EU use volume	25	3	0.2
Emission factor to wastewater [-]	0.0006	0.0006	0.002
Working days	250	250	125
Fraction emission of EU use volume per day, Worst case	$60*10^{-8}$	$7.2*10^{-8}$	$3.2*10^{-8}$
Fraction discharged after treatment*, EU use volume, Worst case	$6*10^{-8}$		

* WWTP onsite

It was concluded that for all compounding scenarios the daily emission to the sewer (ex site) can be estimated by the fraction $8*10^{-8}$ of the total EU use volume.

In the EFFA SPORT scenario it was assumed, as a generic conservative estimate, that the wastewater is discharged to a relatively small municipal STP serving 10,000 population equivalents and a water flow of 2,000 m^3 per day (defaults of the EU-TGD, EC2003). Thus the concentration in the influent of the STP can be calculated. Further generalizations were made in the removal of the fragrance ingredients in the STP, see Table 6. The dilution of effluent discharged into surface water is 1:10.

[1] N.B.: This value of 90% may deviate for some substances. The 90% is based on effective physical removal by skimming, flotation or adsorption or removal of a readily biodegradable substance in a biological STP.

Table 6 Removal in STP, conservative estimates (EFFA SPORT)

Substance characteristic	Removal
Readily biodegradable	95 % ([2])
Non readily biodegradable:	
- log Kow < 4	0 %
- 4 < log Kow < 5	EUSES predictions
- log Kow > 5	80 %

Thus the emission and concentrations in STP effluents and surface water can be estimated in a generic scenario, see Table 7.

Table 7. Emission scenario for estimating the release of fragrance materials during compounding

Variable/parameter	Unit	Symbol	Default	S/D/O/P
Input				
Tonnage of the substance in EU	[tonnes.yr^{-1}]	TONNAGE		S
Fraction of tonnage released to wastewater during compounding	[-]	Fwastewater	8*10^{-8} (or see Table 5)	D/S
Water flow in STP	[m^3. day^{-1}]	$Flow_{STP}$	2000	D
Removal in STP	[-]	$F_{removal\_STP}$	see Table 6	P
Dilution in river water	[-]	DILUTION	0.1	D
Output				
Release during compounding to wastewater	[tonnes.y^{-1}]	$Elocal_{wastewater}$		O
Concentration in effluent	[mg. L^{-1}]	Ceffl		O
Concentration in surface water	[mg. L^{-1}]	Cwater		O
Calculations				
$Elocal_{wastewater}$ = Fwastewater * TONNAGE				
Ceffl = ($Elocal_{wastewater}$ / ($FLOW_{STP}$ * 365)) * (1 – $F_{removal\_STP}$) * 10^6				
Cwater = Ceffl * DILUTION				

All solid waste is collected and may be recycled. Used packaging which have been in contact with chemicals are all incinerated or collected by specified waste companies.

2.4 Emission scenarios for formulation of fragrance materials into consumer products

2.4.1 EU Technical Guidance Document

The EU Technical Guidance Document on Risk Assessment contains a simple scenario for the emission during the production of soaps, fabric washing, dish cleaning and

[2] Well documented experience in AISE with readily biodegradable detergents shows that the removal percentage varies between 96 and 99% (i.d. 1 – 4 % in the effluent). Specific fatty alcohols are even removed for 99.9%. The lower removal figures belong to trickling filter systems, the higher to extended aeration systems. Most detergents consist of alkyl groups such as fatty alcohols, ethoxylates, esters or acids. Biodegradation patterns and removal rates of fragrance oils that consist of alcohols and esters will be very similar.

surface cleaning products (Use Category UC9) and cosmetics (UC15) for personal/domestic use and use in the public domain to wastewater during the formulation (Industrial Categories IC5&6, EC 2003a).

For major production volumes, the loss at production and formulation needs to be quantified for risk assessment purposes. The emission factors given in Table 8 have been generated for high production volume chemicals (HPV, >1,000 $t.y^{-1}$) and, according to the EU-TGD, should be applied as default values for products. They may not necessarily apply for chemicals in low volumes (previously known as ‘new chemicals’). In that case, the default for UC36 ‘Odour agents” may apply, see Table 2 (2% to wastewater for < 1000 $t.y^{-1}$).

Table 8 **Percentage released to wastewater, air, and solid waste during formulation of cleaning/washing agents and cosmetics (Table A2# in Appendix I and Emission scenario description for IC5&6 in EU-TGD, EC2003a)**

	Regular powder	Compact powder	Liquid	Unknown *)
% to wastewater	0.01	0.01 (A2#); [0.001 (ESD IC5**)]	0.09	0.09
% to air	0.02	0.02	0.002	0.02
% to solid waste	0.73	0.81	0.32	0.81

*) Not included in the description for IC5&6

**) It is supposed that this deviating lower value is an error

The A- and B-tables in the EU-TGD give generic release factors in specific industrial categories. In doing so the volume (for formulation) determines whether there are few or many similar production sites in the region (fraction of the main source that is used on a generic site) as well as the number of emission days. The tables relevant for the formulation of detergents and cosmetics are table A2# and B2.1 (for non-HPV) and B2.3 (for HPV) substances.

The generic emission scenario during the formulation of fragrance oils into washing/cleaning agents and cosmetics is described in Table 9. It should be noted that the default values for Fwaste(water) in Table 9 are identical to the most conservative values in Table 8, with the notation that the figures were generated for HPV chemicals (see above). It should be realized that TONNAGE in the table refers to the tonnage of the formulated product, including all ingredients next to the fragrance compound, and that the final emission relates to the individual fragrance ingredient.

Table 9 **Emission scenario for formulation of fragrance oils into detergents and cosmetics, calculating the release to wastewater (EU-TGD, EC 2003a)**

Variable/parameter	Unit	Symbol	Default	S/D/O/P
Input				
Tonnage of the product	[$tonnes.y^{-1}$]	TONNAGE		S
Fraction of fragrance ingredient in compound	[-]	Fsubst		S
Fraction of fragrance compound in product	[-]	Fcomp		S
Fraction of tonnage released to wastewater during formulation	[-]	Fwastewater	0.0009 *	D
Fraction of tonnage released to		Fwaste	0.0081 *	D

Variable/parameter	Unit	Symbol	Default		S/D/O/P
waste during formulation					
Fraction of main source (non-HPVC)	[-]	Fmainsource	< 100 $t.y^{-1}$:	1	D
			100-500 $t.y^{-1}$:	0.6	
			500-1000 $t.y^{-1}$:	0.6	
			≥ 1000 $t.y^{-1}$:	0.4	
Fraction of main source (HPVC)	[-]	Fmainsource	< 3500 $t.y^{-1}$:	1	D
			3500-10000 $t.y^{-1}$:	0.8	
			10000-25000 $t.y^{-1}$:	0.7	
			25000-50000 $t.y^{-1}$:	0.6	
			≥ 50000 $t.y^{-1}$:	0.4	
Output					
Number of emission days	[$d.y^{-1}$]	Temission			
Release of frag.ingred. during life-cycle stage formulation to wastewater	[$kg.y^{-1}$]	$Elocal_{wastewater}$			
Release of frag.ingred. during life-cycle stage formulation to waste	[$kg.y^{-1}$]	$Elocal_{waste}$			
Calculations					
Temission (non-HPVC) =					O
< 100 $t.y^{-1}$	= 2 * Fmainsource * TONNAGE				
100-500 $t.y^{-1}$	= Fmainsource * TONNAGE				
500-1000 $t.y^{-1}$	= 0.5 * Fmainsource * TONNAGE				
= ≥ 1000 $t.y^{-1}$	= 300				
Temission (HPVC)	= 300				O
$Elocal_{wastewater}$ = Fwastewater * Fcomp * Fsubst * TONNAGE * 1000 / Temission					
$Elocal_{waste}$ = Fwaste * Fcomp * Fsubst * TONNAGE * 1000 / Temission					

*) generated for HPV-chemicals; may not necessarily apply for low volume chemicals

2.4.2 OECD emission scenario document

Under the auspices of the OECD Environmental Exposure Assessment Task Force, the US EPA has recently developed a draft Emission Scenario Document (draft ESD, US-EPA 2006): “The blending of fine and functional fragrance oils into commercial and consumer products – emission scenario document for estimating occupational exposures and releases”. This document includes conservative, screening level estimates of release and environmental exposure during formulation. The document states that it is generally assumed that losses of the aroma chemical, as a component of the fragrance oil, are minimized in practice; however, it is the purpose of the ESD to provide conservative, worst case estimates for use in screening level exposure assessments. Many of the environmental release estimates are based on standard CEB release models. CEB has developed a software package ChemSTEER[3] containing these models as well as the CEB defaults.

The document classifies fragrance oils into two categories, fine fragrances, used in formulation of perfumes, colognes and aftershaves; and functional fragrances used in

[3] Chemical Screening Tool For Exposures & Environmental Releases, http://www.epa.gov/oppt/exposure/pubs/chemsteer.htm

personal and household products such as cosmetics, shampoos, detergents, soaps and other cleaning formulations. The only significant difference between the oils is the relative strengths and variety of aroma. Functional fragrance oils are incorporated at concentrations of 2% or less, whereas fine fragrance oils are present in the final products at concentrations of 2 – 12% in men's colognes after shaves up to 15-30% in women's perfumes.

The document considers the production of powdered detergents, liquid detergents or cleaning agents, solid bar soaps and aerosol air fresheners and cleaners and from there it derives a general process description for the incorporation of functional fragrance oil into commercial and consumer products. It also considers the manufacturing of fine fragrances. When the end-use of an aroma chemical is unknown, it is advised to assume that it will be formulated into functional fragrance oils and shipped off-site for formulation into powdered commercial and consumer products as a conservative estimate.([4])

The emission scenario document first describes a generic site, see Table 10. Releases of the product to water or land may occur at three stages during the formulation process: 1) when materials are unloaded from transport or storage containers, 2) when equipment is cleaned after mixing and packaging, and 3) due to conveying of powdered products. The recommended default values used for release and exposure estimates are based on model calculations (Table 11).

Table 10 Generic facility description

Variable/parameter	Unit	Symbol	Default	S/D/O/P
Input				
Annual production volume of aroma chemical	[kg/year]	Q_{chem_year}		S
Average annual use rate of fragrance oil [b])	[kg/site-year]	Q_{oil_year}	19,500 [a)]	D
a. Days of operation OR	[days/yr]	$TIME_{working\ days}$	250 [c)]	D
b. Days in which aroma chemical is used in the manufacture of end products	[days/yr]	$TIME_{working\ days}$		S
Fraction of aroma chemical in fragrance oil	[-]	$F_{chem\ oil}$	0.2	D
Fraction of fragrance oil in final product	[-]	$F_{oil\ final}$	0.02	D
Concentration of aroma chemical in final product	[-]	$F_{chem\ final}$	0.004	S/O
Volume of fragrance oil container	[L/container]	$V_{container\ oil}$	208	D
Volume of final product container	[L/container]	$V_{container\ final}$	3.78	D
Density of fragrance oil	[kg/L]	RHO_{oil}	1	D
Density of final product	[kg/L]	RHO_{final}	1	D
Output				

[4] This may appear as being in contradiction with the higher number of emission days (~$Time_{cleaning}$) associated with "fine fragrances" as shown on page 16. The probable reason to consider formulation in a "functional" product as a conservative estimate is that tonnages used in this type of application are much larger than those used in fine fragrances.

Variable/parameter	Unit	Symbol	Default	S/D/O/P
Daily use rate of fragrance oil	[kg/site-day]	$Q_{oil\ day}$		O
Daily use rate of aroma chemical	[kg/site-day]	$Q_{chem\ day}$		O
Number of sites using the fragrance oil containing the aroma chemical	[-]	N_{sites}		O
Number of transport containers unloaded at each site per year	[container/site-year]	$N_{container\ unload}$		O
Number of transport containers filled at each site per year	[container/site-year]	$N_{container\ filled}$		O

Intermediate calculations

$F_{chem\_final} = F_{chem\_oil} * F_{oil\_final}$

$Q_{oil\_day} = Q_{oil\_yr} / TIME_{working\ days}$

$Q_{chem\_day} = Q_{oil\_day} * F_{chem\_oil}$

$N_{sites} = Q_{chem\_year} / Q_{chem\_day} * TIME_{working\ days}$

Alternative:

$Q_{chem\_day} = Q_{chem\_yr} / (N_{sites} * TIME_{working\ days})$

$N_{container\ unload} = (Q_{chem\_day} * TIME_{working\_days}) / (F_{chem\_oil} * V_{container\_oil} * RHO_{oil})$

$N_{container\_filled} = (Q_{chem\_day} * TIME_{working\_days}) / (F_{chem\_final} * V_{container\_final} * RHO_{final})$

[a]) Estimate for the US

[b]) All sites are assumed to use only one fragrance oil. EPA recognises that facilities will likely formulate multiple products containing different fragrance oils. This assumption is likely to cause an overestimation of the daily use rate of the aroma chemical

[c]) 5-d work week and 2 weeks per year of operation shut down.

The volumes of the transport containers are set at a default value of 208 litre (55 gallon) but other sizes may be more appropriate in specific situations. In the same way the volume of the containers filled with the final product is set at a default value of 3.78 litre, whereas the actual size may vary, depending on the type of end product, from 20 ounce for a fine fragrance up to 55 gallon drums for industrial or institutional use. The default values may be adapted.

Table 11 Sources of release of aroma chemicals to wastewater and models used to estimate release during formulation (models included in ChemSTEER)

Source of release	Model
Container cleaning	EPA/OPPT Bulk Transport Residual Model (e.g., totes, tank trucks, rail cars), Drum Residual Model (20 to 100 gallons), or Small Container Residual Model (< 20 gallons)
Equipment cleaning	EPA/OPPT Multiple Vessel Residual Model (Liquids) or Solid Residues in Transport Containers Model
Conveying powder products	AP-42 Emission Factor (for Soap and detergent industry)

The release estimates are based on the most current versions of the models listed in Table 11. No industry-specific information on transport container cleaning was available. For unloading of the fragrance oil containers the approach is based on rinsing of the container with water or solvent where the residual wash is then released to water or incinerated. If the containers are not washed, they may be sent directly to a landfill or a drum recycler/ reconditioner. If the number of containers used per site per year ($N_{container\_unload,}$ Table 10) is fewer then the days of operation ($TIME_{working\_days}$), the days of release equals the number of containers.

