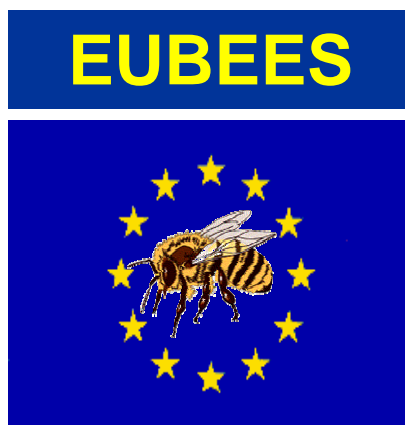


**Supplement to the methodology for risk
evaluation of biocides
Harmonisation of
Environmental Emission
Scenarios for biocides used as
metalworking fluid
preservatives
(Product type 13)**

European Commission DG ENV / RIVM

May 2003



This report has been developed in the context of the EU project entitled "Gathering, review and development of environmental emission scenarios for biocides" (EUBEES 2).

The contents have been discussed and agreed by the EUBEES 2 working group, consisting of representatives of some Member States, CEFIC and Commission. The Commission's financial support of the project is gratefully acknowledged (Ref. ENV.C3/SER/2001/0058).

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FOREWORD

The European Parliament and the Council adopted in 1998 the Directive 98/8/EC on the placing of biocidal products on the market (Biocidal Products Directive, BPD). The background for the directive is a need for harmonisation of the legislation of the Member States regarding this type of chemicals, which are intended for exerting a controlling effect on higher or lower organisms. The Directive requires an authorisation process for biocidal products containing active substances listed in positive lists (Annex I and IA). Active substances may be added to the positive lists after evaluation of the risks to workers handling biocides, risks to the general public and risks to the environment. The risk assessments are carried out for the life cycle of the biocide: risks during and resulting from the application, risks associated with (the use of) the treated product and risks resulting from the disposal of the biocide and the treated product.

For the environmental risk assessment the environmental exposure needs to be assessed. As a tool in this assessment emission scenarios are developed specific for the Product Types distinguished in the Directive. This report gives a description of emission scenarios for Product Type 13, metalworking fluid preservatives.

This report has been developed by Royal Haskoning, The Netherlands, in the context of the EU project entitled "Gathering, review and development of environmental emission scenarios for biocides" (EUBEES 2). The contents have been discussed and agreed by the EUBEES 2 working group, consisting of representatives of some Member States, CEFIC and Commission. The Commissions financial support of the project is gratefully acknowledged (Ref.ENV.C3/SER/2001/0058).

SUMMARY

The European Parliament and the Council adopted in 1998 the Directive 98/8/EC on the placing of biocidal products on the market (Biocidal Products Directive). As an implication an environmental risk assessment is to be carried out. For this purpose a uniform method to predict the potential environmental emissions needs to be available. Therefore emission scenario documents are being developed for the various biocidal product types. This report deals with product type 13, metalworking fluid preservatives.

This report is based on three existing emission scenarios for metalworking fluid preservatives produced in different EU countries, discussions in the working group for the EU project "Gathering, review and development of environmental emission scenarios for biocides (EUBEES 2)" and data supplied by some Member States.

The three emission scenarios are:

- The USES-scenario: developed by Luttik et al (1993), is designed to calculate the environmental release resulting from the industrial use of metalworking fluids;
- The TGD-scenario: included in the former TGD (1996) as an emission scenario document IC8 "Metal extraction industry, refining and processing industry". It assumes that no (relevant) emissions occur during industrial use and is designed to calculate the environmental release resulting from the waste treatment phase of metalworking fluids;
- The UBA-scenario: developed as an update to the former TGD (1996) scenario IC8.

These scenarios are compared and integrated where possible to produce one harmonised, realistic worst case emission scenario for metalworking fluid preservatives.

Emissions during the use phase of metalworking fluids are possible, but according to dummy calculations in this report eventual emissions from industrial use (calculated by USES) are considered not relevant as compared with emissions from waste treatment plant (calculated by UBA/TGD).

When comparing the UBA- and TGD-scenarios several differences are discovered:

- The UBA-method uses defined dimensions for the volume of wastewater caused by the treatment of spent metalworking fluids that is to be treated in the STP, as well as for the STP itself. Because of this, it is possible to use different wastewater volumes for emulsifiable and water-soluble metalworking fluids. The TGD-method uses a fixed dilution factor instead.
- When the concentration of the chemical in the metalworking fluid is not provided by the supplier, the UBA-scenario provides the possibility to calculate this value with help of a pick list.
- A further difference between these two scenarios is the fact that the UBA-method calculates the volume of the water phase of an emulsifiable metalworking fluid which is discharged into the STP (the volume of the emulsifiable metalworking fluid minus the volume of the oil phase, which is separated from the watery phase during the waste treatment).
- Finally, the UBA-method provides the possibility to include the fraction of elimination of the preservative during the physical/chemical waste treatment. The TGD-method does not.

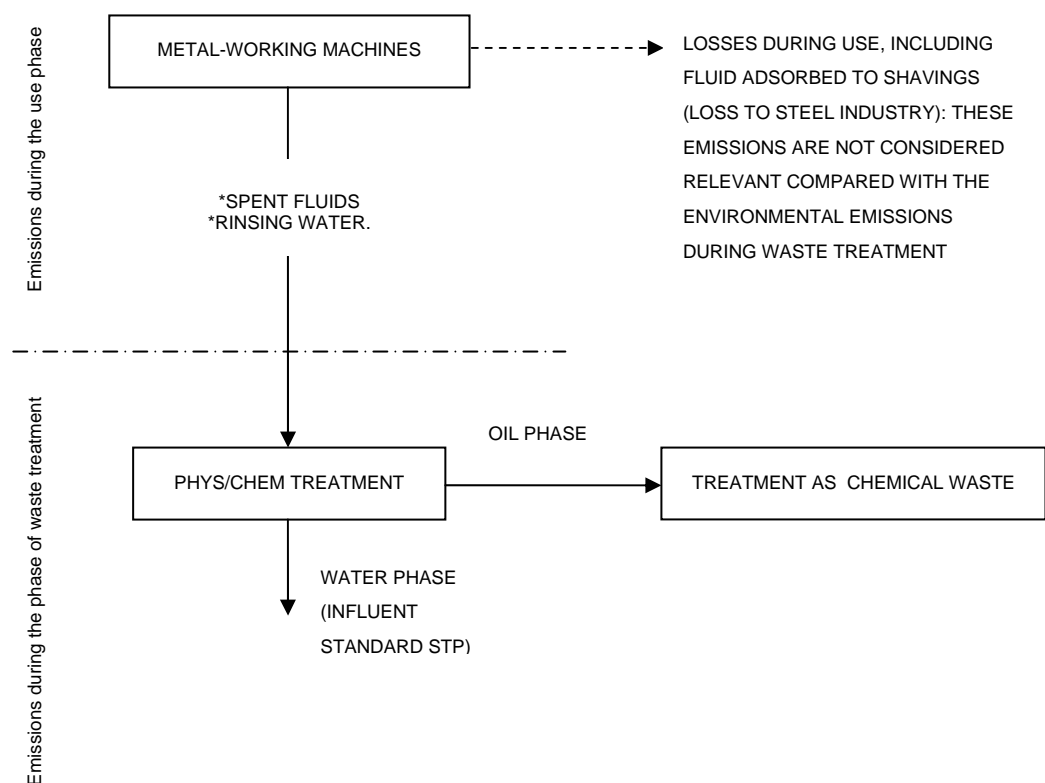
The main conclusion is that the scenario from the German UBA is the best existing scenario for the calculation of environmental emissions. The new TGD (February 2002) has also adopted the approach of the UBA-scenario. Further conclusions are that the UBA-scenario does not consider degradation of the biocide during use of the metal working fluid. This may be important in certain cases. Furthermore, the amount of wastewater coming from the treatment plant for metalworking fluids is a relatively high contribution to the STP. It is not clear whether the ratio wastewater amount/capacity STP (40/2000 for watersoluble metalworking fluids and 200/2000 for emulsifiable metalworking fluids) corresponds with reality.

Based on this conclusion, it is recommended to use a modified version of the UBA scenario.

The modification involves a term for the degradation of biocides during the use phase. The user of this scenario may use this fraction when necessary.

With respect to the capacity of the receiving STP in relation with the amount of wastewater, it is recommended to check on which data this is based on and whether this ratio (amount of wastewater/capacity of STP) corresponds with reality.

In Figure A the recommended scenario is described from metalworking machine up to the influent of the STP.



Legend:
 Not considered in this scenario: - - - - -
 Border of metalworking site: - · - · - · -

Figure A Recommended-scenario

The Tables A and B contain the input parameters and calculations for the UBA scenario from the metalworking machine up to the influent concentration of the STP.

Emulsifiable metalworking fluids

Table A Emission scenario for calculating the releases from preservatives used in emulsifiable (waterbased) metalworking fluids at the life cycle stage of waste treatment (proposed as modified from UBA2001).

Variable/parameter	Unit	Symbol	Value	S/D/O/P
Input				
A) Concentration of the chemical in the concentrated emulsifiable metalworking fluid	[kg.m ⁻³]	C _{proc,emul}		S
B) Weight fraction of chemical in concentrate ²⁾	[-]	F _{conc}		P
Volume ratio concentrate / water phase ³⁾	[-]	F _{conc/water}		S/P
Density of metalworking fluid	[kg.m ⁻³]	RHO _{MWF}	1000	D
Treated volume of metalworking fluid	[m ³ .d ⁻¹]	V _{proc,emul.}	200 ¹⁾	D
Fraction of metalworking fluid with chemical in treated volume	[-]	F _{form}	1	S/D
Fraction of chemical degraded during industrial use	[-]	F _{degr}	0	D
Partition coefficient n-octanol/water	[-]	K _{OW}		S
Fraction of elimination of the chemical during physical or chemical treatment	[-]	F _{elim}	0	D
Volume of the treated water phase	[m ³ .d ⁻¹]	V _{water}		
Concentration of the chemical in the untreated sewage water phase of the metalworking fluid	[mg.l ⁻¹]	C _{water}		
Capacity of the receiving STP	[m ³ .d ⁻¹]	CAP _{STP}	2000	
Output:				
Emission to the STP	[kg.d ⁻¹]	E _{local,water}		
Preservative concentration in the STP-influent	[kg.m ⁻³]	PEC _{influent}		

Model calculations:

Intermediate calculations:

$$C_{\text{proc,emul}} = (F_{\text{conc}} * \text{RHO}_{\text{MWF}}) / (1 - F_{\text{conc}})$$

End calculation:⁴⁾

$$\text{Elocal}_{\text{water}} = C_{\text{proc,emul}} * V_{\text{proc,emul}} * F_{\text{form}} / (F_{\text{conc/water}} * K_{\text{OW}} + 1) * (1 - F_{\text{elim}}) * (1 - F_{\text{degr}})$$

$$\text{PEC}_{\text{influent}} = \text{Elocal}_{\text{water}} / \text{CAP}_{\text{STP}}$$

- 1) It is recognised that this volume is a high contribution to the STP. It is clear that metalworking fluids contain bactericides. With respect to this ratio it will be made clear beforehand whether this ratio corresponds with the practice.
- 2) If the concentration of the chemical in the metalworking fluid has not been provided by the notifier or industry, it can be taken from Tables 6 and 7 from the UBA-scenario, see Appendix 1.
- 3) The values for $F_{\text{conc/water}}$ can be derived from Table 8 from the UBA-scenario, see Appendix 1.
- 4) The end calculation is separated in a calculation of $\text{Elocal}_{\text{water}}$ and $\text{PEC}_{\text{influent}}$. The reason for this separation is to provide the possibility to calculate the concentration in the wastewater coming from the waste treatment plant without using the standard EU STP.

Water-soluble metalworking fluids

Table B Emission scenario for calculating the releases from preservatives used in water-soluble metalworking fluids during the life cycle stage of waste treatment (UBA2001).

Variable/parameter (unit)	Unit	Symbol	Value	S/D/O/P
Input				
Treated volume		$V_{\text{proc,w.s}}$	40 ¹⁾	D
A) Concentration of the chemical in the concentrated water-soluble metalworking fluid	[kg.m ⁻³]	$C_{\text{proc,sol}}$		S
B) Weight fraction of chemical in concentrate ²⁾	[-]	F_{conc}		P
Volume ratio concentrate / water phase ³⁾	[-]	$F_{\text{conc/water}}$		S/P
Density of metalworking fluid	[kg.m ⁻³]	RHO_{MWF}	1000	D
Fraction of chemical degraded during industrial use	[-]	F_{degr}	0	D
Fraction of metalworking fluid with chemical in treated volume	[-]	F_{form}	1	S/D
Fraction of elimination of the chemical during physical or chemical treatment	[-]	F_{elim}	0.8	D
Capacity of the receiving STP	[m ³ .d ⁻¹]	CAP_{STP}	2000	
Output:				
Emission to the STP	[kg.d ⁻¹]	$\text{Elocal}_{\text{water}}$		

Variable/parameter (unit)	Unit	Symbol	Value	S/D/O/P
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Emission concentration in the STP-influent	[kg.m ⁻³]	PEC _{influent}		
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Model calculations:

Intermediate calculations:

$$C_{\text{proc,sol}} = (F_{\text{conc}} * RHO_{\text{MWF}}) / (1 - F_{\text{conc}})$$

End calculation:⁴⁾

$$E_{\text{local,water}} = C_{\text{proc,sol}} * V_{\text{proc,w.s}} * F_{\text{conc/water}} * (1 - F_{\text{elim}}) * (1 - F_{\text{degr}}) * F_{\text{form}}$$

$$PEC_{\text{influent}} = E_{\text{local,water}} / CAP_{\text{STP}}$$

- 1) It is recognised that this volume is a high contribution to the STP. It is clear that metalworking fluids contain bactericides. With respect to this ratio it will be made clear beforehand whether this ratio corresponds with the practice.
- 2) If the concentration of the chemical in the metalworking fluid has not been provided by the notifier or industry, it can be taken from Tables 6 and 7 from the UBA-scenario, see Appendix 1.
- 3) The values for $F_{\text{conc/water}}$ can be derived from Table 8 from the UBA-scenario, see Appendix 1.
- 4) The end calculation is separated in a calculation of $E_{\text{local,water}}$ and PEC_{influent} . The reason for this separation is to provide the possibility to calculate the emission concentration in the wastewater coming from the waste treatment plant without using the standard EU STP.

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1 INTRODUCTION

For product type 13, metalworking fluids, three emission scenarios have been described. These are compared and integrated where possible to produce one harmonised emission scenario.

The methods of estimating the emission rate of metalworking fluid preservatives to the primary receiving environmental compartments (e.g. standard STP) are described. According to Annex VI of the Biocidal Products Directive the risk assessment shall cover the proposed normal use of the biocidal product together with a 'realistic worst case scenario'. For the decision whether to place a biocide on the market or not, the realistic worst case scenario will be used in practice. Therefore only the harmonised realistic worst case emission scenario was selected. The calculation of a realistic worst case PEC using environmental interactions, for example subsequent movement of emissions to secondary environmental compartments (e.g. from soil to ground water), is considered to be subject to fate and behaviour calculations and models, and outside the scope of this Guideline.

The report is based on:

- three emission scenarios produced in different EU countries;
- discussions in the working group for the EU project "Gathering, review and development of environmental emission scenarios for biocides (EUBEES 2)".

The emission scenarios are applicable in all European Union member states.

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 units according to USES are used. 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.

1.1 Description of industry or use area

Metalworking fluid preservatives, biocide product type 13, are used in the metal industry. The metal industry can be divided into different working sectors. These are:

- blast furnaces: production of steel;
- iron foundry: moulding of steel into half- or end-products;
- rolling mills: rolling of steel to half-products to be used by the steel production industry;
- metal forming: forcing of metal products in the shape of the end-product;
- metal cutting: creation of products by cutting away chips of the product;
- galvanic industry: application of protective metal-coatings to metal products.

