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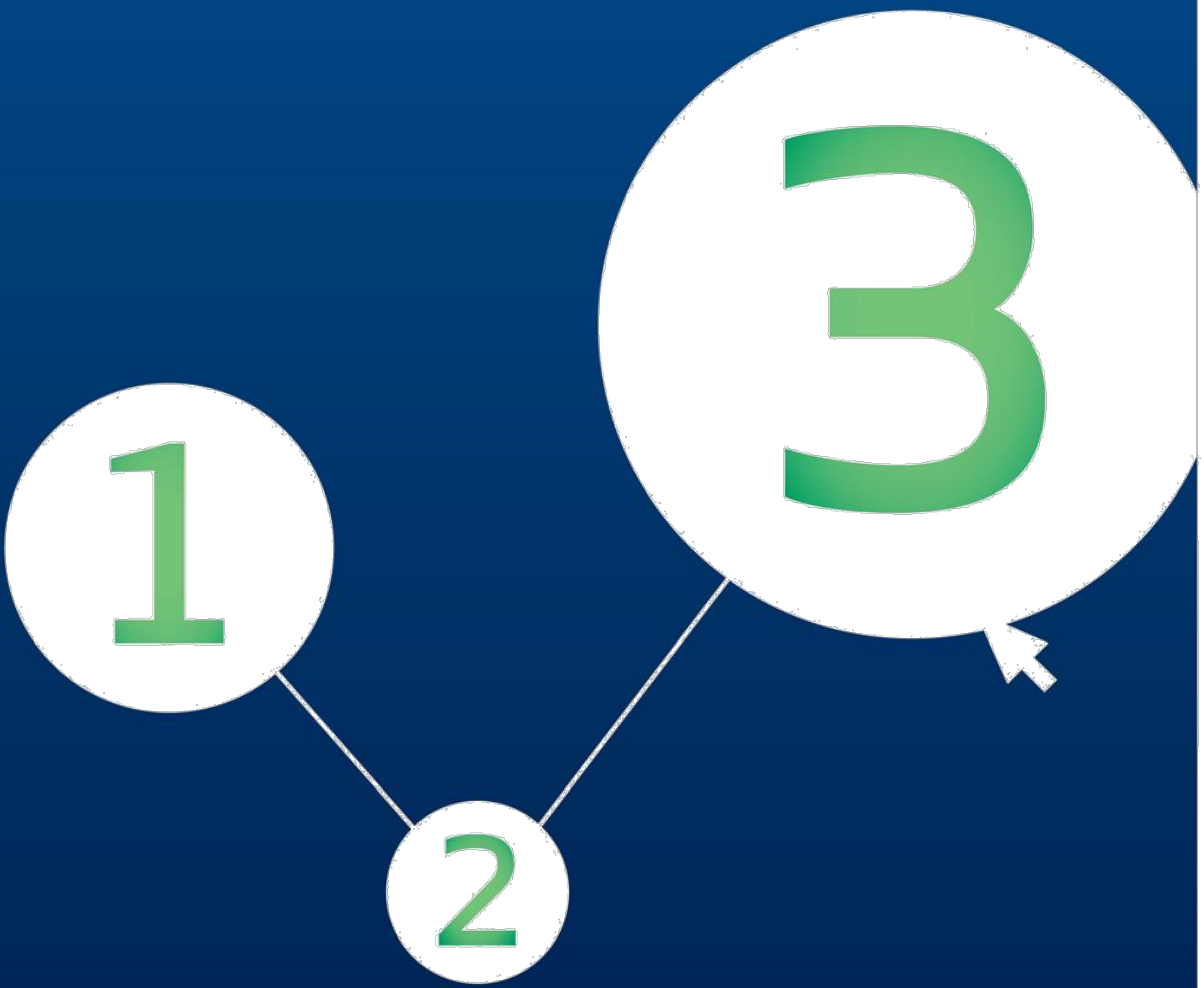
EMISSION SCENARIO DOCUMENT

Refinement of the Emission Scenario Document for Product Type 13

Working or cutting fluid preservatives



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Refinement of the Emission Scenario Document for working or cutting fluid preservatives (PT 13)

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Content

1 INTRODUCTION

The “TEGEWA MWF Working Group”[1] has agreed to fund a project to investigate the handling and disposal of used water miscible metalworking fluids. The project has been placed with the Fraunhofer Institute for Toxicology and Experimental Medicine (Fraunhofer ITEM).

Within this report, the term “water miscible metalworking fluids” (wm mwf) refers to emulsifiable mwf but also water soluble mwf. A third type of metalworking fluids are oils, however, no biocides are needed for these and therefore they are not further discussed in this document. Whereas the previously used EUBEES ESD differentiates between water soluble and emulsifiable mwf, in this document they are usually discussed together, as the amount of water soluble mwf is small compared to emulsions and the resulting waste is mostly treated together with the emulsifiable types. In order to fulfill EU wide legislation concerning the maximum COD (chemical oxygen demand) and other pollutants the oil content has also to be removed for the soluble types, i.e. although there is no actual emulsion, some kind of splitting procedure has to be in place. Thus, the developed scenarios are able to also cover water soluble mwf as a worst case (see also chapter 4.1.1 and detailed information in Excel tables).

The aim / scope of project is to evaluate the available emission scenario documents (EUBEES ESD, OECD ESD No. 28), compare them with actual situations found in industry and other up to date information and to revise the suggested algorithms in order to remove unrealistic assumptions or defaults and obtain a realistic worst case approach to estimate environmental exposure.

In the course of the project different aspects of the environmental exposure to biocides due to use and waste treatment of metalworking fluids have been evaluated in summarised in a number of status reports (see Appendices A-C). It is felt that the information gathered over the last months is now sufficient to derive a reasonable suggestion for a new Emission Scenario Document.

This document includes therefore a short summary of the information gathered so far and the resulting scenarios suggested for the environmental exposure assessment for biocides used in metalworking fluids (chapter 4, Table 11).

[1] TEGEWA: Association for textile auxiliaries (TExtilhilfsmittel), tanning agents (GErbstoffe) and detergent raw materials (WAschrohstoffe); mwf: metalworking fluids

2 AVAILABLE DOCUMENTS

- First report: "Gathering of information for the refinement of the Environmental Emission Scenario for metalworking fluids (PT13) under BPD", presented at TM II in 2013 (an excerpt can be found in Appendix E):
  - o Background information, ESD evaluation (Appendix E), first questionnaire results
- Addendum from October 2013, presented at TM IV (Appendix

  A) o Questionnaire updates, statistical considerations
- Status report from December 2013, discussed in e-consultation group with authorities (Appendix B)
  - o Questionnaire updates, refined analysis of BREF documents
- Available data to be included in ESD suggestions (Appendix C)
  - o Questionnaire updates, evaluation of Pollutant Release and Transfer Register (PRTR)

3 INFORMATION GATHERED IN THE COURSE OF THE PROJECT - SUMMARY

3.1 BACKGROUND INFORMATION

During the first stages of the project background information concerning legislation and available emission scenario documents (ESDs) has been collected, summarised and been presented at TM II in 2013 (Report: "Gathering of information for the refinement of the Environmental Emission Scenario for metalworking fluids (PT13) under BPD/").

It has been shown that in the EU emulsions are categorised as hazardous waste, therefore they are not allowed to be led directly into rivers or other water compartments without prior treatment and removal of the oil content. In addition, a large number of local regulations are available for the different EU countries which regulate allowed concentrations of various hazardous substances in waste water. However, most limitations refer to summary parameters (e.g. biological oxygen demand (BOD)) or substances not related to biocides (e.g. heavy metals). However, limitations concerning the biological or chemical oxygen demand also mean that neither emulsions nor water soluble mwf can be led into surface water compartments or municipal sewage treatment plants without a prior removal of the oil content.

Concerning the available ESDs it has been identified that the two documents under discussion (EUBEES ESD and OECD ESD No. 28) are designed to represent different scenarios. While the EUBEES ESD is intended to reflect waste treatment companies the OECD ESD represents small end-user companies.

In addition a number of inconsistencies have been identified. Overall the findings suggest that neither of the documents should be applied for the environmental exposure assessment concerning biocides used in metalworking fluids and a modified exposure scenario is needed.

3.2 QUESTIONNAIRES (END-USERS AND WASTE MANAGEMENT COMPANIES)

A central part of this project is the circulation of questionnaires to end-users of water miscible metalworking fluids and waste management companies, which may receive used metalworking fluids. The questions contained in these questionnaires are based on the EUBEES ESD approach and given in Appendix D.

Overall, feedback from 28 end-users of wm (water miscible) mwf has been gathered, including 23 responses from Germany, 2 from Austria, 1 from Hungary, 1 from Portugal, 1 from Slovakia and 1 from Spain. In addition, two responses from German manufacturers of mwf and one from a Dutch manufacturer of mwf have been received. Following discussions with authorities in addition 5 datasets from Spain and Italy have been gathered from the PRTR (pollutant release and transfer register) and other available sources of information (see detailed Excel documents and Appendix C for evaluation strategy of PRTR). As in the general, European version of the PRTR no details concerning further handling of waste are summarised (e.g. if the waste is only stored, if PC treatment is performed), its evaluation for end-users is more difficult than for waste treatment companies, who usually provide some information on their webpages. However, the national Spanish PRTR database includes more information (see Appendix

C) and a general internet research resulted in one Italian steel processing company with an on-site treatment facility[2].

Concerning waste management companies we received 9 replies, including 2 from the Netherlands and 7 from Germany. These results were completed by an evaluation of the PRTR (Pollutant Release and Transfer Register) database (see Appendix C).

Detailed results gathered via questionnaires can be found in two additional Excel documents ("end-user results", "waste treatment companies results") which are distributed together with this document. In addition, discussions of subsets of this database are included in the previous status reports (Appendices A-C) and the report presented at TM II in 2013 ("Gathering of information for the refinement of the Environmental Emission Scenario for metalworking fluids (PT13) under BPD").

The information gathered confirms that the available documents are not able to reflect reality in a sufficient way. In contrast to the currently available approaches, two scenarios (one for waste treatment companies and one for end-users of wm mwf) are suggested from the available data. On the other hand it does not seem to be necessary to introduce a separate scenario for water soluble mwf, as these are used in much smaller quantities and usually treated together with the emulsions:

No company was identified who used only water soluble mwf and of the 10 cases where water soluble mwf were mentioned, 8 treated the together with the emulsions while 2 indicated that their treat their emulsions on-site while water soluble mwf are externally treated. Fractions of water soluble mwf range from 2-20% of the overall mwf used by one site/company.

Concerning available treatment techniques for end-users ultrafiltration seems to be the most common one (19 responses), however, evaporation techniques were also indicated frequently (8 responses). No end-user response was identified were only chemical splitting was practiced and only one without details concerning emulsion splitting. Some end-users have both techniques available (6 responses).

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Concerning waste management companies often fewer details were available (e.g. only general reference to PC treatment), however, 4 companies are known to use ultrafiltration while 8 indicated evaporation techniques in their responses or on their webpages.

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Other techniques such as precipitation, osmosis or biological treatment are also mentioned by a number of end-users as well as waste management companies.

Moreover the default values given in the EUBEES ESD are a combination of highly conservative worst case assumptions which leads to unrealistically high overestimations of exposure instead of a reasonable worst case (e.g. 90th percentile, see introductory text of section 4 for further information). This refers for example to the dilution factors, i.e. the ratio between the waste water volume emitted per site and the capacity of the municipal STP ($D_{company->STP} = V_{STP}/V_{company}$) and the ratio between the water emitted by

[2] see http://www.euromec.net/public/files/II-%20WTP%20MINIMEC%20for%20Steel%20Industry%20-%20EN-300.pdf, http://www.euromec.net/public/files/II-%20WTP%20Marcegaglia%20RO%20-%20EN-306.pdf, http://www.euromec.net/public/files/II-WWTP%20Marcegaglia%20Industrial%20WWTP%20-%20EN-92.pdf

the STP and the receiving river ($D_{STP->river}$ = V_{river}/V_{STP}). Furthermore, common biocide concentrations are usually much lower than suggested in the ESD as toxicity and applicable biocide concentrations are not independent of each other.

In most cases the waste water is emitted into a municipal sewage treatment plant and not directly into the receiving compartment. At sites where this is not the case on-site biological treatment is practiced (→ consistent with EUBEES). Apart from that, a number of waste water treatment techniques are applied, including always one step to separate oil and water (ultrafiltration, evaporation, chemical methods etc.; consistent with EUBEES), whereas the oil fraction is usually recycled or incinerated, but also further purification steps for the water phase (e.g. additional biological treatment, precipitation, see BREF document on waste gas and waste water treatment for further examples). Although no standard treatment can be defined it is therefore considered to be very likely that some kind of emission reduction will happen in the process that exceeds the reduction reached via water/oil separation. A value of 0% elimination, as assumed in the EUBEES ESD (F_{elim} = 0, emulsion splitting excluded), is therefore considered to be unrealistic.

3.3 EVALUATION OF POLLUTANT RELEASE AND TRANSFER REGISTER (PRTR)

It became apparent in the course of the project that especially waste management companies from EU countries other than Germany are often reluctant to submit information for this project. It has therefore been decided to amend the data gathered directly from waste management companies by information published in the pollutant release and transfer register (PRTR). Details of this procedure are described in the internal status report from April 2014 (Appendix C). Results have been summarised together with questionnaire responses in the submitted Excel document ("waste treatment companies results"). Although the amount and quality of available information differs between countries it has been possible to identify 29 companies which treat emulsions at their premises. This includes companies in Germany, the Netherlands, UK, Italy, Spain, Hungary and Poland. Additional information found in publicly available French databases has been provided by the French authority.

As a result information concerning treatment techniques, emitted waste water volumes and therefore, also dilution factors for the facilities could be extracted and combined with the questionnaire results (see attached Excel document) in order to verify data gathered via direct contact and give an overall picture which is representative for all regions of the EU.
During later stages of the project also some datasets for end-users of wm mwf have been extracted, including 4 sites from Spain and one from Italy.

3.4 STATISTICAL CONSIDERATIONS

It has been identified during the evaluation of the questionnaire responses and the contents of PRTR, that one crucial point influencing the final exposure values are the dilution factors (see earlier Chapters) . Available data as presented in earlier chapters and the Appendices of this report suggest that the dilution factors given in the EUBEES ESD ($D_{company->STP}$ = 10; $D_{STP->river}$ = 10) are much lower than found in reality, which leads to much higher environmental exposure concentrations than would be realistic.

We have therefore further evaluated the probability that a comparably large waste treatment company will release its waste water into a small municipal treatment plant. Details of this process have been described in the status report presented at TM IV in 2013 (Appendix A)

Taking into account annual tonnages of water based mwf and some general information about STPs and mwf end-users it could be shown that the combination of large waste treatment plants (i.e. 200 or more m^3/day waste water output) and small municipal STPs (i.e. 2000 m^3/day water treatment) is highly unlikely: Theoretically < 1 large waste treatment plant releases its waste water into a small STP in the EU (although in reality it would obviously be either one or no site at all) . This supports the previous finding that dilution factors are usually much higher in this industry sector than currently recommended.

3.5 EVALUATION OF RISK MITIGATION MEASURES (RMMS)

In the “Best available technique reference document” (BREF document) on common waste gas and waste water treatment techniques (see ref. [1], BREF draft version (2011), pp. 175 ff) a number of possible treatment techniques for emulsions is described. Exposure reduction efficiencies are listed for some examples substances, suggesting worst case reduction values, which correspond to the lowest exemplary exposure reduction from the BREF document (rounded down), and are listed in Table 14 in Appendix B.

Most removal efficiencies are substance dependant and it is difficult to derive standard default values or alternatively simple advice for the derivation of a substance specific value. Therefore they have not been included into the final suggestions in section 4.

However, there are some risk mitigation measures for which it is considered to be possible to use them in the course of the exposure assessment with only minor uncertainties:

- *General emulsion splitting techniques (e.g. ultrafiltration, chemical splitting):* This RMM is already implemented in the EUBEES ESD via the partition coefficient and it is considered to be reasonable to keep this part of the algorithm. For ionisable substances a correction may be necessary as described in section 4.1.5.2.

- *Splitting of emulsion by evaporation of the water phase:* In this case a large part of non-volatile substances will remain in the oil content which is usually incinerated or recycled, but not led into surface water. The water phase is collected in a condenser and will often be recycled (especially when the technique is used for on-site treatment), which leads to 0% biocide release into the environment. However, it is also possible that it is led into the responsible municipal sewage treatment plant. According to the BREF document on waste water and waste gas treatment in the chemical sector [2][3] common operating conditions are 12-20 kPa and 50-60°C. The systems are closed in order to avoid release of steam or other substances[4]. The exhaust air will be cleaned with a carbon filter [3]. Furthermore, the condensing steam can be used to heat the evaporating fluid and save energy costs.

  According to further information provided by a representative of the VSI Schmierstoffe (association for lubricants) evaporators are usually equipped with a water jet pump and the resulting vapour phase is led into the distillation tower.

[3] http://eippcb.jrc.ec.europa.eu/reference/BREF/cww_bref_0203.pdf

[4] see e.g. http://www.wastewater-evaporator-h2o.com/en/vacuum-evaporator/vacudest/vacudest-xxl/vacudest-xl-30000-detail; http://www.tieser.de/de/produkte/verdampfer/index.php, http://www.wwdmag.com/wastewater/evaporation-wastewater-treatment-alternative

- The amount remaining in the water phase can theoretically be estimated using the vapour pressure of each substance and compare it with the vapour pressure of water at the same temperature (see Appendix C). However, as modern evaporators are usually operated in series (see footnotes 3 and 4), i.e. the water is purified with several evaporation steps, the final release of biocide into surface water is considered to be negligible as long as the vapour pressure is small enough ($p_{vap} < ½\ p_{vap\ H2O}$). For higher vapour pressures 0% exposure reduction from wastewater can be used as a worst case. *biological waste water treatment:* This RMM is already implemented in EUSES via Simple Treat and the available data suggest that biological treatment is indeed always practiced before waste water is led into a water compartment.