For the cleaning of process equipment it is assumed that the equipment cleaning waste is released to water, incineration or land. Semi-continuous manufacturing equipment is not likely to be cleaned daily; however, the batch equipment used for the formulation of perfumes and colognes may be cleaned after each batch. If the fragrance oil is used in commercial and consumer products containing functional fragrance oil, it may be assumed that cleaning occurs weekly between product changes (50 times/year). Daily cleaning may be assumed for equipment used for products containing fine fragrance oil.

The amount of residual material remaining in the transport container or in the process equipment depends on type of material, volume of the container, type of process equipment and number of cleaning cycles related to the number of batches or capacity of the process. Default values for the residues are set for the residual fractions ($F_{X\_residue}$) as well as for the number of cleaning times ($TIME_{cleaning}$).

Table 12 shows the values for residual fractions given in the draft OECD ESD document (2006). The default value of 0.03 is the one for pumping liquids from 55 gallon (208 litre) containers, whereas the default for solids is 0.01.

Likewise, the equipment cleaning residue $F_{equipment\_residue}$ is defined as the fraction of the amount of the total chemical in the process equipment remaining in the emptied vessels, transfer lines, and/or other pieces. The OECD draft ESD proposes the multiple process vessel residual model with a conservative default value of 0.02. The alternatives are shown in Table 13.

The formulation of fragrance oils in powdered detergents is considered as a ‘worst case’ with a view to emissions because conveying, mixing and packaging powder products may produce dust emissions. Uncontrolled releases of the final product are expected, although pollution control devices will recycle most of the recovered particulate material back into the process with efficiencies of common control devices from 85 to 99.9%. The conservative default value for dust emission is based on the uncontrolled releases from a spray drying unit (for soap and detergents) and is set at 4.5% (45 kg particulate per ton product). A conservative estimate for the control device is 85% efficiency.

Table 12 **Default values (fractions) for residual release fractions of containers $F_{container\_residue}$ (draft OECD ESD alternative default values)**

Chemical form	Container type	Container volume (gallons)		Pouring: Default residual fraction		Pumping: Default residual fraction	
			range	central tendency	high end	central tendency	high end
Liquid	Bottle	1	5	0.003	0.006	< 0.003 >	< 0.006 >
Liquid	Small container	5	5 to <20				
Liquid	Drum	55	20 to <100	0.003	0.006	0.025	0.03 [#]
Liquid	Tote	550	100 to <1000	0.0007	0.002	0.0007	0.002
Liquid	Tank Truck	5000	1000 to <10000				
Liquid	Rail car	20000	10000 and up				
Solid	Any	Any		0.01		0.01	

[#] :selected default in OECD draft document

< x >: it is unclear whether pumping is actually used for emptying these small volumes

Table 13 **Default values for residual fractions of process equipment $F_{equipment\_residue}$ (draft OECD ESD alternative default values)**

Model	Gravity draining: Default residual fraction		Pumping: Default residual fraction
	central tendency	high end	conservative
Single process vessel	0.0007	0.002	0.01
Multiple process vessel		0.02	

Table 14 Emission scenario for calculating the release of aroma chemicals to wastewater and waste during the formulation

Variable/parameter	Unit	Symbol	Default	S/D/O/P
Input				
See also Table 10				
1. Fraction of aroma chemical remaining in the emptied container	[-]	$F_{container\_residue}$	0.03(*)	D
2. Fraction of aroma chemical remaining in the equipment as residue	[-]	$F_{equipment\_residue}$	liquids:0.02 solids: 0.01	D
3. Fraction of final product released as dust	[-]	$F_{dust\_generation}$	0.045	D
Air pollution control device efficiency	[-]	F_{APCD}	0.85	D
Number of cleaning times for process equipment	[yr^{-1}]	$TIME_{cleaning}$	perfume: # of batches; fine frag. 250 funct. 50	S
Output				
1. Container residue release rate	kg/site-day	$Elocal_{container\_residue\_disp}$		O
2. Equipment residue release rate	kg/site-day	$Elocal_{equipment\_residue\_disp}$		O
3. Release rate from dust generation	kg/site-day	$Elocal_{dust\_generation}$		O

Calculations

1. Unloading

If $N_{container\_unload}$ *is fewer than* $TIME_{working\_days}$:

$Elocal_{container\_residue\_disp} = V_{container\ oil} * RHO_{oil} * F_{chem\_oil} * F_{containerresidue} * 1$.

This release will occur over [$N_{container\_load}$] *days/year from* [N_{sites}] *sites*

If $N_{container\_unload}$ *is greater than* TIMEworking_days:

$Elocal_{container\_residue\_disp} = Q_{chem\_day} * F_{container\_residue}$

(also used with unknown container volume or unknown number of containers per site per year)

This release will occur over [$TIME_{working\_days}$] *days/year from* [N_{sites}] *sites*

2. Equipment cleaning

$Elocale_{quipment\_residue\_disp} = Q_{chem\_day} * F_{equipment\_residue}$

This release will occur over [$TIME_{cleaning}$] days/year from [N_{sites}]sites.

3. Release of dust waste

$Elocal_{dust\_generation} = Q_{chem\ day} * F_{dust\_generation} * (1-F_{APDC})$

*) 0.03 is default value (fraction) for high end (for pumping liquid out of the drum); central tendency: 0.025. Alternative default value for high end is 0.006 (for pouring liquid out of the drum) and for central tendency: 0.003, see Table 12.

The media of release for the emissions calculated in Table 14 are water, land or incineration. For the total emission of the site to water, the results of all emissions due to unloading and equipment cleaning and conveying powder products should be summed, taking into account whether the emission is daily or intermittent.

No specific data were found on typical pollution control technologies for water releases in this sector, although it is likely that some sites may implement pre-treatment of their process wastewater and/or controls on their process stacks. The ESD suggests that as a default it is assumed that all aqueous wastes are discharged to surface waters (potentially to a publicly owned treatment works in the U.S.).

2.4.3 Risk Assessment Reports on polycyclic musks

Within the context of the risk assessment for HHCB and AHTN, site-specific information was obtained from two large and from one medium-sized formulator of the polycyclic musks AHTN and HHCB. One smaller site was visited and site-specific emission data was submitted for this site. Additional information was obtained through questionnaires and interviews from larger companies. This information was used to describe site-specific and generic local emission scenarios during formulation. As a result of the limited data set the emission scenarios for formulation are less well founded as compared to the ones described for the large and medium sized compounders. The findings were reported in EU-RAR documents for the polycyclic musks AHTN and HHCB (ECB 2008).

All solid waste is collected and may be recycled. Used packaging which have been in contact with chemicals are all incinerated or collected by waste companies.

Table 15 **Generic emission scenario for calculating the release of AHTN and HHCB during the formulation of cleaning products**

Variable/parameter	Unit	Symbol	Default	S/D/O/P
Input				
a1. Total tonnage of products	[tonnes.y^{-1}]	TONNAGEprod		S
a2. Fraction of fragrance oil in products	[-]	Foil		S
a3. Fraction of substance in fragrance oil	[-]	Fsubst		S
b. Tonnage of substance	[tonnes.y^{-1}]	TONNAGEsubst		S
Working days per year	[days.y^{-1}]	$TIME_{working\_days}$	Large 345 Small 250	
Fraction of products released to wastewater	[-]	Fwastewater	Large 0.0006 Small 0.002	D
Fraction of products released to soil	[-]	Fwaste *	0	D
Output				
Release of fragrance ingredient to wastewater	[kg.d^{-1}]	$Elocal_{wastewater}$		O
Release of fragrance ingredient to waste	[kg.d^{-1}]	$Elocal_{waste}$		O

Calculations

a. $Elocal_{wastewater}$ = TONNAGEprod * Foil * Fsubst * Fwastewater * 1000 / $TIME_{working\_days}$

b. $Elocal_{wastewater}$ = TONNAGEsubst * Fwastewater * 1000 / $TIME_{working\_days}$

$Elocal_{waste}$ = 0

2.4.4 EFFA SPORT

Within the EFFA SPORT exercise an effort was made to generalize the emission scenarios for polycyclic musks and make them applicable for the processes in compounding and formulation companies throughout Europe, see section 2.3.4. The emission scenario is based on the EU use volume for a fragrance ingredient. The data were already presented in section 2.3.4, and the ones relating to formulation are repeated here[5]:

- Some 10 % of the use volume is not mixed by compounders but is directly used by large detergent formulators.
- About 3-4 large size formulators use on average 2 % of the use volume; the maximum is taken to be 5% of the EU use volume.
- There are about 1000 small size formulators. The 'maximum use' for the larger of the small formulators is 0.4 % of the EU use volume.

Emission factors

The emission of fragrance oils during the formulation process was based on the data in the EU-RAR and multiplied by a factor of 2, both for the small and the large formulator. These percentages represent the losses without any treatment. The emissions are not specific for the substances, and hence not influenced by the substance properties. They are based on estimated losses, scrap factors and measurements.

Table 16 Typical plant size and release factors in fragrance industry for compounding

Plants	Large	Small
Number	3	1000
Average % of EU use volume	2	0.004
Worst case % of EU use volume	5	0.4
Emission factor to sewer [-]	0.0004	0.004
Working days	250	250
Fraction emission of EU use volume per day, Worst case	$8*10^{-8}$	$6.4*10^{-8}$

It was concluded that for all formulating scenarios the daily emission to the municipal STP can be estimated by the fraction $8*10^{-8}$ of the total EU use volume.
This is the same conclusion as was drawn for the compounders in section 2.3.4. The further description of the emission scenario is identical to the one described in that section in Table 7.

[5] Can we assume that this distribution for the polycyclic musks is generally valid?

2.5 Non-specified industrial life cycle

2.5.1 IPPC BREF document on organic fine chemicals

The Integrated Pollution Prevention and Control IPPC Reference Document on Best Available Techniques (BREF) for the Manufacture of Oil Fine Chemicals (EC, 2005) was expected to describe batch processes in multi-purpose plants similar to those in the fragrance supply chain. The BREF lists techniques to be considered in the determination of the best risk reduction measures. This document reports emissions to waste water for one reference plant for the production of fragrance compounds. The COD elimination in a WWTP was 96%. Thus the remaining fraction in the effluent is 0.04. The volume flow was 300 m^3/d. After treatment, the effluent was discharged to a river. Currently the document provided no more useful information.

2.5.2 Emission calculation models of API and US EPA

The models of the American Petroleum Industry are focused on the emission to air. This is currently outside the scope of this study.

3 NEW EMPIRICAL DATA ON ENVIRONMENTAL RELEASE

3.1 Introduction

The draft OECD Emission Scenario Document states that approaches used are ‘’intended to provide conservative, screening-level estimates’’ and that resulting ‘’releases and exposure amounts are likely to be higher, or at least higher than average, as compared to amounts that might actually be occurring in a real world setting.’’ In addition it states, ‘’where specific information is available, it should be used in lieu of the defaults presented, as appropriate’’. Also the EU guidance for exposure and risk assessment provides conservative approaches to estimate release from industrial processes and embed this in a tiered approach. The EU Guidance for REACH (R.16, EU 2008([6])) allows for refinement of the release estimation when more specific data is available. As described earlier, several sources of information on releases of fragrance ingredients during the compounding and formulation process are available. The default values used in the emission scenarios are summarized in Table 17. Except for the release factors for the formulation of cleaning/washing products (0.09 and 0.81), the default values were derived for generic industrial processes. Thus more specific information was collected to replace these conservative estimates by more realistic values.

Table 17. Default values to determine the release in OECD and EU emission scenarios

		% of tonnage released to wastewater	% of tonnage released to soil	Source
Compounding				
EU-TGD Emission factors	Cleaning/washing agents and cosmetics (UC9, 15), ESD-IC5	0.09	0.81	Table 2
	Odour agents (UC 36)			
	non-HPV	2	0.01	
	HPV	0.3	0.04	
Formulation				
EU-TGD Emission factors	Cleaning/washing agents (UC9, 15) for HPV ESD-IC5	0.09	0.81	Table 9
OECD draft ESD Residual fractions	Containers - Liquids	3 #		Table 12
	Solids	1		
	Equipment	2		Table 13

Branch-specific information on the emission during the compounding or formulation process is available from various projects. The most recent data was generated by the Questionnaire carried out in the context of this project (2008). The Questionnaire was sent to compounding and formulating companies and responses were received from 7 compounding sites and 8 formulation sites. The responses are summarised in Appendix

[6] EU 2008. Guidance on information requirements and chemical safety assessment, Chapter R.16: Environmental Exposure Estimation, Guidance on the implementation of REACH, European Chemicals Agency, May 2008.

2. General observations of the mixing processes during compounding and formulation are summarised in this chapter.

Attention is also given to empirical data on environmental release during compounding and formulation that was collected before. Information on the release of fragrance ingredients was collected in the EU for the preparation of the risk assessment reports for the polycyclic musks in 2001/2002, whereas in the US data on tank residues during compounding was collected by FMA in 2006. Also the Questionnaire was directed to providing specific details on the release during compounding and formulation of fragrance oils and fragranced products.

Estimates of release factors have been made in a variety of approaches, using for example:

- The scrap factor or the difference between purchased volume and (sold) bottled volume;
- Measurement of residues in empty tanks and process equipment;
- Measurements of the Chemical Oxygen Demand (COD) or Total Organic Carbon (TOC) in waste streams.

This chapter presents the empirical results obtained over the years using the different approaches. More details of the information are given in Appendix 3.