In blast furnaces plants, iron foundry and rolling mills the main activities are carried out at high temperatures. Because of these high temperatures, there is no need for the use of biocides in the working process.

Metal working fluids are used only in the sectors metal forming, metal cutting and in the galvanic industry. In the metal forming industry metalworking fluids are used only in small amounts, but these fluids contain no biocides. In the modern galvanic industry a wide variety of treatments are applied. In most of these treatments no biocides are used. The only technique within the galvanic industry that sometimes does make use of biocides is that of metal degreasing, but no further information is available.

The largest amounts of metalworking fluids are used in the metal cutting industry. A great part of the fluids used here also contain biocides. In section 2.1 of this document a more detailed description of the sector metal cutting is found.

A metalworking fluid passes through several life cycle stages. The scheme of the life cycle stages is presented in Figure 1.

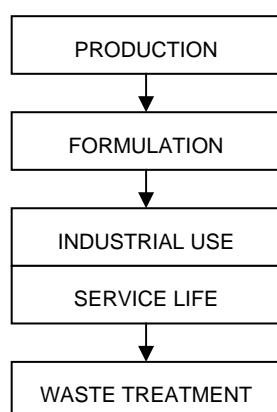


Figure 1 Life cycle scheme

In this document only the life cycle stages industrial use, service life and waste treatment are discussed. For metal working fluids the life cycle stages of industrial use and service life are completely interconnected, unlike for several other products containing biocides such as wood preservatives.
(Source: INFU2000)

1.2 Sources of information for product type 13 (Metal-working fluid preservatives)

The following documents are the main sources of information for the present document:

1. National Institute of Public Health and the Environment (RIVM), Ministry of Housing, Spatial Planning and the Environment (VROM), Ministry of Health, Welfare and Sport (VWS), The Netherlands: Uniform system for the evaluation of substances 3.0 (USES 3.0) (1999) **Code: RIVM1999**
Local exposure scenario derived from Luttkik et al. 1993. Estimates concentration in receiving wastewater from production and product characteristics.

2. European Commission: Technical Guidance Document (TGD) in support of Commission Directive 93/67/EEC on risk assessment for new notified substances and commission regulation (EC) No. 1488/94 on risk assessment for existing substances, part IV (1996) **Code: EC1996**
Emission Scenario for the environmental release of chemicals used in metalworking fluids.
3. Umweltbundesamt (UBA), Berlin: Emission Scenario Document Metal Extraction, Refining and Processing Industry IC 8, Subcategory Metal Processing (2001) **Code: UBA2001**
Emission Scenario for the environmental release of chemicals used in metalworking fluids.
4. Dokkum, H.P. van, D.J. Bakker, M.C.Th. Scholten, TNO-Report: Development of a concept for the environmental risk assessment of biocidal products for authorisation purposes (BIOEXPO).- Part 2: Release estimation for 23 biocidal products types (1998). **Code: TNO1998**
In this report emission estimates for several kinds of metalworking fluid preservatives are described. The environmental compartments to which biocides are most likely emitted (the direct exposure compartments) are identified.
5. Institute for Environmental Research (INFU), University of Dortmund, UBA Berlin: Gathering and review of Environmental Emission Scenarios for biocides (2000) **Code: INFU2000**
In this report general information about emissions is described.
6. OECD: Emission Scenario Document -Lubricants and lubricant additives (2001) **Code: OECD2001**
This document is based on a report produced in 1997 for the UK Environment Agency entitled "Use category document - Lubricants and Lubricant Additives" and incorporates additional information from a report from RIVM in The Netherlands entitled "EUSES Use category Document. Automotive fuels, lubricants and lubricant additives". and the INFU/UBA (Germany) report "Emission Scenario Document – Metal extraction Industry, Refining and Processing Industry IC: Subcategory Metal Processing. Both these reports were produced in order to provide information for the assessment of exposure in risk assessments for new and existing substances in the EU. The descriptions of the industry structure are based on the situation in the UK, The Netherlands and Germany. In some areas wider information on Europe has been included. The data were gathered mostly in the period 1994-1997. The report provides information on the amount of metalworking fluid used, the releases of a substance during use of a fluid, the form of release and the amount released for each of these categories. Waste treatment and recycling of metalworking fluids is also considered.
7. Baumann, W., B. Herberg Liedtke: Chemicalien in der Metallbearbeitung (1996) **Code: BAU1996**
8. Lassen, C., S. Skårup, H. Mikkelsen, J. Kjølholt, P.J. Nielsen, L. Samsøe-Petersen: Inventory of biocides used in Denmark (2001) **Code: LASS2001**

9. OECD: Emission Scenario Document on metal finishing, draft report (2002)

Code: OECD2002

This document deals with metal finishing (e.g. plating, coating), so there is no overlap with metalworking fluid preservatives.

2 TYPES OF APPLICATION OF METALWORKING FLUID PRESERVATIVES

2.1 Processes for application: metal cutting

In metalworking processes the geometry of the object is changed by metal removing and non-metalremoving operations. Metal removing operations are for example turning, drilling, milling, cutting, abrasive blasting, planing and lapping (mechanical polishing). When using non-metal removing operations the workpiece is formed through pressure, compression tension, pulling, bending or pushing.

The main objectives of metalworking fluids are reduction of friction, removal of heat and flushing away metal shavings (or swarf). Metalworking fluids are used during manufacture and production in the metalworking industry. Metalworking fluids fall into the categories pure oils, emulsifiable and water soluble metalworking fluids (see Figure 2).

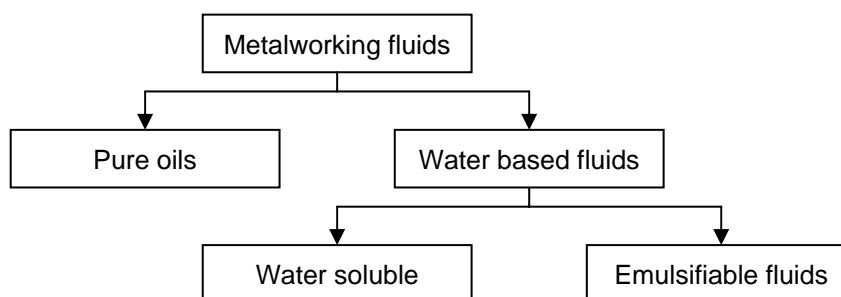


Figure 2 Division of metalworking fluids (Source UBA2001)

In the pure oils cooling lubricants no biocides are used. Water-based cooling lubricants are, due to their composition, an ideal growth medium for micro-organisms. For water-based metalworking fluids a distinction can be made between emulsified and water-soluble metalworking fluids.

Water-based metalworking fluids are often delivered as concentrates, which are diluted with water before use. In many cases water based metalworking fluids are used in circulation systems. To increase the emulsion lifetime and for the suppression of unwanted odours all water-based metalworking fluids contain, in low concentrations, biocides. (Source: TNO1998, INFU2000)

2.2 Description of types of substances used and their function

2.2.1 Composition of metalworking fluids

In this section the composition of the water based metalworking fluids that contain biocides are described. A metalworking fluid is composed of many different substances. The water-based metal working fluids always consist of the basic oil (mineral or synthetic hydrocarbons) and certain additives. Additives are used to improve, among other things, the lubricity, the wear resistance, corrosion inhibition, insusceptibility to ageing and the foaming behaviour of the cooling lubricant.

Metalworking fluid preservatives are used for control of microbial deterioration of metalworking fluids.

Metalworking fluids are a very diverse group of products. There are differences in composition between countries and between different metalworking processes. Therefore the exact composition of a water based metalworking fluid is not available. The most important additives that are used are:

- emulsifiers;
- corrosion inhibitors;
- extreme pressure (EP) additives;
- anti-foaming agents;
- biocides;
- others (including stabilisers and solubilisers).

(Source: TNO1998)

For metal removing processes with a high cutting load and a low cutting speed which require a high lubricity, pure oils are used. Since they have better cooling properties, water-based metalworking fluids are used for those processes with a high cutting speed, when cooling of the metal removing operation is the primary requirement. Water is very suitable for this application, but water is a poor lubricant.

A typical emulsifiable metalworking fluid will therefore contain a mineral oil to improve the lubricating abilities, emulsifiers and additives to improve the corrosion protection, and/or additives that reduce the foaming tendency. To prevent the growth of micro-organisms and extend its useful working life, biocide additives are added. The biocides are often described as bactericides, fungicides or micro-biocides.

Modern water-soluble metalworking fluids or synthetic fluids are used for a variety of metal removing operations, even those requiring heavy duty cutting fluids. These products do not contain mineral oil. Their lubricant properties are entirely derived from the additives. These additives can be non-ionic surfactants, soaps of natural or synthetic fatty acids, polyalkylene glycols etc. Like emulsifiable metalworking fluids also soluble metalworking fluids are complex in composition and there is also a wide diversity in the number and nature of the individual additives.

2.2.2 Preservatives

Baumann (1996) describes in several examples the concentration of metalworking preservatives of the two categories of water-miscible metalworking fluids. The concentrations represent the concentrations in the original fluids before diluting them for use. In Table 1 these concentrations are given.

Table 1 The concentration of preservatives in metalworking fluids

Category	Subcategory	Concentration in wt-%
Emulsifiable metalworking fluids	- conventional oils	Bactericide: circa 4 % Fungicide: 0-1 %
	- semi-synthetic oils	Bactericide: 0-5 % Fungicide: 0-1 %
Watersoluble metalworking fluids		Biocide: 3-4 % Fungicide: 0-1 %

The most important biocides used are formaldehyde-donors. Phenols are also important but the use decreases (TNO1998). Other types of biocides used in metalworking fluids are chlorine-compounds and heterocyclic substances containing S-, N-, S-N. A list of active substances currently notified for PT 13 according to the BPD can be found on the ECB Homepage: <http://ecb.jrc.it/biocides/>.

In the UBA-ESD the composition and mixture ratios of metalworking fluids are presented. Detailed information concerning mixture ratios for the different cutting-processes is described (derived from BAU1996). The average concentrate/water mixture ratio for metal removing processes is considered to be 0,05. With respect to the concentration of biocides in the metalworking fluids this ESD assumes also the values as described by Baumann (Table 1).

In the ESD derived from Luttik et al. (1993) that is included in USES 3.0, the end-use concentrations of biocides in metalworking fluids are presented. A distinction is made between:

- emulsions 0.05 wt-%
- dispersions 0.025 wt-%
- synthetics 0.02 wt-%
- semi-synthetics 0.035 wt-%
- unknown 0.05 wt-%

Conventional soluble oils and semi-synthetic soluble oils as used in the UK consist of 1-2% of biocides. In use, conventional soluble oils are mixed with water to give an emulsion containing typically 5% of the fluid. This product in use contains 0.05-0.1% biocides (Source: OECD2001, INFU2000). Water soluble metalworking fluids as used in the UK consist for 1% of biocides (Source: OECD2001).

According to Haskoning, 1995 (in INFU2000) a concentration of 1-5% of biocide is contained in the concentrated fluid to give a concentration of about 0.15% in the working solution.

2.2.3 Information of the scale or size of the industry area

Information on the amounts of metalworking fluids and/or biocides used in different countries is given below:

The Netherlands: In 1992 the total Dutch industry used 36,000 m³ prepared water-miscible metalworking fluids (Source: CBS, 1992 in TNO1998).

Denmark: The consumption of biocides for preservation of metalworking fluids in Denmark in 1999 is estimated from information from suppliers covering approximately 70% of the market. The total consumption of biocides in 1999 is estimated 10-13 tonnes/year. (Source: LASS2001)

UK: More than 50,000 businesses (estimation) use metalworking fluids in the UK. The total consumption of metalworking fluids is 35,000 tonnes/year (data from 1994-1997):

- emulsifiable metalworking fluids: - conventional oils: 7,700 tonnes/year
- semi-synthetic oils: 8,750 tonnes/year
- synthetic metalworking fluids: 1,050 tonnes/year

(Source: OECD2001)

Germany: The total consumption of water-based metalworking fluids in Germany in 1998 was 30,707 tonnes concentrated liquid and 770,000 tonnes prepared metalworking fluids (Source: statistics from the German Federal Economy Agency (FRG) in UBA2001). When using the average concentration of 4% biocide in the concentrated metalworking fluid (BAU96), this means a total use of approximately 1230 tonnes of biocide per year. These statistics were taken from the official mineral oil data and do not cover mineral oil free cooling lubricants. In 1993, mineral oil free lubricants had a market share of 21.2% of the total amount of water-based cooling lubricants produced.

(Source: BAU1996)

EU: By expanding the national sales of the FRG, the total consumption as calculated for the EU in 1998 was 140,000 tonnes concentrated liquid and 3,500,000 tonnes prepared metalworking fluids. This means a total use of 5600 tonnes of biocide per year. These data do also not cover mineral oil free cooling lubricants. The total scale of metalworking fluids in the EU was estimated in relation to the population. Because of the relatively high use of metalworking fluids in Germany the listed numbers are most probably too high for the EU and therefore only considered a very rough indication. (Source: BAU1996)

This is confirmed when the same exercise is elaborated for the Denmark, where relatively less metalworking fluids are used. The result for the consumption of biocides in the EU is then roughly 780 tonnes a year ($300/5 \cdot 13$ tonnes). This is a factor seven lower than the estimation with data from Germany.

2.3 Identification of the potential points of release in the application and use area

Substantial quantities of metalworking fluids are lost (and sometimes recycled) during use, but because of the wide diversity of operations involving these fluids, generalisation is difficult. This section provides an overview of how and where releases can arise.

The life cycle for biocides in water-miscible metalworking fluids is presented in Figure 3 (Source: TNO1998, OECD2001, RIVM1999).

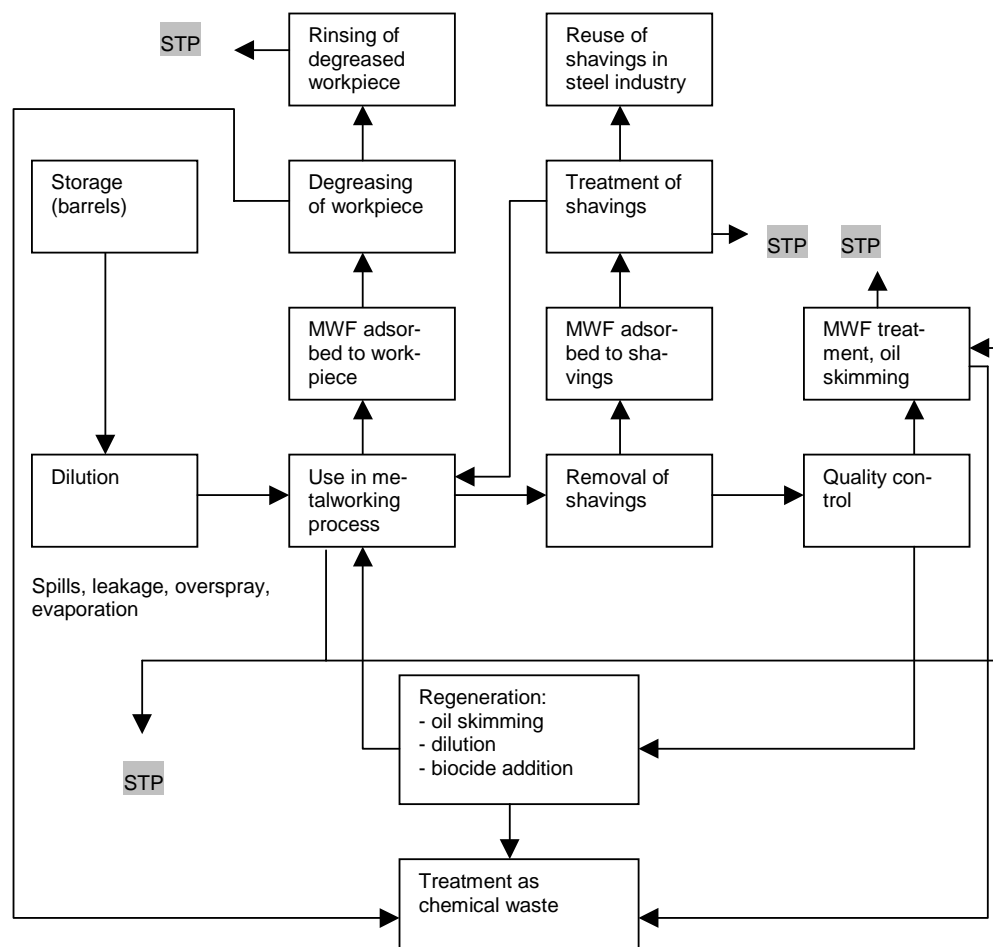


Figure 3 Environmental release of water-based metalworking fluids (MWF) (Source: TNO1998, OECD2001, RIVM1999)

Metalworking fluid concentrates are diluted, and used to cool and lubricate in a circulation system during metalworking processes.