4 SUMMARY AND CONCLUSION: SUGGESTIONS FOR THE REPLACEMENT OF THE EUBEES ESD

On the basis of the information described in the previous chapters and the Appendices a tiered approach for exposure assessment has been developed.

The first step as laid down in chapter 4.1 refers to standard conditions and default values which are intended to represent a reasonable worst case.

The second step is based on step 1, however offers additional risk mitigation measures which are applied in reality but are – as there is no standard treatment for emulsions – not always present. If these have to be applied during the risk assessment it has to be ensured by the manufacturers of the biocide as well as the corresponding end-users and waste treatment companies that these measures are met.

Defaults suggested in the following sections are mostly based on the data obtained via questionnaire responses, from the PRTR and the European STP database as detailed in the separate Excel sheets. Average and median values are included in the sub-sections as far as available.

However, we refrain from a detailed presentation of percentiles, as these are only of limited reliability for databases < 100 datasets: Percentiles divide each set of data points into 100 part with an identical number of data points in each part. This is theoretically possible also for less than 100 datasets, but obviously the informative value is much more limited. A similar example would be a linear regression through a small number of data points - in an extreme case this can mean only 2 data points: Theoretically this is possible and results, as an example, in remarkably low statistical standard errors for the slope. However, the results of this regression are highly influenced by individual errors related to the single data points (large confidence).

Apart from this, using percentiles, especially very conservative ones, for the derivation of input values, results in an accumulation of this conservativeness: If a result is obtained by multiplication of two parameters derived from $90^{th}/10^{th}$ percentiles, the result will represent approximately the 99^{th} or 1^{st} percentile of the actual distribution (0.1 x 0.1 = 0.01). If, on the other hand, $25^{th}/75^{th}$ percentiles are used, the result represents approximately the $95^{th}/5^{th}$ percentile, which is still more conservative than the $10^{th}/90^{th}$ percentile which is often recommended as a worst case approach (see e.g. TGD part 2, ECHA guidance R14 for human exposure, ConsExpo general fact sheet[5]). Thus, although we are aware that there are different approaches (suggesting both higher and lower percentiles than the $90^{th}/10^{th}$ depending on document/model and available database), this is considered to be a reasonable approach.

In other words, the combination of worst case parameters in one scenario is less likely than each of the parameters alone.

[5] R14 (http://echa.europa.eu/documents/10162/13632/information_requirements_r14_en.pdf), p.4: „To address the reasonable worst-case, it is recommended to select the 90th percentile of the exposure distribution over the whole spectrum of likely circumstances of use in a particular scenario (see also Paustenbach 2000)."
TGD part 2 (http://echa.europa.eu/documents/10162/16960216/tgdpart2_2ed_en.pdf), p20: "The mean of the 90th percentiles of the individual sites within one region is recommended for regional PEC determination."

This is most likely also one of the reasons why the EUBEES results cannot reflect the companies represented in the questionnaires and leads to high overestimations.

4.1 TIER 1 ASSESSMENT

4.1.1 Basis of exposure assessment

The equation used for the exposure assessment is based on the EUBEES ESD. However, it has been converted in order to allow for a direct insertion of the dilution factors and the applicable concentration of the biocide substance (see later).

As already explained in earlier chapters, the data suggest the application of two scenarios, one for end-users of wm mwf who treat their waste on-site, and one for waste management companies who receive waste from smaller mwf using companies who do not refer to on-site treatment.

Water soluble and emulsifiable mwf are usually treated together and moreover, the amount of water soluble mwf is comparably small, therefore no separate scenario for water soluble mwf is proposed (see also section 3.2).

All waste waters resulting from the use of wm mwf will be led to biological treatment (mostly to municipal STPs) before discharge into the environment. Concerning the use of STP sludge as a fertiliser it is recognised that this may not be applicable for all member states, as there may be the tendency to use only (or additional) on-site biological treatment before release into municipal STPs in some countries. In these cases the on-site STP sludge will probably be incinerated and the release into soil via agricultural uses will be negligible. However, this situation is highly variable, therefore the standard default application of sludge on agricultural soil as implemented in EUSES is suggested to be used as a worst case.

4.1.2 Concentration of biocide in the machine ($C_{biocide, dil}$)

It has been determined during early stages of the project that there exist many possibilities concerning the actual use pattern of biocides in wm mwf, i.e. regular, almost continuous dosing of biocide to prevent contamination, shock-dosing in case of bacteria/fungi contamination, dosing via treated concentrate, separate dosing of biocide product and all combinations of these sub-scenarios.

The easiest way to combine these possibilities into one algorithm is the direct use of the biocide concentration in the diluted wm mwf as input parameter instead of the fraction of biocide in the concentrate and the fraction of concentrate in diluted mwf. Thus, the EUBEES equation has been converted in order to allow for a direct input of this parameter[6].

As the toxicity of a substance and applicable concentration range are not independent of each other it is highly recommended to use substance specific concentration ranges for the exposure assessment[7].

[6] If only fraction of biocide in the concentrate and the fraction of concentrate in the diluted mwf are known, $c_{biocide, dil}$ can either be derived from these two values or – for the sake of user friendliness – an alternative algorithm can be used as described in section 4.4. This alternative algorithm is in general identical the the one described here, it only has been converted in order to allow for the input of other parameters.

[7] If the biocide is only dosed via concentrate it has to be taken into account for the derivation of $c_{biocide,dil}$ that it depends on the concentration of biocide in concentrate as well as the fraction of concentrate in diluted mwf: If a certain $c_{biocide,dil}$ is to be maintained different concentrations of

As a default for the fraction of concentrate in the mwf the lowest possible value (5%) should be chosen as a worst case in this case in order to maximise the amount of biocide in the water phase after water/oil separation.

The default values currently implemented in the EUSES algorithm and summarised in Table 1 (concentrate fraction F_{conc} = 5-20%, biocide concentration in concentrate $C_{biocide, conc}$ = 4-5%) have been shown to give conservative results and can therefore also be safely applied if no information should be available (see also section 4.4). However, this will usually lead to much higher exposure values beyond the reasonable worst case. This applies to both scenarios, on-site treatment as well as discharge via external waste treatment companies.

Biocide concentrations found in the questionnaire results range from 0.000075-1% (highest concentrations found for system cleaner) in diluted mwf, while those derived with EUBEES ESD / EUSES defaults range from 0.2-1%.

If all applications should be covered and no substance specific application concentrations are available, two worst case scenarios based on the available defaults should be estimated (two scenarios, as the fraction of concentrate in diluted mwf influences the release at two points (derivation of $C_{biocide,dil}$ and distribution between water phase and oil phase during splitting), these influences go in different directions and the resulting overall worst case depends also on the K_{ow}):

- F_{conc} = 5%, $C_{biocide, conc}$ = 5 %, i.e. $C_{biocide,dil}$ = 0.25 %
- F_{conc} = 20%, $C_{biocide, conc}$ = 5 %, i.e. $C_{biocide,dil}$ = 1 %

Table 1: EUSES defaults: Fraction of concentrate in diluted mwf and fraction of biocide in concentrate

Activity	**Fraction of concentrate in diluted wm mwf (applies to all wm mwf)**
Broaching	0.2
thread cutting	0.1
deep hole drilling	0.2
parting off	0.1
cylindrical milling	0.1
turning, drilling, automation work	0.1
Sawing	0.2
tool grinding	0.06
cylindrical grinding	0.05
centreless grinding	0.06
surface grinding	0.05
Type of mwf	**Bactericide fraction in concentrate**
traditional emulsions and water soluble mwf	0.04
synthetic emulsions	0.05
	Fungicide fraction in concentrate
All wm mwf	0.001

biocide in the concentrate may be necessary or, if only one concentration of biocide in the concentrate is available, different resulting $c_{biocide,dil}$ may appear in reality, of which obviously the largest should be chosen as a worst case.

4.1.3 Fraction of waste water caused by mwf (F_{mwf}) / fraction of substance of relevance in mwf (F_{form})

End-users

For many end-user companies it was indicated by the providers of the questionnaire responses that not all of the waste water was caused by wm mwf, i.e. either by cleaning water or even by completely different activities. However, there are also cases where either no information about this was available or all waste water seems to come from the use of wm mwf in the company (see Table 2).

Table 2: End-user results: Fraction of waste water caused by mwf consumption

Company No.	% mwf of waste water[8]
3	0.3
4	4
5a	44
9	100
10	88
11	15
14	100[9]
15	20
17	14
18	0.9
21	20
22	29
24	17
26	28
27	4
28	0.03
32	72
33	15
34	38
35	3
Average	31
Median	19
75 percentile	< 40

Therefore a conservative Factor of 1 is suggested for this parameter in the end-user (on-site treatment) scenario.

The same applies to the fraction of the substance of relevance: There are many companies using several biocide substances depending on application area and purpose (see Table 3). However, there are some which only use one substance, so again a conservative factor of 1 is suggested.

[8] Estimated with mwf waste water amounts and overall waste water amounts if given, otherwise with the concentrate tonnage, 5% concentrate in mwf assumed and overall waste water amounts as given.

[9] Estimated fraction > 100% (e.g. due to concentrate fraction > 5%), therefore set to 100 %.

Table 3: End-user responses: Number of biocides used per site and maximum use fraction (i.e. maximum percentage of mwf equipped with one substance); For details see separate Excel table.

Company No.	Are different biocides used in one company?	Maximum fraction for one biocide (%)
1	no information available	no information available
2	*no information available / no end-user*	*no information available/ no end-user*
3	yes	80%
4	three different biocides (shock dosing, alternating two biocides), fungicide if necessary.	no information available
5a	different biocides depending on solubility for different wmf, not depending on process	80%
5b	different biocides depending on solubility for different wmf, not depending on process.	80%
6	only one biocide	100%
7	*no end-user*	*no end-user*
8	*no end-user*	*no end-user*
9	yes	no information available
10	two biocides	no information available
11	no biocides are used	not applicable
12	three different biocides; all mwf treated with a combination of those	100%
13	different due to different solubilities in soluble/emulsifiable mwf.	30-80%
14	yes, four different substances	100 % for all substances.
15	yes, no separation concerning processes, but one substance cannot be used in soluble.	80%
16	three differenc biocides	Only 10% treated with biocides at all.
17	no information available	no information available
18	yes	30-80%
19	three different substances	100%
20	different biocides specific per application, two substances	100%
21	4 biocides; between 14 and 2400 kg/year per substance	no information available
22	different biocides, > 10 products and substances	50%
23	two biocides for bacteria and fungi	100%
24	three biocides	90%
25	no additional biocides, only pretreatment	no information available
26	different biocides: bactericide, fungicide and system cleaner	up to 100%
27	mwf product 1 only fungicide, product 2 no biocide, product 3 both. Fungicide for central machines as pretreatment measure and bactericide if needed.	100% of mwf with fungicide; 3.6% of mwf with bactericide
28	two biocides for different applications apart from preconservation; 0.18 t/a biocide,	~80% (preconservation). No information about additional dosing.
29	three different biocides for dosing during use; if required shock dosing in addition	25-35% fraction of biocide substances / for preconservation; 75% of the mwf volume shock dosing with one of the biocides

Company No.	Are different biocides used in one company?	Maximum fraction for one biocide (%)
30	two biocides for additional dosing (which of these is used depends on contamination); two as pretreatment	30%
31	**three biocides (three products, 5 substances)**	**80%**
Average		**81 %**
Median		**80 %**
75th percentile		**100 %**

Waste management companies

In contrast to end-users who refer to on-site treatment, it is very unusual for waste management companies to treat only metalworking fluids. Considering the information which was given in the questionnaire responses, approximately 30% mwf in the treated emulsions seems to be a common case and results of the PRTR evaluation suggest that this value may still be highly conservative for a number of companies (see Table 4 for available information on F_{mwf}), resulting in an average mwf fraction of 20 % and a median of 9 %.

Moreover, the values documented in Table 4 are mostly derived from PRTR data and relevant waste codes for emulsions, which will not necessarily consist of 100% water miscible mwf. In general, end-users of mwf tend to store their waste together as far as waste types (i.e. legal restrictions) allow it, therefore often the produced waste may include mwf, other emulsions, cleaning water / solutions and other water / oil mixtures (see also Table 2). This supports that a fraction of 50% mwf in waste (f_{mwf}) is indeed a conservative choice for this parameter concerning the external waste treatment scenario.

The same arguments apply for the fraction of one biocide substance in this mixture: As these companies usually collect their waste from different companies it is very unlikely that all companies will contribute the same biocide substance in the wm mwf. In addition, already at end-user sites often several biocidal substances are used, depending on the type of mwf, process and dosing strategy (shock dosing, pretreatment etc.) (see Table 3), and although this information is not considered to be sufficient for a reduction of F_{form} for the end-user scenario it further decreases the probability for waste management companies to receive only used mwf which are treated with one specific substance.

Overall it is therefore suggested to use a conservative factor of 0.5 as a default for the fraction of mwf in the treated emulsions as well as for the fraction of the substance of relevance (i.e. 50% mwf in waste and 50% biocidal substance in mwf).

Table 4: Fraction of metalworking fluid in treated waste (waste management companies, for details see separate Excel table).

Company number[10]	Maximum fraction of mwf in waste (%)
4	9
5	40
8	30
12	35
27	9
28	2
31	3
32	0.4
33	2
34	100
35	3
36	11
37	9
38	16
39	10
40	1
41	4
42	53
43	16
44	50
45	17
Average	20
Median	9
75^{th} percentile	< 40

4.1.4 Dilution factors ($D_{overall} = D_{company\text{->}STP} \cdot D_{STP\text{->}river}$)

In general, the dilution factor for the release from a company (end-user or waste treatment site) is defined as follows:

$D_{company\text{->}STP}$
$= CAP_{STP} / V_{wastewater}$
$\approx CAP_{STP} / V_{proc,emul}$

With CAPSTP being the capacity of the receiving sewage treatment plant, $V_{wastewater}$ being the volume of the released waste water and $V_{proc,emul}$ being the volume of the corresponding mwf.

The dilution for the second release step is defined in a similar way:

$D_{STP\text{->}river}$
$= V_{river}/CAP_{STP}$

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10 Overall, 39 replies from waste management companies have been received. For companies not listed in this table no information about the fraction of mwf could be gathered.

With V_{river} being the daily flow rate of the receiving river.

The data obtained via questionnaires and from publicly available sources of information (PRTR, EU STP database, various local sources of information; for detailed information see separate Excel tables: “end-user results”, “waste treatment companies results”) strongly suggests that standard dilution factors of 10 for release into the municipal STP and for release into the river (i.e. overall dilutions of 100) as suggested by the EUBEES ESD are unrealistically low.

This is also in line with the plausibility check detailed in Appendix A.

One explanation for this could be a dependence between city size and usual size of allocated companies: There is a high variability concerning release waste water volumes, i.e. there may exist large companies with high releases of waste water, however, these are not connected to small sewage treatment plants. A large company with many employees is usually not located in a small town as all employees need housing space and a certain infrastructure which leads to a larger municipal sewage treatment plant.

Therefore, the equation Table 6 has been converted to allow for a direct insertion of the dilution instead of release volumes.

End-users

Available data for end-users of wm mwf from questionnaires have been used to derive dilution factors for these sites. The results bare some uncertainty, as not always the overall amount of waste water was given but sometimes only the waste water from emulsions or only the amount of waste, which would lead to higher dilutions. However, this is not expected to lead to underestimations of the risk as the fraction of mwf in the waste is suggested to be 1 as a default for this scenarios (chapter 4.1.3), i.e. even if the actual amount of waste water would be larger due to cleaning water or other wastes, the higher dilution factor would be compensated by the neglect of the reduced fraction of mwf in the waste water.

The results of this evaluation lead to an average overall dilution factor of ~499106 ($D_{overall} = D_{company->STP} \cdot D_{STP->river}$), a dilution factor for release into the municipal STP of 10592[11] ($D_{company->STP}$), and a dilution for the release into a river of 13084 ($D_{STP->river}$).[12] The corresponding median values are 970 ($D_{company->STP}$), 297 ($D_{STP->river}$) and an overall dilution $D_{overall}$ of 329364 (see also Figure 1, Figure 2 and Table 5). 25th percentiles are > 160 ($D_{company->STP}$) and > 40 ($D_{STP->river}$).

Although some isolated dilution factors for the first or the second dilution step are below 100, these are in almost all cases compensated by the other one, resulting in only one site with an overall dilution below 10000 (5th percentile $D_{overall}$ > 15000).

Especially concerning the first dilution steps results are supported by general, statistical considerations concerning average end-user company outputs in combination with average STP capacities as extracted from the EU wastewater treatment database (see Appendix F).

Thus, it is considered to be a reasonable worst case to use 150 for the first dilution step ($D_{company->STP}$) while keeping the standard default of 10 for the second step ($D_{STP->river}$),

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[11] When both was available, the dilution of the overall amount of waste water has been chosen and not the dilution only related to mwf.
[12] The three average values were estimated separately, for details see attached Excel documents.

resulting in an overall dilution of 1500, which is more than a factor of 10 below the 5th percentile of the collected data points.

This applies to release into a river, while for release into a lake or the sea a standard dilution of 100 for the release from the STP is commonly applied.