3.2 Observations on compounders and formulators based on the Questionnaire

3.2.1 Compounders

Responses to the questionnaire of 2008 were received from 7 compounding sites with varying size and varying degree of emission control. The main objective of the questionnaire was to obtain information on the emission to water and soil during the compounding process. The responses have been analyzed and a validation step was carried out to clear some uncertainties. The responders did not supply all requested information. The results are presented in Appendix 2 and summarized in Table 18.

Observations

- The size of operations ranges from some 100 tons per year to some tens of thousands per year;
- Compounding is carried out as a batch-wise process. The number and sizes of batches is variable. A small compounder indicates to produce a little more than 1 batch per day, whereas another small one makes 15 batches per day. Also in the group of large compounders the same variability is observed, with 13 to 140 batches per day. It is obvious that the small number of batches is produced in larger quantities.
- In the smaller facilities, dosing is mainly a manual process, whereas in the larger facilities a mixture of automatic and manual dosing is reported. After each batch a number of mixing vessels will need to be cleaned;
- The delivery area is a contained area so spills and contaminated rain is drained to the water treatment system. Generally the empty containers are not cleaned. They are either dedicated containers or they are recycled by an external company. Pumps may be cleaned with water and the water is discharged into the drains. Some minor losses may occur there. Estimated losses range from <<0.01% to 0.08%;
- Mixing vessels and batch sizes span a large volume range, from a few litres to many cubic meters. The main release occurs after the mixing process when containers,

pumps and other equipment are cleaned with water, detergent and sometimes steam or alcohol. The average releases range from 0.015 to 0.1%, with higher estimates for small batches (< 60L) up to 0.3%. These results are based on measurements.

- During the filling of all finished products, rinsing or cleaning procedures are directed towards avoiding emissions to wastewater. Estimated emissions are in the range of 0.01%.
- Floors are mopped and the water is discharged to the sewer system; spills are absorbed and treated as chemical waste, although small spills may be washed down the drain;
- Waste is treated under national regulations. Spills are absorbed and collected as chemical waste. The same is true for samples, packaging materials and sludge residues from water treatment. It is disposed of to an outside contractor and may be treated, incinerated on put in a landfill, according to local regulations;
- Compounders treat their wastewater on site. This includes physical/chemical treatment and in some cases also a biological treatment system is in place. If not, the treated water is discharged to a local sewage treatment plant for further biological treatment;
- Most responses showed that the COD in wastewater was caused mainly by the presence of fragrances in the water. Based on indications of the COD and the production volumes, and assuming that the COD of most of the fragrance ingredients in wastewater = 3 mg O/mg substance (see Appendix 4), it was possible to estimate the release of products to wastewater. This fraction, prior to any treatment, ranges from 0.2 to < 0.43 % for the small compounders whereas for the large compounders the estimates range from 0.01 to 0.15%.
- On-site physical-chemical treatment generally resulted in a removal of 70%, whereas for the biological treatment plant a general figure of 90% was given.

Table 18. Summary of results of the Questionnaire (2008) for 7 compouders

	Compounders
Size of operation	
Small ($t.y^{-1}$)	<1000
Medium ($t.y^{-1}$)	1000 – 10,000
Large ($t.y^{-1}$)	> 10,000
Number of working days	230 - 250
Delivery and storage	
Release to water	<< 0.01% to 0.08%
Dosing and Mixing	
Vessels	< 60 L up to 35 m^3
Residues in empty vessels	0.02 – 0.3%
Finished products	
Wastewater treatment	phys-chem treatment and biological (on site or STP)
Release to water	0.01 - < 0.1 %
Overall	
Estimated release in process (COD or kg)	Small: 0.2% - <0.43%
	Large: 0.007 – 0.15%
Estimated release (including treatment)	Large: 0.01 – 0.07%

3.2.2 Formulators

Responses were received from 8 production sites producing a varying range of products. Some responders supplied very limited background information but they did present overall estimates for their emissions to water.

The product categories on which information has been obtained, include:

- Soap bars
- Formulation of liquid and granular detergents
- Conditioners
- Liquid cleaners
- Shampoos and shower gels
- Liquid creams and lotions
- Fine fragrances and perfumes

The responses have been analyzed and in some cases some additional clarification was obtained. The answers were less detailed than for the compounding facilities. The results are presented in Appendix 2 and summarized in Table 20.

Observations

- The size of operations ranges from less then 1000 tons per year to over 100,000 tons per year. The size of operation is to be considered on a different scale, depending on the type of products being produced. This is summarized in Table 19.

Table 19. Size of operations for formulation of consumer products

	Medium, ton/year	Large, ton/year
Fine Fragrances	< 1000	> 1000
Liquid creams and lotions	> 1000	> 10,000
Soap bars	> 1000	> 10,000
Granular Detergents	> 10,000	> 100,000
Liquid cleaners, conditioners, shampoos, shower gel	> 10,000	> 100,000

- The production of granular powder in a large-scale plant is a continuous process. As far as the data are available, the production of the other products is carried out as a batch-wise process. The number and sizes of batches is highly variable but there is not sufficient data for a generalization;
- The concentration of fragrance oils (mixture) in a final product ranges from below 1% to 15% or more. However, when individual ingredients are considered, the concentrations vary over many orders of magnitude. For an assessment per substance, an indication of the concentration per substance is needed;
- As for the compounding facilities, the delivery area is a contained area so there is no emission of spills and contaminated rain to surface water. Empty containers are generally not cleaned. They are either dedicated containers or they are recycled by an external company;

Table 20. **Summary of results of the Questionnaire (2008) for formulation**

	Hard Soap	**Granular Detergents**	**Liquid cleaners, conditioners, shampoos, shower gel**	**Liquid creams and lotions**	**Fine Fragrances**
General characteristics					
Size of operation	L	L	M/L	L	M/L
Number of working days		260	250		312
Total % of fragrance in product	0.5% [1)]	0.4% [1)] , 2 % (dw)	0.2 – 0.3% [1)]		10 – 15%
Examples for individual substances		0.002 – 0.12%	0.33% (incl. water)		0.00003 – 0.8%
Delivery and storage					
Release to water	no release	only spills	no release	no release	<1% (off-site)
Dosing and Mixing					
Vessels		> 1 m^3	> 1 m^3		
Residues in empty vessels	Minimised by recycling into product	Residue reblend or recycling of washing water	Low due to recycling of water; to 3.3% [2)]	Low due to incorporation back into process or disposal into solid stream	0 (cleaning with alcohol) to 0.5 %
Finished products	no release	no release	no release	no release	little residue, little cleaning needed
Release estimates					
Estimated release to solid waste	0.06%	0.06 %	0.14%	0.085%	no loss
Wastewater treatment	biological	physico-chem	phys.chem and biological	biological	no water to drain
Estimated release in process to waste water before treatment	0.03%	0.08%	0.027%	0.8%	0 – 1.5%
Estimated emission in wastewater (after treatment on site)	0.003%	0.003 – 0.007%	0.007% - 0.008%; 0.13 [2)]	0.08%	not applicable

1) Source: RIVM 1997, Report 601503008, Environmental Risk Assessment of the Polycyclic Musks AHTN and HHCB according to the EU-TGD.

2) 3.3% is considered to be very high; the responder emphasised that measures are taken to adapt the process and that this value is not to be considered representative for the scenario development. Wastewater treatment efficiency 96%.

- After the mixing process, containers, pumps and other equipment are cleaned with water. Many responders stated that the washing water is recycled back into the formulation process to reduce the loss of products. Residues or samples of soap or powdered detergent are reused in the production. For some perfume alcoholic products, alcohol is used for cleaning. The alcohol is then recovered without any loss to water. Release during the dosing and mixing of the various formulations varies from 0 to 1.5%.
- During the filling of all finished products, procedures of rinsing and cleaning are used that avoid losses. Waste from change-overs is minimized and if it cannot be incorporated in the next batch it is collected and disposed in the solid waste stream.
- It is general practice that spills are vacuum-cleaned or absorbed and treated as chemical waste, although small spills may be washed to the drain;
- Packaging materials are cleaned and/or recycled by specialized contractors. Waste is treated under national regulations. Spills are absorbed and collected as chemical waste. The same is true for sludge residues from water treatment. It is disposed of to an outside contractor and may be treated, incinerated or put in a landfill, according to local regulations;
- Most formulators treat their wastewater on site. This includes physical/chemical treatment and in some cases also a biological treatment system is in place. If not, the water is discharged to a local sewage treatment plant for further biological treatment;
- Based on indications of the COD of the products and the production volumes it was possible to make an estimation of the release of products to wastewater. For the formulated products the ThOD (without water) was taken to be 2 g O per gram product (see Appendix 3). In general the release is far below 1%.
- The emission from the site, i.e. after on site wastewater treatments, was specified by a number of responders. In particular for bulk products like soap, detergents, cleaning agents and conditioners, the emission after treatment was below < 0.01%.

3.3 Scrap factor or difference between purchased and sold volume

The scrap factor is a term for the amount that is produced in surplus to the ordered amount to take into account volumes needed for sampling, residues in various containers, volatilization, etc. during the process. Generally customers also receive slightly more than the ordered volumes to prevent complaints on the delivered quantities. The scrap is high for small volumes, due to the relative large sample size, whereas it is small for higher volumes. The scrap factor is an empirical factor specific for the processes on site. An example from a large compounder is given in Table 21.

Table 21 Scrap factor for a large European compounding site (data from 2001/2002)

Size	volume	scrap factor	Remarks
Small batches	1.5 kg	8%	
Medium size	200 kg	0.3 %	
Larger size	>> 200 kg	0.15 %	class forms 50% of production
average scrap factor		*0.2%*	

For a small formulator the loss of products was estimated on the basis of data on yearly production versus bottled volumes. The average over 2 years was 0.5%. These losses were due to fillings in the bottle above the minimum and to cleaning/rinsing during production. Only the latter is released to the sewer system, and this fraction was estimated at 60%. Thus actually 0.3% of the production volume is released to the sewer.

Using the scrap factor or the difference between purchased and sold volume as an indication for the volume released to wastewater is to be considered as an overly conservative approach. Not all of this 'lost' volume is released to the water phase: the main part is sold as surplus in the bottle, whereas another part is used for sampling and will be disposed of in another way. This approach is to be seen as a first estimate in the early years before more accurate estimations were made.

3.4 Tank and equipment residues

The residual fraction is the fraction of a substance that is left in a container after emptying. It is expressed as the 'amount (kg) of substance left in the empty container divided by the total amount (kg) of substance in the full container', $F_{container\_residue\_}$.

The residual fraction is (amongst others) dependent on:
- Intrinsic properties of the substance (e.g. viscosity).
- Container type (e.g. bottle, drum, etc.).
- Method used for emptying the container (pouring, pumping).

The general trend is that the residual fraction increases with:
- Increasing substance viscosity (due to the substance adhering to the container surface).
- Decreasing container size (larger surface/volume ratio of smaller containers).
- Pumping instead of pouring as a method of emptying containers, since pumping is an inherently less efficient emptying method.

Empirical data was collected in the period 2002 and 2003 in preparation for the EU Risk assessment for the polycyclic musks (EC 2008). The data are summarized in Table 22. More details are given in Appendix 3.

Table 22. Tank and equipment residues, % of total production, data from 2001/2002, See Appendix A3.1

Compounding		Residue	Remarks
Loss at delivery, Galaxolid50	200 l drum, vacuum pumping	100 g = 0.05%	Determined by weight
Large site Overall residue in mixing vessels	batch size 3 kg – 17 m^3	0.12%	Determined by weight (Scrap factor was 0.2%)
Large site Overall residue in mixing vessels and pumps	1000 and 6300 L	0.15% $^{++}$	Determined by weight, $^{++}$): probably overestimation
Overall residue in mixing vessels and pumps	water from washing of 15 mixing tanks (90 to 580 kg)	0.015%	Determined by TOC analyses and volume of washing water

Members of the FMA have undertaken three studies on the two basic drum handling scenarios (pumping and pouring) described in the OECD draft ESD in an effort to provide realistic values for the parameters $F_{container\_residue}$. The results are summarized in Table 23. More details are included in Appendix 3.

Table 23 **Summary of results of 3 studies on tank residues in varying tank sizes, compounding (FMA 2006), see Appendix A3.2**

	Pumping 20 – 100 gallon	**Pouring 20 – 100 gallon**	**55 gallon**	**15-gallon**	**30-gallon**	**55-gallon**
	95th perc.	95th perc.	90th-perc.<			
Fragrance ingredients	0.572%	0.530 %		0.5% [1)]	no data	0.15%
Fragrance compounds	0.309%	0.172 %	0.5%	no data	0.12%	0.11%

[1)] Result of only one weighing

Following the Questionnaire of 2008, responses were received from 7 compounding sites with varying size and varying degree of emission control. From the Questionnaire specified empirical data on residues in mixing vessels have been obtained from two different compounding sites. One site also specified the residues during pumping and cleaning of tank trucks, IBCs and drums, see Table 24.

Table 24 **Residues in tank for fragrance compounds, specified for two sites (Questionnaire 2008, compounding), see Appendix A3.3**

Mixing vessel	**Tank residue Site A**	**Tank residue Site B**	**Equipment residue Site B**
< 60L (< 15 Gallon)	0.32%		
60 – 200 L (15 – 55 Gallon)	0.25%		
90 kg		0.033%	
200 – 1000 L (55 – 265 Gallon)	0.195%		
215 kg		0.027%	
580 kg		0.072%	
> 1 m^3 (> 265 Gallon)	0.091%		
7 – 30 m^3		0.08%	
Indicated average tank residues for the site	0.1%	0.07%	
Loss due to pumping containers			0.08%
Combined loss tank and equipment		0.15%	

It should be realized that the residues washed from the containers and equipment are collected to the sewer on site and treated in a physico-chemical and/or biological treatment system before the water leaves the site. Thus the emission from the site is to be corrected for the efficacy of these treatments.

3.5 Estimations based on wastewater analyses

Another way to approach the release is by analysis of the wastewater. In this approach the Chemical Oxygen Demand of the waste streams is determined. In this approach it is assumed that all ingredients behave similarly during the mixing and cleaning process. The COD-load in the wastewater reflects the release of compounded or formulated products.