The quality of the used fluid is examined for recycling. Depending on the condition of the fluid, the fluid can be regenerated first or the fluid can be in such condition that it is collected for disposal. The oil and water phase can be separated, and the oil phase is treated as hazardous waste. The water phase is emitted to the sewer, and finally to a STP, or to the water treatment plant of the factory.

The shavings are removed from the fluid. On many sites the shavings are separated from the metalworking fluid adsorbed to it, for example by spin-drying. The spin-dried

shavings are re-used in the steel-industry. Because this separation is not perfect and because not all the shavings will be treated, it is assumed that still a part of the fluid remains on the shavings. Emissions from metalworking fluid preservatives during re-use of the shavings in the steel-industry are considered negligible. The preservatives will be destroyed during the processes, that are carried out at high temperatures. The separated oil is normally recycled. It is possible that, due to leaking from the shavings followed by cleaning operations, a direct emission to the sewer occurs. In the scenario USES 3.0 leak out of chips is assumed, but this is considered less relevant as compared with other emissions occurring during use of metalworking fluids (see section 3.1.1).

Depending on the country and the size of the metalworking plant spills, leaked fluid, overspray and evaporation are collected as much as possible for waste treatment or are directly emitted to the sewer. In Germany, for example, the majority of losses from equipment in use is collected and sent to external treatment plants for disposal. The use of completely encapsulated machine tools helps to make this possible. In these situations, releases from the waste treatment sites will be more significant, and releases from the actual use sites are considered to be negligible. In other countries, for example in the UK, larger sites may collect releases or treat them on site, but emissions to the environment during use of the metalworking fluids can occur from smaller sites (Source: OECD2001).

The work-pieces may be degreased for further processing. Degreasing will usually take place by using an alkaline degreasant. Oils (including metalworking fluids), greases and dirt are removed. The spent degreasant will be treated as chemical waste. After the object is degreased the greater part of the degreasant will be removed by leaching, but rinsing with clean water is always necessary to remove the last remains. The rinsing water is usually emitted to the waste water. According to the fact that the fraction of metalworking fluid adsorbed to workpieces is relatively low compared with other emission routes and only a small part of these fluid ends up in the rinsing water, this emission route is considered negligible (Source: Samsom2001).

2.3.1 Discharge of the used metal-working fluid

The rate of degradation of additives in metalworking fluids is generally low. The service life of these products is generally limited by the accumulation of contaminants rather than by reduced performance. In water based metalworking fluids the service life is limited by microbial contamination. The concentrations of chemicals in used synthetic fluids are similar to those in unused fluids. The concentrations in an emulsifiable fluid will be somewhat higher than in the unused fluid (110%), because there is a preferential loss of water by evaporation and because a certain amount of time will have passed since the last replenishment. Periodic replenishment of the metalworking fluid is necessary to compensate the metalworking fluid that is lost by drag-out on shavings and evaporation. An average replenishment rate of +/- 10% per week is typical to compensate for loss of fluid by adsorption on shavings, evaporation, leaks etc. Depending on the possibilities for recycling in the metalworking plant, the replenishment fluid can consist of fresh metalworking fluid or already used and recycled fluid. Since there is a preferential loss of water by evaporation, the replenishment package used is often a diluted version of the original oil concentration, typically 50% of the normal working concentration of the emulsion or synthetic fluid. To compensate degradation of biocides or the adaptation of micro-organisms to certain biocides, extra biocides or a different type of biocide have to be added in certain cases.

(Source: OECD2001)

2.3.2 Estimates of the amounts of substance released at these points

In the literature several estimates of emissions of metalworking fluids occurring at various emission points are to be found. It must be noted that the concentrations of biocides vary between the different emission amounts. Several estimates are presented below.

Table 2 Loss of metalworking fluid as a percentage of the total loss

Losses	STIMULAR, 1993	Loos, 1992	Bremmer, 1988
Evaporation and spray	25-30	25-60	30
Adsorbed to workpieces	15-20	15-20	15
Leaking and spilling	25-30	20-35	35
Adsorbed to shavings	25-30	5-20	20
Chemical wastes	5-20		
	100 %	100 %	100 %

(Source: TNO1998)

The following Table 3 summarises the loss of soluble oils.

Table 3 Losses of metalworking fluids as percentage of the total loss

Losses/annum	%	Emissions to
Evaporation and spray	5	Air
Overalls	2	Water
Leaking and spilling	3	Waste oil/water
Adsorbed to shavings	87	(78 %) 90% oxidised oil to air (9 %) 10% to landfill
Adsorbed to workpiece	3	(1 %) Water (2%) Chemical waste – alkaline degreasant

(Source: OECD2001)

The fractions in Table 3 seem to deviate from the fractions in Table 2. In Table 2 the losses are almost equally divided over the various emission points. In Table 3 the main emission route during use of the metalworking fluid is adsorption to the shavings. The origin of the data in Table 3 is not clear.

An explanation could be that the OECD report assumes that treatment of shavings does not take place in case of water-based metalworking fluids, so all fluid adsorbed to the shavings is lost. The information in the other Table is based on Dutch data and assumes probably that shavings in most cases are treated (see also the scenario description of USES 3.0 in section 3.1.1). When the OECD report does consider treatment of shavings and recycling of the oil (for example in the case of neat oils) the actual loss is 30% instead of 87%, which corresponds with the value in Table 2. In appendix 3 the losses for neat oils with and without treatment of shavings and recycling of oil, according to OECD2001, are described.

As described in section 2.3 the loss of preservatives adsorbed to shavings is not considered relevant for the environment. The preservatives that are not recycled and thus remain on the shavings are destroyed during re-use of the shavings in the steel industry

2.4 Waste treatment

Waste fluid is likely to be heavily contaminated with metal fines from the cutting process.

Spent emulsions of conventional soluble oils can be split before disposal to minimise the volume of liquid waste. In the UK emulsion splitting or post-treatment of spent metalworking fluids only occurs in the largest machine shops (which represent some 40% of the machining industry in the UK). In Germany treatment of spent metalworking fluids is much more common.

Emulsion-splitting techniques are:

- chemical methods;
- reverse osmosis;
- evaporation methods;
- biological treatment (is more effective for semi-synthetic or synthetic fluids where normal physical-chemical processes are not so effective).

External recycling of metalworking fluids is limited to neat oils based on mineral hydrocarbons. Neat oils do not contain biocides. In the case of water-based cutting fluids, on-site treatment normally takes place, which can be a form of recycling (see also Figure 3)

(Source: OECD2001)

The emission scenario as described in the TGD (IC-8) assumes that spent emulsifiable metalworking fluids are submitted to emulsion breaking during the waste treatment step. In general four steps are employed:

- oil/water emulsion breaking;
- oil phase separation;
- secondary treatment of the water phase in a STP;
- secondary treatment of the oil phase.

The separation of the oil phase and water phase may take place by physical (ultrafiltration or adsorption processes) and chemical processes (by adding salts, acids).

After this the water phase is discharged to a company biological wastewater treatment plant.

The German UBA scenario (IC-8) shares the point of view that prior to discharge in a waste water treatment plant the spent emulsifiable fluids are separated in an oil and a water phase.

The treatment according to this scenario consists of the following steps:

- separation of unemulsified foreign oils (contamination) through skimming;
- separation of solid materials through filtration or settling;
- oil/water emulsion breaking;
- secondary treatment of the separated water, removal of dissolved heavy metals and organic substances, neutralisation;
- secondary treatment of the oil phase to reduce the water content.

With respect to water-soluble metalworking fluids this scenario assumes that some materials can be removed with filters, oil skimmers or decanters. Next, the fluids are treated with reverse osmosis or evaporation.

The scenario included in USES 3.0 does not consider emissions during the life cycle phase of waste treatment.

3 EMISSION SCENARIOS FOR METALWORKING FLUID PRESERVATIVES

3.1 Description of available scenarios

Scenarios for preservatives in metalworking fluids have been developed for the EU Technical Guidance Document (1996), by the German UBA and by Luttik et al. (included in USES 3.0). In this section the three available emission scenarios for metalworking fluids are described and compared. For every scenario a short description is given. To be able to clearly understand and compare each of the scenarios they are presented as flow diagrams in Figure 4. Each of the flow diagrams shows the potential emission routes in each scenario and whether they are actually considered in each model as significant routes of exposure.

Table 4 contains information on the dimensions of the emission sources of metalworking fluids during industrial use and waste treatment. Next to this the nature and dimensions of the primary receiving compartments are described. Information on the calculation methods provided with the original scenarios is given in section 3.2. Emissions to the environment during the production and formulation of metalworking fluids and possible discharges other than those from their intended use and disposal are not considered in these emission scenarios.

3.1.1 USES 3.0: emissions during industrial use

USES 3.0 includes an emission scenario for preservatives used in water-based metalworking fluids. The scenario has been derived from the original scenario described by Luttik et al. (1993). The defaults for that scenario originate from Van der Poel and Ros (1987). In this model the sources of emissions leading to wastewater during the life cycle step of industrial use are determined as:

- evaporation and misting, followed by deposition and cleaning operations;
- leakage, splashing and spills;
- degreasing of processed materials by means of alkaline aqueous systems;
- leak out of shavings and spin drying of shavings before recycling.

The former two are considered to be the main sources of discharges into wastewater during industrial use. It is assumed that this wastewater is treated in a standard EU STP with a capacity of 2,000 m³/day. The removal of the active ingredient can be calculated with the SimpleTreat model.

(Source: RIVM1999, USES 2.0 documentation)

USES 3.0 describes a worst case situation for a medium-sized user of metalworking fluids. At the daily practice of the time it was written, it was assumed that all of the metalworking fluid released during metal removing operations (i.e. the fraction supplemented per day) ends up in the wastewater. The used fluids, after replacing the whole content of the machines, were supposed to go to the hazardous waste treatment according to legislation.

The waste treatment stage is not considered at all in the scenario, because it was not considered very significant at the time it was written. In TNO1998 environmental losses, during use of the metalworking fluids, of 51-85 % for 9 factories in the Netherlands are mentioned (data from 1994 and 1995). But the spreading of the emissions among the different emission routes is not clear. In other words, it is not known whether metalworking fluids adsorbed to workpieces and shavings are included as losses to the environment, as waste oil or to the steel industry.

Splashes and such will get to the floor, machinery, clothing, etc., and the mists will rather set as aerosol than escape as vapours. Because of better controls – such as capturing mechanisms or total encapsulated machines – losses will get smaller, leading to larger volumes of waste at the periodical cleaning stage of the whole system.

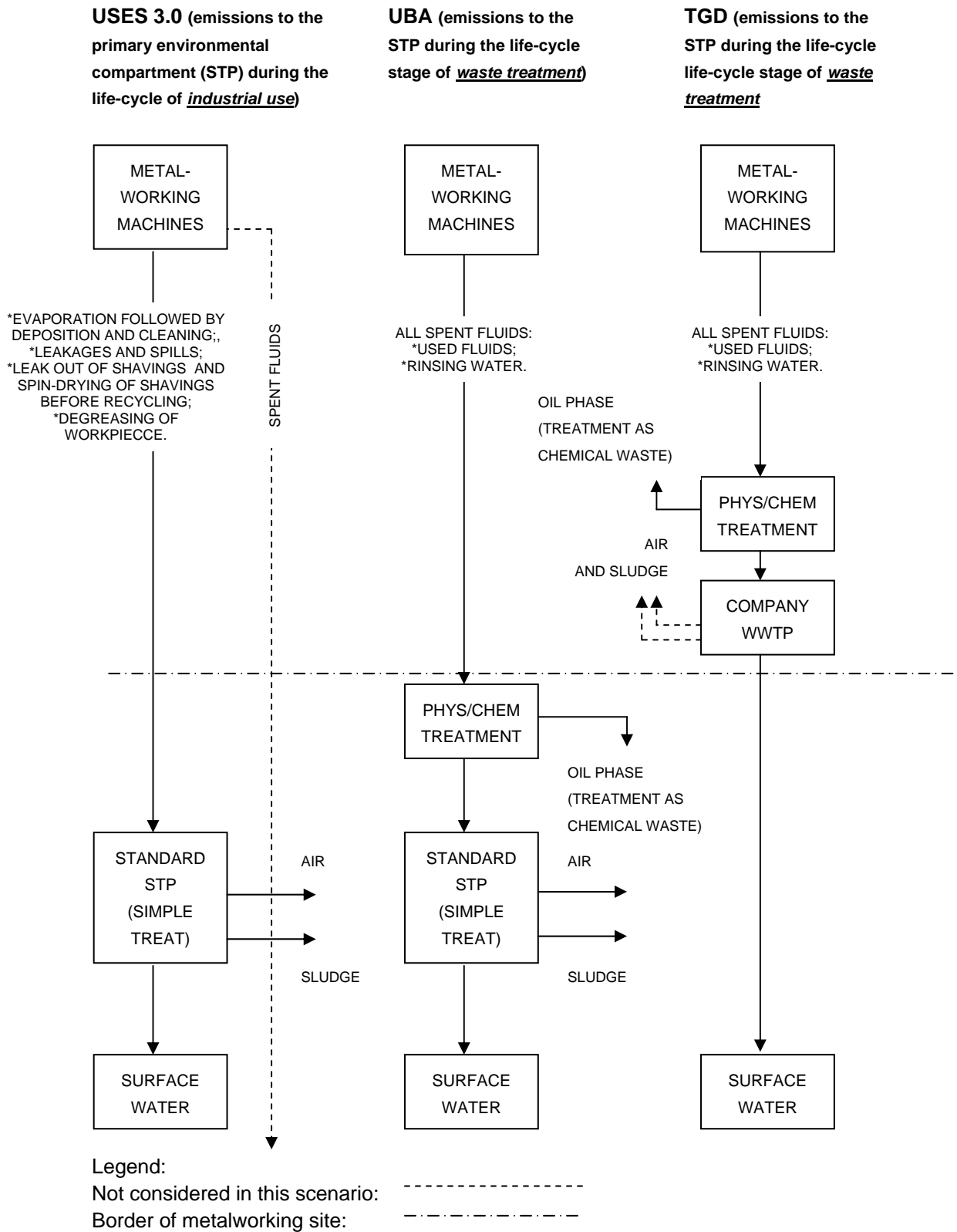


Figure 4 Graphic comparison of scenarios

3.1.2 UBA IC8: emissions during waste treatment

The Emission Scenario Document Metal Extraction, Refining and Processing Industry IC8 (ESD IC8), as described in the UBA-document, estimates the release to wastewater of chemicals that can be found in water-based metalworking fluids. A distinction is made between emulsifiable and water-soluble metalworking fluids. Emissions of water based metalworking fluids, both emulsifiable and water soluble, during use and during waste-disposal by external waste treatment plants are considered.

To conform with all European legislation (EURAL) all spent metalworking fluids are to be disposed of as hazardous waste. In view of this requirement and because of the fact that this scenario is based on German data (see section 2.3), this ESD assumes that (relevant) emissions to wastewater only take place during the life cycle step of waste treatment.

To be able to estimate releases a representative emission source is considered. Due to the high number of industrial users of metal working fluids and since most of these are medium sized companies, and do not have inner company waste and wastewater treatment facilities, it is assumed that all spent metalworking fluids as well as cleaning water of mixing containers or workpieces are disposed of as waste to an external treatment plant. This external treatment plant will be used as the point source for the life cycle step waste treatment. The assumed ratio between the capacities for the treatment of emulsifiable and water-soluble fluids reflects the market share of emulsifiable metalworking fluids in Germany (see section 2.2.3).