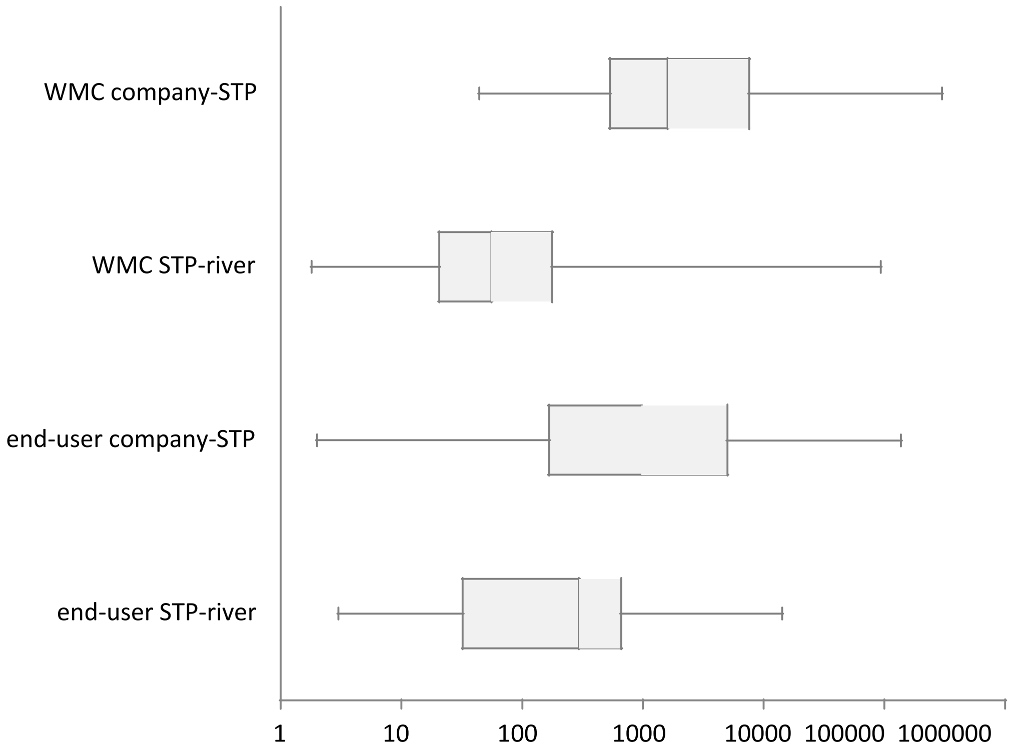

Figure 1: Dilution factors for both separate dilution steps ($D_{company->STP}$, $D_{STP -> river}$) for waste management companies (WMC) and end- users. Boxes: 25th and 75th percentile. Whiskers: Complete range.

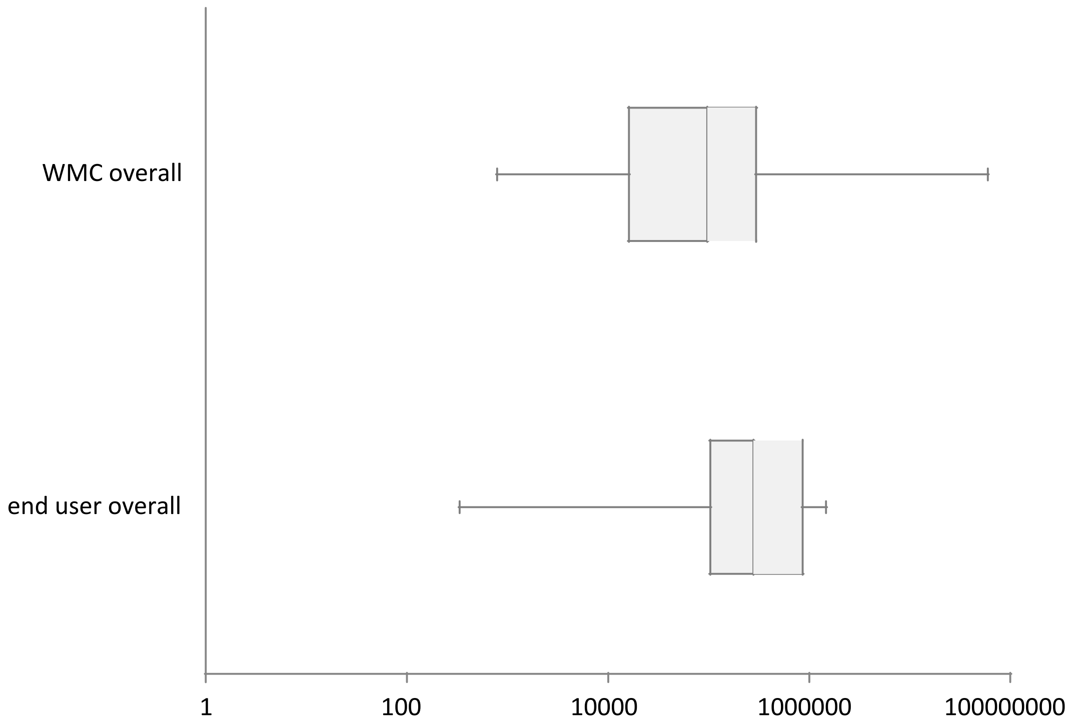

Figure 2: Overall dilution factor $D_{overall}$ for end-users and waste management companies (WMC). Boxes: 25th and 75th percentile. Whiskers: Complete range.

Table 5: Statistical information on dilution factors for end-users and waste management companies.

End users	$D_{company \rightarrow STP}$	$D_{stp \rightarrow river}$	$D_{overall}$ **(derived from single data sets)**
number of values	21	17	18
Average	10592	13084	499106
Median	970	297	329364
	25th percentile > 160	25th percentile > 40	25th percentile > 100000 5th perentile > 15000
Waste management companies	$D_{company \rightarrow STP}$	$D_{stp \rightarrow river}$	$D_{overall}$ **(derived from single data points)**
number of values	35	27	28
Average	15807	3784	3540640
Median	1600	56	97013
	25th percentile > 530	25th percentile > 15	25th percentile > 15000 5th percentile > 4500

Waste management companies

All dilution factors from questionnaire responses are based on overall amount of waste water. In some specialised cases this may refer to 100% waste water originating from mwf, but in most cases it reflects a mixture of liquid, water based wastes.

In case of the PRTR evaluation this was not possible, however, as most PRTR versions do not discriminate between different types of waste the results are still expected a reasonable worst case concerning the overall amount of waste water (for details see Appendix C).

An evaluation of the dilution factors derived from questionnaire responses and the PRTR database lead to an average value of 15807 for the release of waste water into the municipal sewage treatment plant, an average value of 3784 for the release from STP into the river system or sea[13] and an overall average dilution factor of 3540640.

Corresponding median values are 1600 for the first dilution step, 56 for the release from STP to river and 97013 for the overall dilution (see also Figure 1, Figure 2 and Table 5). Of the available dilution factors concerning the step from waste treatment facility to STP only two are smaller than 100 (which however both still lead to overall dilutions above 10000), while for the second dilution step (STP→ river/sea) 13 facilities seem to have values lower than 100. These values can at least partly be explained by a number of uncertainties, e.g. river volumes are sometimes not available for the exact location of the STP or even only as an average for the whole river. Moreover there is a number of locations / rivers systems, where no volume per day value could be identified at all for the river in question.

Thus, overall the information currently available on waste management companies is not sufficient to support dilution factors above 10 in case of this second dilution step ($D_{STP->river}$) but it is considered to be more than sufficient to justify the application of a dilution factor of 100 for the release of waste water into the municipal sewage treatment system ($D_{company->STP}$) This leads to an overall dilution factor ($D_{overall}$) of 1000, which is a factor of ~5 below the 5th percentile concerning the collected data points.

4.1.5 Elimination before the municipal treatment plant

4.1.5.1 Degradation during industrial use (F_{degr})

In the original EUBEES ESD no degradation during use is assumed (F_{degr} =0) . In many cases this will be overly conservative as it is often practiced to stop dosing of the biocide some time before the mwf is removed from the installation in order to save biocide and, as a consequence, money. However, there is not enough information available to derive a refined default for this parameter.

Instead, it is suggested to remove this parameter completely from the equation. The time between the last biocide dosing and the removal of mwf is considered to be included in the degradation during storage ($F_{elim,storage+more}$ see section 4.3.2).

[13] For comparison:
The EUBEES ESD suggests 10 for both dilution steps, i.e. an overall dilution of 100.
In earlier stages of the project dilution factors of 100 for both steps (i.e. an overall dilution of 10000 from facility to river) had been suggested.

4.1.5.2 Biocide removal during splitting of emulsion **($F_{split,evap}$ or $F_{split,kow}$)**

The EUBEES ESD already uses the partition coefficient (K_{OW}) in order to implement the removal of biocide from the water phase via emulsion splitting.

As our research has shown that emulsion splitting is always done before further treatment and release into surface water compartments this approach is considered to be reasonable.

The implementation of K_{ow} covers the most commonly applied emulsion splitting techniques (e.g. chemical splitting, ultrafiltration) and therefore the majority of cases.

For ionisable substances, a correction of the available partition coefficient may be necessary, as the K_{OW} usually refers to the neutral species. A correction factor (corr) for this purpose, which has to be multiplied with the available K_{ow}, can be found in the Technical Guidance Document (TGD Part II, Appendix XI on inonisable chemicals [4]):

$$Corr = (1+10^{A\,(pH - pKa)})^{-1}$$

where:
A = 1 for acids, -1 for bases
pH = pH-value of the environment: For used mwf the pH is usually at approximately 8. However, if more specific information about the pH is available concerning the waste mixture during emulsion splitting, this may be used instead.
pKa = acid/base dissociation constant

If it is known that a substance is ionisable but necessary data for a correction are not available, as a worst case 100% release into the water phase should be assumed.

In cases where a D_{OW} is available (distribution between octanol and water corresponding to the sum of all species) this value can be used instead of K_{ow} and no correction is necessary.

Splitting via evaporation of the water phase, which is also practiced sometimes in reality, is not covered by this approach, as in this case the removal efficiency depends on the biocide's vapour pressure.
It is therefore suggested to perform exposure estimations for both versions according to the defaults and algorithms suggested in Table 6. For a tier 1 assessment both techniques should lead to a safe scenario.

This applies to both scenarios, on-site treatment as well as treatment by external waste management companies.

4.1.5.3 Biocide removal during further physico chemical (PC) treatment ($F_{elim,\,x}$)

As detailed in section 3.5 this subject is difficult to implement on a general basis, as there is no standard treatment for emulsions, except the fact that the emulsion is always splitted before further treatment and in general, the non-water fraction of the mwf has to be removed in order to meet laws regulating the maximum chemical or biological oxygen demand (COD or BOD). Some suggestions for refinements concerning PC treatment are given in chapter 4.2 for a tier 2 assessment, however, at this point it is considered to be reasonable to include no further options except elimination in the course of emulsion splitting (discussed separately in chapter 4.1.5.2).

Table 6: Suggestions for an ESD revision (adapted version of Table 15). Suggestions are mainly Tier 1 level. For refinement options see section 4.3 and Table 9.

Variable/parameter	Unit	Symbol	Value (release into municipal STP)		S/D/O/P
			end-user + on-site treatment	external waste treatment company	
Input					
Concentration of the chemical in the diluted metalworking fluid in the machine	[kg.m-3]	$C_{biocide, dil}$			S
Fraction of concentrate in diluted metalworking fluid	[-]	F_{conc}			S/P
Dilution factor company-> municipal STP[14]	[-]	$D_{company\text{->}STP}$	150	100	D/S
Fraction of metalworking fluid in treated volume	[-]	F_{mwf}	1	0.5	S/D
Fraction of metalworking fluid with chemical of interest in treated volume	[-]	F_{form}	1	0.5	S/D
Partition coefficient n-octanol/water, corrected if necessary (see discussion)	[-]	K_{OW}			S

14 The exact value for the dilution factor has to be calculated using the volume of waste water emitted from the company. However, for the sake of simplicity it has been assumed that the volumes of water and wm mwf ($V_{proc,emul}$) are the same. As the oil content of the mwf is usually well below 10% the uncertainty caused by this is considered to be negligible.

Variable / parameter	Unit	Symbol	Value (release into municipal STP)		S/D/O/P
			end-user + on-site treatment	**external waste treatment company**	
Input					
Fraction of elimination of the chemical during physical or chemical treatment	[-]	F_{elim}	0 (Tier 1) see Text (Tier 2)	0 (Tier 1) see Text (Tier 2)	S
Fraction of elimination of the chemical during emulsion splitting: Evaporation of water	[-]	$F_{split,evap}$	$p_{vap} <= ½\ p_{vap\ H2O}$: 0 $p_{vap} > ½\ p_{vap,H2O}$: 1	$p_{vap} <= ½\ p_{vap\ H2O}$: 0 $p_{vap} > ½\ p_{vap,H2O}$: 1	
Fraction of elimination of the chemical during emulsion splitting: All other splitting methods	[-]	$F_{split,kow} = (F_{conc} \cdot (1-F_{conc})^{-1} \cdot K_{ow}+1)^{-1}$			
Dilution factor municipal STP-> river (needed for estimation of PECfreshwater, see standard EUSES algorithm for details)	[-]	$D_{STP->river}$	10	10	D
Overall dilution	[-]	$D_{overall} = D_{company->STP} \cdot D_{STP->river}$	1500	1000	D
Number of release days (only required for regional concentrations)	[-]	N	300	300	D
Output					
Preservative concentration in municipal STP influent, with F_{split} being either $F_{split,evap}$ or $F_{split,kow}$	[kg m^{-3}]	$C_{STP,inf} = C_{biocide,dil} \cdot D_{company->STP}^{-1} \cdot F_{form} \cdot F_{split} \cdot (1-F_{elim}) \cdot F_{mwf}$			O

15 For a temperature of 25°C p_{vapH2O} = 3158 Pa (http://intro.chem.okstate.edu/1515sp01/database/vpwater.html)

4.2 COMPARISON WITH OTHER APPROACHES

An extensive comparison of the OECD No. 28 ESD and the EUBEES ESD has been done during the first stages of the project (see Appendix E). In addition, basic concepts and parameters of the OECD approach, the EUBEES ESD and the revised parameters discussed in this report have been summarised in Table 7. Not all parameters are comparable due to the different concepts used. However, the summary may give a general idea of differences concerning algorithm and default parameters.

Table 7: Comparison of available ESDs and new suggestions

			New suggestions	
	OECD ESD No. 28	EUBEES ESD	Suggestions: End-user, On-site treatment	Suggestions: Waste management company
General	No information	Release into municipal STP	Release into (municipal) STP	Release into (municipal) STP
Waste treatment	Splitting of emulsion (non-substance specific TOC reduction efficiency for chemical emulsion breaking (50 %) + ultrafiltration (70%))	Splitting of emulsion	Splitting of emulsion (two approaches)	Splitting of emulsion (two approaches)
	non-substance specific TOC reduction efficiency for precipitation (8 %)	F_{elim} = 0	F_{elim} = 0 (Tier1) see Text (Tier 2)	F_{elim} = 0 (Tier1) see Text (Tier 2)
Dilution factor STP-> river: $D_{company\text{->}STP} = V_{STP} / V_{company}$	No information	~10	150	100
Dilution factor company -> STP $D_{STP\text{->}river} = V_{river} / V_{STP}$	No information	~10	10	10
Overall dilution $D_{overall} = D_{company\text{->}STP} \cdot D_{STP\text{->}river}$	No information	~100	10000	1000
Fraction of biocide in concentrate	2 %	4 - 5%	substance specific	substance specific
Fraction of concentrate in diluted mwf	3-10%	5 - 20%	5 - 20% or substance specific	5 - 20% or substance specific
Fraction of metalworking fluids within the overall amount of emulsions (F_{form})	No information	100%	100%	50%
Fraction of mwf that is treated with one specific substance	No information	100%	100%	50%

Release days per year	247	300	300	300
Released biocide kg/day (before emulsion splitting or other treatment)	1.3-3.6 kg/day	500-2000 kg/day	not applicable (approach concentration based)	not applicable (approach concentration based)

In addition to the available ESD documents an approach has been developed by the Netherlands which combines features of the EUBEES ESD and the OECD ESD. It consists of two basic parts:

Tier 1: This part is almost identical to the EUBEES approach; however, the volume ratio V_{conc}/V_{H2O} in the diluted mwf has been set to 0.05[16] for emulsions and to 0.2 for water soluble mwf, which results in concentrate fractions of 0.048 and 0.17. Concentrations of biocide can be given in concentrate or in the diluted mwf. Releases per site range from 400-476 kg/day (50 g/l =5%, biocide in concentrate assumed, no emulsion splitting).

Tier 2: An annual mwf use per company is estimated with information from the OECD ESD via annual releases per installation and an average number of installations per site. Emulsion splitting as treatment technique is implemented and releases are considered separately for daily release (shavings, cleaning etc.) and release in the course of maintenance, when the installations are emptied completely.
Releases per site range from 7-321 kg/day (50 g/l =5% biocide in concentrate assumed, no emulsion splitting).

It is not further explained how the tiered approach has been developed, i.e. why OECD volumes (→ small US metalworking companies) are considered to be a refinement of the EUBEES (→ German waste management companies) (see also Appendix E; the approach and data background of both ESDs is fundamentally different).

[16] Volume ratio of 0.05 for emulsions not necessarily worst case: for a fixed concentration of biocide in the concentrate higher fractions of concentrate in mwf mean higher release (two influences: distribution via Kow and amount of biocide in concentrate), see also section 4.1.2.

4.3 TIER 2 ASSESSMENT

While the Tier 1 approach described in section 4.1 allows for a reasonable worst case assessment on the basis of default values in the course of both substance and product authorisation, the Tier 2 level includes several possibilities to refine the estimate with measured exposure data, region specific information concerning specific commonly applied techniques etc. While refinements with experimental data are in general possible during substance and product authorisation, region specific data (e.g. for dilutions or national restrictions) can only be implemented during product authorisation. A general comparison of Tier 1 and Tier 2 aspects of the risk assessment is given in Table 9.