The data collected in the period 2002 and 2003 for the EU-RAR for the polycyclic musks (EC 2008) included COD analyses of the wastewater. This data was converted to the mass of the products and compared to the total production volume of the site. The data are summarized in Table 25. More details are given in Appendix 3.

Table 25. Fwastewater as a % of total production, data from 2001/2002

	Analysis	Average release to water	Remarks
Compounding			
Large site Release to external STP after phys/chem. treatment on site	COD analysis of wastewater	0.02%	Includes phys/chem. treatment App. A3.1
Large site Release to external STP after oil separation	COD analysis of wastewater	0.05%	Includes phys/chem. treatment App. A3.1
Formulation			
Large site Overall release		0.017%	No further specifications RARs PCM 2008
Small site Release to external STP	Actual COD release vs annual purchase raw materials;	0.07 – 0.22%	App. A3.5
	COD fraction of products	0.14%	

Some of the responders to the Questionnaire (2008) supplied information on the COD load of their wastewater, so in combination with their production volumes the fraction released to wastewater was estimated, see Table 26. For this calculation it was assumed that the COD for a fragrance mixture is 3 mg O/mg substance, whereas the COD for a formulated product is 2 mg O/mg substance (see Appendix 4). More detailed data are presented in Appendix 2 and 3.

Table 26. Fwastewater as a % of total production, data from 2008 Questionnaire. Release in COD is related to production volume, see Appendix 2

	Average release to waste water	Remarks [1)]
Compounding		
Small site		
Release to external STP	0.43%	
Large site		
Release to phys.chem treatment	0.007 – 0.016%	Phys/chem. 32% removal
Release to from site	0.005 – 0.01%	
Formulation		
Hard soap		
Release to internal WWTP	0.03%	WWTP 90 % removal
Release from site	0.003%	
Gran. Detergent		
Release to internal WWTP	0.08%	WWTP 90 – 96 %
Release from site	0.003% - 0.007%	removal
Liquid cleaners, conditioners, shampoos, shower gel		
Release to internal WWTP	0.027 to 3.3% [#]	WWTP 70 – 96 %
Release from site	0.007 – 0.008%; 0.13 [#]%	
Liquid creams and lotions		
Release to internal WWTP	0.8%	WWTP 90%
Release from site	0.08%	
Fine fragrances		
Release from site	0 to 1.5%	

[#] 3.3% is considered to be very high; the responder emphasized that measures are taken to adapt the process and that this value is not to be considered representative for the scenario development

[1)] It should be remarked that removal by physical-chemical treatment and even more by biological treatment depends on substance properties such as log Kow and the biodegradability. Thus the removal percentages should be considered with care and the validity of these generalizations is to be challenged for hydrophilic substances in oil/water separators as well as for poorly degradable substances in a biological treatment plant.

3.6 Comparison of the empirical data with the default values proposed in the emission scenarios

Sections 2.3 and 2.4 presented the existing emission scenarios and described the various default values. Table 17 presented a summary of the default values in the OECD proposal and the EU scenarios. These data are intended to be conservative. From earlier projects as well as from the responses to the inquiry a large number of empirical data have become available. The focus was mainly on obtaining supporting data for reducing the values for the release factors in the scenarios. An overview of the release factors for compounding is given in Appendix 3, Table A3.6 and for formulation in Table A3.7. The results for compounding are summarized in Table 27 and in Table 28 for formulation. It is clear that the empirical data are lower than the conservative proposals in the OECD-ESD.

Conclusions on the container residue are:

- Across a wide range of viscosities, the residue in a 55 gallon-tank is not above 0.5% for individual fragrance ingredients, whereas for fragrance compounds it is not above 0.3% (from Table 22, Table 23 and Table 24, Figure A3.1);
- For smaller containers, the residue is higher in percentage, but the volumes in the smaller containers contribute little to the total release of a site.
- Data obtained from one company over time seem to illustrate that also awareness contributes to lower residues and thus a low overall value of 0.15% was reported.
- Many measurements are available for the container residues during compounding. The data refer to the residues of single fragrance ingredients in containers emptied after delivery and storage, as well as to compound oils for vessels used to mix the oils. Thus the latter results can also be assumed to be representative for containers received by the formulators when they dose the fragrance oils in their end product.
- The consistency (viscosity) of the formulated end product, however, is quite variable and it may also be assumed that the size of the mixing vessels differs among the different product types with the larger volumes used for granular detergents and smaller sizes for the fine fragrances. The higher viscosity of liquid cleaning products and conditioners would yield higher container residues, but at the same time it apparently stimulated the development of recycling of wash water into the process to reduce product loss.
- On the other hand, the smaller volumes used in fine fragrances and the need to avoid contamination of the characteristic odours causes a higher emission when washed with water.
- Not for all sizes of operation data was obtained. Yet it is clear that the size of the facilities influences the release factors. This is due to the distribution of the container volumes: with a higher share of larger vessels, the container residues are reduced. Thus as a conservative approach, for smaller facilities a higher release factor is proposed.
- Based on the empirical data, in

Table 27 and Table 28 proposals are derived for the release factors for the various scenarios, representing the emissions from the process before any wastewater treatment:

- Compounding:
  - Large/Medium facility: 0.2%
  - Small facility: 0.5 %
- Formulation of
  - Soap Bar: 0.05 % (Large facility)
  - Granular Detergents: 0.1 % (Large facility)
  - Liquid cleaners, conditioners, shampoos, shower gel:
    Large facility: 0.1 %
    Small facility: 0.2 %
  - Liquid creams and lotions: 1%
  - Fine fragrances and perfume products: 1.5%,
    but 0 % if alcohol is used for cleaning.

Table 27. Comparison of empirical data with default values for compounders

	Temission (days)	Fwastewater (%)	Treatment on site	Fraction in site effluent (%)
EU-TGD Cleaning/washing agents and cosmetics (UC9, 15), ESD-IC5	300	0.09		
Odour agents (UC 36) non-HPV HPV	< 50 - 300	 2 0.3		
Empirical Results	(230 -) 250	Prior to on site treatment L/M: 0.007 – 0.016, 0.015 - 0.15, 0.03 – 0.15 S: 0.22, <0.43 0.16, 0.08	Phys.chem treatment (30 –)70 % removal	0.02 - 0.07
Proposed scenario	**250**	Prior to on site treatments: **Large/Medium sites: 0.2** **Small sites: 0.5**	Phys-chem. treatment **50 % removal**	

Table 28. Comparison of release factors for formulation (in %)

	Generic defaults	Hard Soap	Granular Detergents	Liq.Cleaners Conditioners Shampoos Shower gel	Liquid creams and lotions	Fine Fragrances
Draft OECD Defaults						
Release to water from containers	3					
Release to water from equipment	2					
EU-scenario Emission days	0.09 300 days	0.01	0.01	0.09	0.09	0.09
Empirical data Inquiry 2008 and Data 2002/2003*						
Emission days	250 – 345 days					
Estimated release to wastewater (Based o COD) prior to treatment		0.03	0.08	L/M: 0.027, 0.06, <3.3#> S*: 0.07 – 0.22	0.8	0 1.5
Estimated emission (after treatment on site)		0.003	0.003 – 0.007	0.007 – 0.008; 0.13	0.08	--
Proposed scenario, Fwastewater prior to on-site treatment	**250**	**Large: 0.05** **Small: 0.1**	**Large: 0.1** **Small: 0.2**	**Large: 0.1** **Small: 0.2**	**1**	**1.5** **0 if cleaned with alcohol**
On-site treatment		**yes**	**yes**	**yes**	option	option

The wastewater treatment on site is variable. For compounders there is at least a physico-chemical treatment system with an efficacy of 50% or more, but of course this also depends on the substance characteristics. This is also the case for biological treatment plants that are often present on the larger industrial sites. Thus a conservative removal percentage of 50% is proposed as a default value.

For formulators there were not sufficient details on the type of wastewater treatment for all product types. Thus the removal after on-site treatment, as well as the receiving system of the discharged water can only be assigned on a case by case basis.

The release factors are derived relative to the daily or yearly production. However, this assumes that the release is continuous during all days of the year. If the specific fragrance ingredients is present only occasionally in the fragrance oils mixed into the end products, a correction needs to be made for the lower number of emissions days (Temission). The proposed number of emission days is also presented in the proposed scenarios. However, for sites where the wastewater is treated in a continuous system, the buffering capacity of the treatment system should be taken into account when establishing the daily emission from the site.

4 CALCULATED EXAMPLES FOR COMPARISON

For comparison, the results are used in the scenarios as proposed by the draft OECD ESD and the EU-TGD and they are compared to the results using the release factors proposed here (RIFM). The calculation is performed for the liquid cleaner, which has the higher release factor. The results are summarized in Table 29. The results are linearly dependent on the release factor, so the effect of a change is evident.

The EU-TGD scenario for formulation uses relatively low release factors, which is quite unusual. The highest release factor is 0.09%. This is lower than any of the values proposed in this study. Moreover, the number of emission days in the EU-TGD scenario is taken as 293 instead of 250, which also reduces the daily emission rate. These choices are not expected to be representing a “reasonable worst case”.
The OECD scenario mainly differs from the RIFM calculations in the more differentiated values for the release factors.

Table 29. Comparison of the emission scenarios

Variable/Parameter	Unit	Remarks	RIFM	OECD ESD	EU TGD
Annual tonnage of final product	Ton/yr		975		975
Annual production volume of aroma chemical	kg/y			10000	-
Average annual use rate of fragrance oil	kg/y/site		19500	19500	19500
Daily use rate of aroma chemical	kg/y/site			-	-
Days of operation or days in which aroma chemical is used in the manufacture of end products	d/y	with low# containers:		250 lower	
Faction of aroma chemical in fragrance oil	-			0.2	-
Fraction of fragrance oil in final product	-			0.02	-
Volume of fragrance oil container	L/container			208	-
Volume of final product container	L/container			3.78	-
Density of fragrance oil	kg/L			1	-
Density of final product	kg/Ll			1	-
Fraction of aroma chemical remaining in the emptied container	-	Liquid Solid		0.03 0.01	
Fraction of aroma chemical remaining in the equipment as residue	-			0.02	-
Fraction of tonnage released to wastewater during formulation		Compounding L/M	0.002	-	0.02
		Compounding. Small	0.005		
		Soap, Large/ Small	0.0005/ 0 001		
		Granular Det, Large/ Small	0.001/ 0.002		0.0001
		Liq. cond, cleaners, Shampoo, shower gel Large/Small	0.001/ 0.002		0.0009
		Creams, lotions	0.01		
		Fine Fragr.	0.015		

Variable/Parameter	Unit	Remarks	RIFM	OECD ESD	EU TGD
Number of cleaning times for process equipment	y^{-1}	Perfumes		# of batches	-
		Fine Fragr.		250	
		Func. Fragr		50	
Number of cleaning days for process equipment	y^{-1}			"	
Number of emission days	d/y				Depends on tonnage
Fraction of final product released as dust	-			0.045	-
Air pollution control device efficiency	-			0.85	-
Fraction of tonnage released to waste during formulation	-			-	0.0032
Fraction of main source (non-HPVC)		< 100 $t.y^{-1}$			1
		100-500 $t.y^{-1}$			0.6
		500-1000 $t.y^{-1}$			0.6
	-	>1000 $t.y^{-1}$		-	0.4
Fraction of main source (HPVC)	-	< 3500 $t.y^{-1}$		-	1
		3500-10000 $t.y^{-1}$			0.8
		10000-25000 $t.y^{-1}$			0.7
		25000-50000 $t.y^{-1}$			0.6
Calculations					
Fchem_final = Fchem_oil * Foil_final	-			0.004	
$Q_{oil\_day} = Q_{oil\_yr} / TIME_{working\ days}$	kg/site/day			78	
$Q_{chem\_day} = Q_{oil\_day} * F_{chem\_oil}$	kg/site/day			15.6	
$N_{sites} = Q_{chem\_year} / Q_{chem\_day} * TIME_{working\ days}$	-			3	
$N_{container\ unload} = (Q_{chem\_day} * TIME_{working\_days}) / (F_{chem\_oil} * V_{container\_oil} * RHO_{oil})$	-			94	
$N_{container\_filled} = (Q_{chem\_day} * TIME_{working\_days}) / (F_{chem\_final} * V_{container\_final} * RHO_{final})$	-			257937	

OECD/EPA draft					
Container unload release					
$Elocal_{container\_residue\_disp} = V_{container\ oil} * RHO_{oil} * F_{chem\_oil} * F_{containerresidue} * 1$. for Ncont_unload < working days	kg/site/day			1.25	
$Elocal_{container\_residue\_disp} = Q_{chem\_day} * F_{container\_residue}$ for Ncont_unload > working days	kg/site/day			0.468	
Release from Equipment Cleaning					
$Elocale_{quipment\_residue\_disp} = Q_{chem\_day} * F_{equipment\_residue}$	kg/site/day			0.312	
Release from Conveying, mixing, packaging powdered detergents					
$Elocal_{dust\_generation} = Q_{chem\ day} * F_{dust\_generation} * (1-F_{APDC})$	kg/site/day			0.105	

Variable/Parameter	Unit	Remarks	RIFM	OECD ESD	EU TGD
EU_TGD (LIQUIDS)					
Temission (non HPV)	d/y	< 100 $t.y^{-1}$			1950
		100-500 $t.y^{-1}$			585
		500 - 1000 $t.y^{-1}$			292.5
		> 1000 $t.y^{-1}$			300
Temission HPV		HPV			300
$Elocal_{wastewater}$ = Fwastewater * Fcomp * Fsubst * TONNAGE * 1000 / Temission	kg/y				0.012
RIFM (LIQUIDS)					
$Elocal_{wastewater}$ = Fwastewater * Fcomp * Fsubst * TONNAGE * 1000 / Temission					0.031
Temission	d/y		250		

		RIFM	OECD ESD	EU TGD
Total release per site	**kg/site/day**	**0.31**	**1.56**	**0.012**

5 RECOMMENDED SCENARIO

Following the results of this study, the recommended scenario for the compounding and formulation of fragrance ingredients is summarized in Table 30. The newly derived default values for the release factors to the waste water compartment are shaded in the table. It is remarked that the number of emission days for the substance should be considered with care. For ingredients that are not often used, the number of days should be reduced in order not to underestimate the daily emission per event.