According to the UBA-scenario the wastewater from the waste treatment plants can be treated in a related industrial wastewater treatment plant (1000 m³/day) or in a standard EU STP (2000 m³/day). Because of the fact that the UBA-scenario uses the standard STP in its examples, the assumption is made that the wastewater is treated in the standard EU STP. As described in the scenario of USES 3.0, the removal of the active ingredient can be calculated with the SimpleTreat model. (Source: UBA2001)

3.1.3 TGD IC-8: emissions during waste treatment

This Emission Scenario Document is described in the first Technical Guidance Document (EC1996). It estimates the concentration of the preservative in recipient surface waters resulting from the discharge of the treated water phase from a large metal working plant with its own biological waste water treatment plant (WWTP). This ESD is related to the scenario described in the UBA-document: the scenario in the UBA-document originates from this ESD. As in the UBA-document the emission is caused by the discharge of spent metalworking fluids into wastewater. This scenario also distinguishes between emulsifiable and water-soluble metalworking fluids.

The internal disposal of used emulsions via the waste water is not allowed, therefore all used metal working fluids as well as cleaning water are disposed of as waste. For this ESD this implies that the discharge into the compartment water only takes place during the life cycle step waste treatment (physical/chemical). The wastewater from the physical or chemical treatment is finally treated in the company WWTP. In

contrast with the scenario as described in the UBA-document, this is not a standard EU STP.

The calculation method for the removal of the active ingredient is presented in the scenario description of the TGD. (Source: EC1996)

Figure 4 summarises the emission routes taken into account by the various scenarios. In Table 4 the scenarios are compared with respect to the required input to carry out the calculations.

Table 4 Comparison of scenarios

Original source	Unit	UBA IC-8	TGD IC-8	USES 3.0
Metalworking plant		Large metalworking plant and indirect discharging	Large metalworking plant with its own WWTP	
System capacity	[kg]			100
Fraction of fluid supplemented per day	[d ⁻¹]			0.035
Fraction of active ingredient in (diluted) fluid	[-]			Emulsions: 0.0005 Dispersions: 0.00025 Synthetics: 0.0002 Semi-synthetics: 0.00035 Unknown: 0.0005
External waste treatment plant				
Processing capacity for cooling lubricants	[m ³ /day]	200		
Processing capacity for aqueous cooling lubricants	[m ³ /day]	40		
Primary receiving compartments				
Dimensions sewerage treatment plant (STP)				
Capacity of STP	[m ³ /day]	2000		2000
Size of STP	[eq]	10000		10000
Depth of water in primary settler	[m]	4		4
Depth of water in	[m]	3		3

Original source	Unit	UBA IC-8	TGD IC-8	USES 3.0
Metalworking plant		Large metalworking plant and indirect discharging	Large metalworking plant with its own WWTP	
aeration tank				
Depth of water in solid/liquid separator	[m]	3		3
Depth of sediment in primary settler	[m]	1		1
Depth of sediment in solid/liquid separator	[m]	0.5		0.5
Dimensions company wastewater treatment plant (WWTP)				
Internal dilution factor for a larger metal working plant	[-]		10	

Calculations				
Method provided by		UBA IC-8	TGD IC-8	USES 3.0
Required input (D = default available)		<p>Emission of emulsifiable metalworking fluids</p> <ul style="list-style-type: none"> - Concentration of the chemical in the untreated sewage water of the lubricant - Concentration of the chemical in the cooling lubricant - Treated volume of cooling lubricant per day (average) (D) - Volume of the treated water phase - Volume ratio concentrate / water phase - Partition coefficient between n-octanol and water (K_{ow}) - Fraction of elimination of the chemical during physical or chemical treatment - Fraction of metalworking fluid with chemical in treated volume - capacity of STP (D) - elimination in the STP <p>Emission of water-soluble metalworking fluids</p> <ul style="list-style-type: none"> - concentration of the chemical in the aqueous cooling lubricant - treated volume (D) - volume ratio concentrate / water phase - fraction of elimination of the chemical during physical or chemical treatment - fraction of metalworking fluid with chemical in treated volume - capacity of the STP (D) 	<p>Emission of emulsifiable metalworking fluids</p> <ul style="list-style-type: none"> - concentration of the chemical in the untreated sewage water of the lubricant - concentration of the chemical in the cooling lubricant - volume ratio concentrate / water phase - partition coefficient between n-octanol and water (K_{ow}) - fraction of metalworking fluid with chemical in treated volume - internal dilution factor for a larger metal working plant (D) - elimination in the STP <p>Emission of water-soluble metalworking fluids</p> <ul style="list-style-type: none"> - concentration of the chemical in the aqueous cooling lubricant - fraction of metalworking fluid with chemical in treated volume - internal dilution factor for a larger metal working plant (D) - elimination in the STP 	<p>Emission of metalworking fluids</p> <ul style="list-style-type: none"> - system capacity (D) - fraction of fluid supplemented per day (D) - type of preservative - fraction of active ingredient in (diluted) fluid (D) - number of emission days for preservative - capacity of the STP (D) - elimination in the STP
Output		Preservative concentration in the STP-effluent	Preservative concentration in the STP-effl.	Preservative concentration in the STP-effl.

In all three scenarios only the emissions to waste water (during waste treatment or industrial use) are described. None of the scenarios take into account the fluid adsorbed to the shavings (to steel-industry, see section 2.3).

Furthermore, the scenarios do not consider the fact that the concentration of biocides in a spent metalworking fluid is often lower than the original concentration. This is caused by degradation of the biocide. In certain cases extra biocides are added periodically to compensate degradation of biocides during the use phase. But in case of a spent fluid a certain amount of time will have past since the last replenishment (see section 2.3.1).

All scenarios assume that finally all spills, spent fluids and emissions originating from misting or evaporation of the fluid end up in the waste water and that emissions to other compartments only take place during waste water treatment. Emissions from the wastewater treatment plants to the compartments surface water, air and sludge are considered when the standard EU STP is involved (SimpleTreat). In the TGD scenario with the on-site company WWTP, emissions to compartments other than surface water are not considered.

The scenario included in USES 3.0, is clearly different from the other scenarios. In contrast to the other two scenarios, this scenario assumes that there is a direct release of metalworking fluids to the wastewater during the industrial use phase (service life) in the metalworking plant. This scenario does not include the emissions coming from spent fluids after their service life.

The scenarios from the TGD and the German UBA share the point of view that all spent metalworking fluids are disposed of as hazardous waste. Accordingly, relevant emissions to the wastewater only take place during waste treatment and not during industrial use. The scenarios from the TGD and the German UBA both assume that all spent metalworking fluids are being treated in a physical and/or chemical waste treatment step. The TGD-scenario assumes on-site waste treatment whereas in the UBA-scenario waste treatment takes place in a specialised external waste treatment plant.

After the waste treatment step the aqueous phase of the treated metalworking fluids is discharged into a sewage water treatment plant.

A difference is that the TGD scenario uses a fixed dilution factor to calculate the concentration in the influent of the receiving wastewater treatment plant, whereas the UBA-scenario distinguishes two waste streams depending on the type of fluid (water soluble or emulsifiable) with different volumes.

Another difference is that the wastewater in the scenario from the TGD is being treated in a company WWTP, whereas the wastewater in the UBA-scenario is being treated in a standard EU STP. Both scenarios consider emissions from the treatment of the separated oil phase negligible because of the high temperatures used.

3.2 Overview of methods

In the original source documents for the described emission scenarios calculations were provided. Although two of the described scenarios are essentially the same, different calculation methods are applied. The original methods are presented in appendix 1 of this document. This section aims to present the calculation methods in a comparable way as far as possible, as to identify the main differences and similarities between them.

The calculation methods are given below. To facilitate comparison, some modifications to the original descriptions are made, which concern the following points:

- a standard notation and format is applied;
- percentages are replaced by dimensionless fractions;
- formulas within a calculation are united or disunited to obtain a similar notation of the several calculations.

3.2.1 USES 3.0

Table 5 Emission scenario for calculating the releases from preservatives used in water based metalworking fluids during the life cycle stage industrial use (RIVM1999).

Variable/parameter	Unit	Symbol	Value	S/D/O/P
Input:				
System capacity	[kg] ¹⁾	Q _{sys}	100	D
Fraction of fluid supplement per day	[d ⁻¹]	F _{suppl}	0,035	D
Fraction of chemical ingredient in (diluted) fluid	[-]	F _{proc}		D
- emulsions			0.0005	P
- dispersions			0.00025	P
- synthetics			0.0002	P
- semi-synthetics			0.00035	P
- unknown			0.0005	P
Capacity of the receiving STP	[m ³ .d ⁻¹]	CAP _{STP}	2000	D
Fractions of the chemical directed to the compartments surface water, air and sludge	[-]	F _{STP,water} F _{STP,air} F _{STP,sludge}		O
Output:				
Preservative concentration in the STP-effluent	[kg.m ³]	PEC _{effluent}		
Model calculations:				
$PEC_{influent} = (Q_{sys} * F_{suppl} * F_{proc}) / CAP_{STP}$				
$PEC_{effluent} = PEC_{influent} * F_{STP,water}$				

1) Amount of metalworking fluid in system of machinery used

Table 6 Parameters required for distribution modules of USES 3.0

Parameters required	Symbol	Unit	Value
Number of emission days	Temission ₃	[d]	300

3.2.2 UBA: ESD IC8

Emulsifiable metalworking fluids

Table 7 Emission scenario for calculating the releases from preservatives used in emulsifiable (water based) metalworking fluids during the life cycle stage of waste treatment (UBA2001).

Variable/parameter	Unit	Symbol	Value	S/D/O/P
Input				
A) Concentration of the chemical in the concentrated emulsifiable metalworking fluid	[kg.m ⁻³]	C _{proc,emul}		S
B) Weight fraction of chemical in concentrate ¹⁾	[-]	F _{conc}		P
Volume ratio concentrate / water phase ²⁾	[-]	F _{conc/water}		S/P
Density of metalworking fluid	[kg.m ⁻³]	RHO _{MWF}	1000	D
Treated volume of metalworking fluid	[m ³ .d ⁻¹]	V _{proc,emul.}	200	D
Fraction of metalworking fluid with chemical in treated volume	[-]	F _{form}	1	S/D
Partition coefficient n-octanol/water	[-]	K _{OW}		S
Fraction of elimination of the chemical during physical or chemical treatment	[-]	F _{elim}	0	D
Volume of the treated water phase	[m ³ .d ⁻¹]	V _{water}		
Concentration of the chemical in the untreated sewage water phase of the metalworking fluid	[mg.l ⁻¹]	C _{water}		
Capacity of the receiving STP	[m ³ .d ⁻¹]	CAP _{STP}	2000	
Fractions of the a.i. directed to the compartments surface water, air and sludge	[-]	F _{STP,water} F _{STP,air} F _{STP,sludge}		O
Output:				
Preservative concentration in the STP-effluent	[kg.m ⁻³]	PEC _{effluent}		

Model calculations:

Intermediate calculations

$$C_{\text{proc,emul}} = (F_{\text{conc}} * RHO_{\text{MWF}}) / (1 - F_{\text{conc}})$$

With the concentration of the chemical in the untreated sewage water phase

$$C_{\text{water}} = (C_{\text{proc,emul}} * F_{\text{form}} * (F_{\text{conc/water}} + 1)) / (F_{\text{conc/water}} * K_{\text{OW}} + 1) * (1 - F_{\text{elim}})$$

$$V_{\text{water}} = V_{\text{proc,emul}} / (F_{\text{conc/water}} + 1)$$

The emission concentration is calculated as follows:

$$PEC_{\text{influent}} = (C_{\text{water}} * V_{\text{water}}) / CAP_{\text{STP}}$$

$$PEC_{\text{influent}} = (C_{\text{proc,emul}} * V_{\text{proc,emul}} * F_{\text{form}} / (F_{\text{conc/water}} * K_{\text{OW}} + 1) * (1 - F_{\text{elim}})) / CAP_{\text{STP}}$$

$$PEC_{\text{effluent}} = PEC_{\text{influent}} * F_{\text{STP,water}}$$

- 1) If the concentration of the chemical in the metalworking fluid has not been provided by the notifier or industry, it can be taken from Tables 6 and 7 from the UBA-scenario, see Appendix 1.
- 2) The values for $F_{\text{conc/water}}$ can be derived from Table 8 from the UBA-scenario, see Appendix 1.

Water-soluble metalworking fluids

Table 8 Emission scenario for calculating the releases from preservatives used in water-soluble metalworking fluids during the life cycle stage of waste treatment (UBA2001).

Variable/parameter (unit)	Unit	Symbol	Value	S/D/O/P
Input				
Treated volume		$V_{\text{proc,w.s}}$	40	D
A) Concentration of the chemical in the concentrated water-soluble metalworking fluid	$[\text{kg} \cdot \text{m}^{-3}]$	$C_{\text{proc,sol}}$		S
B) Weight fraction of chemical in concentrate ¹⁾	[-]	F_{conc}		P
Volume ratio concentrate / water phase ²⁾	[-]	$F_{\text{conc/water}}$		S/P
Density of metalworking fluid	$[\text{kg} \cdot \text{m}^{-3}]$	RHO_{MWF}	1000	D
Fraction of metalworking fluid with chemical in treated volume	[-]	F_{form}	1	S/D
Fraction of elimination of the chemical during physical or chemical treatment	[-]	F_{elim}	0.8	D
Capacity of the receiving STP	$[\text{m}^3 \cdot \text{d}^{-1}]$	CAP_{STP}	2000	
Fractions of the a.i. directed to the compartments surface water, air and sludge	[-]	$F_{\text{STP,water}}$ $F_{\text{STP,air}}$ $F_{\text{STP,sludge}}$		O

Output:

Emission concentration in the STP-
effluent [kg.m⁻³] PEC_{effluent}

Model calculations:

Intermediate calculations

$$C_{\text{proc,w.s.}} = (F_{\text{conc}} * RHO_{\text{MWF}}) / (1 - F_{\text{conc}})$$

End calculations

$$PEC_{\text{influent}} = (C_{\text{proc,sol}} * V_{\text{proc,w.s.}} * F_{\text{conc/water}} * (1 - F_{\text{elim}}) * F_{\text{form}}) / CAP_{\text{STP}}$$

$$PEC_{\text{effluent}} = PEC_{\text{influent}} * F_{\text{STP,water}}$$

- 1) If the concentration of the chemical in the metalworking fluid has not been provided by the notifier or industry, it can be taken from Tables 6 and 7 from the UBA-scenario, see Appendix 1.
- 2) The values for F_{conc/water} can be derived from Table 8 from the UBA-scenario, see Appendix 1.

(Source: UBA2001)

3.2.3 TGD IC-8

Emulsifiable metalworking fluids

Table 9 Emission scenario for calculating the releases from preservatives used in emulsifiable (waterbased) metalworking fluids during the life cycle stage of waste treatment (EC1996).

Variable/parameter (unit)	Unit	Symbol	Value	S/D/O/P
Input				
Concentration of the chemical in the metalworking fluid	[kg.m ⁻³]	C _{proc,emul}		S
Concentration of the chemical in the untreated sewage water phase of the metalworking fluid	[kg.m ⁻³]	C _{water}		S
Fraction of metalworking fluid with chemical in treated volume		F _{form}	1	S/D
Volume ratio concentrate / water phase	[-]	F _{conc/water}	0.05	S/D
Partition coefficient n-octanol/water	[-]	K _{OW}		S
Internal dilution factor for a larger metal working plant	[-]	DILUTION	10	D
Fraction of the a.i. directed to the compartment surface water	[-]	F _{STP,water}		O
Output:				
Emission concentration in the WWTP- effluent	[kg.m ⁻³]	PEC _{effluent}		

Model calculations:

$$PEC_{\text{influent}} = (C_{\text{water}} * F_{\text{form}}) / \text{DILUTION}$$

$$C_{\text{water}} = C_{\text{proc,emul}} * (F_{\text{conc/water}} + 1) / (K_{\text{ow}} * F_{\text{conc/water}} + 1)$$

$$PEC_{\text{influent}} = ((C_{\text{proc,emul}} * (F_{\text{conc/water}} + 1) * F_{\text{form}}) / (K_{\text{ow}} * F_{\text{conc/water}} + 1)) / \text{DILUTION}$$

$$PEC_{\text{effluent}} = PEC_{\text{influent}} * F_{\text{STP,water}}$$

Water-soluble metalworking fluids

Table 10 Emission scenario for calculating the releases from preservatives used in water-soluble metalworking fluids during the life cycle stage of waste treatment (EC1996).