In addition, in the following sub-sections some risk mitigation measures will be discussed, which have been mentioned in some of the questionnaire responses and the available BREF document [1] and are therefore considered to be reasonable choices for waste water treatment in case of mwf.

The data basis is considered to be sufficient to assign default exposure reduction values for these RMMs. However, not all companies who treat waste (waste management or end-user) refer to these techniques. Thus, if they are applied during the exposure assessment, it has to be ensured with relevant data during product authorisation that only companies actually referring to these RMMs will treat the used mwf.

If more than one elimination factor can be determined (e.g. if several treatment techniques are applied), the final reduction factor is estimated as the product of all factors: $(1-F_{elim}) = \Pi(1-F_{elim,x})$

4.3.1 Recycling of waste water ($F_{elim,recycle}$)

If the emulsion is split via evaporation of water it will be clean enough to be re-used. This practice has not been mentioned yet very often during the evaluation of questionnaires. However, due to financial reasons (water costs) it is considered to be likely that it will become more common in the future.

If the waste water is recycled, no biocide is released into the environment independant on other waste treatment steps:

$$F_{elim} = F_{elim,recycle} = 1$$

4.3.2 Degradation since last dosing (operating time since last biocide dosing, storage at end-user site, transport to waste management facility, storage at waste management site; $F_{elim,storage+more}$)

In general, degradation of biocide between the last dosing and the start of waste treatment will further reduce the biocide concentration. However, for an accurate estimation of the exposure reduction information about the degradation in used mwf has to be available. As there is no standard algorithm that can be used to derive such degradation rates it is suggested to estimate those experimentally for substances where the available defaults for exposure estimations (section 4.1) are not sufficient.

Applicable sampling techniques may depend on the substance and the required limit of detection. One possible technique applicable to many substances is the isotopic ratio mass-spectrometry (IRMS)[17], however, also other techniques may be possible.

Available information about common time intervals between the last dosing and the start of waste treatment operations as described below can be used for this purpose, however, should be amended by further information obtained in the course of the experimental studies as far as possible.

As an example, total rate constants for degradation in MWF and tank water k_{deg} can be used together with the corresponding duration t to estimate the final elimination factor as follows:

$$F_{elim,storage+more(t)} = 1 - \exp(-k_{deg} \cdot t)$$

Alternatively, degradation factors or substance concentrations before release can be measured directly.

Waste management companies

It is considered to be reasonable that small companies, who do not refer to on-site treatment, will store their waste for at least one week due to organisational and financial reasons: Costs will be higher for more visits from the waste management company and at some point it will make more sense to refer to on-site treatment instead. Available information from end-users who refer to external waste management is summarised in Table 8 and suggests a minimum time of t = ~7 days between the last biocide dosing and the start of waste treatment (PC, biological treatment etc.).

In addition to storage on end-users' sites this parameter includes the time between the last biocide dosing and removal of mwf from the machine, transport time (waste management companies will probably collect waste from several companies before the mixture is treated) and possibly storage at the site of the waste management company.

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17 One application of the isotopic ratio mass spectrometry techique is compound-specific isotope analysis (CSIA), where the change in the ratio of naturally occuring isotopes for instance can be studied over time (using samples from for instance the MWF-tanks at different time points). Such changes only occur when chemical bonds are broken, in essence when degradation of the biocide has occurred

Table 8: End-users, who refer to external waste treatment and gave information about the release frequency or storage times before waste collection (see separate Excel tables for details)

Company number	Information concerning on-site storage / discharge days per year	resulting storage time (days)
6	once per year and installation discharge to external company	number of installations not known
8	once per week collection by external company	7
12	storage, then external treatment	not known
13	storage, then external treatment (soluble) or on-site (emulsifiable)	not known
18	every 4 weeks disposal at other site	28
19	storage in 1 m^3 tanks, 1-2 days release per year	183
23	2 times per year to external company	183
25	1-4 days per year collection by external company	91
31	storage in 50 m^3 tanks (50 t/a concentrate indicated, i.e. ~1000 t/a diluted mwf, i.e. 20 50 m tanks → ~ 20 times per year)	20
Average		85
Median		60

End-users

Of the companies who refer to on-site treatment, some also indicated storage of waste before treatment. Even odour development was observed during this time, which suggests an almost complete degradation of the biocide and an increased growth of microorganisms.

The currently available data do not allow for a general statement about common storage times before treatment, although a certain degree of degradation (e.g. during the time span between last dosing and emptying of the machine) will certainly be present.

4.3.3 Biocide removal during further physico chemical (PC) treatment ($F_{elim, x}$)

As mentioned in section 4.1.5.3 the derivation of default reduction efficiencies is difficult, as for most techniques efficiencies are substance specific.

Thus, if other techniques than those described in the previous sections shall be evaluated or suggested defaults shall be refined, exposure reductions have to be determined experimentally for each substance individually.

Applicable sampling techniques may depend on the substance and the required limit of detection. One possible technique applicable to many substances is the isotopic ratio mass-spectrometry (IRMS), however, also other techniques may be possible.

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[18] Overall, 11 companies from the survey results refer to external waste treatment companies. For companies not listed in this table, no information could be gathered on this question.

Table 9: Comparison of Tier 1 and Tier 2 aspects

	Tier 1: substance and product authorisation		Tier 2: substance authorisation		Tier 2: product authorisation
	end-user	waste manage-ment company	end-user	waste management company	End-user and waste management company
Dilution factor company→ municipal STP: $D_{company->STP}$	150	100	x		refinement with region specific data about dilution factors possible
Fraction of metalworking fluid in treated volume: F_{mwf}	1	0.5	x		refinement with region specific data about F_{mwf} possible
Fraction of metalworking fluid with chemical of interest in treated volume: F_{form}	1	0.5	x		refinement with region specific data about F_{form} during product authorisation possible
Fraction of elimination of the chemical during physical or chemical treatment (except oil/water splitting): F_{elim}	0		Refinement of fraction of elimination with measured data is possible for all treatment techniques. However, as long as several treatment techniques are possible, the lowest available elimination fraction should be used as a worst case. Special case waste water recycling: $F_{elim,recycle}$ = 1, no release of biocide as no waste water is released		Refinement of fraction of elimination with measured data is possible for all treatment techniques. If several treatment techniques are possible, it has to be ensured with relevant data that the respective technique is applied as necessary RMM on a national level. Special case waste water recycling: $F_{elim,recycle}$ = 1, no release of biocide as no waste water is released

	Tier 1: substance and product authorisation	Tier 2: substance authorisation		Tier 2: product authorisation
Degradation of biocide since last dosing: $F_{elim,\ storage+more}$	1 (no degradation assumed)	Refinement of fraction of elimination with measured data is possible.	$F_{elim,storage+more}(t) = 1 - \exp(-k_{deg} \cdot t)$ Refinement of fraction of elimination with measured data is possible. A time span of 7 days between last dosing and PC treatment is suggested as a default.	$F_{elim,storage+more}(t) = 1 - \exp(-k_{deg} \cdot t)$ Refinement of fraction of elimination with measured data is possible. The time span between last dosing and PC treatment can be refined with region specific data about time spans between last dosing and PC treatment
Fraction of elimination of the chemical during emulsion splitting: Evaporation of water: $F_{split,evap}$	$p_{vap} \leq \frac{1}{2}\, p_{vap\ H2}$: 0; $p_{vap} > \frac{1}{2}\, p_{vap,H2O}$: 1	Refinement of fraction of elimination with measured data is possible.		Refinement of fraction of elimination with measured data is possible.
Fraction of elimination of the chemical during emulsion splitting: All other splitting methods: $F_{split,kow}$	$(F_{conc} \cdot (1-F_{conc}) \cdot K_{ow}+1)^{-1}$ (correction of ionisable substances may be necessary (see text))	Refinement of fraction of elimination with measured data is possible. However, as long as several treatment techniques are possible, the lowest available elimination fraction should be used as a worst case.		Refinement of fraction of elimination with measured data is possible. If several treatment techniques are possible of which only some are safe, it has to be ensured with relevant data that the respective technique is applied as necessary RMM on a national level.

	Tier 1: substance and product authorisation		Tier 2: substance authorisation		Tier 2: product authorisation
Dilution factor STP→ river (needed for estimation of PECfreshwater, see standard EUSES algorithm for details): $D_{STP\text{->}river}$	10		x	x	refinement with region specific data about dilution factors possible
Overall dilution: $D_{overall} = D_{company\text{-> }STP} \cdot D_{STP\text{->}river}$	1500	1000	x	x	refinement with region specific data about dilution factors possible
Number of release days (only required for regional concentrations): N	300		x	x	refinement with region specific data about number of release days possible
concentration of biocide in the machine: $c_{biocide,dil}$	substance specific information (defaults from original EUBEES approach only if no other information available ("Tier 0"); of all possible uses the worst case result should be chosen (see text for details).		substance specific information (defaults from original EUBEES approach only if no other information available ("Tier 0"); of all possible uses the worst case result should be chosen (see text for details).		substance specific information (defaults from original EUBEES approach only if no other information available ("Tier 0"); if only some applications (e.g. certain fractions of concentrate) lead to a safe use it has to be ensured with relevant data that the respective technique is applied as necessary RMM on a national level.

4.4 ALTERNATIVE ALGORITHM

If no information about the concentration of biocide in diluted metalworking fluid is available but only the concentration of biocide in mwf concentrate ($C_{biocide, conc}$) and the fraction of mwf concentrate in diluted mwf (F_{conc}), an alternative version of the exposure algorithm may be used. This applies also to cases where no substance specific information concerning applicable concentrations is available (see old defaults in Table 1). Differences between this approach and the algorithm described previously are pointed out in the table below. All variables and equations not mentioned here are identical to the previous approach.

If the fraction of biocide in concentrate and the fraction of concentrate in mwf are known, $C_{biocide, dil}$ can be derived from them. Moreover, in the course of the authorisation process the ideal in-use concentration of a biocidal substance has to be determined and applied by the end-user, therefore a complete ignorance of the applicable concentrations is considered to be highly unlikely. Thus, this additional equation is not strictly necessary but only aims to increase the user friendliness of the final ESD.

Table 10: Suggestions for an ESD revision: Alternative algorithm

Variable / parameter	Unit	Symbol	Value (release into municipal STP)		S/D/O/P
			end-user + on-site treatment	external waste treatment company	
Concentration of biocide in mwf concentrate	[kg.m-3]	$C_{biocide, conc}$			S
Concentration of the chemical in the diluted metalworking fluid in the machine		$C_{biocide, dil} = F_{conc} \cdot C_{biocide, conc}$			
Output					
Preservative concentration in municipal STP influent	[kg m-3]	$C_{STP,inf} = F_{conc} \cdot C_{biocide, conc} \cdot D_{company\text{-}>STP}^{-1} \cdot F_{form} \cdot F_{split} \cdot (1-F_{elim})\ F_{mwf}$			O

5 CONCLUSION

As a summary, it could be shown in the course of this project that neither of the currently available ESDs (OECD ESD No. 28, EUBEES ESD) should be used for the environmental exposure assessment related to wm mwf due to the following reasons:

- Both ESDs are based on comparably old (1990s) and limited data.
- Both ESDs are not able to reflect the release paths appropriately and in a complete way:
  - The OECD approach intends to estimate only the release from small end-user companies.
  - The EUBEES approach on the other hand only intends to represent large waste treatment companies. In addition, it is based on the assumption that biocide is only dosed via treated concentrate, while in reality dosing via concentrate as well as direct dosing (shock dosing or continuous, precautionary dosing) are practiced.
- Moreover, both ESDs use unrealistic defaults:
  - The EUBEES approach assumes very low dilution factors for the release into STP and into the surface water compartments.
  - The EUBEES approach assumes very high biocide concentrations, which are rarely reached in reality (only for system cleaners in rare cases)
  - Although the EUBEES approach intends to represent waste treatment companies which usually collect waste from different end-users it assumes that the whole amount of treated emulsions consists of mwf which are all treated with the same biocide. No reduction of the biocide concentrations due to RMMs or storage of waste is implemented although it has been observed in reality that even odour development occurs if used mwf are not treated at once.
  - The OECD on the other hand suggests efficiencies for treatment techniques, but does not discuss if these efficiencies apply to all substances. As an example this approach assumes 70% emission reduction by ultrafiltration as a standard – a treatment technique which is not suitable to eliminate small molecules such as biocides[19]. Exposure reduction in the course of ultrafiltration is only caused by the partition between water and oil phase and thus, is substance specific and already covered by the implementation of the partition coefficient.
  - The OECD approach also includes assumptions concerning adsorption on shavings or container residues without discussing substance dependence of these parameters.
  - The companies represented by the OECD usually refer to waste management companies, therefore these release volumes are not representative for the waste water amounts released into municipal STPs.

Thus, the ESDs are not able to represent reality appropriately and lead to scientifically unjustified and unrealistic results. We therefore propose to replace the existing ESDs by the suggestions described in section 4.

19 Some reduction corresponding to partition coefficient - this is covered by the splitting of emulsions.

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APPENDIX A: GATHERING OF INFORMATION FOR THE REFINEMENT OF THE ENVIRONMENTAL EMISSION SCENARIO FOR METALWORKING FLUIDS (PT13) UNDER BPD/R: ADDENDUM 1

INTRODUCTION

The “TEGEWA MWF Working Group” has agreed to fund a project to investigate the handling and disposal of used metalworking fluids (cooling lubricants). The project has been placed with the Fraunhofer Institute for Toxicology and Experimental Medicine (Fraunhofer ITEM).

In the course of the project different aspects of the environmental exposure to biocides due to use and waste treatment of metalworking fluids will be evaluated. These include relevant regulatory information such as the Water Framework Directive or Waste Framework Directive, which interact with the waste handling or use of metalworking fluids, and best available techniques as laid down in publicly available documents and guidelines. Metalworking fluids are considered to be hazardous wastes, and they cannot be led directly to a river without an appropriate prior treatment. Moreover the applicability of the current emission scenario documents like the EUBEES ESD representing the waste companies, the OECD ESD representing mostly small USA end-user companies, and available national scenarios from European countries will be evaluated using information collected from European metalworking industries as well as waste management companies dealing with the handling and treatment of used metalworking fluids (common industrial practice and parameters relevant for the exposure estimation).

First results of this project and data which may be used to refine the available ESDs have been presented at TM II in 2013 (see also Report “Gathering of information for the refinement of the Environmental Emission Scenario for metalworking fluids (PT13) under BPD/R [5]). A short summary of these first results can be found in Chapter 1.

Additionally it was agreed to form a working group including industry members and representatives of the competent authorities with the aim to gather more information and data supporting the first results. The final goal of this working group is to develop a refined and harmonised ESD that can be used for environmental exposure estimations for water miscible metalworking fluids and represents a realistic worst case situation based on up-to-date data from the European metalworking sector.

It is furthermore seen as a reasonable step to form a working group under the BPC (Biocidal Products Committee) with the aim to evaluate suggestions about the general harmonised assessment of environmental exposure to biocides.

This document is designed to be an Addendum to the report “Gathering of information for the refinement of the Environmental Emission Scenario for metalworking fluids (PT13) under BPD/R” [5] and includes additional information that has been gathered in the meantime in order to support the refinements suggested at TM II (2013).

1 STATE OF AFFAIRS AFTER TM II 2013: SUGGESTIONS FOR A REFINEMENT OF THE EUBEES ESD DEFAULT PARAMETERS

The information gathered in the first part of this project suggests the following modifications of the EUBEES ESD (slightly adapted excerpt from [5]):

The database for water soluble metalworking fluids is considered not sufficient at the moment to make a detailed differentiation between emulsifiable and water soluble metalworking fluids. However it has been confirmed that emulsifiable metalworking fluids are much more common and used in higher tonnages (as suggested in the EUBEES ESD). Dilution factors are expected to be similar to (or – due to the lower tonnages – even higher than) those for emulsifiable metalworking fluids. In addition, no clear directions or specifications exist whether both kinds of water miscible metalworking fluids are treated together or not. It is assumed that often both are collected in the same reservoir for treatment together with other cleaning solutions. In conclusion, it is expected that both types of water miscible metalworking fluids can be represented by the same scenario(s).

However, based on the information gathered it is suggested to use at least two different scenarios: one for companies with on-site waste treatment who discharge to the municipal sewage treatment plant and one for companies who refer to external treatment companies (see description below and summary in Table 11).

Discharge without previous treatment in the municipal treatment plant has not been mentioned in the previous survey replies and is thus considered to be not the common case. However, the few companies practicing this approach will most likely be quite large and use on-site biological treatment plants. Thus, they are considered to be covered by the scenario suggested for the combination of on-site treatment and release into a municipal STP.

Table 11: Suggestions for refinement of EUBEES ESD default parameters.

	EUBEES ESD	Suggestions: On-site treatment	Suggestions: Waste management company
General	Release into municipal STP	Release into municipal (or on-site) STP	Release into municipal STP
Waste treatment	Splitting of emulsion	Splitting of emulsion	Splitting of emulsion
Dilution factor company -> STP $D_{company/WTP\text{->}STP} = V_{STP}/V_{PROC}$ [20]	~10	100	100
Dilution factor STP-> river: $D_{STP\text{->}river} = V_{river}/V_{STP}$	~10	100	100
Overall dilution $D_{overall} = D_{company/WTP\text{->}STP} \cdot D_{STP\text{->}river}$	~100	10000	10000
Fraction of biocide in concentrate	4 - 5%	0.1 - 4%	0.1 - 4%
Fraction of concentrate in diluted mwf	5 - 20%	2.5 - 15%	2.5 – 15 %
Fraction of metalworking fluids within the overall amount of emulsions (F_{form})	100%	100%	50%
Fraction of mwf that is treated with one specific substance	100%	100%	50%
Number of release days	300	300	300

[20] In general V_{PROC} can be interpretted either as the emitted waste water volume of a waste treatment plant or an end-user of metalworking fluids.