Moreover, this study showed that it is common practice that the waste water is treated in a physical-chemical system before it is discharged into a biological wastewater treatment plant on-site or in a municipal sewage treatment plant.

Table 30. Recommended emission scenario

Variable/Parameter	Unit	Symbol		S/D/O/P[1)]
Input				
Annual tonnage of final product	[Ton/yr]	TONNAGEproduct		S
Average annual use rate of fragrance oil	[kg/y/site]	TONNAGEoil		S
Number of emission days of aroma chemical	[d/y]	Temission	250	S/D
Faction of aroma chemical in fragrance oil		Fsubst_oil		S
Fraction of fragrance oil in final product	[-]	Foil		S
Fraction of tonnage released to wastewater	[-]	Fwastewater		
Compounding Large+Medium/ Small			0.002/ 0.005	D
Soap Large/ Small			0.0005/ 0.001	D
Granular Detergents Large/ Small			0.001/ 0.002	D
Liquid conditioners, cleaners, Shampoo, Shower gel - Large/ Small			0.001/ 0.002	D
Creams, lotions			0.01	D
Fine fragrances (if not cleaned with alcohol)			0.015	D

Output			
Faction of aroma chemical in final product		Fsubst_prod	O
Release to wastewater during life-cycle stager formulation	[kg/d]	$Elocal_{wastewater}$	
Calculations			

Fsubst_prod = Fsubst_oil * Foil

1. $Elocal_{wastewater}$ = Fwastewater * Fsubst_prod * TONNAGEproduct * 1000 / Temission

OR

2. $Elocal_{wastewater}$ = Fwastewater * Fsubst_oil * TONNAGEoil * 1000 / Temission

1) **S** data to be Set by the user
D Default, parameter has a standard value but can be changed by the user

A COMPANY OF

ROYAL HASKONING

Appendix 1
Questionnaire distributed to compounders and formulators

Questionnaire on emissions to water and waste during fragrance compounding and formulation

Research Institute for Fragrance Materials
RIFMResearch Institute for Fragrance Materials

28 April 2008

9S3975.01

A COMPANY OF

ROYAL HASKONING

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Date/initials check	28 April 2008	………………….
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Date/initials approval	28 April 2008	………………….

Responsible for filling the questionnaire:	
Company:	
Name:	
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1. INTRODUCTION

During compounding of fragrance ingredients and formulation of the fragrance oils into consumer products, some emission of ingredients or products cannot be avoided. In the past, generic tables were developed within the EU Technical Guidance Documents for Risk Assessment to describe the emissions as a percentage of the total volumes produced on per site. These percentages are rather high to take a precautionary approach to protection of the environment.
In environmental exposure assessments for some specific substances is was already shown that the actual emission is lower than the prediction of these generic tables. Within the context of the OECD, EPA has produced a draft Emission Scenario Document (2006) that still takes a rather conservative approach.

In an effort to bring these estimates to a more realistic level, the Research Institute for Fragrance Materials RIFM has commissioned Royal Haskoning to improve the description of the emission estimates based on realistic data from the fragrance industry and its downstream users. The results of the project will be used by RIFM in contacts with the OECD and regulatory authorities in the USA and Europe.

For the further development of these emission scenarios it is essential that we obtain more detailed information on the process and equipment used during compounding and formulation.
The basic question that needs to be answered is:

"How much fragrance goes to wastewater during compounding / formulation?"

Royal Haskoning has prepared a questionnaire that intends find an answer to this question. The questionnaire presents a number of approaches that may lead to an answer, but there more alternative approaches possible. If the reviewer has alternative data or methods to provide us with the answer to the above question, he is invited to do so.

However, next to deriving a figure for a specific site, we intend to generalise the information for the generic categories of large/medium compounders and small compounders as well as for the categories of large/medium formulators and small formulators. Therefore we ask more questions than needed for finding the answer for a specific site. We would appreciate to obtain information on your processes and equipment enabling us to couple your emission data to these categories. Only in this way we are able to describe generic emission scenarios. It goes without saying that the results will be treated confidentially and that they will only be presented in an aggregated form.

We propose that our questionnaire will be answered by the company expert on site. The expert may consider using it during an internal site visit, to ensure an accurate description of the situation.

2. GENERAL STRATEGY

During the discussion with the Environmental Task Force one of its members proposed that he would use the questionnaire during actual visits to two of his sites. This seems to be a perfect way to collect the requested information in cooperation with the HSE-manager, operators, sales department, etc. When relevant information (e.g., monitoring data) is available on paper, it is suggested to return it with the completed questionnaire to Royal Haskoning.

Confidentiality of data
The information will not be reported for each site individually. Available information will be evaluated and summarized in several generic scenario(s). Thus, in the final report it will not be possible to trace the data back to individual sites or companies. The report will show a summary of the results, grouped in categories, as support for the choices and categories proposed for relevant generic emission scenarios and emission levels.

3. INFORMATION NEEDED

To answer the basic question: *"How much fragrance goes to wastewater during compounding / formulation?"* a series of more detailed questions can be posed, see Box 1. The questionnaire presented in section 4, formulates further questions to assist in finding a answer to the basic question.

Box 1. Questions related to emissions on site

Handling of the 100% Fragrance material
- How do fragrances enter your plant? (e.g. 55 gallon barrel, 1000 L cubitainer)
- How are they stored?
- How do you protect from spills? What is done with spilled fragrance materials? Are spilled materials washed into drains? (If so, how frequently and how much?)

- How are these materials transferred within the plant?
- How do you protect from spills during the transfer process? What is done with fragrance materials spilled during transfer? Are spilled materials washed into drains? (If so, how frequently and how much?)
- What is done with the empty fragrance containers? (e.g. returned to supplier, cleaned and recyled, etc.?)
- Are empty containers washed out on-site? If so, is the wash and rinse water released to wastewater?

Product Types
- What types of products containing fragrance materials are formulated at the plant? (e.g. liquid detergent, granular detergent, shampoo, fine fragrance, etc.)
- For each major product category, what is the
    - Annual tonnage produced?
    - Physical form of the finished product (i.e. solid or liquid)?
    - Approximate percent (%) of fragrance in the product?
    - Approximate level of water in liquid products?

Formulation into solid products or into liquid products
- How do you prevent and protect from spills of finished product? What is done with spilled finished product as a function of product type or physical form? Is spilled finished product washed into drains? (If so, how frequently and how much?)
- How do you clean your equipment between batches or production runs? If wash and rinse water are released to drains, how frequently does this occur and how much product is being washed down the drain?
- How many days per year are solid and/or liquid products produced at the site?

Wastewater Releases
- What is the total COD (BOD) released from your site on an annual basis?
- What fraction of this COD (BOD) is associated with formulation of products containing fragrance materials?
- What happens to the wastewater? (i.e. treated on site? Sent to a publicly operated STP? released to surface water without treatment?)

In a generic scenario the emissions to the environment are most often expressed as a fraction of the volume of used fragrance ingredients or a fraction of the produced product.

The exposure and emissions due to the activities during compounding and formulation can be divided in the following activities (see figure 1):

A) Delivery of feedstock ([7]);
B) Storage of feedstock;
C) Filling process equipment and metering procedures;
D) Mixing of feedstock and cleaning procedures;
E) Handling finished product;
F) Treatment of solid waste
G) Wastewater handling and treatment.

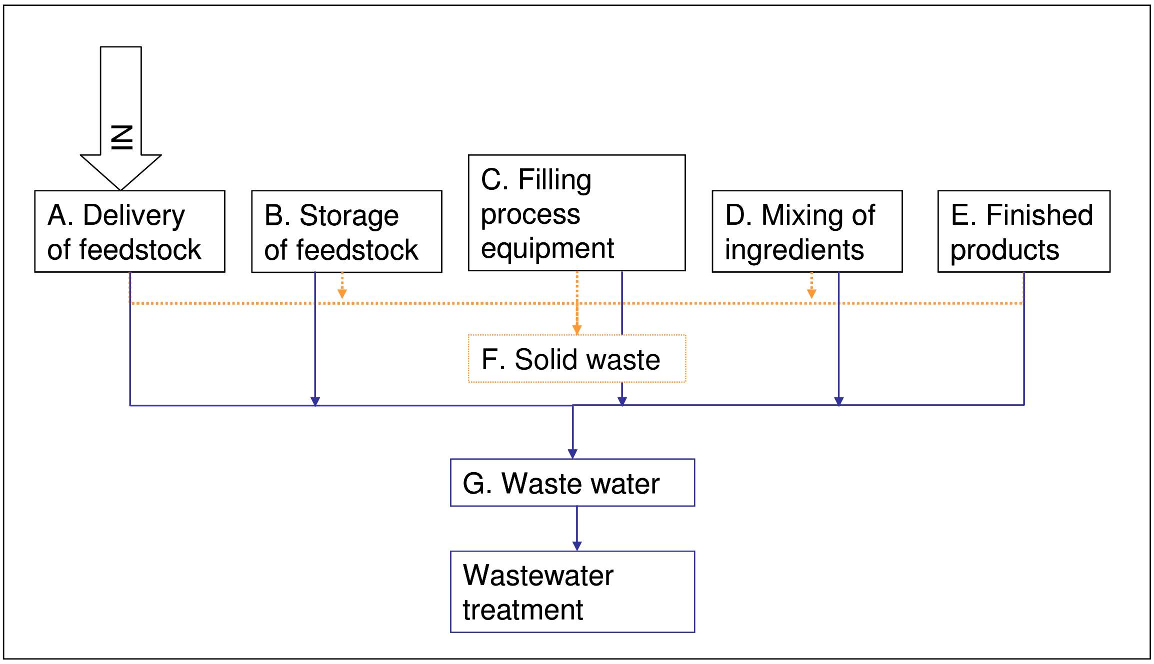

Figure 1. Activities during compounding or formulation

Approaches to assess the release of ingredients or products to waste water are, for example:

1. Comparison of the Chemical Oxygen Demand COD or the Total Organic Carbon TOC in the wastewater coming from the mixing plant to the COD or TOC in the total feedstock at delivery or to the total in the finished products. This ratio represents the loss during the process. If COD or TOC can be measured only after a phys-chemical treatment, it presents an overall release ratio after initial treatment.
2. Using the scrap factor under the assumption that all feedstock filled into the mixing equipment but missing in the finished products, was discharged to wastewater.
3. Determination of residues in mixing vessels and pumping equipment, for example by weighing containers before and after emptying and cleaning.

Combinations of these approaches and alternatives are possible as well.

([7]) Feedstock: Fragrance ingredient or fragrance oil (compound)

As already stated in the introduction, however, we also intend to generalise the information for the generic categories of large/medium compounders and small compounders as well as for the categories of large/medium formulators and small formulators. Therefore the questionnaire contains more questions so we can couple your emission data to these categories. Only in this way we are able to describe generic emission scenarios. Thus we would appreciate to receive answers to the other questions as well.

Compounders of fragance oils

For each of the activities in Figure 1, we need information describing the volumes of fragrance ingredients, the type of containers used for storage and mixing and losses to water, etc. It is understood that this cannot be done for the numerous ingredients that are being used by the fragrance industry and their downstream users. Yet for certain regulations, for example for REACH, the emission should be assessed for individual substances. For compounding we can adopt an approach using 'marker ingredients' representing different aroma chemicals categories with a range of physico-chemical properties, in particular with respect to Log Kow, vapour pressure and viscosity. We ask you to keep such example substances as in table 1 in mind when collecting your information.

Table 1. Examples of substances representing a variety of physico-chemical properties

Name	Category	CAS nr	Vapour pressure (mm Hg, 25 ºC)	Log Kow	Density
1. Benzyl acetate	Ester	140-11-4	0.177	1.96	1.06
2. Citronellol	Alcohol	106-22-9	0.0441	3.91	0.86
3. Citral	Aldehyde	5392-40-5	0.0913	3.45	0.89
4. Limonene	Hydrocarbon	138-86-3	1.55	4.57	0.84
5. Carvone	Ketone	99-49-0	0.16	3.07	0.96
6. Coumarin	Lactones	91-64-5	0.00098	1.39	0.94
7. Galaxolide	Ether	1222-05-5	0.000545	5.9	1.00
8. Cinnamonitril	Nitrile	4360-47-8	0.0129	1.84	1.03
9. Isoeugenol	Polyfunctional	97-54-1	0.012	3.04	1.09

Please select circa 3 marker substances.

If on your site these substances are not relevant (in frequency of use or volume throughput), please feel free to consider other 'marker substances'.

Our questionnaire asks information that is specific for your site as well as for the marker substances. For the substance-specific information we ask you to fill the tables separately (replicate) for each of the marker substances for your site.

Formulators of consumer products

For the activities in figure 1 we need information describing the volumes of fragranced oils and final product, along with a description of its characteristics (liquid/viscosity of oils, and for the product also liquid/viscosity or solid, powder), the type of equipment used for storage and mixing and losses to water, etc.

4. QUESTIONNAIRE

General information on the mixing plant (for compounding or formulation)

	Please answer in this column:
- Number of working days per year:	
For formulators: - Composition of selected product(s):	Typical percentage of fragrance ingredients in final product: % Typical percentage of marker ingredient in final product: %
- Total production volume of selected product(s) per year:	Per Product: kg/year
- Number of batches per operating day (per selected product category)	Per Product: batch/day
- Is production continuous or batch wise? o If in batches: how many days per year?	continuous / batch wise (8)
How would you classify the activities of the mixing plant (on your site), first qualitative indication ([8]):	
- Relative size of operation:	in the EU among the (number……) largest medium-sized / smallest (8)
- Degree of control of emissions to water:	low (no treatment) / medium (e.g. phys.chem. treatment) / high (e.g. phys.chem + biol. treatment, on site or communal) (8)
- Is your Environmental Management System operational?	fully (yearly certified report) / half-way (under development)/ incomplete (8)

([8]) This is to check whether there is a relation between the size of operations and the level of control.