Variable/parameter (unit)	Unit	Symbol	Value	S/D/O/P
Input				
Concentration of the chemical in the untreated sewage water phase of the metalworking fluid	[kg.m ⁻³]	C _{water}		S
Fraction of metalworking fluid with chemical in treated volume		F _{form}	1	S/D
Internal dilution factor for a larger metal working plant	[-]	DILUTION	10	D
Fraction of the a.i. directed to the compartment surface water	[-]	F _{STP,water}		O
Output:				
Emission concentration in the receiving surface water	[kg.m ⁻³]	PEC _{effluent}		
Model calculations:				
$PEC_{\text{influent}} = (C_{\text{water}} * F_{\text{form}}) / \text{DILUTION}$				
$PEC_{\text{effluent}} = PEC_{\text{influent}} * F_{\text{STP,water}}$				

3.3
Qualitative comparison of the methods

It is not relevant to compare the calculation of the STP-influent concentration from the ESD according to USES 3.0 with the other calculations, because the scenario is completely different from the other two scenarios. The further calculation of the concentration in the receiving surface water is comparable to the other methods.

The calculation according to USES 3.0 is only made to be able to answer the question if an eventual emission caused during industrial use is negligible or not in comparison with the emission caused during waste treatment.

In this section are discussed:

- the methods for calculation of the STP-influent concentrations (primary receiving compartment) used by the TGD and the German UBA;
- the methods for the calculation of the concentration in the secondary receiving compartments surface water, sludge and air.

The first step in the calculation of environmental concentrations is to calculate the emission, in a second step this quantity is divided by the dimensions of the compartment. The main similarities and differences between the methods are indicated below for both steps.

Calculation of emissions

- **quantity emitted:** in the UBA approach, the quantity of preservatives emitted during waste treatment is calculated by multiplying the concentration in the watery phase of the metalworking fluid and the capacity of the waste treatment plant. The TGD does not calculate the quantity emitted, but uses only the concentration of preservatives in the watery phase of the metalworking fluid and an internal dilution factor for the discharge into a STP. Both methods have in common that the concentration in the watery phase of an emulsifiable metalworking fluid is calculated by using the “Nernst partition law”.

A further difference is the fact that the UBA-method also calculates the volume of the water phase of an emulsifiable metalworking fluid which is discharged into the STP: the volume of the emulsifiable metalworking fluid minus the volume of the oil phase, which is separated from the watery phase during the waste treatment.

In contrast to the TGD approach, the UBA-method provides the possibility to include the fraction of elimination of the preservative during the physical/chemical waste treatment. If the concentration of the chemical in the metalworking fluid has not been provided by the notifier or industry, the UBA-scenario provides the possibility to choose from a picklist (Tables 6 and 7 from the UBA-scenario: see Appendix 1). The UBA-scenario also provides a list with volume ratios concentrate/water phase for different kinds of water-based metalworking fluids (Table 8 from the UB-scenario: see Appendix 1). In contrast with this, the TGD-scenario uses a default value for this ratio.

- **time:** In the UBA-method the parameter time is processed in the capacities of the waste treatment plant and the receiving STP, both in [$m^3 \cdot d^{-1}$]. Time is not defined as a separate parameter in the formulas of the TGD, but is implicitly part of the calculation because the dilution factor used is in fact the ratio between the capacity of the waste treatment and the capacity of the related STP.

Calculation of the environmental concentration

In the primary compartment STP

- **STP:** As already described, the TGD-method uses a dilution factor instead of defined dimensions of the receiving STP. The UBA-method divides the amount emitted by the defined capacity of the receiving STP.

In the secondary compartments surface water, sludge and air

- **Surface water:** All methods calculate the emission to the surface water by multiplying the influent concentration of the STP with the fraction of the active ingredient directed to water. The fraction of the active ingredient directed to surface water for the UBA- and USES 3.0-scenario is calculated by using the SimpleTreat model. This fraction is determined by the substance specific value of K_{OW} . The scenario described in the TGD does not consider a defined value for this fraction. In an example-calculation described in this scenario a fraction of 0.2 is assumed.
- **Air and sludge:** Emissions from the STP to air and sludge are not considered in the TGD-scenario. For the UBA- and USES 3.0-scenario these emissions are calculated by using the SimpleTreat model.

3.4 Detection of similarities and differences, comparison and examples

To show how the differences between the calculation methods work out for different scenarios, an example is elaborated in detail. The scenarios for emulsifiable metalworking fluids of UBA and the TGD are chosen for this exercise, because they are built up in the same way but differ in their description of the dimensions of the waste treatment plant or facility and the receiving STP. For both scenarios, the $PEC_{influent}$ is calculated using the methods of UBA and the TGD with similar input values.

An example is taken for a “dummy” substance. The “dummy” input variables for this substance ($\log K_{OW} = 2.3$, solubility = 500-5000 [mg.l⁻¹], vapour pressure = 1 Pa) were estimated on the basis of properties of several biocides that could be used as metalworking-preservatives.

The input values are listed in Table 11 below, where the parameters are indicated as “dummy”, “default” or “result”. Dummy means that this is a chosen value and default is a value that is given in the original scenarios or methods. Results are calculated from dummies and defaults.

The fractions of the active ingredient directed to the compartments surface water, air and sludge are obtained from a calculation with the SimpleTreat model. The calculated fractions (results) are given in Table 11.

Table 11 Input values for the calculation of $PEC_{influent}$.

Parameter	Parameter type	Symbol	Unit	Value
Input				
Concentration of the chemical in the water based metalworking fluid	Dummy	$C_{proc,emul}$	[kg.m ⁻³]	2.5
Fraction of metalworking fluid with chemical in treated volume	Dummy	F_{form}	[-]	1
Volume ratio concentrate / water phase	Default/ dummy	$F_{conc/water}$	[-]	0,05
Internal dilution factor for a larger metal working plant in the untreated sewage water phase of the metalworking fluid	Default	Dilution	[-]	10
Partition coefficient between n-	Dummy	logKow	[-]	2.3

octanol and water				
Treated volume of emulsifiable metalworking fluid in an external waste treatment plant	Default	$V_{proc,emul}$	$[m^3 \cdot d^{-1}]$	200
Treated volume of water soluble metalworking fluid in an external waste treatment plant	Default	$V_{proc,w.s.}$	$[m^3 \cdot d^{-1}]$	40
Fraction of elimination of the chemical during physical or chemical treatment	Default	F_{elim}	[-]	Emulsifiable metalworking fluid: $F_{elim} = 0$ Watersoluble metalworking fluid: $F_{elim} = 0.8$
Fractions of the chemical directed to the compartments surface water, air and sludge	Result	$F_{STP,water}$ $F_{STP,air}$ $F_{STP,sludge}$	[-]	0.988 0.0005 0.011

A summary of calculated $PEC_{effluent}$ is given in Tables 12 and 13. In these Tables, the $PEC_{effluent}$ in $[mg \cdot m^{-3}]$ for the scenarios for emulsifiable and water-soluble metalworking fluids of UBA and the TGD is given as calculated with methods of UBA and TGD. The full calculations are given in appendix 2.

Table 12 $PEC_{effluent}$ in $[mg \cdot m^{-3}]$ for the UBA and TGD scenario for emulsifiable metalworking fluids, calculated with methods of UBA and TGD

Calculation method	Scenario UBA	Scenario TGD
UBA	0.221 (kg/m ³)	0.221 (kg/m ³)
TGD	0.232 (kg/m ³)	0.232 (kg/m ³)

Table 13 $PEC_{effluent}$ in $[kg \cdot m^{-3}]$ for the UBA and TGD scenario for water-soluble metalworking fluids, calculated with methods of UBA and TGD

Calculation method	Scenario UBA	Scenario TGD
UBA	0.0005 (kg/m ³)	0.0025 (kg/m ³)
TGD	0.0025 (kg/m ³)	0.0124 (kg/m ³)

Differences between scenarios within a calculation method

To identify the parameters that determine the outcome of the calculations, the differences between scenarios within a calculation method are calculated. For each calculation method (rows in Tables 12 and 13), the $PEC_{effluent}$ for the TGD-scenario is divided by the $PEC_{effluent}$ of the UBA-scenario. These ratios, further referred to as difference factors, are presented in Tables 14 and 15.

Table 14 Difference between scenarios for emulsifiable metalworking fluids within a calculation method

Calculation method	Ratio TGD/UBA
UBA	1.0
TGD	1.0

Table 15 Difference between scenarios for water-soluble metalworking fluids within a calculation method

Calculation method	Ratio TGD/UBA
UBA	5.0
TGD	5.0

The difference, shown in Table 15, is caused by the use of an average dilution factor within the TGD-scenario versus the use of defined capacities for the waste treatment plant and the STP. The ratio between the capacity of the standard EU STP (2000 m³.d⁻¹) and the daily treated volume of water-soluble fluids (40 m³.d⁻¹) is exactly 5 times the dilution factor for the company WWTP (10).

The difference is not detected in the case of emulsifiable metalworking fluids (Table 14), because the ratio between the capacity of the standard EU STP (2000 m³.d⁻¹) and the daily treated volume of emulsifiable fluids (200 m³.d⁻¹) is exactly 10 (the dilution factor for the company WWTP).

Possible differences that can occur between the two scenarios with respect to the treatment in a standard EU STP versus the treatment in a company WWTP are not visible here, because identical values for the fraction of the a.i. directed to the compartment surface water were used.

The differences between calculation methods within a scenario can also be illustrated in this way. For each scenario (columns in Tables 12 and 13), the PEC_{effluent} calculated with different methods are compared pairwise. The difference factors are described in Tables 16 and 17.

Table 16 Difference between calculation methods within a scenario for emulsifiable metalworking fluids

Scenario	TGD method versus UBA method
UBA	1.05
TGD	1.05

Table 17 Difference between calculation methods within a scenario for water-soluble metalworking fluids

Scenario	TGD method versus UBA method
UBA	5.0
TGD	5.0

Differences between calculation methods for emulsifiable metalworking fluids are caused by the fact that the calculation method of the UBA-scenario, in contrast to the TGD-scenario, takes into account the volume of the separated and removed oil phase during physical/chemical treatment.

The difference between the methods for water-soluble metalworking fluids is caused by the considered elimination factor (0.8) for physical/chemical treatment in the method of UBA. This factor is also included in the UBA-method for emulsifiable metalworking fluids, but there it is assumed to have a value of 0. This is because of the fact that water-based metalworking fluids, in contrast with emulsifiable fluids, can not be separated by simple emulsion splitting. They have to be treated by, for example, reversed osmosis.

Conclusions

The following conclusions can be derived from these exercises:

- 1) For a given scenario, the differences in the concentrations of the STP-effluent are determined by:
 - the ratio between the capacity of the STP or WWTP and the daily physical/chemical treated volume of metalworking fluids;
 - the fraction of the a.i. directed to the compartment surface water from the STP or WWTP.
- 2) Different calculation methods yield the same results for a scenario when the elimination factor for physical/chemical treatment in the UBA-method equals 0.

3.5 Comparison between scenarios for waste treatment (UBA and TGD) and the scenario for emissions during industrial use (USES3.0)

The scenarios of UBA and TGD both calculate emissions caused during the waste treatment of spent metalworking fluids. The USES-scenario calculates the emission caused by industrial use. For countries like Germany, where advanced metalworking machines are common use, it is assumed that (relevant) emissions only occur during the life cycle step of waste treatment. In other countries, for example in the UK, significant emissions during use may occur in smaller metalworking plants. In this section the calculated emission of the USES-scenario is compared with the emission of the UBA- and TGD-scenario. For the calculation the same input values as described in Table 11 are used. In addition to this the system capacity of a metalworking plant (100 l) and the fraction of supplemented fluid per day (0,035), as described in Table 5, are used for the USES3.0-scenario. In appendix 2 the influent concentrations of the STP are calculated. In Table 18 the influent concentrations for the different scenarios are given.

Table 18 Difference between calculated influent concentrations of the STP for different scenarios

Scenario	PEC _{influent} (kg/m ³)	PEC _{influent} (mg/l)
<i>Emissions during industrial use</i>		
USES3.0 (both emulsifiable and water soluble MWF)	0.000022	0.022
<i>Emissions during waste treatment</i>		
UBA (emulsifiable MWF)	0.224	224
UBA (water soluble MWF)	0.0005	0.5
TGD (emulsifiable MWF)	0.235	235
TGD (water soluble MWF)	0.0125	12.5

The influent concentration for a metalworking fluid with a certain biocide-concentration calculated with the USES3.0-scenario is lower than the concentrations calculated with the other scenarios. In case of an emulsifiable fluid the difference is even 4 orders of magnitude. This is caused by the fact that the value for the fraction of elimination during physical or chemical treatment is 0.

The scenario of USES3.0 assumes a system capacity of a metalworking plant of 100 litres. As described before, emissions during industrial use will mainly occur in smaller plants. The USES3.0-scenario represents a worst-case situation for a medium-sized plant during the phase of industrial use. Due to the use of more advanced metalworking machines, the loss of fluid during use will only decrease more in time. Because of this, it is not likely that the influent concentration calculated with USES 3.0 is higher in practice, and therefore it will be less significant compared with the influent concentrations caused by waste treatment of spent metalworking fluids.

4 DISCUSSION

4.1 Dimensions and characteristics of the point sources and the receiving waste water treatment plants

The scenarios as described in USES 3.0 on the one hand, and the scenarios of UBA and the TGD on the other hand were developed from different viewpoints. The scenario of USES is designed to calculate emissions resulting from the industrial use of metalworking fluids directly to a STP, whereas the other scenarios assume that no (relevant) emissions occur during industrial use. The possibility of recollection and recycling of metalworking fluids lost through evaporation and misting will strongly depend upon the type of collection system. The direct release of metalworking fluids is not allowed conform European legislation, as described earlier in this document, but can occur in practice mainly in smaller machine shops.

According to section 3.5 the emissions from the waste treatment plant (UBA/TGD-scenarios) are more relevant compared with eventual emissions from industrial use (USES-scenario). In the case of emulsifiable fluids the emissions during industrial use are even negligible. It is not logical to assume that both the emissions from industrial use and the emissions from waste treatment end up in the same STP. A smaller plant where emissions during the use-phase will mainly occur, is not likely to have an own waste treatment plant. Therefore, for the calculation of a reasonable worst case concentration in the environment, a scenario that describes the emissions during waste treatment (UBA or TGD) is sufficient.

The UBA-scenario has defined and traceable dimensions for both the specialised waste treatment plant and the subsequent treatment in a sewage water treatment plant. The parameters of the TGD-scenario could not be traced. The description of the company wastewater treatment plant is very brief.

Although the dimensions of the UBA-scenario are traceable it is questionable whether it is realistic to assume that a wastewater stream of 200 m³/day (for emulsifiable fluids) ends up in a STP of 2000 m³/day. This is a relative high contribution to the amount of wastewater that is to be treated in the STP, particularly because the wastewater contains bactericides. In certain concentrations these may be toxic for the bacteria in the STP.

In both the UBA and TGD-scenarios the emissions from the disposal of all spent fluids, including rinsing water, are considered. The emissions coming from leakage, spills, evaporating and misting are considered negligible. The loss of fluid adsorbed to the shavings is not considered in these scenarios. Both scenarios assume that all fluid is removed from the shavings by, for example, spin-drying and that the fluid is recycled again. As described earlier in this report, in practice a major part of the fluid adsorbed to the shavings is not recycled but is a loss to steel industry. However, due to the high temperatures used in the steel industry, this does not lead to environmental emissions.