On-site treatment:

It is expected that a splitting of emulsions (by ultrafiltration, chemical splitting, evaporation etc.) will usually be practiced (consistent with EUBEES ESD) as recommended by regulatory information for emulsions. Moreover, release of the aqueous phase into STP but not directly into river is the usual case (consistent with EUBEES ESD) . It is recognised that large volumes of used mwf refer usually to large companies with a high number of employees. Therefore, the cities where these companies are located as well as the corresponding municipal sewage treatment plants are also expected to be larger than the standard size used for common risk assessment, i.e. the parameters for STP volume and release of waste water per site are not independent of each other. This explains that the dilution factors $D_{company\text{-}>STP}$ and $D_{STP\text{-}>river}$ [21] are usually much higher in reality than anticipated in the EUBEES ESD approach. In order to deal with this dependency dilution factors have been suggested and the volumes have been scaled to match the commonly used standard STP (see also external waste treatment below). The information gathered during this project would suggest the following refinement of parameters for an exposure assessment in case of water miscible metalworking fluids:

- Standard dilution factors of 100 for the release from company to STP and from STP to river ($D_{company\text{-}>STP}$ = 100 and $D_{STP\text{-}>river}$ = 100, i.e. $D_{overall} = D_{company\text{-}>STP} \cdot D_{STP\text{-}>river}$ = 10000 overall dilution, see
- Table 11) (EUBEES ESD: overall dilution $D_{overall} \approx 10 \times 10 = 100$). If the volume of a standard STP with 2000 m^3/day is assumed this will lead to approximately 20 m^3 release of used metalworking fluid per day and a river flow of 198000 m^3/day.
- Concentrations of biocide in concentrate of 0.1 – 4% (EUBEES ESD: 4-5%)
- Concentrations of concentrate in mwf 2.5 - 15 % (EUBEES ESD: 5-20%)

External treatment

Again the release after treatment will usually happen not directly into a water body but into the local STP.

[21] Volume of water emitted by STP divided by volume of water emitted by the company: $D_{company\text{-}>STP} = V_{STP}/V_{PROC}$;
Volume of river divided by volume of water emitted by the STP: $D_{STP\text{-}>river} = V_{river}/V_{STP}$; all volumes in m^3/d
Overall Dilution: $D_{overall} = D_{company\text{-}>STP} \cdot D_{STP\text{-}>river}$

The information gathered during this project would suggest the following refinement of parameters for an exposure assessment in case of water miscible metalworking fluids:

- Standard dilution factors of 100 for the release from waste treatment company to STP and from STP to river ($D_{company\text{-}> STP}$ = 100 and $D_{STP\text{-}>river}$ =100, i.e. $D_{overall}$ = 10000 see
- Table 11 (EUBEES ESD: overall dilution of approximately $D_{overall}$ ≈ 10 x 10 = 100 (depending on fraction of concentrate in metalworking fluid)). If the volume of a standard STP with 2000 m^3/day is assumed this will lead to approximately 20 m^3 release of used metalworking fluid per day and a river flow of 198,000 m^3/day.
- Concentrations of biocide in mwf concentrate of 0.1 – 4% (EUBEES ESD: 4-5%)
- Concentrations of concentrate in mwf 2.5 - 15 % (EUBEES ESD: 5-20%)

External waste treatment facilities will usually receive emulsions from different companies and applications, therefore it is suggested to assume that 50% of the treated waste volume are used metalworking fluids and 50% of these metalworking fluids are treated with one substance (i.e. F_{form} = 0.5; EUBEES ESD: F_{form} = 1, 100 % waste from water based metalworking fluids). As it is expected that already at end-user premises only ~50% of the collected waste will consist of pure used metalworking fluids (see Chapter 5 and Appendix 3 in Ref. [5]) this approach is considered to be conservative.

As a first approach the TGD default of 300 release days per year may be used for on-site as well as for external waste treatment (see also EUBEES ESD).

As an additional simplification it is suggested to use the parameter “concentration of biocide in metalworking fluid” instead of the fractions of concentrate in mwf and of biocide in the concentrate. This approach would facilitate the exposure assessment for end-users who add biocide separately (not via concentrate), it would also be applicable and maybe even easier in all other cases (external treatment, dosing of biocide via concentrate) and would neither change the basic algorithm nor the exposure result.

The suggestions listed above may still not cover all possibilities; however they could be used as a first approach to refine the existing EUBEES ESD that should be underlined with further data as soon as this would be available.

It is recognised that there may be situations in the EU where a parameter is not represented by these suggested parameters. However, as they were chosen on a realistic worst case basis it is expected that these rare deviations will be even overcompensated by the conservativeness of the other variables. A combination of worst case parameters as used in the EUBEES ESD is – in accordance with the information gathered during this project - expected to be highly unlikely.

In conclusion, a first step for the refinement of the EUBEES ESD could be the implementation of refined parameters as suggested above. As soon as possible additional information about usage and waste treatment of metalworking fluids should be collected and used to verify the suggested values and/or to add further refinements if possible.
If monitoring data should become available these could also be used to validate exposure estimates provided by the resulting model algorithm.

2 UPDATE: STATISTICAL ANALYSIS

2.1 PLAUSABILITY CHECK OF DILUTION FACTORS IN THE EUBEES ESD FOR PT13

As already detailed in the former Ref. [5] and summarised in Chapter 1, the main reason for an overestimation of the PEC_{STP} and $PEC_{freshwater}$ (and thus also PEC_{soil} and $PEC_{groundwater}$, which are based on the releases into water) is seen in unrealistic assumptions about the dilution of produced waste water in the available municipal treatment plant in the currently used EUBEES ESD [6].

The dilution factor suggested in this ESD is estimated as follows:

Waste water volume: $V_{PROC/WTP} \approx 200\ m^3/day$

According to the original UBA ESD [7] this volume is intended to reflect the volume emitted by a waste treatment company. It is – in accordance with the data collected in the first part of the project - considered to be a worst case, i.e. a comparably large amount of waste water.

Volume of sewage treatment plant: $V_{STP} = 2000\ m^3/day$.

The latter volume is – in accordance with the data collected in the first part of the project - considered to be a worst case, i.e. a comparably small municipal treatment plant.

Dilution: $D_{company\text{-}>STP} = V_{STP}/V_{PROC/WTP} = 10$

2.1.1 Possible release pathways

In reality, different pathways are possible for the waste water produced by the use of water miscible metalworking fluids (see also Figure 3)[22]:

Non-discharge: The end-user uses recycling measures (e.g. evaporation systems), which allow for a re-use of oil and water phase. Non-dischargers do obviously not provide a risk for the receiving compartment as they do not release any waste water into the environment.

According to recently gathered information (exemplary representative German company from the mwf sector; personal communication) this option is already practised in some companies and it is expected to gain more relevance in the future due to rising water costs.

Direct discharge: The end-user refers to on-site waste treatment measures. The waste water is not led into a municipal sewage treatment plant before it is released to the surface water.

As already shown in the first part of the project direct discharge is very rare. None of the received replies from end-users of mwf during the first project part indicated that this was their common way of waste water discharge. General information received from industry representatives suggests that the few direct dischargers are comparably large companies which will use on-site biological treatment plants and in addition elaborated

[22] It is recognised that in the available literature partly other definitions (direct/indirect/non-discharger) are used. It is therefore recommended to include corresponding definitions in the final ESD.

PC treatment techniques, i.e. PEC_{STP} is not relevant in this case and

$PEC_{surfacewater}$ is considered to be most likely very low [7].

Indirect discharge: The end-user refers to external waste- and waste water treatment facilities.

A fourth option is the release from end users into a municipal STP after on-site PC treatment, which is however considered unlikely to lead to high effluent concentrations, as large companies are likely to also have on-site waste water treatment facilities including biological treatment (Ref. [7], see also Chapter 0). General control measures at industrial sites are more defined, i.e. it is possible to control the level of contamination in on-site biological treatment plants or emitted waste water in a more specific way than in case of waste treatment companies which have to treat mixtures containing a much higher variety of different contaminants.

This assumption is also supported by data gathered in the first part of the project, general experience of industry representatives in this project and exemplary information submitted by a representative German end-user company of metalworking fluids who was able to deliver some new details via personal communication since TM II 2013. Apart from the common on -site waste treatment techniques (ultrafiltration, evaporation) during storage time of used emulsion unpleasant odour caused by anaerobic degradation of various fluid components has also been observed, which strongly indicates the absence of biocide as otherwise the fluid components could not be degraded.

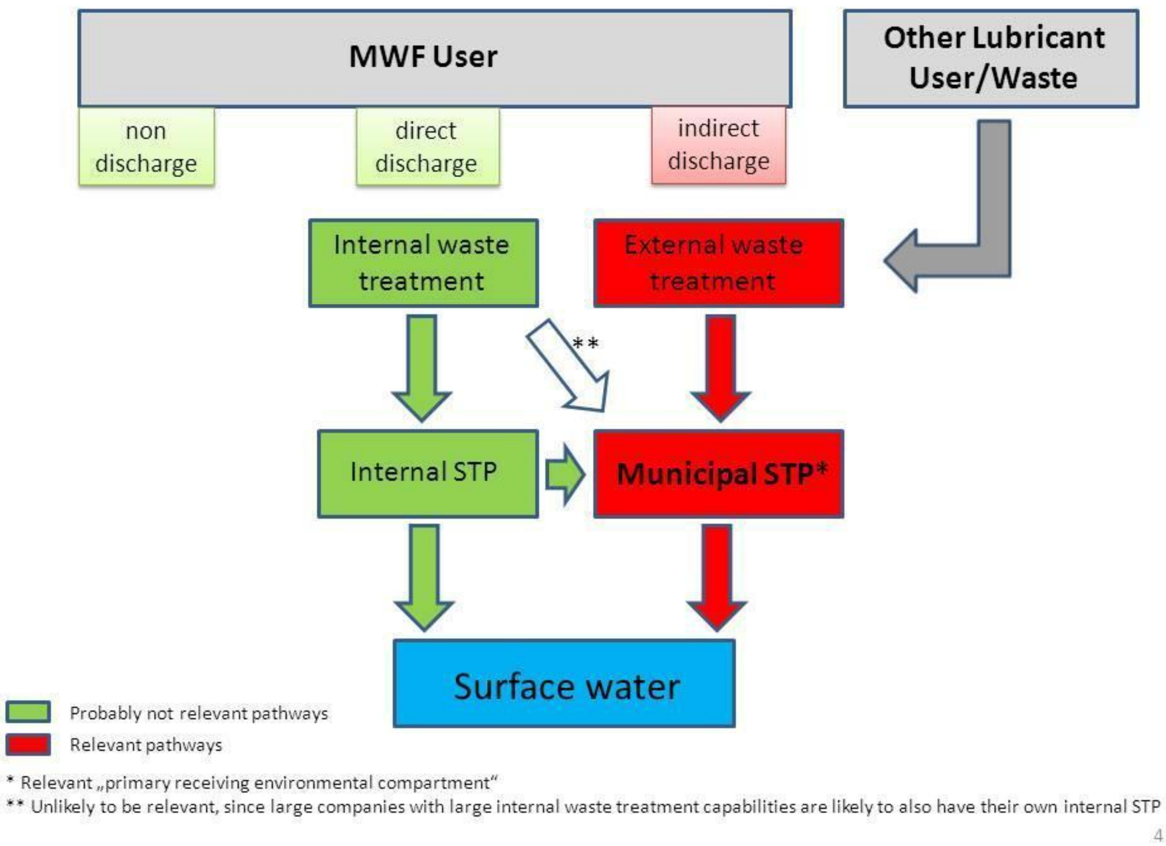

Figure 3: MWF discharge pathways.

Thus, the most relevant point in the context of risk assessment is the release of waste water from external waste management companies into municipal sewage treatment plants.

A more detailed differentiation of the various possible pathways related to the indirect discharge of mwf is shown in Figure 4. There are some pathways which are considered to be unlikely to occur (dotted arrows) as it is unreasonable to assume that, as an example, large end-users with a high output of waste water will refer to small waste management companies which may not be able to provide the capacities to treat all generated waste water in a reliable way.

Moreover, taking into account the definition of the dilution factor (ratio between volume of STP and volume of emitted waste water) and the possible combinations between small/medium/large end-users and waste treatment plants (WTP) some assumptions about the most relevant pathways, i.e. the lowest dilution factors can be made (combination between comparably large emitter (~ 200 m^3/day) and small STP (10.000 p.e. or smaller, red arrows).

Overall the release path with the highest probability of resulting in high environmental concentrations, i.e. the worst case, is considered to be the release from large waste treatment facilities into small municipal sewage treatment plants.

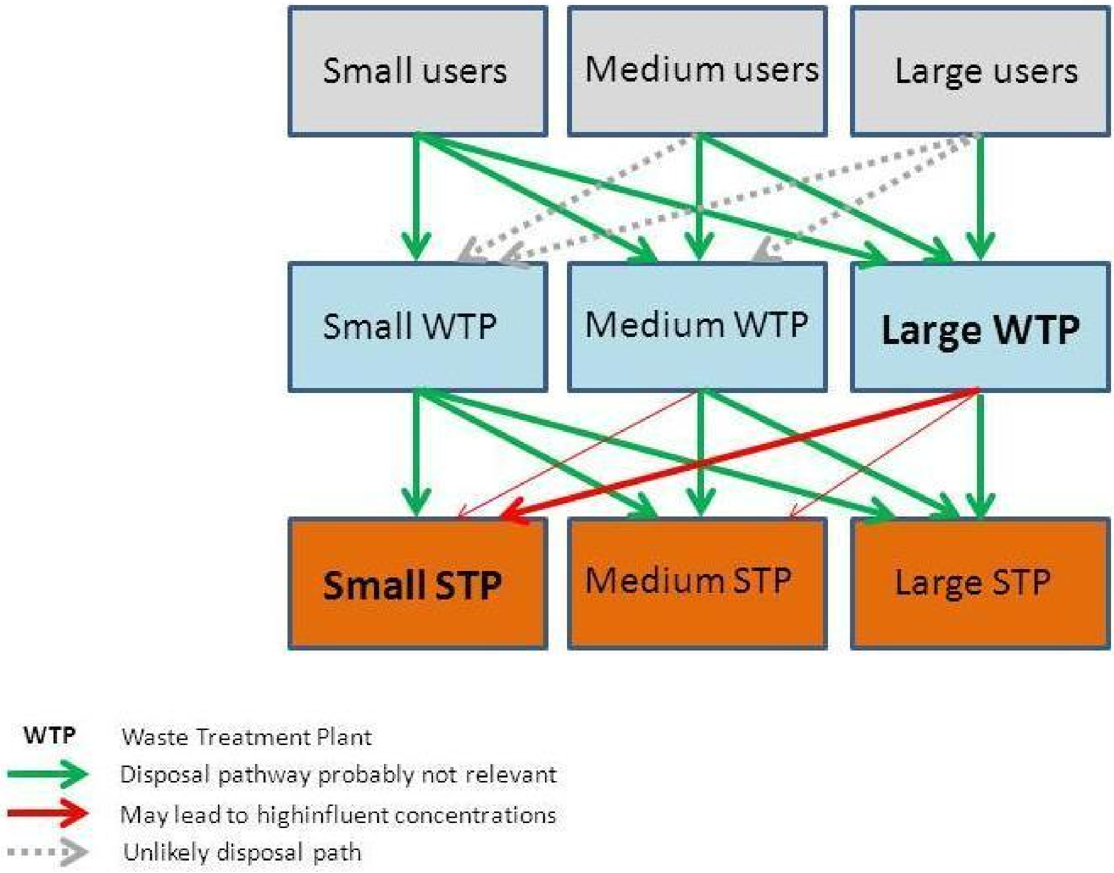

Figure 4: MWF discharge pathways. Differentiation into small, medium and large end-user companies.

2.1.2 Evaluation of available STPs in Europe

Statistical analysis of potentially receiving STPs in Europe shows that there are overall at least 23.282 STPs in Europe (as registered in the Waterbase_UWWTD [8]) . Of those 22.797 have a capacity of more than 10 population equivalents (p.e.) and will be considered in the further analysis. The summed up capacity of these 22.797 STPs is 760.236.457 p.e. (see Table 12 for details).

Only 13.658 STPs have capacities below or equal to 10.000 p.e. and are therefore considered to be small STPs, representing a total of 59.171.336 p.e. or 7.8 % of the overall STP capacity in Europe. These STPs are considered to be the worst case for the European STP capacity as they refer to STPs smaller than or equal to the standard of 10.000 p.e.

Table 12: Evaluation of STP capacities in Europe

p.e. Distribution (to ...)	Number STPs accumulated	Number STPs in Segment	p.e. in Segment	% p.e. in Segment	% p.e. accumulated
5000	9204	9204	25708068	3.38	3.38
10000	13658	4454	33463268	4.40	7.78
20000	16892	3234	48419945	6.37	14.15
50000	20051	3159	103530777	13.62	27.77
100000	21464	1413	103892912	13.67	41.44
200000	22197	733	105247790	13.84	55.28
300000	22429	232	57864797	7.61	62.89
400000	22536	107	38383906	5.05	67.94
500000	22616	80	35991374	4.73	72.68
1000000	22741	125	89197111	11.73	84.41
12000000	22797	56	118536509	15.59	100.00
			760236457	***100.00***	

2.1.3 Evaluation of the term "large waste treatment plant"[23]

The per year consumption of water miscible metalworking fluids in the EU is extrapolated to be approximately 3.000.000 t/year (diluted mwf). This number is based on a market share of ~25% for metalworking fluids of Germany in the EU [9], an amount of ~20.000-30.000 t/year concentrate in Germany (see [5], Chapter 6.1, and refs. [7, 10]) and an average concentrate fraction in the emulsion of ~4%[24].