A. Delivery of feedstock and B. Storage of feedstock

Requested data are relevant for emissions due to delivery at site and storage of feedstock.
The information is related to the packaging used for delivery at site; method for storage of feedstock; throughput of feedstock; relevant properties of feedstock; cleaning method or disposal of delivered / stored packaging

Tables 1a (Delivery of feedstock) and 1b (Storage of feedstock) provide an overview of requested data.

Table 1a Overview of the required information for A. Delivery of feedstock

[Please Replicate for each Marker Substance (Compounders) or Formulated product (Formulators)] < @: where relevant >

Data for Substance 1/ Product 1: …[*NAME*] ……………….	**Tank truck**	**Container**	**IBC**	**Big bags**	**Drum**	**Cans**
- Volume [m^3]	[m^3]	[m^3]	[m^3]	[m^3]	Liter	Liter
- Number per year						
- Throughput [kg/year, m^3/year]						
- Powder or liquid						
- Properties of feedstock - solid / powder / liquid - temperature range of feedstock - volatility (e.g. in mbar at delivery temp.)@ - dyn. viscosity (e.g. Pa.s, N sec/m^2) - specific gravity (kg/m^3)						
Storage Indoor or Outdoor						
Storage above or underground						
Cleaning on site, give description / procedure: e.g. water only / detergent; temperature; manually/automated;						

Data for Substance 1/ Product 1: …[*NAME*] ……………….	**Tank truck**	**Container**	**IBC**	**Big bags**	**Drum**	**Cans**
closed/open system						
Containment of water in delivery area (rain water, spills)?						
Estimate of residual product lost by cleaning (percentage of volume of absolute amount)						
Treatment of empty vessels:	- cleaning on site; - cleaning off-site; - dedicated use without cleaning;	- cleaning on site; - cleaning off-site; - dedicated use without cleaning;	- cleaning on site; - cleaning off-site; - dedicated use without cleaning; - disposal without cleaning	- cleaning on site; - cleaning off-site; - dedicated use without cleaning; - disposal without cleaning	- cleaning on site; - cleaning off-site; - dedicated use without cleaning; - disposal without cleaning	- cleaning on site; - cleaning off-site; - dedicated use without cleaning; - disposal without cleaning
Equipment used during pumping		*<e.g., submersion pump with vapour recycling>*				
Frequency and time spent for pumping						
Cleaning procedure for pumping equipment						
Discharge of water to:	- surface water - wastewater tank - water treatment system					
Equipment used during sampling						
Volume for sampling						

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Table 1b Overview of the required information for B. Storage of feedstock

[Please Replicate for each Marker Substance (Compounders) or Formulated product (Formulators)]

Data for substance 1/ Product 1: …[*NAME*] ……………….	**Storage tank**	**Container**	**IBC**	**Big bags**	**Drum**	**Cans**
- Volume [m^3]						
- Number per year						
- Throughput [m^3/ year, ton/year]						
- Percentage storage - indoor - outdoor						

Equipment used during pumping						
Average temperature indoors, ºC						
Cleaning procedure for equipment and containers e.g. water only / detergent; temperature; manually/automated; closed/open system						
Estimate of residual product lost by cleaning (percentage of volume of absolute amount)						
Discharge of water						

C. Filling process equipment and D. mixing feedstock and cleaning procedures

Requested data are relevant to estimate emissions due to filling and cleaning of process equipment, and mixing of feedstock. The information concerns:

- the range of volumes of the mixing vessels; the diameter of the mixing vessels; normally applied maximum filling of a mixing vessel;
- the number of mixings per day; cleaning procedures for vessels, dosing and mixing equipment;
- availability of measurements on the residues left in the vessels and dosing equipment before cleaning

Please summarize the requested information in table 2.

Table 2 Overview of the required information for C. Filling process equipment and D. Mixing feedstock

Volume of mixing vessel [kg]	**Diameter mixing vessel [m]**	**Normally applied maximum filling mixing vessel [%]**	**Average number of mixing per day [-]**	**Transfer of stored product to the process equipment, % automatic and % by hand**	**Residue of product in vessel just before cleaning [g] or %**	**Cleaning procedure and discharge of water**
< 60 Litre				- automatic: - manual:		
60 – 200 Litre				- automatic: - manual:		
200 L – 1 m^3				- automatic: - manual:		
> 1 m^3				- automatic: - manual:		

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We assume that the (marker) fragrance ingredients or the formulated products are used in smaller as well as in large volume compounds. Is this correct?	YES/ NO, Remarks:
Is data available on measurements in discharged water from the hall?	TOC, name of fragrance ingredients, typical levels and conditions
Number of (non-automated) pourings per day	# non-automated: # automated:
Number of (non-automated) weightings per day	# non-automated: # automated:
Number of (non-automated) mixings per day	# non-automated: # automated:
Number of (non-automated) pumpings per day	# non-automated: # automated:
Number of samples taken per day	
Number of washings per day	
Type of personnel protection equipment used	always: sometimes:
Additional information	

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E. Handling finished products

After processing the product will be filled into a storage tank or directly into other containers. Please give an overview of the fractions of finished product filled into containers in table 3 below.

Table 3 Overview of information for D. Handling of finished products

Filling Volume of vessel	Average number per day	Fraction of total production	% automatic and % by hand	Cleaning procedure of filling equipment	Estimated residue lost by transfer, [g] or %
< 60 Litre			- automatic: - manual:		
60 – 200 Litre			- automatic: - manual:		
200 L – 1 m^3			- automatic: - manual:		
> 1 m^3			- automatic: - manual:		

F. Treatment of waste

Please describe the procedure for the disposal of solid or liquid waste:

Collection of spills	
Cleaning of floors	
Samples for quality control (number, volume, frequency, disposal)	
Packaging material	
Residues in solid/liquid separation units	

G. Handling of waste water and wastewater treatment

Requested data is relevant for quantifying the emissions to wastewater and surface water. Losses are due to residues from containers or from spills of fragrance ingredients / formulated products. Finally it is the aim of the emission scenarios to enable estimation of the emission to surface waters.

Description of drainage system on site:	
- For process water, wash water and cleaning water from mixing rooms;	
- For drainage water of delivery and storage areas;	
- Water flow (m^3/hour) from the mixing plant;	
- Total water flow from the site (if mixed with flow of mixing plant);	
- Removal of spills inside and outside of mixing plants;	
- Contribution of TOC (Total Organic Carbon per liter) or COD (Chemical oxygen Demand) of the mixing plant to the total TOC of the waste water;	
- Fraction of TOC in waste water (~ fragrances) from mixing plant to TOC of total production volume (fragranced products) to determine the fraction of production volume lost via waste water.	
(Alternative solutions are welcomed as well).	
Is there a wastewater treatment on site?	
Process description:	
- mechanical/physical/chemical	
- and/or biological	
- flow (m^3/hour),	
- COD removal efficiency	
Measurement results if available.	
Is the waste water transported to a waste water treatment plant of a third party (e.g. municipal sewage treatment plant)?	

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Appendix 2
Results of the Questionnaire

Results for Compounders

Product type	Fragrance formulations	Fragrance formulations	Fragrance formulations	Fragrance formulations	Fragrance formulations	Fragrance formulations	Fragrance formulations
Number of working days	250	250	246	250	230	245	250
Relative size of operation	Small	Small	Medium	Medium	Large	Large	Large
Percentage of fragrance in product	≥ 99.9%	2% (fragr. ingred.) Ingr A: 0.002-0.2% Ingr B: 0.12%	1 %, no water	-	100% (fragr. ingred) Ingred A: 3.6% Ingred B: 7% Ingred C: 1.4%	100% (fragr. ingred)	100% (fragr. ingred) Ingredient A: 1.5% Ingredient B: 0.5% Ingredient C: 4.5%
Degree of control of emissions to water	Complete effluent treatment done on site	High	High	High	Medium	High	High
EMS operational?	Incomplete	Half-way to fully	Half-way, under development	Half-way	Yes, fully (yearly certified report)	Yes, fully (yearly certified report)	Yes, fully (yearly certified report)
A. Delivery and B. Storage of feedstock							
Container types	General: 1000 L cubitainers, 100 – 200 L drums, 10-50 L pails and < 1L allum. bottles **A:** 200 L drums **B:** 1 m3 IBC **C:** 200 L drums	**A.** Drums **B.** Containers **C.** Drums	32 - 210 L drums 10 – 32 L cans	**A.** Tanktrucks 10.000 m^3	***A:*** 1000L IBC ***B:*** drums (10, 20, 60, 100, 200L) ***C:*** Tanktrucks	***A:*** Tank trucks 15 - 22 tonnes ***B:*** IBC (1 m3 or 800 kg) ***C:*** Drums 50 - 200 L	***A:*** Road tanker 20 ton ***B:*** 50 kg in fibre drum C: Road tankers and 200 L drums
Deliveries	--	**A.** 20 drums **B.** 22 containers **C.** 23 drums	drums 256 /year cans 120/year	**A.** 7 times/yr	***A:*** 42 times /yr ***B:*** 28/yr ***C:*** 53/yr	***A:*** 2.2 per day (all) ***B:*** 15 / day (all) ***C:*** 150 per day	***A:*** 10 – 12/yr ***B:*** -- ***C:*** 23 tankers /yr

Product type	Fragrance formulations	Fragrance formulations	Fragrance formulations	Fragrance formulations	Fragrance formulations	Fragrance formulations	Fragrance formulations
Emissions to wastewater and waste	No washing on site. Empty containers sold for recycling No water containment in delivery area Packaging material: **A.** Disposal without cleaning, final destination is external recycling **B.** dedicated use without cleaning **C.** disposal without cleaning to drum receiving vendor Spills materials are absorbed and disposed to chem. waste;	Containers not washed on site. - Air pumps; cleaned with detergent and rinse, once/week; Discharge to *surface water* - Mechanical pumps; cleaned with detergent and rinse/steam; estimated loss 0.01% Discharge into drains **A.** Disposal without cleaning **B.** Dedicated use without cleaning **C.** Disposal without cleaning	Vessels: dedicated use without cleaning Pumping equipment is cleaned with water, to waste water treatment system; 0.1% lost as residue from pumping -	Contained area Positive displacement pumps with internal recycle, when washed with hot water, loss ca. 5 kg/tanker, but dedicated use without cleaning Contaminated water from tanker offloading to treatment plant, other bunds after assessment to surface water or water treatment	***A, B and C*** Contained delivery area - all the water goes to WWTP Estimated loss of residual product by cleaning < 0.025% ***A** and **C:*** Disposal without cleaning ***B:*** Tank truck cleaned off site by contractor Dedicated use of storage tank without cleaning	Contained delivery area ***A:*** Residue 2 kg/pumping to wastewater, no cleaning on site ***B:*** automated cleaning with hot water + detergent, < 1.0 kg residue lost, 1 kg lost by pumping = 11 times per day ***C:*** automated cleaning etc. < 200 g lost for 180 kg drum, 0.2 kg lost by pumping = 30 times per day **A**. dedicated use without cleaning B& C. Cleaning on site, to WWTP. Loss for logistics 0.08% (weight) Cardboard packaging material and can is disposal without cleaning	Contained delivery area - all the water goes to WWTP Road tanker and drums are cleaned off-site

Product type	Fragrance formulations	Fragrance formulations	Fragrance formulations	Fragrance formulations	Fragrance formulations	Fragrance formulations	Fragrance formulations
C. Filling process equipment and D. Mixing of ingredients							
Type of process	Batch wise, 15 batches per day Vessels range from < 60 L to > 1 m^3.	Batch wise, 1.25 batch per day Manual dosing Vessels <60 –200 L and > 1 m^3	Batch wise, 30 batches per day Manual filling Vessels range from < 60 L to > 1 m^3.	Batch wise, 50 batches per day All sizes of vessels are used, from < 60 L to > 1 m^3 80% automatic dosing, 20% manual	Batch wise, Per product: perfume & flavour = 13 batches per day 155 L, 234 L, 1400L; 4, 10, 18, 20, 35 m^3	Batch wise, 140 batches per day 90 L, 215 L, 580 L, both automated and manually dosing 7 – 30 m^3 automatic dosing Indication of residue for dosing and mixing 0.07% (weight)	Batch wise, 80 batches per day Vessels range from < 60 L to > 1 m^3.
Emissions to wastewater	Cleaning: 1. Alcohol, disposed to waste, thermal destruction; 2. Water, to treatment plant; 3. Water and detergent. 11.45 L fragrance materials lost per day Residue in vessels: < 60 L: 0.32% 60 – 200 L : 0.25% 200 – 1000 L: 0.195% > 1 m^3: 0.091 % (average 0.1%) 20 washings per day Floors are mopped,	Washed with detergent – rinse, steam residue < 1 kg 2 washings per day	cleaning with hot water and detergent. 120 washings per day residue < 0,1 %. Wash /cleaning water from Fragrance workshop 60 – 72 m^3/day ; 72-94 m^3/day wastewater (includes also Flavors prod.)	All mixing vessels are washed with water, some smaller in machine with detergent 150-200 washings per day	Steam condensate of all mixing vessels goes to waste water treatment (residue in vessel before cleaning: max 0.1%) 2 washings per day	Analysis of waste water of 15 mixing vessels (3.36 g TOC/L in 210 L) of 5885 kg production: emission 0.015%. Total loss for logistics and dosing/mixing 0.08% +0.07% = 0.15% (weight)	Residue in vessel before cleaning is 100 – 500 g Cleaning with hot water 160 washings per day *(Loss 160 * 100 – 500 g) = 16 – 80 kg/day*