The separated oil phase coming from the waste treatment is in both scenarios assumed to be treated as hazardous waste (incineration or controlled dumping). It is assumed that the biocides do not end up in the environment in their original form after treatment.

Finally, both scenarios (UBA and the TGD) do not consider the fact that the concentration of biocides in a spent metalworking fluid is often lower than the original concentration due to degradation of the biocide. (see also sections 2.3.1 and 3.1).

4.2 Conclusions

The UBA-scenario is the best described scenario for the calculation of the emission to the receiving STP and, finally the surface water. The new TGD (February 2002) has also adopted the approach of the UBA-scenario in the new Technical Guidance Document for New and Existing Chemicals and for Biocidal Products: "IC-8 Metal extraction industry, refining and processing industry. Assessment of environmental release of chemicals used in metal cutting and -forming fluids".

The loss of metalworking fluid to the steel industry (adsorbed to shavings) is not considered in this scenario. But since the loss causes no emissions of the original biocides to the environment this is not relevant.

Further, the UBA-scenario does not consider degradation of the biocide during use of the metal working fluid. This may be important in certain cases.

And finally, the amount of wastewater coming from the treatment plant for metalworking fluids is a relatively high contribution to the STP. It is not clear whether the ratio wastewater amount/capacity STP corresponds with reality.

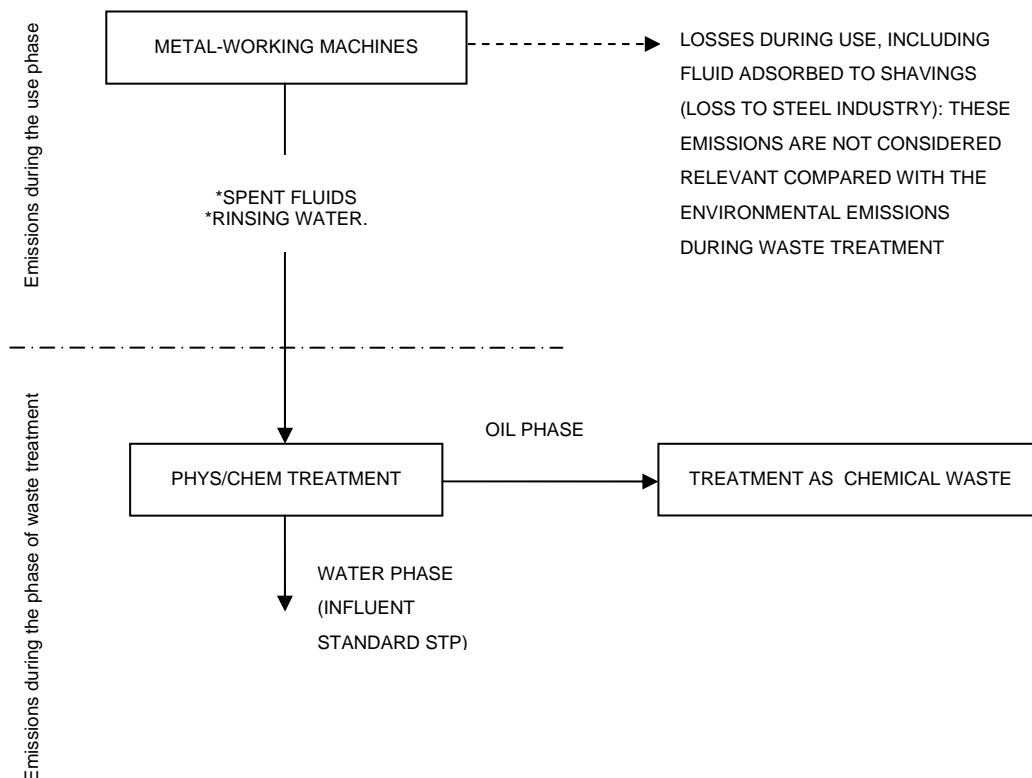
4.3 Recommended scenario

Based on the results of this report it is recommended to use a modified version of the new TGD scenario (this is the UBA scenario), as described in section 3.1.2, to calculate the release of biocides into a standard STP.

The original scenario is slightly modified by adding a fraction for degradation of biocides during the use phase. The value for this fraction is 0 by default. The user of this scenario may change this value when necessary.

With respect to the capacity of the receiving STP in relation with the amount of wastewater, it is recommended to check whether this ratio (amount of wastewater/capacity of STP) corresponds with reality.

In Figure 5 the recommended scenario is described from metalworking machine up to the influent of the STP.



Legend:

Not considered in this scenario: -----

Border of metalworking site: -.-.-.-.-

Figure 4 Recommended-scenario

The Tables 19 and 20 contain the input parameters and calculations for the UBA scenario from the metalworking machine up to the influent concentration of the STP.

Emulsifiable metalworking fluids

Table 19 Emission scenario for calculating the releases from preservatives used in emulsifiable (waterbased) metalworking fluids at the life cycle stage of waste treatment (proposed as modified from UBA2001).

Variable/parameter	Unit	Symbol	Value	S/D/O/P
Input				
A) Concentration of the chemical in the concentrated emulsifiable metalworking fluid	[kg.m ⁻³]	C _{proc,emul}		S
B) Weight fraction of chemical in concentrate ²⁾	[-]	F _{conc}		P
Volume ratio concentrate / water phase ³⁾	[-]	F _{conc/water}		S/P
Density of metalworking fluid	[kg.m ⁻³]	RHO _{MWF}	1000	D
Treated volume of metalworking fluid	[m ³ .d ⁻¹]	V _{proc,emul.}	200 ¹⁾	D
Fraction of metalworking fluid with chemical in treated volume	[-]	F _{form}	1	S/D
Fraction of chemical degraded during industrial use	[-]	F _{degr}	0	D
Partition coefficient n-octanol/water	[-]	K _{OW}		S
Fraction of elimination of the chemical during physical or chemical treatment	[-]	F _{elim}	0	D
Volume of the treated water phase	[m ³ .d ⁻¹]	V _{water}		
Concentration of the chemical in the untreated sewage water phase of the metalworking fluid	[mg.l ⁻¹]	C _{water}		
Capacity of the receiving STP	[m ³ .d ⁻¹]	CAP _{STP}	2000	
Output:				
Emission to the STP	[kg.d ⁻¹]	E _{local} _{water}		
Preservative concentration in the STP-influent	[kg.m ⁻³]	PEC _{influent}		

Model calculations:

Intermediate calculations:

$$C_{\text{proc,emul}} = (F_{\text{conc}} * RHO_{\text{MWF}}) / (1 - F_{\text{conc}})$$

End calculation:⁴⁾

$$E_{\text{local}}_{\text{water}} = C_{\text{proc,emul}} * V_{\text{proc,emul}} * F_{\text{form}} / (F_{\text{conc/water}} * K_{\text{OW}} + 1) * (1 - F_{\text{elim}}) * (1 - F_{\text{degr}})$$

$$PEC_{\text{influent}} = E_{\text{local}}_{\text{water}} / CAP_{\text{STP}}$$

- 1) It is recognised that this volume is a high contribution to the STP. It is clear that metalworking fluids contain bactericides. With respect to this ratio it will be made clear beforehand whether this ratio corresponds with the practice.
- 2) If the concentration of the chemical in the metalworking fluid has not been provided by the notifier or industry, it can be taken from Tables 6 and 7 from the UBA-scenario, see Appendix 1.
- 3) The values for $F_{\text{conc/water}}$ can be derived from Table 8 from the UBA-scenario, see Appendix 1.
- 4) The end calculation is separated in a calculation of $E_{\text{local}}_{\text{water}}$ and PEC_{influent} . The reason for this separation is to provide the possibility to calculate the concentration in the wastewater coming from the waste treatment plant without using the standard EU STP.

Water-soluble metalworking fluids

Table 20 Emission scenario for calculating the releases from preservatives used in water-soluble metalworking fluids during the life cycle stage of waste treatment (UBA2001).

Variable/parameter (unit)	Unit	Symbol	Value	S/D/O/P
Input				
Treated volume		$V_{\text{proc,w.s}}$	40 ¹⁾	D
A) Concentration of the chemical in the concentrated water-soluble metalworking fluid	[kg.m ⁻³]	$C_{\text{proc,sol}}$		S
B) Weight fraction of chemical in concentrate ²⁾	[-]	F_{conc}		P
Volume ratio concentrate / water phase ³⁾	[-]	$F_{\text{conc/water}}$		S/P
Density of metalworking fluid	[kg.m ⁻³]	RHO_{MWF}	1000	D
Fraction of chemical degraded during industrial use	[-]	F_{degr}	0	D
Fraction of metalworking fluid with chemical in treated volume	[-]	F_{form}	1	S/D
Fraction of elimination of the chemical during physical or chemical treatment	[-]	F_{elim}	0.8	D
Capacity of the receiving STP	[m ³ .d ⁻¹]	CAP_{STP}	2000	
Output:				
Emission to the STP	[kg.d ⁻¹]	$\text{Elocal}_{\text{water}}$		
Emission concentration in the STP-influent	[kg.m ⁻³]	$\text{PEC}_{\text{influent}}$		

Model calculations:

Intermediate calculations:

$$C_{\text{proc,sol}} = (F_{\text{conc}} * \text{RHO}_{\text{MWF}}) / (1 - F_{\text{conc}})$$

End calculation:⁴⁾

$$\text{Elocal}_{\text{water}} = C_{\text{proc,sol}} * V_{\text{proc,w.s}} * F_{\text{conc/water}} * (1 - F_{\text{elim}}) * (1 - F_{\text{degr}}) * F_{\text{form}}$$

$$\text{PEC}_{\text{influent}} = \text{Elocal}_{\text{water}} / \text{CAP}_{\text{STP}}$$

- 1) It is recognised that this volume is a high contribution to the STP. It is clear that metalworking fluids contain bactericides. With respect to this ratio it will be made clear beforehand whether this ratio corresponds with the practice.
- 2) If the concentration of the chemical in the metalworking fluid has not been provided by the notifier or industry, it can be taken from Tables 6 and 7 from the UBA-scenario, see Appendix 1.
- 3) The values for $F_{\text{conc/water}}$ can be derived from Table 8 from the UBA-scenario, see Appendix 1.
- 4) The end calculation is separated in a calculation of $\text{Elocal}_{\text{water}}$ and $\text{PEC}_{\text{influent}}$. The reason for this separation is to provide the possibility to calculate the emission concentration in the wastewater coming from the waste treatment plant without using the standard EU STP.

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Appendix 1: The original descriptions of methods

USES3.0

USES 3.0 (RIVM, VROM, VWS, 1999) includes an emission scenario for preservatives used in water based metalworking fluids. The scenario has been derived from Luttik et al. (1993) and the defaults for that scenario originate from Van der Poel and Ros (1987). A description of this scenario is presented below.

In metal industry large amounts of metalworking fluids are used for their cooling and lubricating abilities. In many cases water-based metalworking fluids are used, often in circulation systems. According to Pijnenburg (1992) some 10 tonnes/year of biocides are in use for preservation of these fluids (assuming 0.5% of biocide in metalworking fluids). Water-based metalworking fluids are delivered as concentrates which are diluted with water before use. The dilution is depending on the type of water-based fluid (i.e. emulsion, dispersion, synthetic or semi-synthetic) and the type of machining. Though spent fluid has to be treated as hazardous waste, a part of the fluid will be discharged into the waste water (sewerage). These emissions are not taken into account here.

Emissions leading to discharges to waste water are:

- evaporation and misting, followed by deposition and cleaning operations;
- leakage, splashing and spills;
- degreasing of processed materials by means of alkaline aqueous systems;
- leak out of chips and spin drying of chips before recycling.

The former two are the main sources of discharges to waste-water. The latter two are minor ones; degreasing of the processed materials occurs in many cases not at the same place. It is assumed that the waste water is treated in an STP (2,000 m³/day); the removal of the a.i. is calculated with the standard module of USES.

The emission scenario is presented in Table 13.1. The parameters required for the distribution model are presented in Table 13.2.

Table 13.1: Emission scenario for calculating the releases from preservatives used in metalworking fluids

Variable/parameter (unit)	Symbol	Default	S/D/O/P
Input:			
System capacity ¹ (kg)	Qsyst	100	D
Fraction of fluid supplemented per day (-)	Fsuppl	0,0035	D
Fraction of active ingredient in (diluted) fluid:			D
• Emulsions		0,0005	
• Dispersions		0,00025	
• Synthetics		0,0002	
• Semi-synthetics		0,00035	
• Unknown		0,0005	
Output:			
Elocal _{3,water} = Local emission to wastewater during episode (kg.d ⁻¹)			
Model calculations:			
Elocal _{3,water} = Qsyst * Fsuppl * Fproc			(13.1)

1) Amount of metalworking fluid in system of machinery used

Table 13.2: Default values of parameters required for distribution models of USES 3.0

Parameters required	Symbol USES 3.0	Symbol for this scenario	Symbol for this report	Value
Number of emission days (d)	Temission	Temission _{pres}	Temission ₃	300

(Source: RIVM1999, USES2.0-documentation)

TGD IC-8

1. Introduction

Objective of this document is to represent "realistic" scenarios for environmental release of chemicals that can be found in cooling lubricants used for metal working (UC-29, UC-35).

Calculated assessments should relate to the metalworking fluids as marketed under normal use conditions but realistic worst case considerations should be included. Environmental releases during the production of metalworking fluids and possible discharges other than those from using process e.g. disposal are not subject of this document.

2. Main processes

In metal forming processes the geometry of the object to be treated is changed by cutting and non-cutting forming. Metal cutting processes are for example turning, drilling, milling, cutting, abrasive blasting, planing and lapping. When using non-cutting forming the work piece is formed through pressure (e.g. rolling), compression-tension (e.g. deep drawing), pulling bending or pushing.

Water-miscible and non-water-miscible cooling lubricants are used in metal working to reduce the friction, to remove arising heat and to sweep away metal chips from the cutting place. For water miscible cooling lubricants a distinction can be made between emulsified and water-soluble cooling lubricants (see Figure 1).

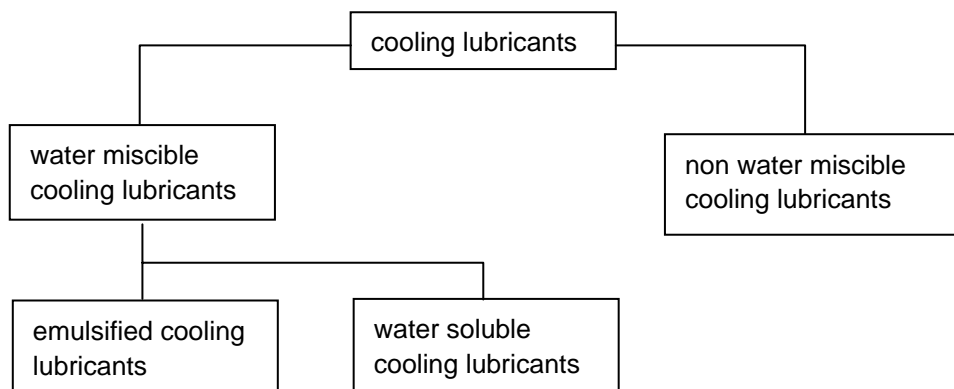


Figure 1: Classification scheme of cooling lubricants

Depending on the requirements of the special working procedure water-miscible or non-water-miscible cooling lubricants are used. The water-miscible cooling lubricants are mixed prior to use with water in a ratio of between 1:5 to 1:100. As a consequence either permanent aqueous cooling lubricant solutions are obtained (from water-soluble substances) or cooling lubricant emulsions (from emulsified substances), i.e. water-in-oil or oil-in-water emulsions.

3. Composition of cooling lubricants and application

The composition of ready-to-use cooling lubricants, or more precisely, of water-miscible or non-water-miscible cooling lubricants is shown in Figure 2.