[23] All densities are assumed to be equal to 1 for the sake of simplicity

[24] Gräfen et al.: ~30000 t/y concentrate in Germany and 744000 t/y emulsions and solutions created from water miscible mwf concentrates result in approximately 4% concentrate fraction.

This approach is considered to be more reasonable than a scaling procedure using the population, as the population of a country not necessarily relates to the relevance of metalworking companies. Moreover it represents a reasonable worst case compared to EUBEES defaults and information gathered in the first project part.

In combination with 300 release days per year (see Ref. [6] and first part of the project) this means ~10.000 t/day discharged emulsions which approximately equals the amount of discharged waste water.

In addition it is assumed that, as a worst case, ~10% of the used mwf are discharged indirectly [25] into large waste treatment facilities and thus 200 t/day release would lead to a total number of ~5 large waste treatment facilities in Europe.

Interpreted as an overall number of waste treatment facilities per country this value is obviously highly unrealistic (see also similar plausibility checks in [5], Chapter 6.1). However, it can be used as a realistic worst case for the number of large plants in Europe, as a higher number of waste treatment facilities in combination with the overall amount of consumed wm mwf could only result in a smaller average volume treated per facility or – if a probability distribution of plant sizes is assumed – a smaller possible number of large facilities with a volume of 200 t/day.

2.1.4 Conclusion

The combination of chapters 2.1.2 (7.8% small STPs in Europe) and 2.1.3 (~5 large WTFs in Europe) results in a maximum of 1 large plant (0.078*5 = 0.39) in Europe which would probably hit a small municipal sewage treatment plant.

This estimation is still considered to be conservative as in reality large waste treatment companies will (similar to large companies from the metalworking sector) most probably not be located in small towns offering small STP capacities (company size and STP volume are not independent – see also [5], Conclusion) . In addition, discharge permits would be required before a waste treatment facility will be allowed to discharge into the municipal STP by the local authorities (see. e.g. urban waste water directive [11, 12]). Thus, overall the evaluation of statistical data supports the suggestions already made in the first part of the project: A low dilution factor is highly unrealistic and therefore will lead to overestimations of exposure.

Apart from these statistical evaluation other aspects of the risk assessment which have already been discussed in the first part of the project do still apply: The waste considered so far is most likely to be diluted with other waste emulsions, i.e. on the one hand the probability that a small STP is hit by a large WTP may be larger (inclusion of other wastes will lead to higher EU waste tonnages) but on the other hand the concentrations of actual metalworking fluid and thus, the substance of interest in the resulting waste water, will be lower (F_{form} < 100%). The biocides will most likely already be degraded to a certain amount due to PC/biological on-site treatment or simply a longer storage time before discharge, i.e. even if it should happen that a large WTP releases into a small STP it is considered to be unlikely that high concentrations environment would be reached.

[25] Baumann et al: 83% of the mwf tonnage are discharged directly (few companies with high tonnages). Of the remaining 17% which are indirectly discharged only a certain fraction will meet the “worst case definition” large WTP. This fraction is assumed to be 10% of the mwf tonnage (59% of the indirectly discharged tonnage). Taking into account the probable size distribution of WTPs this assumption is considered to be conservative.
However, if enough up-to-date information will be gathered in the course of this project this value can be verified and, if necessary, adapted.

2.2 OUTLOOK: TOWARDS A BETTER UNDERSTANDING OF THE EUROPEAN MWF WASTE TREATMENT INDUSTRY STRUCTURE AND A MORE REALISTIC DISCHARGE VOLUME V_{PROC}

In the following, an approach is described to derive a refined value for one of the key parameter $V_{PROC/WTP}$ (treated volume of metalworking fluid per waste treatment facility) in the current EUBEES PT 13 ESD, with the aid of some publically available data sources and furthermore some logical assumptions.

The current very high default value of V_{PROC} of 200 m^3/d has been questioned in the past, and even in the ESD it is mentioned that "*It is not clear whether the ratio wastewater amount/capacity STP corresponds with reality*" (p. 35), indicating clearly difficulties and doubts to properly derive and justify this important input parameter
In the original UBA ESD [7] it is indicated that this release volume is intended to represent a waste treatment plant and not an end-user of metalworking fluids ($V_{PROC/WTP}$).

In order to make an attempt to define a more realistic worst case emission scenario and derive a corresponding value for $V_{PROC/WTP}$, the parameter $V_{PROC/WTP}$ can be assigned on a large metalworking fluid waste treatment plant, which (indirectly) discharges into a small municipal STP.

Some useful information can be found in the "TGD on Risk Assessment (2003), Part IV, IC-8, p.80" [13] and the original UBA ESD on metalworking fluids [7]. These documents teach that in Germany "*83% of the [metalworking fluid] amount is used by direct dischargers. The direct dischargers are usually large companies with their own private wastewater treatment plant.*" Consequently ~17% of the metalworking fluid waste is indirectly discharged into municipal STP and therefore considered as most relevant (see Chapter 2.1 for details).

However, another independent attempt to derive a value for $V_{PROC/WTP}$ can be made based on data which is available in the "FWC Sector Competitiveness Studies – Competitiveness of the EU Metalworking and Metal Article Industries, Final Report 18th November 2009" [9]. Among others this report gives information about the percentage of metal processing enterprises and the metal article output for each country in Europe. From this, the following useful values can be estimated/derived by logical assumptions for each European country:

1. Metalworking fluid consumption per country

2. Average relative size of metal processing company

3. Metalworking fluid use density (metalworking fluid consumption per area)

Furthermore, in order to draw conclusions from those values and data, the following logical assumptions can be considered:

- The smaller the metal processing companies in a country, the larger the amount on indirectly discharged metalworking fluid (small metal processing companies are less likely to have their own waste treatment plant).

- The higher the metalworking fluid use density in a country, the smaller should be the (theoretical) metalworking fluid collection area of a waste treatment company. (→ more disposal into large waste treatment plants)

Implementing the above mentioned data and assumptions into a “disposal distribution model”, attempts can be made to estimate/derive $V_{PROC/WTP}$ for each European country. Of course this theoretical approach is based on statistical information and includes a number of assumptions. However, it may be able to give a general overview about reasonable volumes treated in an average large waste treatment facility.

Industry would welcome the opportunity to present and discuss this approach and results in detail with member states.

3 UPDATE: ADDITIONAL INFORMATION ABOUT A DUTCH WASTE TREATMENT FACILITY

Some information about a Dutch waste treatment facility was provided via personal communication by a member state representative.

The visited plant uses a two-step process which includes a separation of the solid phase by sedimentation, filtration and centrifugation as a first step.

The aqueous phase is then purified biologically at the facility and afterwards led to the sewer, i.e. a second biological treatment is done in the municipal treatment plant. No information about released tonnages or the corresponding river/STP is available, i.e. no dilution factors can be derived.

However, the available information suggests that no harm is expected for the municipal STP as the on-site biological treatment plant may be seen as a test station for the sensitivity of microbiological organisms to the various waste components.

4 UPDATE: ADDITIONAL INFORMATION ABOUT A GERMAN END-USER OF METALWORKING FLUIDS

An additional response to our survey from the first part of the project has been received. The end-user of metalworking fluids is located in Germany and uses exclusively emulsifiable metalworking fluids. The consumption of concentrate per year is ~2300 t/a, however it is indicated that no biocides are used in this company and thus, no release of those substances will happen. This approach is possible for some situations where, due to specific process characteristics (e.g. a high temperature), the growth of bacteria and fungi is prevented or where it does not influence process outcome and/or worker health in a negative way.

The fraction of concentrate in water ranges from 3-9% and the waste treatment happens in a continuous way together with other emulsions and oil-water mixtures. The company discharges directly into a river and refers to a number of on-site waste treatment techniques: Standing times of the metalworking fluid are increased by filtration and internal oil recovery measures. The used mwf is split into oil- and water phase by distillation and the aqueous phase is further purified by flotation to remove oil residues. Afterwards it is led into an on-site biological waste treatment plant from where approximately 600 m^3/day waste water are emitted into a river with 172.800.000 m^3/day volume flow. This means an overall dilution factor of 288.000 or 1.920.000 if only waste water from oil-water mixtures is taken into account (~15%).

This piece of information therefore supports the suggestions made in part 1 of the project and detailed in Chapter 1 to be a realistic worst case assumption.

APPENDIX B: GATHERING OF INFORMATION FOR THE REFINEMENT OF THE ENVIRONMENTAL EMISSION SCENARIO FOR METALWORKING FLUIDS (PT13) UNDER BPD/R: STATUS REPORT DECEMBER 2013

QUESTIONNAIRE RESPONSES SINCE THE FIRST PROJECT PART

End-users

- In the first project stage we had responses from 10 sites, amongst these 3 manufacturers of mwf, 1 of these manufacturers from the Netherlands, rest of responses from Germany
- Now: 31 responses including the sites from the first project part. Some of the responses are from one company: 31 sites and 10 companies overall;
- 6 additional (potential) end-users from NL contacted (contact data from http://www.metaalbewerking-info.nl/azindex.php), no response so far.
- amongst the received responses there are 6 sites which are not in Germany: 1 Portugal, 1 Spain, 1 Slovakia, 2 Austria, 1 Hungary (+ 1 manufacturer from the Netherlands from the first project part)
- overall dilutions of > 100 · 100 for Germany are supported by the new data (sometimes one dilution factor below 100 but overall dilution always above 10000)
- for the non-German sites only dilution factor information is available for Portugal and Slovakia: one site (Portugal) has unfortunately indicated a low dilution. (3 * 111 = 333 overall dilution). However, it is not known if this is representative for Portugal.

➔ Currently no representative amount of data for other EU countries than Germany is available, therefore more data from other EU countries would be needed to show that dilution factors of >/= 100 · 100 apply also to other EU countries.

Concentrations of biocide in diluted mwf according to the the EUBEES scenario are 0.005-0.02% (fungicides) and 0.1-1% (bactericides in traditional or synthetic emulsions), but the reported values in the questionnaires in diluted mwf range from 0.00018-3% (highest concentrations found for system cleaner), i.e. the possible range of concentrations is clearly much larger than suggested by EUBEES.

The reason for this is, that concentrations of biocides in mwf recommended to be effective are substance specific and have to be derived from suitable efficacy studies. A general default value for the concentration over the range of different biocides is therefore not reasonable. Moreover, the environmental limit values and the concentration in mwf are not independent of each other, therefore the corresponding risk assessments will not be able to provide reasonable results if worst case concentrations are used.

Thus, the biocide concentration (fungicide and bactericide) should be a substance specific parameter within the algorithm that is given by the manufacturer and no default.
As in case of pretreated concentrates not only one biocide concentration will appear in reality ideally a range could be given by the concentrate manufacturer which reflects the maximum and minimum usual fractions of concentrate and therefore can be used to derive the relevant biocide concentrations.

However, it still has to be discussed how this can be combined with the existing biocides regulation to ensure that all needed information is available to the person assessing the risk for a biocidal substance.

Furthermore, the new data support the first impression that the real scenario is more complicated than illustrated in the EUBEES:

- some companies only use biocide which is introduced by the pretreated concentrate
- some companies add additional biocide to the diluted mwf
- some companies only directly add biocide to the diluted mwf
- some companies perform continuous dosing, some shock dosing (i.e. only addition of biocide in case of contamination a few times per year, -> intermittent exposure!); there may be also mixtures between these two extremes
- sometimes fungicide and bactericide are separate substances, but sometimes only one biocidal product is used for both purposes.
- number of biocidal substances used per site: sometimes different biocides are used for different mwf products or applications, but for end-users the maximum fraction for one biocide can be quite high (often 80% or higher)

The new information still supports treating emulsifiable mwf as the main release path. Soluble mwf scenarios are covered by them (smaller volumes for soluble mwf).

Waste treatment companies

- In the first stage of the project we had responses from 5 waste treatment companies, including one from the Netherlands which however did not include information about the dilution factor(s)
- Now: 6 responses (one additional from the Netherlands) but no further information about dilution factors
- Information from 6th response: solid phase is first separated from the aqueous phase by sedimentation (enforced by the addition of chemicals such as iron-chloride), filtration, and centrifugation. The aqueous phase is subsequently purified biologically, discharged to the sewer, and purified again in the municipal STP (sewage treatment plant). The solid phase is burned. Samples from the incoming waste and the effluent are analysed on organic compounds in general (chemical and biological oxygen demand), total chlorinated hydrocarbons, dioxins, PCBs and various metals. The plant claimed an efficiency of about 80% hydrocarbon removal based on COD. The waste water's organic load is almost entirely releated to hydrocarbons and not to biocides. No information about discharge volumes or the municipal STP is available.
- Several further waste treatment companies were contacted since the first project part (14 from GB, 4 from NL, 6 from Germany, 1 from Spain, 2 from Austria, 1 from Hungary), but only two responses (1 from NL, 1 from GB) indicating that the corresponding companies do not treat these wastes.
- Contacts have been found via questionnaire responses from end-users, http://www.freeindex.co.uk/categories/manufacturing_and_industry/industrial_services/hazardous_waste_management/, https://www.gov.uk/hazardous-waste-disposal

OPTIONS TO REFINE THE EXPOSURE ASSESSMENT

As already suggested in part 1 of the project the basic equation used in the EUBESS ESD can be used (in a slightly adapted form) for the refined version as well.

However, with the current knowledge some approaches could be identified to refine the exposure estimation and to get a realistic worst case result.

Table 13: Suggestions for an ESD revision - current state of affairs (December 2013)

Variable/parameter	Unit	Symbol	Value (release into municipal STP)		S/D/O/P
			end-user + on-site treatment	external waste treatment company	
Input					
Concentration of the chemical in the diluted emulsifiable metalworking fluid	$[kg.m^{-3}]$	$C_{biocide,\,dil}$			S
Volume ratio concentrate / water phase	[-]	$F_{conc/water}$			S/P
Dilution factor company-> municipal STP	[-]	$D_{company\text{->}STP} = V_{STP}/V_{company}$	100	100	D/S
Capacity of the receiving municipal STP	[m .d]	CAPSTP	2000	2000	D
Treated volume of metalworking fluid	[m .d]	$V_{proc,emul.} = D_{company\text{->}STP}^{-1} \cdot CAPSTP$	20	20	O
Fraction of metalworking fluid in treated volume	[-]	F_{mwf}	1	0.5	S/D
Fraction of metalworking fluid with chemical of interest in treated volume	[-]	F_{form}	1	0.5	S/D
Fraction of chemical degraded during industrial use	[-]	F_{degr}	0	0	D
Partition coefficient n-octanol/water	[-]	K_{OW}			S

Fraction of elimination of the chemical during physical or chemical treatment	[-]	F_{elim}	see below	see below	S
Dilution factor municipal STP-> river	[-]	$D_{STP\text{->}river} = V_{river} \cdot V_{STP}$	100	100	D
Overall dilution	[-]	$D_{overall} = D_{company\text{->}STP} \cdot D_{STP\text{->}river}$	10000	10000	D
River flow rate	[m^3 d^{-1}]	$V_{river} = CAP_{STP} \cdot D_{STP\text{->}river}$	198000	198000	O
Number of release days (only required for regional concentrations)	[-]	N	300	300	D
Output					
Emission to municipal STP	[kg d]	$E_{local,water} = C_{biocide,dil} \cdot V_{mwf,dil} \cdot F_{form} \cdot (F_{conc/water} \cdot K_{ow}+1) \cdot (1-F_{deg}) \cdot (1-F_{elim})\ F_{mwf} = C_{biocide,dil} \cdot D_{company\text{->}STP} \cdot CAP_{STP} \cdot F_{form} \cdot (F_{conc/water} \cdot K_{ow}+1) \cdot (1-F_{deg}) \cdot (1-F_{elim})\ F_{mwf}$			O
Preservative concentration in municipal STP influent	[kg m^{-3}]	$PEC_{STP} = E_{loc,water} \cdot CAP_{STP}^{-1} = C_{biocide,dil} \cdot D_{company\text{->}STP} \cdot F_{form} \cdot (F_{conc/water} \cdot K_{ow}+1)^{-1} \cdot (1-F_{deg}) \cdot (1-F_{elim})\ F_{mwf}$			O
Preservative concentration in river water (for further details see standard EUSES algorithm)	[kg m]	$PEC_{freshwater} \approx PEC_{STP} \cdot D_{STP\text{->}river}$			O

A summary of the algorithm and its defaults as suggested by the current stage of knowledge is given in Table 14. Details will be discussed in the following sub-sections.

S: set – free user input
D: default – value set by model algorithm
O: output - result or intermediate result of model algorithm
P: Pick-list - several defaults to choose from (e.g. depending on specific process (grinding, turning etc)

Dilution factors

As already proposed in the first project part the data collected so far via questionnaires suggest the use of revised dilution factors, i.e. higher ratios between the river and the STP volume as well as between the STP volume and the discharged waste water volume. The data gathered so far suggest dilution factors of 100 · 100 = 10000 overall. However, most data are still from Germany. Plausibility checks performed by Frank Bienewald suggest that the resulting release volumes are a reasonable worst case, but more datasets for end-users and waste treatment companies especially from EU countries other than Germany would be preferable.

Substance specific biocide concentrations

As mentioned above in section 0, the concentration in the diluted mwf is substance specific and should be given by the applicant based on the efficacy studies considering a buffer. If the concentration will be given as final (recommended) concentration in the diluted mwf, the algorithm will be more flexible and simultaneously simpler (see Table 14).

Ideally the basis of the exposure estimation should be the possible range of final biocide concentrations in the diluted mwf.

This approach would lead to more realistic – but still worst case - exposure results, as required concentrations and toxicity are both substance specific and not independent of each other.

Localised controls – risk mitigation measures (RMMs)

It had already been shown in the first project part and been confirmed in the last months, that there is always a selection of PC treatment techniques and partly also biological treatment present before the waste water is released into an STP or a water compartment, i.e. RMM efficiencies may be one additional, reasonable and realistic possibility for refinement.