Product type	Fragrance formulations	Fragrance formulations	Fragrance formulations	Fragrance formulations	Fragrance formulations	Fragrance formulations	Fragrance formulations
	water discharged to WWTP. Spills may be washed down the drain to WWTP						
E. Finished products							
Emissions to waste or wastewater	-	Manual filling of 20 kg and 170 kg vessels, Estimated loss 0.01%	-	99% Manual filing Vessels range from < 60L to 1 m3 equipment is washed using water and compressed air First ½ kg goes to waste oil; no loss to water	Dedicated use without cleaning; in exceptional cases cleaning with steam & nitrogen (estimated residue loss by transfer for each volume < 0.1%)	Mainly automated filling. No emission to waste water	Filling equipment is drained and rinsed out with 5 kg product of the next batch Estimated residue lost by transfer 0-200 g/batch for each volume. Av. 70 colli per day Loss: 70*100 = 7 kg/day
F. Treatment of waste							
Waste collection and cleaning	Spills are absorbed, to waste treatment or washed to drain. Packaging material is segregated for recycling	Large spills recycled or removed in spill kit, small washed to drain, Floors are mopped, to drain Waste disposal to outside contractor	Samples 1 kg/day Disposal by drum Residues from phys.chem treatment are collected to drum. Drums are passed to chemical waste treatment	Vast majority ends up in waster oil/oily solid waste. small drips mopped or washed to WWTP Medium spills sorbed and to solid oily waste Larger taken up by	Spills and samples are collected for special disposal	Large spills are collected in retention basin; small spills with adsorbing material, incinerated; pipettes cleaned with solvent, flasks incinerated with remaining content	Spills and samples are collected for incineration

Product type	Fragrance formulations	Fragrance formulations	Fragrance formulations	Fragrance formulations	Fragrance formulations	Fragrance formulations	Fragrance formulations
			company	suction and disposed via waste oil. Packaging material is recycled or landfill for non-recyclables, oily waste for incineration			
G. Handling of waste water and waste water treatment							
Drainage system on site and WWTP	Entire in-house drainage is collection system for the WWTP: water flow from site: 100 m^3/day Physical/chemical and biological treatment	Total water flow from mixing plant 3070 m^3/y Spills 1.6 m^3*/h (?)*	Treatment: Fence-adjective pool Anaerobic/aerobic biological *4000* m^3 */hour*	On site treatment. Retention tank with settling, phys-chem treatment and separation water/oil/sludge. Incineration or treated elsewhere. Flow FR to treatment plant *15* m^3*/h, total 16* m^3*/h* Flow in treatment plant 25L.min (8h, 5d per week = *2.900* m^3*/y*	Collecting tank – elutriator–oil separator–reaction container– emulsion cracking facility – communal waste water after oil-separator & measurement (COD, BOD and pH). When the values are OK, pass wastewater to the communal waste water treatment	Sewerage system total flow WWTP 1'200'000 m3/year (site + some domestic) or 137 m3 per hour phys-chem and biological treatment TOC removal > 90% Excess sludge is digested in local plant for biogas, residue is incinerated	Oil separator, activated carbon filter, pH adjustment FR 1350 m^3/yr (2 m^3/hr) mixes in 506,445 m^3/yr (60-70 m^3/hr) on site;

Product type	Fragrance formulations	Fragrance formulations	Fragrance formulations	Fragrance formulations	Fragrance formulations	Fragrance formulations	Fragrance formulations
Wastewater transported to a 3rd party waste water treatment plant?	To municipal wastewater collection system, discharges into river	Yes, Drain water to local municipality treatment plant	Yes, after internal treatment the waste water is discharged to municipal treatment plant	Only in exceptional circumstances.	Yes, to communal waste water treatment		Yes, to communal STP
Measurements	Physical/chemical and biological treatment 90% COD removal	COD < 500 mg/l	90-95% COD contribution from mixing plant; *TOCfragr/TOC prod = 0.1%*	Estimated contribution of Fragr. materials to total TOC = 95% 130 mg COD/l, 30 mg BOD/l	overall COD removal 32%		COD Fr. 26800 kg O_2 COD total 746000 kg O_2 Fragr: 3.5%
H. Loss estimates							
Estimated loss factors	Residues average 0.1% (specified per volume); Daily loss to wastewater/total production = 0.22%	COD loss related to production volume gives loss in process of < 0.43%			COD loss related to production volume gives loss in process of 0.007 – 0.016%, phys/chem removal = 32%	Indication of loss: 0.015% based on cleaning water evaluation (TOC); Total loss = 0.15% based on process analysis.	loss based on kg related to production 0.03 – 0.15% COD loss related to production volume gives loss of 0.07% (includes water treatment)

Results for formulators

Product type	Hard Soap	Granular detergent	Detergents (gran&liq) & conditioners	Liquid cleaners & conditioners	Shampoos and shower gels	Liquid creams & lotions	Perfume alcoholic products	Fine fragrance
Number of working days		260			250	-	250	312
Relative size of operation	Large	Large	Large	Large	Medium	Large	Medium	Large
Percentage of fragrance in product	Soap bar 2.5 kg COD/L	2% (prod. no water) Ingredient A: 0.002-0.2% Ingredient B: 0.12%	fabr.cond. 560 g COD/L Liq Det. 450 g COD/L (av. 505 g COD/L)	fabr.cond. 560 g COD/L HHcleaners 177 g COD/L Hand dishwash 790 g COD/L (av. 509 g COD/L)	0.33% (product incl. water) 4% based on TOC	Shampoo 350 g COD/L Creams/lotions 750 g/L	--	10-15% (frag. ingr.) (10 – 15% water) marker ingredients: Ingr.A: 0.8% ingr.B: 0.07% Ingr.C: 0.00003%
Degree of control of emissions to water	High	High	high	High	High	High	There is no emission to water	Low (no treatment)
EMS operational?		Yes, fully (yearly certified report)			Yes, fully (yearly certified report)		Yes, fully (yearly certified report)	Yes, fully (yearly certified report)
A. Delivery and B. Storage of feedstock								
Container types		1000L-cubitainers			--		--	200 L barrels
Deliveries		29 times per year			--		--	< 10 times per year
Emissions to wastewater	Contained area	Separate containment of	Storage in contained area	Controlled storage of drums/IBCs	-	Minimisation of environmental	None	Discharge to spill pit.

Product type	Hard Soap	Granular detergent	Detergents (gran&liq) & conditioners	Liquid cleaners & conditioners	Shampoos and shower gels	Liquid creams & lotions	Perfume alcoholic products	Fine fragrance
		rain water. Possible contaminated rain water goes through waste water treatment plant. Closed spill protection for perfume spills.				exposure by controlled areas		Cleaning of empty vessels off-site and estimated loss of residual product by cleaning < 1%)
Emissions to waste		Empty vessels dedicated use without cleaning (send back to supplier)			-		-	-
C. Filling process equipment and D. Mixing of ingredients								
Type of process		Continuous process, Automated Vessels > 1 m^3			Batch wise, 14 batches per day Manual filling Vessels > 1 m^3		--	Batch wise, 0.0256 batch per day (for marker ingredient)
Emissions to wastewater	Minimised by recycling into product	No cleaning with water; 0% loss from vessel > 1 m^3 due to residue reblend)	Recycling of most of change-over and washing water	Rinsing and cleaning procedures directed towards recycling into product	There is a procedure to clean the vessels with water and discharge wastewater to the	Liquid waste to on-site WWTP Reduction of waste by incorporation back into process.	No discharge to water. Procedure to clean the vessels with alcohol and	Cleaned with water, residue to spill pit (residue in vessel before cleaning: 0.5%

Product type	Hard Soap	Granular detergent	Detergents (gran&liq) & conditioners	Liquid cleaners & conditioners	Shampoos and shower gels	Liquid creams & lotions	Perfume alcoholic products	Fine fragrance
		Small spills to wastewater Floors are mopped for cleaning *2 washings per shift*			on site WWTP (residue in vessel before cleaning: 3.3% in vessel of > 1 m^3) 14 washings per day	If not possible to incorporate back into process, waste is disposed in solid stream.	recover the alcohol	in vessel of < 60 L) 1 washing per day
E. Finished products								
Emissions to waste or wastewater		No residue lost by transfer Flying change over, in case of cleaning necessary: central vacuum system and recycled		Empty drums including residues, are sent to special waste handling	See info for C and D		None	Extreme little residue lost by transfer and dedicated cleaning procedure. Little cleaning needed
F. Treatment of waste								
Waste collection and cleaning		Spills are cleaned with vacuum cleaners Large spills are recycled; if not possible → L/M spills to waste handling	Empty drums including residues, are sent to special waste handling		Spills and samples are incinerated Packaging materials are recycled Residues from phys.chem treatment are	Empty drums including residues, are sent to special waste handling		

Product type	Hard Soap	Granular detergent	Detergents (gran&liq) & conditioners	Liquid cleaners & conditioners	Shampoos and shower gels	Liquid creams & lotions	Perfume alcoholic products	Fine fragrance
		Spills removed as hazardous waste			treated biologically by subcontractor (96% efficiency)			
G. Handling of waste water and waste water treatment								
Drainage system on site and WWTP	on site biological treatment plant, 90% COD removal	On site waste water treatment plant: pH-neutralisation biological treatment COD Removal 96%	Recycling of most of change-over & washing water, thus low concentration at the end	Chemical Treatment Plant, 70% COD removal	Separate network for industrial wastewater to onsite WWTP Mixing plant flow 10 m^3/h Residues from phys.chem treatment are treated biologically by subcontractor (96% efficiency)	No effluent treatment on site	There is no wastewater	No
Wastewater transported to a 3rd party waste water treatment plant?	yes	No, discharge into river	Yes	yes	Yes, after internal treatment effluent is again treated in municipal treatment plant	Yes	There is no wastewater	Yes, waste water to spill pit and publicly operated STP
Measurements		COD Removal 96%		On site 70% COD removal	Fraction fragrances / total products = 4%			

Product type	Hard Soap	Granular detergent	Detergents (gran&liq) & conditioners	Liquid cleaners & conditioners	Shampoos and shower gels	Liquid creams & lotions	Perfume alcoholic products	Fine fragrance
H. Loss estimates								
Estimated loss factors	0.06% to solid waste. 0.03% to biological WWTP (COD related to prod. volume), then 90% COD removal, next to STP with 90% COD removal. Overall loss to water after treatments on site = 0.003%	loss from process to wastewater 0.08% before treatment (COD loss related to production volume). After phys/chem. and biological treatment (96% removal), overall removal = 0.003%	0.06% loss to solid waste, controlled; 0.013% general waste; 0.007% after treatment on site	0.14% to solid waste. 0.027% to wastewater (before treatment) 0.008% after treatment on site	3.3% loss to wastewater during process <but process is being adapted to reduce loss>; 0.13% after WWTP treatment	0.8% after process to wastewater, next to external STP; 0.085% to waste	no waste water	1.5% loss from process to waste water (COD related to production volume)

Appendix 3
Branch-specific information on environmental emission

BRANCHE-SPECIFIC INFORMATION ON ENVIRONMENTAL EMISSION

A range of branch-specific information on losses during the compounding or formulation process is available. Much effort was made to obtain data on the residual fraction: the fraction of a substance that is left in a container after emptying. Alternatively, COD or TOC analyses of the wastewater also contributed to the information on environmental emissions.

1 INFORMATION SUPPLIED BY EUROPEAN COMPOUNDERS PRIOR TO 2003

Loss at delivery
At delivery, 200 l drums with Galaxolid50™ contain, after vacuum pumping, a residue of approx. 100 g. This results in a drum residue of circa 0.1/200 = 0.05%.

Scrap factor
The scrap factor is a term for the amount that is produced in surplus to the ordered amount to take into account volumes needed for sampling, residues in various containers, volatilisation, etc. during the process. Generally customers also receive slightly more than the ordered volumes to prevent complaints on the delivered quantities. The scrap is high for small volumes, due to the relative large sample size, whereas it is small for higher volumes. The scrap factor is an empirical factor specific for the processes on site. An example is given in Table A31. To use the scrap factor as an indication for the residue in a mixing vessel is to be considered as an overly conservative approach. This was a first estimate before a more accurate estimation was made (reported in the next paragraph).

Table A31 Scrap factor for a European site

Size	volume	scrap factor	Remarks
Small batches	1.5 kg	8%	
Medium size	200 kg	0.3 %	
Larger size	>> 200 kg	0.15 %	class forms 50% of production
average scrap factor		*0.2%*	

Residues in mixing vessels
The amount of product released per day due to washings of the mixing vessels has been determined by weighing the amount in the vessel before and after washing (and drying), and the average number of washings per day. The size of the vessels ranged from 3 to 1200 kg. For the large batches from 4 to 17 m^3 the loss was derived from the empirical scrap factor. This results in an average release to water of 0.12% of the total production.

Residue in process equipment
Water used for washing containers and filtration pumps was collected. The cleaning process was studied for two containers: 1000 and 6300 liter. The volume of the water used and the TOC were determined. In this way the general release of ingredients during the cleaning process was estimated at 0.16 %.

Measurement of COD or TOC in waste stream
The emission to trade effluent expressed as COD is assumed to consist entirely of fragrance compounds (with COD = 3g O/g substance)[9]. Next it is assumed that the concentration ratio of fragrance X to total COD in the effluent is in proportion to the ratio of fragrance X to the total fragrance production volume on the site. For the particular lipophilic substance this was an overly conservative assumption, as the wastewater was first treated in a physico-chemical treatment system. In this way an overly conservative overall emission factor was obtained of 0.02% of the use volume of fragrance X on the site.

In another site, measuring the COD in process water after passing through an oil separator resulted in an estimated release of 0.05% of fragrance ingredient X.

Due to the prior water treatment system, it should be realized that these overall figures are not directly comparable to the release fractions determined at earlier stages in the process.