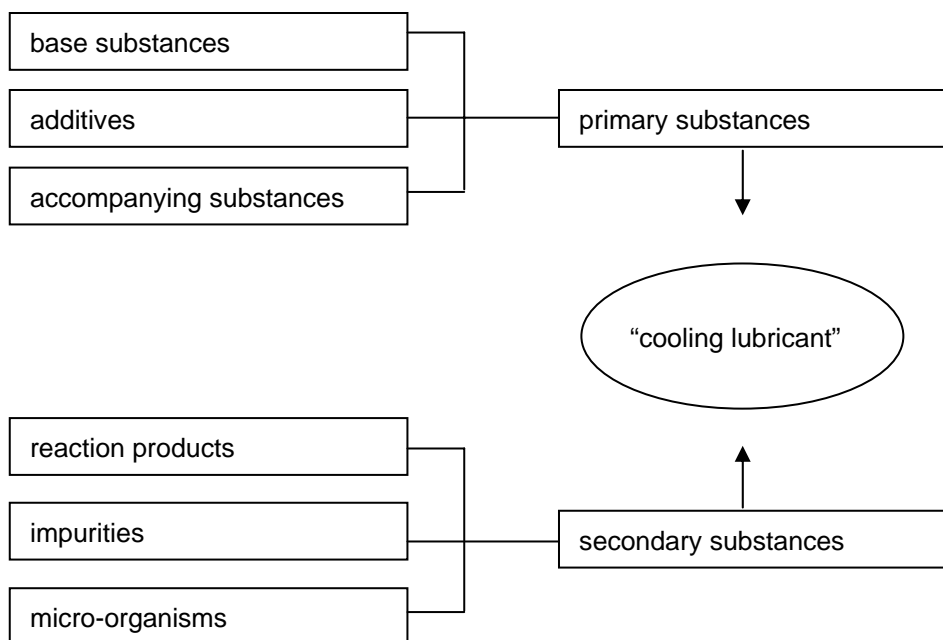


Figure 2: Composition of cooling lubricants (BIA, 1991)

The following definitions have been used:

Primary substances (deliberate constituents of lubricants):

- **Base substances:** Base substances are those substances (e.g. mineral oils) or a mixture of individual substances which constitute the matrix of the cooling lubricant;
- **Additives:** Substances which are added in small quantities to achieve the designed chemical and physical properties of the lubricant fluid. For the different additives, see Table 1;
- **Accompanying substances:** Accompanying substances arise as by-products during the synthesis of the base substances or additives.

Secondary substances (arising during use or storage of lubricants):

- **Reaction products:** Newly formed products e.g. from thermal decomposition or microbial degradation. These substances might change the chemical and physical properties of the cooling lubricants.

Table 1: Additives used in cooling lubricants

Type of additive ¹	Purpose
Oxidation inhibitors	Minimisation of the formation of resin, lacquer, sludge, acidic and polymeric compounds
Corrosion inhibitors	Protection of bearing and other metal surfaces from corrosion
Rust inhibitors	Protection of ferrous metal surfaces from rust
Metal deactivators	Prevention of catalytic effect on oxidation and corrosion
Anti-wear additives	Reduction of excessive wear between metal surfaces
Anti-scuffing	Prevention of micro-seizure additives between metal surfaces during extreme pressure and at high temperatures
Friction modifier	Reduction of friction between metal surfaces
Viscosity index improver	Reduction of the dependence of viscosity on temperature
Foam inhibitors	Prevention of stable foam formation
Adherence improver	Emulsification of oil in water
Biocides	Prolongation of the emulsion's lifetime Prevention of disagreeable odours
Detergent additives	Reduction or prevention of deposits at high working temperatures
Dispersant additives	Prevention or delay of sludge formation and deposit at low working temperatures

¹ Due to the different chemical classes for each type of additive specific default values for the percentage content in the lubricant are not suggested here. In most cases these values (as a range) are supplied by the notifier/industry/user.

- **Impurities:** Impurities which reach the lubricants during their use from outside; mainly originating from impurities of the treated material;
- **Micro-organisms:** Micro-organisms reach the cooling lubricant either via primary substance or by contamination from outside. During multiplying of the number of micro-organisms occurs, particularly in the case of emulsions impinging the life time of the fluid.

During mechanical working procedures the cooling lubricant, which absorbs abrasion, chips and rests of oil from the surface of the working pieces, is run in closed circuits. The central supplying system comprises separators to remove bore chips, splints, shavings etc. and a unit for fine purification (band filter). Absorbed oil to metal surfaces is removed beforehand in an oil separator.

The circulation period of emulsions is not unlimited. The content of foreign matter gradually increases and microbial decomposition processes may occur, causing disagreeable smells or sedimentation of sludge in pipes etc. Single machines and small central suppliers contain up to 5 m of cooling lubricants while large central systems may have up to 100 m and more. Common time intervals between replacements range from 6 months to 1 year.

4. Environmental exposure to chemicals used in cooling lubricants

4.1 General

The assessment of environmental inputs from chemicals used in water-miscible cooling lubricants is based on the assumption that the main environmental inputs take place during the phase of industrial use. Figure 3 shows schematically the internal substance-flow of a cooling lubricant in a metalcutting or metalforming plant. Sewage water contamination arises from:

- used cooling lubricant emulsions (waste emulsions);
- washing and scouring solutions from cleaning machines, tools, pipes and work pieces.

The used non-water-miscible cooling lubricants are subjected to treatment (refining) and, depending on the constituents, disposed of as hazardous substances (incineration).

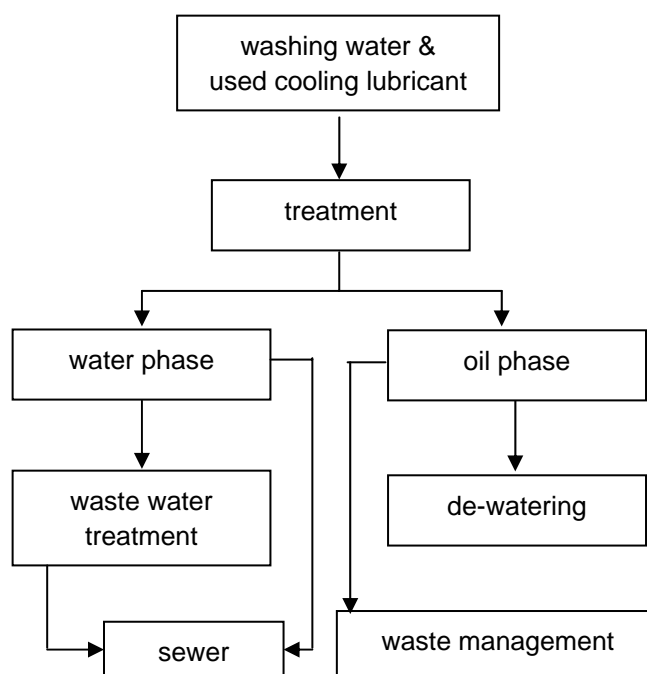


Figure 3: Flow diagram of sewage water and sewage water treatment (UBA, 1994)

4.2 Emulsion breaking and secondary treatment

Spent solutions of cooling lubricants which suffer from severe microbial degradation and advanced pollution and which no longer can be strengthened are submitted to emulsion breaking. In general four steps of treatment are employed:

- oil/water emulsion separation;
- oil phase separation;
- secondary treatment of the water phase;
- secondary treatment of the oil phase.

Breaking of emulsions may be performed by chemical processes (e.g. induced by salts, acids or cationic polymers) or by physical processes (e.g. ultra filtration or adsorption processes). Chemical breaking destroys emulsions by adding acids and metal salts. The

oil phase and water phase are separated. Physical separation processes avoid salting of the solution. Solutions having passed through ultra-filtration show an oil content of less than 20 mg/l and may be discharged if no other constituents (e.g. heavy metals) require additional adsorptive treatment.

In most cases secondary treatment steps of the aqueous phase are necessary prior to discharge. If using chemical separation processes for breaking emulsions, the water has to be neutralised subsequent to phase separation. Heavy metals may need removal. This is preferably achieved by precipitation after neutralisation of the solution. After neutralisation, flocculation and sludge filtration, the water phase generally is discharged.

Additional treatment of the separated oil phase may also be necessary. It may still have residual water contents of 50 - 60 %. Small amounts of oil concentrate from single plants are recycled or disposed of.

4.3 Calculation of the PEC

Because of the complex and inhomogeneous structure of the metal-cutting "industry" (no real branch) the following calculation is suggested for a large metal working plant. This scenario is in agreement with a reasonable worst case approach.

The PEC for using lubricants, resulting from the discharge of the water phase into running waters from a larger metal working plant with an own biological WWTP is calculated according to:

$$PEC_{local\ water} = \frac{C_{wp} * f_r}{ID * D} * \frac{100 - P}{100}$$

Explanation of symbols:

C_{wp}	concentration of the chemical in the untreated sewage water phase of the lubricant (see chapters below)	[mg.l ⁻¹]	
f_r	factor of relevance for the additive percentage of elimination in the WWTP	[%]	1
P	internal dilution factor for a larger metal working plant	[-]	
ID	(e.-. car manufacturing industry)(default value see UBA, 1994)		10
D	dilution factor for the discharge into running waters	[-]	10

4.3.1 Aqueous cooling lubricant solutions

For water-soluble cooling lubricants the concentration of the chemical in the untreated water phase of the lubricant (C_{wp}) is similar to the concentration of the substance in the lubricant solution (C_{lub}) that is either given by the notifier or calculated from the lubricant to water mixture ratio.

4.3.2 Cooling lubricant emulsions

A distribution of the regarded chemical between the oil phase and the water phase during the use of the emulsion is assumed and described with the n-octanol/water partition coefficient for an initial approximation. Due to the "partition law" of Nernst, C_{wp} is calculated as follows:

$$C_{wp} = C_{emul} * \frac{m + 1}{Kow * m + 1}$$

Explanation of symbols:

C_{emul}	concentration of chemical in the emulsion	[mg.l ⁻¹]
m	volume ratio oil phase/water phase	[-]
Kow	the partition coefficient between n-octanol and water	[-]

4.3.2 Non water-miscible lubricants

A release of additives in non-water-miscible lubricants (pure oils) is given via the waste water from washing (e.g. tools, work pieces) and scouring aqueous solutions. As a generic scenario for this release is not available now, the estimation should be carried out with the default emission factors presented Appendix I of Chapter 3 of the TGD.

5 Example for calculating the PEC of an additive in a cooling lubricant

Data specification:

Function: Corrosion inhibitor in water miscible emulsified cooling lubricant	
Concentration in cooling lubricant emulsion (information by producer):	500 mg.l ⁻¹
Volume ratio for mixture with water (default):	1:20
logKow (Kow)	2.3 (200)
Factor of relevance (there are different corrosion inhibitors used in a large plant with several types of lubricants):	20%
Internal dilution factor (default)	10
Elimination in WWTP (fictitious)	80%
Dilution factor D (discharge into running water) (default)	10

$$C_{wp} = 47.8 \text{ mg.l}^{-1} \text{ (from equation 1)}$$

$$PEC_{local_{water}} = 19 \text{ } \mu\text{g.l}^{-1} \text{ (from equation 2)}$$

6 References

WHG (1992), *Hinweise und Erläuterungen zum Anhang 40. - Metallbearbeitung, Metallverarbeitung - der Allgemeinen Rahmen-Verwaltungsvorschrift über Mindestanforderungen an das Einleiten von Abwasser in Gewässern; erarbeitet vom Gesprächskreis 33/35 zu § 7a WHG (1992).*

BIA (1991), BIA-Report 3/91, Kühlschmierstoffe, Schriftenreihe des Hauptverbandes der gewerblichen Berufsgenossenschaften, Berufsgenossenschaftliches Institut für Arbeitssicherheit.

UBA (1994), Private communication between German Federal Environmental Agency and German car manufacturing industry.

UBA IC-8

4.2 Emission by water-based cooling lubricants

4.2.1 Emission of cooling lubricant emulsions

Water-based cooling lubricants are concentrates, regardless of whether they are cooling lubricant emulsions or -solutions. Before use they are mixed with water. During the dilution of the usable cooling lubricant, a contamination of the compartment water can take place during the cleaning of the mixing containers.

- the cleaning of mixing containers used for diluting the cooling lubricant emulsion or - solution to the working concentration
- the cleaning of the worked part (the washing water may also contain cleaning agents and surfactants which are used to improve the cleaning effect. Larger companies usually use cleaning water in a circulating system, disposing it as waste, once it has reached a certain saturation)
- the cleaning of the facility (usually the company has at least an oil separator with coalescence step).

4.2.1.1 Emission during industrial use

A cooling lubricant emulsion contains about 95% water. Spillage and carry off loss can amount to 100% of the bath volume in one month. This is called process losses. The process losses for water-based cooling lubricants are not as high as for their pure oils counterparts.

Large wastewater amounts are a result of rinsing and pre- cleaning steps.

The internal disposal of used emulsions via the waste water is not allowed, therefore all used cooling lubricants as well as the rinsing water are disposed of as waste. For this ESD that means that the discharge into the compartment water takes place during the life cycle step waste/recovery.

4.2.1.2 Emission during waste/recovery treatment

A CL-emulsion which is to be disposed contains about 90% water, in addition to the CL concentrate, impurities and system cleaning agents will be found. Sample values for used cooling lubricants as relevant to waste water are shown in Table 5 (BAU96). Spent emulsions are complex mixtures due to the formula of the concentrate and the various impurities introduced during the processes.

Table 5 Composition of spent emulsions

Parameter	Average value of the emulsion
pH-value	7-10
oil content	2-20%
solid material content	20-100 mg/l
heavy metals	up to 100 mg/l
Nitrite	up to 150 mg/l
COD	5000-20000 mg/l

When processing the old emulsions, the water and oil phase are to be completely separated. The emulsion breaking process consists of the following steps (ABA92):

- Separation of the unemulsified foreign oils through skimming, possibly with support (for example flotation);
- Separation of the solid materials through filtration and/or settling in a settling tank;
- Emulsion breaking;
- Treatment of the separated water, removal of dissolved heavy metals and organic substances (COD), neutralization;
- Possibly further treatment of the separated oil phase to reduce the water content.

Processes used in the treatment of used emulsions are, among others, chemical separation processes (organic, inorganic), membrane processes, ultra filtration, reverse osmosis, evaporation processes, electrochemical processes, flotation, coagulation and adsorption. The washing emulsions are disposed of with the water miscible cooling lubricants. The old oils produced in the circulating system are disposed of directly.

Water-based cooling lubricants are often treated with ultra filtration or emulsion splitting. The remaining CL-content is then below 10 mg/l. The remaining water content in the oil phase is about 40%.

Only large companies have disposal and recycling systems for used cooling lubricants. The companies dispose off the waste water as waste, therefore the greatest part of substances from cooling lubricants reaches the waste water during reprocessing and disposal in the treatment plants.

The discharge into the environmental compartment water takes place after emulsion breaking. The oil phase is turned over to the thermal or substance exploitation (75/439/EEC).

During incineration in special waste disposal incinerators, no release into the compartment water takes place. The reprocessing of the used cooling lubricants of high quality, like the production, also causes no contamination of the compartment water (BAU96).

The estimation of the release of a cooling lubricant additive in the watery phase is done with the aid of the Nernst distribution law. Therefore to determine the release of a substance or the appropriate cooling lubricant additive, specific substance data have to be available. In addition to this, the capacity of the point source is required. If only a fraction of whole amount to be disposed of containing the substance, the default value $f = 1$ can be lowered if appropriate information is provided by the notifier or the industry about the relevance of the substance.