RMM efficiencies are always substance specific, i.e. an exact but commonly applicable efficiency value cannot be derived.

However, the BREF document on common waste gas and waste water treatment techniques includes a number of examples substances on whose basis it has been tried to derive worst case efficiencies. These can be applied by an educated person, who is aware of possible substance specific problems or complications, to develop safe use scenarios. In addition, some general conclusions concerning the splitting of emulsions using evaporation of the water phase and corresponding efficiencies for a set of vapour pressure categories can be made (see paragraphs below the table).

The results of these evaluations can be found in Table 14.

Table 14: Suggestions for commonly used waste treatment techniques

Technique	Suggested efficiency	Examples / discussion
Sedimentation of solids	0%	BREF document[26]: Only applicable to particles or (for flotation) droplets not solved. Small efficiencies may be possible due to adsorption on solids, however, this is an individual process whose efficiency depends on the amount of solids and the adsorption coefficient. No derivation of a worst case default possible.
Flotation	0%	
Filtration / Microfiltration	0%	
Ultrafiltration	according to partition coefficient	BREF: Cut-off size for molecules in solution 1000-100000 g/mol, i.e. biocide molecules are usually only removed if they are solved in the oil fraction

[26] BREF document (best available technique reference document): Common waste gas and waste water treatment techniques, draft version (2011), summary of pp. 175 ff

Technique	Suggested efficiency	Examples / discussion
		Yordanov: 98-99% fat removal for ultrafiltration[27] (fats and suspended substances from poultry slaughterhouses)
Reverse Osmosis	80%	BREF document: Several examples which all show efficiencies above 80%, ranging up to 100% (e.g. Atrazine, DDT, Aldrin, Dieldrin, Dichlorvos, Malathion) Substance must be above 50-200 Daltons (50-200 g/mol cut-off, depending on filter material), or an ion.
Nanofiltration	70%	BREF document: Several examples which all show efficiencies above 70%, ranging up to 96% (e.g. mercury, organic mercury, tetrachloromethane, trichlorobenzence, atrazine). Even up to 100%. Substance must be above 200-1000 Daltons (depending on filter material, cut-off 200-1000 g/mol), i.e. 1000 g/mol molecular weight, or a multivalent ion. According to information sources in footnote also smaller molecular weights are possible depending on the used membrane (down to 100 g/mol).
Oil-water-separators (only in combination with other emulsion splitting technique, e.g. using waste acids and waste alkalis for emulsion splitting, organic breaking up agents for emulsion splitting)	according to partition coefficient	BREF document: 80-95% oil removal
Storage of waste	no default efficiency	It has been indicated by some questionnaire responses that after a certain time of storage the biocide is already degraded (-> odour development indicates bacteria growth). However, the degradation rate is both substance and media dependant, therefore it still has to be discussed in which form this degradation process can be used during a risk assessment.
wet oxidation with H_2O_2	90%	BREF document. Several examples (e.g. pesticides as a summary parameter, phenols, chlorophenols, toluence, alcohols, organic acids, MIBK, MTBE, HEPES, Ethanol, Acetone, Aniline, Pyrazole, Notrobenzenes, Pyridine) which all show efficiencies above 90%, sometimes even higher than 99%. Not enough data in BREF for other oxidation reagents.
chemical oxidation with chlorine/hypochlorite	0%	BREF document: Between 30% and more than 90% effiency; this suggests a very high variability, and only a small number of examples (phenols, oil, PAH, summary parameters AOX and TOC) therefore an efficiency of 0% is suggested.
Super critical water oxidation (new, not common technique)	*99%*	*efficiencies between 99 and 99.9% efficiency reported in BREF (e.g. DDT, Dioxin, "organic compounds, 1,2,4-Trichlorobenzene")*
High pressure wet air oxidation	60%	According to BREF document: Several examples which all show efficiencies above 60%, ranging up to 99% (e.g. Nitro compounds, Aromatic amines, Oxygen heterocycles). Fife pesticides show 97- >98% efficiency (Aldrin, DDT, Endosulfan,

27 http://www.agrojournal.org/16/06-06-10.pdf

28 ~~http://www.geafiltration.com/applications/nanofiltration_whey.asp~~
http://membranes.trisep.com/category/nanofiltration-membranes

Technique	Suggested efficiency	Examples / discussion
		Endrin, 2,4-Dichlorophenol).
Adsorption (PAC or GAC; granular of powdered active carbon)	65%	No data in BREF for other adsorption materials. Efficiencies for these materials range from 70% to 99.9% (e.g. for DDT, Aldrin, Dieldrin, Atrazin, Dic[redacted]exachloro-cyclohexane).
Extraction	0%	No default possible, efficiency depends on partition coefficient between water and the solvent which is used for extraction.
Splitting of emulsion by evaporation / distillation (see below for explanation)	0%	$p_{vap} > 1/2\ p_{vapH2O}$
	50%	$1/2\ p_{vapH2O} \geq p_{vap} > 1/10\ p_{vapH2O}$
	90%	$1/10\ p_{vapH2O} \geq p_{vap} > 1/100\ p_{vapH2O}$
	99%	$1/100\ p_{vapH2O} \geq p_{vap} > 1/1000\ p_{vapH2O}$
	99.9%	$p_{vap} \leq 1/1000\ p_{vapH2O}$
	100%	If the treated waste water is re-used in the process and not released into STP or a surface water compartment
		99% general efficiency for contaminants is reported in BREF document.
Stripping	no default efficiency	Only applicable to volatile substances (e.g. phenols, ammonia, dichloromethane) ideally higher volatiliy than water). Most biocides are not volatile, therefore it is not reasonable to suggest this technique in this context.
biological treatment	no default efficiency	Simple Treat estimation possible
Incineration of emulsion / oily waste	100%	Waste gases from these process have probably to be treated with further PC treatment techniques to prevent large releases of SO_2, CO etc. However, biocidal substances will be destroyed during the incineration process.

Tier 1 estimation: influence of vapour pressure on the RMM measure "evaporation"

The critical question is, if the substance of concern will remain in the oily residue or if it will evaporate together with the water.
In the following paragraphs it will be tried to estimate the efficiency of the evaporation process in relation to the contained biocide, i.e. how much differs the concentration after evaporation from the concentration before. In general this process can be quite complex, however a simplified tier 1 estimation is possible under the assumption of ideal behaviour. Special cases have to be taken into account (e.g. formaldehyde).

Ideal mixture:

$$p_{vap,overall} = p^0_{H2O}\ x_{H2O} + p^0_{oil}\ x_{oil} + p^0_{biocide}\ x_{biocide} + p^0_{other}\ x_{other} \qquad \textit{Raoults law}$$

$$p_{vap,overall} = p_{H2O} + p_{oil} + p_{biocidee} + p_{other} \qquad \textit{Daltons law}$$

p^0: vapour pressure of pure substance
p: partial pressure of a substance above the mixture
x: mole fraction of compound in liquid mixture

p_{oil} is almost 0 at the boiling point of water

$p^0_{other}\ x_{other}$ can most likely be neglected as the concentration of other substances are expected to be low compared to the concentration of water.

$$\Rightarrow \quad p_{vap,overall} \approx p^0_{H2O}\ x_{H2O} + p^0_{biocide}\ x_{biocide}$$

Example:

$x_{biocide}$ [g/g] = 0.01 (1%);
$p_{biocide}^{0} = p_{H2O}^{0}$
x_{water} [g/g] = 0.9 (90%);
9% oil content with very low vapour pressure

It is assumed that mole fraction and mass fraction are approximately the same. This is not completely correct as the molecular weight of the average biocide will be several times higher than the weight of a water molecule (exceptions are possible, e.g. formaldehyde). Thus, it will lead to an overestimation of the molecular fraction.

➔ $p_{vap,overall} = p_{H2O}^{0}\ 0.9 + p_{H2O}^{0}\ 0.01$

The vapour pressure is proportional to the number of molecules in a volume, i.e. the concentration in mole (or number of molecules) per cubic metre. Therefore, the following mole fractions are expected in the mixture:

x_{H2O} = 0.9/(0.9+0.01) = 99%

$x_{biocide}$ = 0.1/(0.9+0.01) = 1.1%

As expected this is approximately the same fraction as before the distillation process. Here again it is assumed that the mass fraction is identical to the mole fraction. Again this leads to uncertainties, but as this assumption has been made twice for conversions in different directions some error compensation will be present which will reduce the uncertainties in this approach.
If the vapour pressure of the pure biocide is assumed to be 1/10 of the vapour pressure of pure water the following concentrations in the resulting, evaporated water are expected:

➔ $p_{vap,overall} = p_{H2O}^{0} \cdot 0.9 + p_{H2O}^{0} \cdot 0.01 \cdot 0.1 = 0.901 \cdot p_{H2O}^{0}$

x_{H2O} = 0.9/(0.9+0.001) = 99.9%

$x_{biocide}$ = 0.01/(0.9+0.001) = 0.11%

This means a reduction of approximately 90%.

Similar calculations can be made for other vapour pressures and lead to efficiencies of ~50% ($p_{biocide}^{0} = 0.5 \cdot p_{H2O}^{0}$), ~99% ($p_{biocide}^{0} = 0.01 \cdot p_{H2O}^{0}$); ~99.9% ($p_{biocide}^{0} = 0.001 \cdot p_{H2O}^{0}$) and ~99.99% ($p_{biocide}^{0} = 0.0001 \cdot p_{H2O}^{0}$).

Summary

We are confident that enough data are available to support dilution factors of $D_{overall}$ = 100·100 = 10000 for end-users in Germany.

To support the revised dilution factors for other countries and waste treatment companies more data from waste treatment companies and end-users especially for other EU countries than Germany are needed.

There are also other possibilities to refine the exposure scenario which do not depend on the questionnaire. In particular, the default biocide concentrations can be replaced by substance specific values and applicable RMMs can be identified using worst case efficiencies derived from example efficiencies reported in the BREF document (Common waste gas and waste water treatment techniques).

APPENDIX C: GATHERING OF INFORMATION FOR THE REFINEMENT OF THE ENVIRONMENTAL EMISSION SCENARIO FOR METALWORKING FLUIDS (PT13) UNDER BPD/R: STATUS REPORT APRIL 2014

INTRODUCTION

Since the last status report from December 2013 three further replies concerning our questionnaire have been received from German waste treatment companies. No further replies from mwf end uses have been received.

However, we had the opportunity to visit a meeting of the German BDE[29] in order to gather further information. Following suggestions given during this meeting, we have started to evaluate the PRTR (pollutant release and transfer register). This database contains information about the release of certain pollutants (e.g. heavy metals) and in addition the amount of waste (hazardous and non-hazardous) which is transferred by the different facilities.

Exemplary waste management facilities, which are known to or at least likely to treat used mwf, have been extracted including the amount of waste. In addition – as far as publicly available within PRTR or other sources of information – treatment techniques, corresponding sewage treatment plants into which the waste water is released, receiving water compartments and their volumes have been identified in order to create further data points that complement the information already gathered via personal communication and answered questionnaires.

EVALUATION STRATEGY

The PRTR database mainly consists of one centralised, EU wide database[30]. In addition local PRTR versions, which are sometimes more up to date than the EU wide version and usually in the language of the country, are also available for some of the member states[31].

Member states

To gain a representative insight into the waste management sector examples from a selection of members states have been searched and extracted from PRTR (2-5 example facilities for each, depending on availability of information) and evaluated.

So far, examples from the following countries are included:

- Germany
- Poland
- Hungary
- The Netherlands
- Italy
- Spain
- UK

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[29] Bundesverband der Deutschen Entsorgungs-, Wasser- und Rohstoffwirtschaft (Federal association of German waste management -, water – and feedstock industry)

[30] http://prtr.ec.europa.eu/, most recent year reported: 2011 (state of affairs: 06.05.2014)

[31] e.g. Spain: http://www.prtr-es.es/; Germany: http://www.thru.de/; UK: http://prtr.defra.gov.uk/

- F (information extracted and provided by S. Alexandre)

This selection is considered to be representative for the EU wide treatment of used mwf, as it includes the most prominent market sectors concerning metalworking and production of metal articles (see Ecorys, 2009[32], Figure 5).

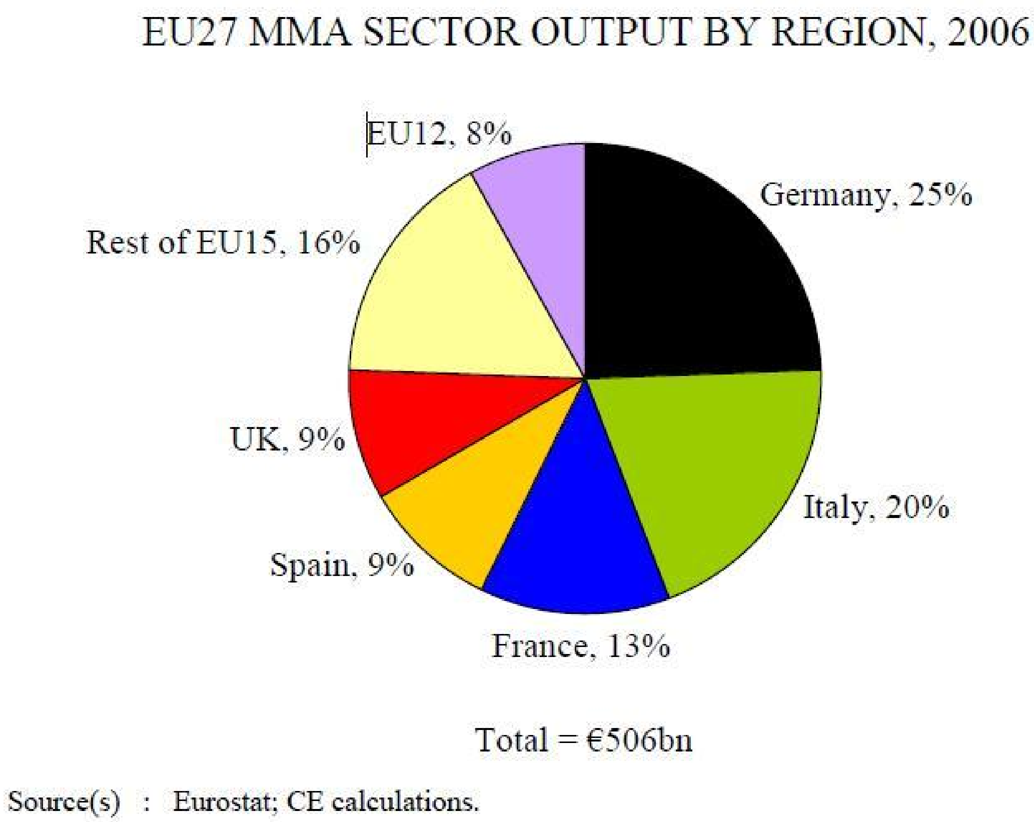

Figure 5: Metalworking and metal articles sector output (source: Ecorys 2009).[33]

Selected facilities

For the selection of example facilities the database has been filtered concerning the NACE Code[34], i.e. only facilities filed under "waste and waste water treatment: disposal and recovery of hazardous waste" (code 38.22) have been listed for further evaluation. However, this category may include a large variety of wastes, e.g. batteries, pure oils and other solid wastes like contaminated soil or minerals. Therefore usually the companies' homepages were also inspected to identify those which may treat significant amounts of emulsions. The amount and quality of available information varies greatly between countries and facilities (see following sub-chapters).

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32 http://ec.europa.eu/enterprise/sectors/mechanical/files/metalworking/mma_final_report_181109_final_en.pdf

33 **EU12**: Bulgaria, Czech Republic, Estonia, Hungary, Latvia, Malta, Poland, Romania, Slovenia, Slovak Republic (since 1. May 2004)
EU15: Austria, Belgium, Denmark, Finland, France, Germany, Greece, Ireland, i.e."rest of EU15" refers to Austria, Belgium, Denmark, Finland, Greece, Ireland.

34 **NACE:** Nomenclature statistique des activités économiques dans la Communauté européenne

Extraction of information

The following information has been extracted from PRTR:

- Waste transfers (recovery and disposal added up for domestic transfer of hazardous waste).

  Assumption: The amount of transferred waste is identical to the amount of hazardous waste treated at this site. 300 release days per year and ~95% water content have been assumed in order to estimate the released waste water per day.

- Location and name of facility.

  Assumption: The nearest municipal sewage treatment plant is responsible and receives the corresponding waste water from the used mwf. In case of doubts the smaller STP was chosen as a worst case assumption.

STP capacities have been extracted from the EU wide STP database.[35] The receiving water compartments were located via Google Maps and river volumes searched via Google search in various sources of information.

OVERVIEW OF RESULTS

EU

Overall 2158 facilities are registered in 2011 for waste and waste water treatment (disposal and recovery of hazardous waste) in the EU.

Germany

Overall 844 facilities are registered within PRTR for 2011. This corresponds to approximately 40% of all waste treatment facilities in the EU.

6 example facilities were extracted from PRTR for which physico chemical treatment / treatment of emulsions was indicated on the companies' webpage and/or on other, local resources of information[36]. It is considered to be possible to find further examples in order to increase this selection.