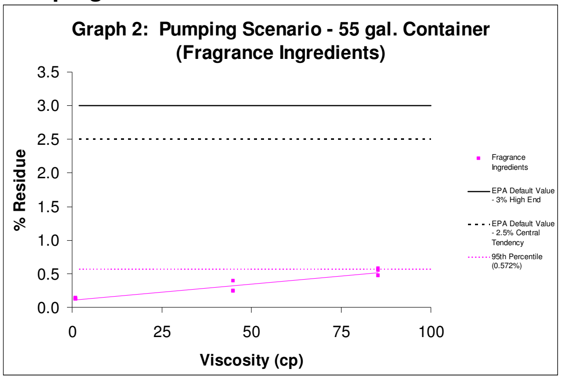
2 DATA ON TANK RESIDUES OBTAINED THROUGH FMA (COMPOUNDERS)

The Fragrance Materials Association (FMA) has reviewed the default input values for container residue or the fraction of chemicals remaining in the container proposed in the draft OECD ESD. Members of the FMA have undertaken three studies on the two basic drum handling scenarios (pumping and pouring) for EPA when estimating the drum residue of containers in the 20 to 100 gallon range in an effort to provide new and more realistic default values for the parameters $F_{container\_residue}$.

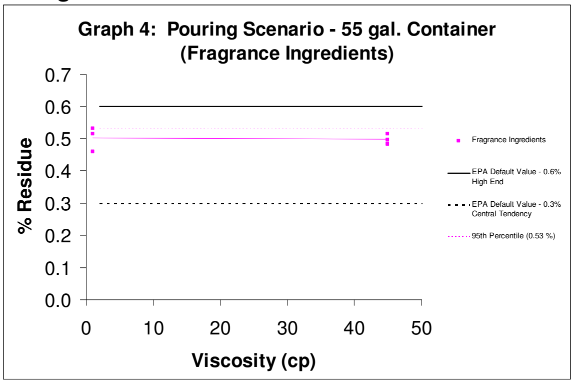
The amount of container residue generated when pumping out the contents of a 55-gallon drum was measured and found to be less than the ESD default values. The results are summarised in Table A32 and in Figure A3.1.

Figure A3.1 Results of studies on 55-gallon tank residues (33 data points, IFF 2006)

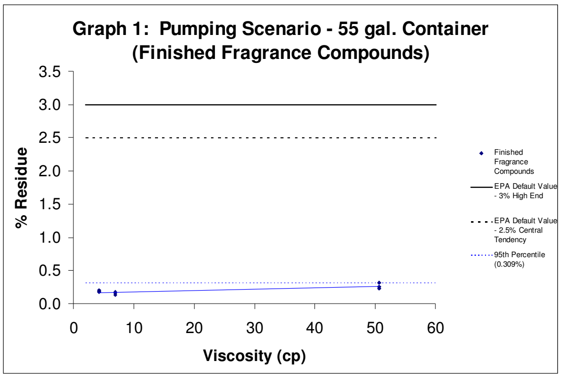
Pumping

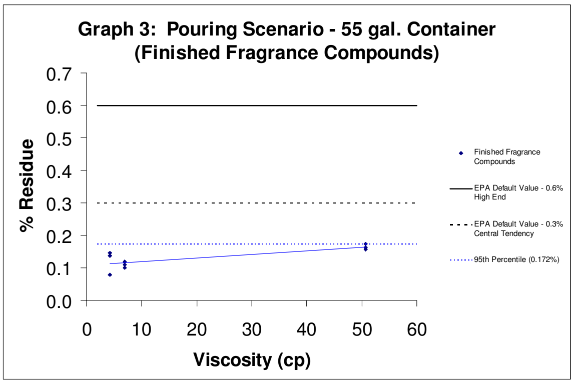


Pouring



[9] The background is given in Appendix 4.





Research by another FMA member including 22 55-gallon drums demonstrated that 64% of the drums had a residue smaller than 0.25% and that 95% of the drums had a residue smaller than 0.5%. Only one drum had a residue above 0.5% (0.56%). This value was obtained for the most viscous fluid. As in the first study a positive correlation between fluid viscosity and residual fraction was established.

A third FMA-member company established the residues in tanks of 15, 30 and 55 gallon. The weighings are an average of multiple weighings for each drum group. These represent different methods of emptying, including gravity and mechanical pumping. The results are given in Table A32.

Table A32 Summary of results of studies on tank residues in varying tank sizes (FMA)

	15-gallon	**30-gallon**	**55-gallon**	**55 gallon**	**Pumping 20 – 100 gallon**	**Pouring 20 – 100 gallon**
					95th perc.	95th perc.
Fragrance ingredients	0.5% 1)	no data	0.15%		0.572%	0.530 %
Fragrance compounds	no data	0.12%	0.11%	64th-perc.< 0.25% 90th-perc.< 0.5%	0.309%	0.172 %

1) Result of only one weighing

3 MORE DATA ON RESIDUES IN MIXING VESSELS (COMPOUNDERS)

From the questionnaire more empirical data on residues in mixing vessels have been obtained, see Table A33.

Table A33 Residues in tank for fragrance compounds (questionnaire, compounding)

Mixing vessel	**Tank residues**	
< 60L (< 15 Gallon)	0.32%	
60 – 200 L (15 – 55 Gallon)	0.25%	
90 kg		0.033%
200 – 1000 L (55 – 265 Gallon)	0.195%	
215 kg		0.027%
580 kg		0.072%

> 1 m^3 (> 265 Gallon)	0.091%	
7 – 30 m^3		0.08%
Indicated average for the site	0.1%	0.07%

4 OVERALL ANALYSIS FOR A LARGE COMPOUNDER

One compounder supplied complete details for the releases from the site. The release per operation step was measured by establishing the residues in empty drums by weighing. The results were related to the total daily production. The analysis showed that release to waste water occurs at delivery due to the cleaning of pumps and containers (0.08%) as well as the cleaning of mixing vessels (0.07%), so a total release of 0.15%.

At the same time an estimate was made based on the TOC of the waste water, indicating a total release of 0.015%. It was concluded that the estimate of 0.07% was probably conservative. The results are presented in Table A34.

Table A34. Determination of the release to wastewater

Compounding plant, 250 working days per year			
1. Logistics			
Fragrance ingredients enter the plant in tank trucks, 1000-L containers, 200-L steel drums and plastic-lined cardboard boxes for solids. Liquids are pumped into tanks of different sizes. Material is released to waste water when pumps are cleaned. Waste water is treated in the on-site WWTP.			
1.1. Cleaning of pumps (per day)			
Loading of:	**Volume/unit (kg)**	**loss/unit (kg)**	**%**
Large tanks	20000	2	0.010
Small tanks	3000	1	0.033
Drums	200	0.2	0.100
Weighted average			0.026
Empty containers are cleaned on site, except tank trucks (cleaned off-site or re-used without cleaning) and cardboard boxes (incinerated)			
1.2. Cleaning of containers (per day)			
	Volume/unit (kg)	**loss/unit**	**%**
Drums	180	0.2	0.111
Containers	800	1	0.125
Weighted average			0.115
Total for logistics (weighted average)			**0.080**
2. Mixing operation			
Fragrance materials are mixed in tanks of different sizes and in large mixers. All are cleaned with water + detergent which is drained to the on-site WWTP. A number of tanks of each type were weighed before and after cleaning, the weight difference representing the release to WW. For large mixers, an estimation was made from data provided by the engineering department.			

Cleaning of mixing vessels (per day)			
	Volume/unit (kg)	**loss/unit (kg)**	**%**
Vessel	580	0.418	0.072
Vessel	215	0.058	0.027
Vessel	90	0.03	0.033
Total			0.062
Large mixers	7 - 30 m3		0.080
Weighted average			**0.073**
Total for logistics + mixing operation			**0.153**

3. Estimation based on Total Organic Carbon measurement of waste water

Waste water from the cleaning of 15 mixing tanks was collected and TOC was analysed. The average carbon content of fragrance materials is assumed to be 80%. The results are not considered to be fully representative of the cleaning operation because the number of each type of cleaned tanks does not correspond to the average. However, this shows that the above estimation (0.073%) is probably conservative.

TOC	**TOC in waste water (g/l)**	**TOC of detergent (g/l)**	**TOC of fragrance (g/l)**
	3.43	0.0676	3.3624
	Volume/unit (kg)		**% released to WW**
MA580	580		
MA215	215		
MA90	90		
Total			**0.015**

5 INFORMATION SUPPLIED BY SMALL EUROPEAN FORMULATORS

Derivation of release factor

For a small formulator the loss of products to the sewer was estimated in a number of ways, as summarised in Table A35:

a. Loss of products can be estimated on the basis of data on production versus bottled volumes. The average over 2 years was 0.5%. These losses were due to fillings in the bottle above the minimum and to cleaning/rinsing during production. Only the latter is released to the sewer system, and this fraction was estimated at 60%. Thus 0.3% of the production volume is released to the sewer.

b. The COD and average flow of the wastewater were determined and the yearly release was compared to the annual use of raw materials in production. Thus the release presents 0.07% to 0.22% of the raw materials.

c. For a range of raw materials the COD was estimated to range from 500 to 2800 g/l, with an average set at 1600 g/l. Based on the volume of raw materials versus end products ratio of 0.32, the overall water content was 68%. Thus the average COD of a product (continuous production) was calculated 0.32 * 1600 g/l. The discharge to the sewer turned out to be 0.14% of the total production volume.

Table A35. Derived release factors for a small formulator

Approach	Loss of raw materials	Loss of production
a. Loss of product	0.3% of production volume	
b. COD fraction of raw materials	0.07 to 0.22% of raw materials	
c. COD fraction of products		0.14% of production volume

6 COMPARISON OF THE RESULTS WITH DEFAULT VALUES

Tables A3.6 and A3.7 present a summary of the results collected in this Appendix and compares the data to the defaults proposed in the emission scenarios of the OECD and the EU for compounding and formulation.

Table A36. Comparison of release factors for fragrance oil (in %)

	Formulation			Compounding							
	Draft OECD ESD			FMA Fragrance oils					Inquiry 2008 and Data 2001/2002*		
Container type	**Container volume (gallons)**	**Pouring**	**Pumping**	**Pouring**	**Pumping**	**Residues**		**Residues**	**Residues**	**Vessels +equipm.**	**Scrap factor**
	range	high end	high end	95th-perc.	95th-perc.	64th-perc.	95th-perc.				
Vessel											8
Bottle	5	0.6	<0.6>								
Small container	5 to <20							0.5	0.033 - 0.32		
Drum	20 to <100	0.6	**3** #	0.172	0.309	0.25	0.5	0.12	0.027 - 0.25		0.3
Vessel	55 to 265								0.072 - 0.195		
Vessel	> 265								0.091	0.16	0.15 ##
Tote	100 to <1000	0.2	0.2								
Tank Truck	1000 to <10000										
Rail car	10000 and up										
Release to water from equipment			**2**								
Total Residue			**5**	0.12 – 0.5 for containers < 100 gallon					total: 0.12	total: 0.03 - 0.15	Scrap Factor: Weighted average 0.2
Total estimated release based on COD in wastewater versus COD of total production									Prior to treatment: 0.16*, 0.08* Large/Medium Site: 0.007 – 0.016, 0.015 - 0.15, 0.03 – 0.15 Small Site: 0.22, <0.43 After on-site treatment: 0.02*, 0.05*, 0.07		

\# default in OECD draft ESD

\## 0.15 represents 50% of the production

Table A37. Comparison of release factors for formulation (in %)

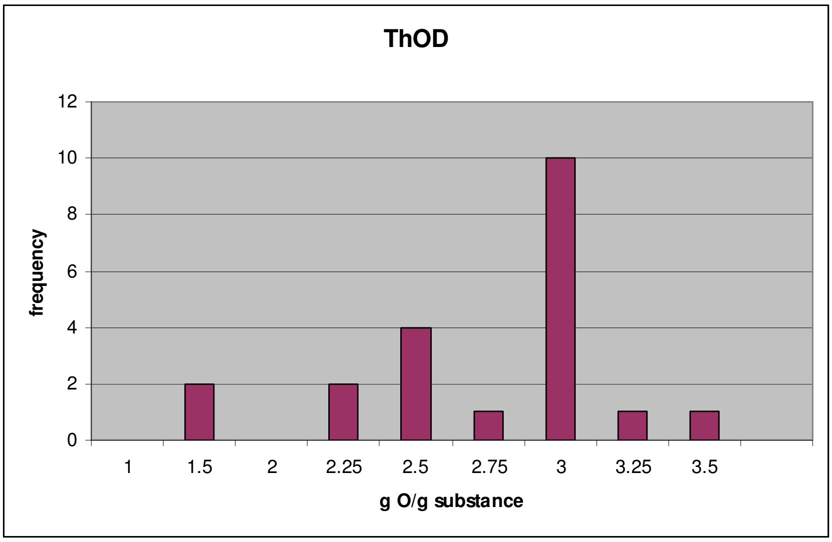
	Generic defaults	Hard Soap	Gran. Detergents	Liq.Cleaners, Conditioners, Shampoos, Shower gel	Liquid creams and lotions	Fine Fragrances
Draft OECD Defaults Release to water from containers Release to water from equipment	3% 2%					
EU-scenario	0.09 %	0.01 %	0.01 %	0.09 %	0.09 %	0.09 %
Empirical data Inquiry 2008 and Data 2001/2002*						
Estimated release to wastewater (Based on COD) prior to treatment		0.03 %	0.08 %	L/M: 0.027%, 0.06, <3.3%#> S*: 0.07 – 0.22%	0.8 %	0 % 1.5 %
Estimated emission (after treatment on site)		0.003 %	0.003 – 0.007 %	0.007 – 0.008 %; 0.13 %	0.08%	--

#) 3.3% is considered to be very high; the responder emphasised that measures are taken to adapt the process and that this value is not to be considered representative for the scenario development. Wastewater treatment efficiency 96%.

Appendix 4
Estimation of ThOD for fragrance ingredients

Estimation of ThOD for fragrance ingredients

For estimating the emission of the production site, often data on the chemical oxygen demand (COD) in the waste water or in the effluent of the site is given.
The COD value is not always available for a substance, but is can be estimated from the Theoretical Oxygen Demand (ThOD).
In order to estimate a generic ThOD, the ThOD was estimated for a range of fragrance ingredients. The results are presented below. The median value for 21 randomly chosen substances was 2.84 g O/g substance. Thus for the calculations a ThOD of 3 g O/g substance was used.



The ThOD for a number of surfactants was in the range of 2 g O/g substance.