If a chemical or physical treatment takes place the fraction of elimination can be considered with the concentration of the chemical in the untreated sewage water phase

$$C_{\text{water}} = C_{\text{chem}_{\text{emul}}} \cdot \frac{f \cdot (m+1)}{(m \cdot K_{\text{ow}} + 1)} \cdot (1 - f_{\text{elim}}) \quad \text{and} \quad V_{\text{water}} = \frac{V_{\text{prod}}}{m+1}$$

the release is calculated as follows:

$$E_{\text{local}_{\text{water}}} = C_{\text{chem}_{\text{emul}}} \cdot V_{\text{prod}} \cdot f / (m \cdot K_{\text{ow}} + 1) \cdot (1 - f_{\text{elim}})$$

Symbols:

Explanation	Symbol	Value	Units	1)	Origin
Input					
Concentration of the chemical in the untreated sewage water phase of the lubricant	C_{water}		mg.l ⁻¹		
Concentration of the chemical in the cooling lubricant	$C_{\text{chem}_{\text{emul}}}$		kg.m ⁻³	A,D	from notifier or industry see chapter 4.4
Treated volume of cooling lubricant per day (average)	V_{prod}	200	m ³ .d ⁻¹	D	see chapter 4.1.2
Volume of the treated water phase	V_{water}		m ³ .d ⁻¹		
Volume ratio concentrate / water phase	m	1 : 20	-	A	from notifier or industry
Partition coefficient between n-octanol and water ($K_{\text{ow}} = 10^{\log K_{\text{ow}}}$)	K_{ow}		-	A	from notifier or industry
Fraction of elimination of the chemical during physical or chemical treatment	F_{elim}	0	-	A	from notifier or industry
Factor of relevance	f	1	-	A	from notifier or industry
Output					
Emission per day	$E_{\text{local}_{\text{water}}}$		kg.d ⁻¹	O	

1) A = based on information from notifier or industry

D = default

O = output

4.2.2 Aqueous cooling lubricant solutions

4.2.2.1 Emission during industrial use

Cooling lubricant solutions are used mainly for grinding processes. The oil content is about 2 to 3%. Some materials can be removed with filters, oil skimmers or decanters (ABA92).

During the processing stage, no discharge into the compartment water takes place. The used solutions are disposed of as waste.

4.2.2.2 Emission during waste/recovery treatment

For water-soluble cooling lubricants the concentration of the chemical in the untreated water phase of the lubricant is calculated from the lubricant to water mixture ratio.

Once the contamination resulting from the specific process has been removed from the synthetic cooling lubricant solution, the cooling lubricant solutions are treated with reverse osmosis or evaporation. A mixing with cooling lubricant emulsions results in an inseparability of the dissolved oils. During the separation process, the oil part remains in the watery phase, leading to a high percentage of leftover oil in the water phase. Due to the high COD-content, a discharge into the compartment water is therefore impossible.

The release is calculated as follows:

$$E_{\text{local}_{\text{water}}} = C_{\text{chem}_{\text{aq}}} \cdot V_{\text{water}} \cdot m \cdot (1 - f_{\text{elim}}) \cdot f$$

Parameters:

Explanation	Symbol	Value	Units	1)	Origin
Input					
Concentration of the chemical in the aqueous cooling lubricant	$C_{\text{chem}_{\text{aq}}}$		(kg.m ⁻³)	A,D	from notifier or industry see chapter 4.4
Treated volume	V_{water}	40	(m ³ .d ⁻¹)	D	see chapter 4.1.2
Volume ratio oil phase / water phase	m	1 : 20	(-)	A	from notifier or industry
Fraction of elimination of the chemical during physical or chemical treatment	F_{elim}	0,8	(-)	A	from notifier or industry
Factor of relevance	f	1	(-)	A	from notifier or industry
Output					
Emission per day	$E_{\text{local}_{\text{water}}}$		(kg.d ⁻¹)	O	

- 1) A = based on information from notifier or industry
 D = default
 O = output

4.3 Release determination parameter

To calculate the emission, the concentration of the substance assessed in the cooling lubricant is required in equation 1 and 2. If the concentration has not been provided by the notifier or industry, it can be taken from the Tables 6 and 7. Table 8 is for the determination of m . By assuming a density $RHO_{form}=1 \text{ kg.l}^{-1}$ of the ready to use water-based cooling lubricant and by assuming that 1 kg of lubricant contains $0,01 \cdot Q_{sub}$ [kg] of additive and $(1 - 0,01 \cdot Q_{sub}) / RHO_{form}$ [l] of lubricant base, C_{CLE} or C_{ACL} can be calculated as follows:

$$Cchem_{emul} \text{ or } Cchem_{aq} = \frac{0,01 \cdot Q_{sub} \cdot RHO_{form}}{(1 - 0,01 \cdot Q_{sub})}$$

or in recommended units:

$$Cchem_{emul} \text{ or } Cchem_{aq} = \frac{10 \cdot Q_{sub} \cdot RHO_{form}}{(1 - 0,01 \cdot Q_{sub})} \quad [\text{kg.m}^{-3}] \quad (3)$$

Table 6 Composition of selected cooling lubricants (substance groups) [BAU96]

traditional emulsifiable cooling lubricant (SEM)		semi synthetic emulsifiable cooling lubricant (SEM)	
	Q_{sub} wt-%		Q_{sub} wt-%
base oil	about 60	base oil	about 30
emulsifier (anionic)	15-20	emulsifier (not ionic)	10-15
solubilizer	about 5	solubilizer	about 5
friction modifier	0-5	friction modifier	5-10
aliphatic acids	about 5	corrosion inhibitor, bacteriostatic agent	20-25
corrosion protection agent	about 5	boric acid (biocide/emulsifier)	0-3
neutralization agent	0-3	carbon acid (emulsifier, corrosion protection, cutting facilitation substance)	5-15
bactericide	about 4	corrosion protection	0-10
fungicide	0-1	bactericide	0-5
		fungicide	0-1
		water	0-10
aqueous cooling lubricant (mineral oil free) (SES)		copper corrosive pure oils cooling lubricant (SN)	
	Q_{sub} wt-%		Q_{sub} wt-%
corrosion protection	20-40	base oil	87-95
neutralization agent (soaping)	15-25	sulphur	about 0,5
solubilizer	10-20	sulphurized ester or sulphurized olefin	3-6
friction modifier	5-10	organic phosphor compounds and calcium sulfonate	0-3
water	5-30	carbon acid ester (anion active surfactant)	0-3
biocide	3-4	mist inhibiting agent	0,5-1
fungicide	0-1	antioxidant	about 0,2

Table 7 Concentration percentages by additive class

class	Q_{sub} wt-%	water miscible CL	non-water miscible CL
anionic surfactants	1-25	x	x
anti-wear agents	up to 5	x	x
biocides	2-5	x	
complex builders	5	x	
corrosion inhibitors	1-20	x	x
detergents	up to 3		x
dispersants	up to 3		x
emulsifier	up to 20	x	
extreme pressure additive	up to 50	x	x
foam inhibitors	0,1-0,3	x	x
friction modifiers	10-100	x	x
fungicides	0,5	x	
lubricant base	0-100	x	x
metal deactivators	up to 1	x	x
mist inhibitors	up to 0,5		x
neutralization agent	5-25	x	
non-ionic surfactants	10	x	
oxidation inhibitors	up to 0,3		
pour point depressor	up to 5		x
solubilizer	5-10 (up to 50)	x	
tackifier	5		x
viscosity index improvers	up to 5		x

Table 8 Mixture relations of cooling lubricant emulsions for different processes

cutting process	concentration [%]	water : concentrate
broaching	10 - 20	1:10 - 1:5
thread cutting	5 - 10	1:20 - 1:10
deep hole drilling	10 - 20	1:10 - 1:5
parting-off	5 - 10	1:20 - 1:10
milling, cylindrical milling	5 - 10	1:20 - 1:10
turning, drilling, automation work	3 - 10	1:33 - 1:10
sawing	5 - 20	1:20 - 1:5
tool grinding	3 - 6	1:33 - 1:17
cylindrical grinding	2 - 5	1:50 - 1:20
centre less grinding	3 - 6	1:33 - 1:17
surface grinding	2 - 5	1:50 - 1:20

Appendix 2: Calculation results

EMISSIONS DURING WASTE TREATMENT

EMULSIFIABLE METALWORKING FLUIDS

Dimensions UBA/UBA-method

$$C_{\text{water}} = (C_{\text{proc,emul}} * F_{\text{form}} * (F_{\text{conc/water}} + 1)) / (F_{\text{conc/water}} * K_{\text{OW}} + 1) * (1 - F_{\text{elim}}) \text{ and}$$

$$V_{\text{water}} = V_{\text{proc,emul}} / (F_{\text{conc/water}} + 1)$$

$$PEC_{\text{local}3,\text{infl}} = (C_{\text{proc,emul}} * V_{\text{proc,emul}} * F_{\text{form}} / (F_{\text{conc/water}} * K_{\text{OW}} + 1) * (1 - F_{\text{elim}})) / CAP_{\text{STP}}$$

$$PEC_{\text{local}3,\text{infl}} = (2.5 * 200 * 1 / (0.05 * 200 + 1) * (1 - 0) / 2000) = 0.0227 \text{ [kg.m}^{-3}\text{]}$$

$$PEC_{\text{effluent}} = PEC_{\text{influent}} * F_{\text{STP,water}} = 0.0227 * 0.988 = \underline{0.0225} \text{ [kg.m}^{-3}\text{]}$$

Dimensions TGD/UBA-method

$$C_{\text{water}} = (C_{\text{proc,emul}} * F_{\text{form}} * (F_{\text{conc/water}} + 1)) / (F_{\text{conc/water}} * K_{\text{OW}} + 1) * (1 - F_{\text{elim}}) \text{ and}$$

$$V_{\text{water}} = V_{\text{proc,emul}} / (F_{\text{conc/water}} + 1)$$

$$PEC_{\text{local}3,\text{infl}} = (C_{\text{proc,emul}} * V_{\text{proc,emul}} * F_{\text{form}} / (F_{\text{conc/water}} * K_{\text{OW}} + 1) * (1 - F_{\text{elim}})) / CAP_{\text{STP}}$$

$$PEC_{\text{local}3,\text{infl}} = (2.5 * 1/10 * 1 / (0.05 * 200 + 1) * (1 - 0) / 1) = 0.0227 \text{ [kg.m}^{-3}\text{]}$$

$$PEC_{\text{effluent}} = PEC_{\text{influent}} * F_{\text{STP,water}} = 0.0227 * 0.988 = \underline{0.0225} \text{ [kg.m}^{-3}\text{]}$$

Dimensions TGD/TGD-method

$$PEC_{\text{influent}} = (C_{\text{water}} * F_{\text{form}}) / ID$$

$$C_{\text{water}} = C_{\text{proc,emul}} * (F_{\text{conc/water}} + 1) / (K_{\text{OW}} * F_{\text{conc/water}} + 1)$$

$$PEC_{\text{local}3,\text{infl}} = ((C_{\text{proc,emul}} * (F_{\text{conc/water}} + 1) * F_{\text{form}}) / (K_{\text{OW}} * F_{\text{conc/water}} + 1)) / ID$$

$$PEC_{\text{influent}} = (2.5 * (0.05 + 1) * 1) / (200 * 0.05 + 1) / 10 = 0.0239 \text{ [kg.m}^{-3}\text{]}$$

$$PEC_{\text{effluent}} = PEC_{\text{influent}} * F_{\text{STP,water}} = 0.0239 * 0.988 = \underline{0.0236} \text{ [kg.m}^{-3}\text{]}$$

Dimensions UBA/TGD-method

$$PEC_{\text{influent}} = (C_{\text{water}} * F_{\text{form}}) / ID$$

$$C_{\text{water}} = C_{\text{proc,emul}} * (F_{\text{conc/water}} + 1) / (K_{\text{OW}} * F_{\text{conc/water}} + 1)$$

$$PEC_{\text{local}3,\text{infl}} = ((C_{\text{proc,emul}} * (F_{\text{conc/water}} + 1) * F_{\text{form}}) / (K_{\text{OW}} * F_{\text{conc/water}} + 1)) / ID$$

$$PEC_{\text{influent}} = (2.5 * (0.05 + 1) * 1) / (200 * 0.05 + 1) / (2000/200) = 0.0239 \text{ [kg.m}^{-3}\text{]}$$

$$PEC_{\text{effluent}} = PEC_{\text{influent}} * F_{\text{STP,water}} = 0.0239 * 0.988 = \underline{0.0236} \text{ [kg.m}^{-3}\text{]}$$

WATERSOLUBLE METALWORKING FLUIDS:

Dimensions UBA/UBA-method

$$PEC_{\text{influent}} = (C_{\text{proc}} * V_{\text{water}} * F_{\text{conc/water}} * (1 - F_{\text{elim}}) * F_{\text{form}}) / CAP_{\text{STP}}$$

$$PEC_{\text{influent}} = (2.5 * 40 * 0.05 * (1-0.8) * 1) / 2000 = 0.0005 \text{ [kg.m}^{-3}\text{]}$$

$$PEC_{\text{effluent}} = PEC_{\text{influent}} * F_{\text{STP,water}} = 0.0005 * 0.988 = \underline{0.0005} \text{ [kg.m}^{-3}\text{]}$$

Dimensions TGD/UBA-method

$$PEC_{\text{influent}} = (C_{\text{proc}} * V_{\text{water}} * F_{\text{conc/water}} * (1 - F_{\text{elim}}) * F_{\text{form}}) / CAP_{\text{STP}}$$

$$PEC_{\text{influent}} = (2.5 * 1/10 * 0.05 * (1-0.8) * 1) / 1 = 0.0025 \text{ [kg.m}^{-3}\text{]}$$

$$PEC_{\text{effluent}} = PEC_{\text{influent}} * F_{\text{STP,water}} = 0.0025 * 0.988 = \underline{0.00049} \text{ [kg.m}^{-3}\text{]}$$

Dimensions TGD/TGD-method

$$PEC_{\text{influent}} = (C_{\text{water}} * F_{\text{form}}) / ID$$

$$PEC_{\text{influent}} = (2.5 * 0.05 * 1) / 10 = 0.0125 \text{ [kg.m}^{-3}\text{]}$$

$$PEC_{\text{effluent}} = PEC_{\text{influent}} * F_{\text{STP,water}} = 0.0125 * 0.988 = \underline{0.0124} \text{ [kg.m}^{-3}\text{]}$$

Dimensions UBA/TGD-method

$$PEC_{\text{influent}} = (C_{\text{water}} * F_{\text{form}}) / ID$$

$$PEC_{\text{influent}} = (2.5 * 0.05 * 1) / (2000/40) = 0.0025 \text{ [kg.m}^{-3}\text{]}$$

$$PEC_{\text{effluent}} = PEC_{\text{influent}} * F_{\text{STP,water}} = 0.0125 * 0.988 = \underline{0.0124} \text{ [kg.m}^{-3}\text{]}$$

EMISSIONS DURING INDUSTRIAL USE

CALCULATION ACCORDING TO THE USES-SCENARIO

$$PEC_{\text{influent}} = (Q_{\text{syst}} * F_{\text{suppl}} * F_{\text{proc}}) / CAP_{\text{STP}}$$

$$PEC_{\text{influent}} = (100 * 0.0035 * 2.5 * 0.05) / 2000 = \underline{0.000022} \text{ kg.m}^{-3}$$

Appendix 3: Tables OECD2001

Tables OECD2001

Table 1 Losses of neat oils with treatment of shavings and recycling of oil

Losses/annum	%	Emissions to
Evaporation and spray	2	Air
Overalls	2	Water
Leaks	2	Water/collected for re-use as waste oil
Internal reprocessing	1	Water/collected for re-use as waste oil
External reprocessing	10	Re-use as waste oil
Adsorbed to shavings	30	(27 %) 90% oxidised oil to air (3 %) 10% to landfill
Adsorbed to workpiece	3	(1 %) Water (2%) Chemical waste – (solvents/degreasants)

(Source: OECD2001)

Table 2 Losses of neat oils without treatment of shavings and recycling of oil

Losses/annum	%	Emissions to
Evaporation and spray	2	Air
Overalls	2	Water
Leaks	3	Water/collected for re-use as waste oil
Adsorbed to shavings	90	(81 %) 90% oxidised oil to air (9 %) 10% to landfill
Adsorbed to workpiece	3	(1 %) Water (2%) Chemical waste – (solvents/degreasants)

(Source: OECD2001)