- Blum GmbH in Melle:
  - PRTR entry: http://prtr.ec.europa.eu/FacilityDetails.aspx?FacilityId=43623&ReportingYear=2011
  - PC treatment indicated on webpage: http://www.blum-gruppe.de/index.php/industrie-entsorgung
  - List of accepted waste types includes emulsions: http://www.blum-gruppe.de/images/AVV-Katalog_Blum_GmbH.pdf
- GSB Sonderabfall-Entsorgung in München

35 http://www.eea.europa.eu/data-and-maps/data/waterbase-uwwtd-urban-waste-water-treatment-directive-3/dataset_view#previous-versions

36 e.g. http://www.abfall-nrw.de/aida/, http://www.lfu.bayern.de/abfall/verwerterdatenbank/recherche/index.htm

- PRTR entry: http://prtr.ec.europa.eu/FacilityDetails.aspx?FacilityId=45687&ReportingYear=2011
- Description of emulsion treatment techniques: http://www.inters-ora.bayern.de/verwerter/php/selektVerfahren.php?VERFAHREN_ID=114324&VW_ID=37211&AVV_ID=120109&AVV_BEZEICHNUNG=halogenfreie_Bearbeitungsemulsionen_und_-l%F6sungen
- List of facilities: http://www.gsb-mbh.de/leistungen.php

- Lobbe in Iserlohn
  - PRTR entry: http://prtr.ec.europa.eu/FacilityDetails.aspx?FacilityId=74088&ReportingYear=2011
  - Emulsion treatment / PC treatment indicated on http://www.abfall-nrw.de/aida/einzel.php?objtype=ens&eanl_id=633; http://www.abfall-nrw.de/aida/amedaausw.php?gid=E96295164&c|thema=enseinzel&r|thema=abfart&r|level=1&action=run
- GSB Sonderabfall-Entsorgung in Ebenhausen:
  - PRTR entry: http://prtr.ec.europa.eu/FacilityDetails.aspx?FacilityId=45686&ReportingYear=2011
  - treatment of emulsions indicated on http://www.lfu.bayern.de/abfall/verwerterdatenbank/recherche/index.htm; http://www.gsb-mbh.de/leistungen.php
- BAUFELD-Oel GmbH in Chemnitz:
  - treatment of emulsions: http://www.inters-ora.bayern.de/verwerter/php/selektVerfahren.php?VERFAHREN_ID=115547&VW_ID=30331&AVV_ID=130105&AVV_BEZEICHNUNG=nichtchlorierte_Emulsio nen
  - German PRTR entry (from 2012, no entry for 2011 found): http://www.thru.de/search/?c=search&a=detail&betriebId=29768&kalendarjahr=2012&view=betriebe
- Remondis in Schwentinental
  - German PRTR information (from 2012, no entry for 2011 found): http://www.thru.de/search/?c=search&a=detail&betriebId=40120&kalendarjahr=2012&view=betriebe
  - indication of PC treatment: http://www.remondis-industrie-service.de/uploads/tx_3slocations/WHG_Klausdorf_nae._Pruef._2015-Mai_vom_2013-06-10.pdf
  - indication of emulsions: http://www.remondis-industrie-service.de/uploads/tx_3slocations/Efb_RIS_Klausdorf_-_bis_2014-10-08_-__vom_2014-02-06.pdf

Poland

Overall 31 facilities are registered within PRTR for 2011. This corresponds to ~1.4% of all facilities within the EU.

Only very few information was found that indicated physico chemical treatment of emulsions. Mostly incineration was indicated, e.g. in construction industries. For other facilities the major responsibility seemed to be ship / tanker cleaning, i.e. emulsions may be involved but most likely not from the use of mwf. However, 4 examples were extracted from PRTR which are considered to be likely to treat emulsions.
The apparently small number of facilities using PC treatment correlates with the small market sector for metal articles and metalworking activities identified in Ecorys (2009).

In general, it is difficult in case of Poland to locate STPs as the coordinates filed in the STP database seem to be erroneous and names are not always related to the city where the STP is located. Therefore, in two cases the STP volume was estimated using the population of the corresponding town and the standard value of 200 l/p.e./day.

- Spółka Wodna "Międzyodrze" w Szczecinie, Zakład in Stettin
  - PRTR entry: http://prtr.ec.europa.eu/FacilityDetails.aspx?FacilityId=21194&ReportingYear=2011;
  - Emulsions treatment indicated on homepage: http://translate.google.de/translate?hl=de&sl=pl&u=http://www.miedzyodrze.pl/&prev=/search%3Fq%3Do%2509Sp%25C3%25B3%25C5%2582ka%2BWodna%2B%2522Mi%25C4%2599dzyodrze%2522%26client%3Dfirefox-a%26hs%3DLx1%26rls%3Dorg.mozilla:de:official%26channel%3Dsb
- Awas Serwis in Zyrardow
  - PRTR entry: http://prtr.ec.europa.eu/FacilityDetails.aspx?FacilityId=81548&ReportingYear=2011
  - emulsions indicated on homepage: http://www.awas- serwis.pl/oferta/utylizacja
- Art-Eko Utylizacja, Asenizacja, Recykling Sp.zo.o., Oczyszczalnia ścieków przemysłowych in Świdnicy
  - PRTR entry: http://prtr.ec.europa.eu/FacilityDetails.aspx?FacilityId=21176&ReportingYear=2011
  - List of accepted wastes: http://translate.google.de/translate?hl=de&sl=pl&u=http://www.scieki.pl/&prev=/search%3Fq%3D%25E2%2580%25A2%2509Art-Eko%2BUtylizacja%26client%3Dfirefox-a%26hs%3DEE2%26rls%3Dorg.mozilla:de:official%26channel%3Dsb
- Pressekko in Bolechowo
  - PRTR entry: http://prtr.ec.europa.eu/FacilityDetails.aspx?FacilityId=21165&ReportingYear=2011
  - PC treatment and treatment of emulsions indicated on homepage: http://translate.google.de/translate?hl=de&sl=pl&u=http://www.presseko.pl/&prev=/search%3Fq%3Dhttp://www.presseko.pl%2523%26client%3Dfirefox-a%26hs%3DQbh%26rls%3Dorg.mozilla:de:official%26channel%3Dsb

The collection of more examples facilities for Poland is considered to be difficult, as the overall number of facilities as well as the corresponding amount of information about them is limited.

Hungary

Overall 25 facilities are found for 2011 in the PRTR database. This corresponds to ~1.2 % of all facilities within the EU.

As in case of Poland, often no web-page with information on treated wastes or techniques could be found. However, 3 examples have been extracted which seem to indicate that emulsions are treated:

- Palota Környezetvédelmi Kft. in Budapest
    - o PRTR entry: http://prtr.ec.europa.eu//PopupFacilityDetails.aspx?FacilityReportId=584944;
    - o Accepted waste types listed on homepage: http://www.palotakft.hu/palota/KTVF14661-16-2012veszhszalleng.pdf
- HAJDU Infrastruktúra in Telep
    - o Emulsions and PC treatment indicated on homepage: http://www.hajduiparipark.hu/content/en/public-utilities.html;
    - o PRTR entry: http://prtr.ec.europa.eu//PopupFacilityDetails.aspx?FacilityReportId=5853 70
- Győri Hulladékégető Kft. in Gyor
    - o PRTR entry: http://prtr.ec.europa.eu//PopupFacilityDetails.aspx?FacilityReportId=5851 22
    - o Emulsions listed on homepage: http://www.gyhk.hu/index.php?m=egetheto

A collection of more examples for Hungary is considered to be difficult, as the overall number of facilities is limited and it is often not known which types of waste are treated and how.

Netherlands

Overall 68 facilitites are listed for 2011. This correspons to approximately 3.2% of all facilities in the EU.

2 examples have been extracted.

- Central Mudplant and Fluid Services BV (CMF) in Velsen
    - o PRTR entry: http://prtr.ec.europa.eu//PopupFacilityDetails.aspx?FacilityReportId=557807
    - o Distillation of cutting fluids etc. indicated on homepage: http://www.cmfservices.nl/NL/
- bcultrafiltratie in Uden
    - o PRTR entry: http://prtr.ec.europa.eu//PopupFacilityDetails.aspx?FacilityReportId=557815

- o emulsion treatment indicated on homepage: http://www.bcultrafiltratie.nl/

The collection of more examples from the Netherlands is considered to be possible

Italy

Overall 203 facilities are registered in Italy in the year 2011. 2 Examples have been extracted.

- A.O.C. s.r.l. in Genova
  - PRTR entry: http://prtr.ec.europa.eu/FacilityDetails.aspx?FacilityId=176916&ReportingYear=2011
  - emulsions as well as PC treatment indicated on homepage: http://www.aoc-genova.it/download/AIA_990_del_21-02-2011_Relazione.pdf
- ASPIRECO Srl in Gavardo
  - treatment of wastes from metalworking industries indicated on homepage: http://www.aspireco.it/en/waste-treatment.html,
  - PRTR entry: http://prtr.ec.europa.eu//PopupFacilityDetails.aspx?FacilityReportId=555236);

The extraction of more example facilities for this country is considered to be possible.

Spain

For Spain, overall 97 facilities are registered in PRTR in 2011 (~4.5% of all facilities in the EU) and 108 in 2012 (according to the local Spanish PRTR database).

In contrast to the other member states evaluated in case of Spain comparably detailed information is available in the local PRTR database. This includes transferred tonnages per waste type for each facility within the database and also the intended fate of the waste (storage, transport, biological treatment, PC treatment etc.) [37].

Waste types are differentiated following the European list of wastes[38]. Waste types considered to be relevant in this case are mostly those with code numbers 120108 and 120109 (machining emulsions and solutions containing halogens or no halogens), but also 130104 and 130105 (chlorinated/ not chlorinated emulsions) or 130802 (other emulsion) may include used mwf emulsions.

Of the facilities listed in the Spanish, local PRTR database (2012) 8 indicate PC treatment of emulsions, 1 indicates incineration of emulsions, 2 indicate storage of emulsions, 1 indicates oil refining and 2 indicate organic substance recycling in relation to emulsions. For this project physico chemical treatment (code number D9) is considered to be most relevant and these sites have been used for the extraction of examples.

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37 www.sepa.org.uk/waste/waste_data/reporting_definitions_and_term/idoc.ashx?docid=4ddf5800-b9a1-49bc-9cd4-f773203bc0b7&version=-1

http://www.nwcpo.ie/forms/EWC_code_book.pdf 38 http://www.nwcpo.ie/forms/EWC_code_book.pdf

The extracted information in case of Spain includes the amount of waste related to emulsions (see above) which has been assumed to consist completely of used mwf, and the summed up amount of waste intended for PC treatment, which has been used to estimate the amount of emitted waste water (assumption: ~95% water content, 300 emission days per year as mentioned above).

6 examples have been extracted from the database:

- BEFESA GESTIÓN DE RESIDUOS INDUSTRIALES, SL (CENTRO DE DERPIN) in MONTORNES DEL VALLES
    - PRTR entry: http://www.prtr-es.es/informes/fichacomplejo.aspx?Id_Complejo=355
- FCC AMBITO S.A. - PLANTA GEMASUR in Cordoba
    - PRTR entry: http://www.prtr-es.es/informes/fichacomplejo.aspx?Id_Complejo=635
- Ecologica Chimica in Sant Celoni
    - PRTR entry: http://www.prtr-es.es/informes/fichacomplejo.aspx?Id_Complejo=2755
- Ecocat Vila Real in Vila-Real
    - PRTR entry: http://www.prtr-es.es/informes/fichacomplejo.aspx?Id_Complejo=2785
- SERTEGO CENTRO DE CARTAGENA (AUREMUR) in Cartagena
    - PRTR entry: http://www.prtr-es.es/informes/fichacomplejo.aspx?Id_Complejo=3211
- FCC ÁMBITO, S.A. in Barcelona
    - PRTR entry: http://www.prtr-es.es/informes/fichacomplejo.aspx?Id_Complejo=2874

UK

Overall 328 facilities are registered in PRTR for 2011. This corresponds to approximately 15.2% of all facilities registered within the EU.

Two examples have been extracted:

- tradebe, site Cheshire
    - PC treatment indicated on homepage: http://www.tradebe.co.uk/business-areas/44-waste-management/80- physio-chemical-treatment
    - PRTR entry: http://prtr.ec.europa.eu//PopupFacilityDetails.aspx?FacilityReportId=580347
- arrow environmental in West Bromich
    - PRTR entry: /http://prtr.ec.europa.eu//PopupFacilityDetails.aspx?FacilityReportId=582511

- o Oily waste water treatment indicated on homepage: http://www.arrow- environmental.co.uk/oily-water.asp

The collection of more example facilities for this country is considered to be possible.

France

Information for France has been searched and provided by S. Alexandre from the French Agency for Food, Environmental and Occupational Health Safety.

The information has been extracted from the following sources of information and transferred into the established excel template afterwards.

- French register of pollutant emissions: http://www.pollutionsindustrielles.ecologie.gouv.fr/IREP/index.php?adr=http://www.pollutionsindustrielles.ecologie.gouv.fr/IREP/
- http://assainissement.developpement-durable.gouv.fr/
- French database Hydro: http://www.hydro.eaufrance.fr/presentation/procedure.php

The reported mwf amounts include synthetic machining oil, mineral machining oil with or without halogens (not under emulsions or solutions), machining emulsions and solutions with or without halogens as well as readily biodegradable machining oil.

VERIFICATION OF EVALUATION METHOD

To get information about the accuracy of the approach used for the evaluation of the PRTR database, entries for the datasets already available via personal communication / questionnaires has been searched and the PRTR entries have been compared with the transmitted information.

Of 9 received questionnaires, for 8 corresponding PRTR entries could be identified while for one the company name was not available and therefore the PRTR could not be searched. Of the 8 entries analysed, for 5 facilities the waste amounts indicated by the received questionnaires show comparable orders of magnitude to the PRTR amount of transferred, hazardous waste. In one of the questionnaires only the waste water amount (and not the amount of waste) was indicated: In this case the waste water amount in the questionnaire is 3 times larger than the amount estimated from the PRTR entry, however, the questionnaire also indicated that only one third of the waste water originates from used mwf.

Of the remaining two questionnaire replies one indicates larger amounts of waste than in PRTR (possible reasons for this may be the difference between waste transfer and waste treatment or fluctuations between different years) and one smaller amounts (a possible reason for this may be waste without water content / not intended for PC treatment).

Overall it can therefore be concluded that, although there may sometimes be differences between the information found in PRTR and the information gathered directly from facility owners, the applied approach will be able to give reasonable results. Over- and underestimations of the emitted volumes are in general possible but are expected to compensate each other at least partly and, moreover, do not seem to be the normal case.

SUMMARY / CONCLUSION

As already established during earlier stages of the project emulsions such as used mwf are considered to be hazardous waste. Therefore emulsions are not allowed to be led directly into water compartment without further treatment. These treatment techniques always include some kind of emulsion splitting (e.g. via ultrafiltration, acid splitting) and further PC treatment techniques as well as biological treatment. It could be confirmed by analysis of PRTR and various Internet sources including the facility homepages, that there is no standard procedure or technique for the treatment of emulsions, however, some kind of treatment is always applied.

No further information about the number of directly discharging companies (i.e. which do not refer to the municipal STP but discharge waste water directly into rivers or the sea) could be gathered. However, following the information gathered during earlier stages of the project, it is considered to be likely that most waste management facilities will lead their waste water to the responsible sewage treatment plant. If this is not the case, biological sewage treatment is usually performed directly at the waste treatment facilities site. Therefore this assumption will not lead to an underestimation of the risk.

Furthermore, to avoid underestimations of exposure and risk in case of doubts, i.e. if several STPs are near the evaluated facility, the STP with the smallest capacity has been chosen for the estimation of the dilution factor. Slight underestimations of the concentration in the STP may appear due to the usage of capacities from the EU database instead of minimum capacities. However, these deviations are considered to be comparably small and at least partly compensated by other worst case assumptions such as the dilution factor of 100 (facility -> STP) which is still highly conservative regarding the available information.

Furthermore, it has been shown that the general approach of PRTR evaluation (waste transfer = waste treatment) is sufficiently reliable. Therefore it is overall expected that the results presented in this status report represent a realistic picture of the treatment of used mwf in waste treatment facilities in Europe.

Evaluation of the dilution factors derived from the PRTR database show an average value of 18441 for the release of waste water into the municipal sewage treatment plant and an average value of 5103 for the release from STP into the river system or sea[39].

Of the available dilution factors concerning the step from waste treatment facility to STP only two are smaller than 100, while for the second dilution step (STP→ river/sea) 13 facilities seem to have values lower than 100. These values can at least partly be explained by a number of uncertainties, e.g. river volumes are sometimes not available for the exact location of the STP or even only as an average for the whole river. Moreover there is a number of locations / rivers systems, where no volume per day value could be identified at all for the river in question.
Thus, overall the current state of affairs including the information gathered in the course of PRTR evaluation is not sufficient to support dilution values above 10 in case of this second dilution step but it is considered to be more than sufficient to justify the application of a dilution factor of 100 for the release of waste water into the municipal sewage treatment system.

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39 For comparison:
The EUBEES ESD suggests 10 for both dilution steps.
In earlier stages of the project dilution factors of 100 for both steps (i.e. an overall dilution of 10000 from facility to river) has been suggested.

Moreover, available information on the fraction of mwf within the overall amount of treated waste in PRTR suggests that an assumption of 50% mwf in waste is still very conservative, i.e. the value previously proposed is supported.

This results in the following exposure scenario (adapted version of Table 1 from Status report / December 2013; changes have been marked red).

Table 15: Suggestions for an ESD revision - current state of affairs (May 2014)

Variable/parameter	Unit	Symbol	Value (release into municipal STP)		S/D/O/P
			end-user + on-site treatment	external waste treatment company	
Input					
Concentration of the chemical in the diluted emulsifiable metalworking fluid	$[kg.m^{-3}]$	$C_{biocide,\ dil}$			S
Volume ratio concentrate / water phase	[-]	$F_{conc/water}$			S/P
Dilution factor company-> municipal STP	[-]	$D_{company\text{->}STP} = V_{STP}/V_{company}$	100	100	D/S
Capacity of the receiving municipal STP	[m .d 1]	CAPSTP	2000	2000	D
Treated volume of metalworking fluid	[m .d]	$V_{proc,emul.} = D_{company\text{->}STP}^{-1} \cdot CAPSTP$	20	20	O
Fraction of metalworking fluid in treated volume	[-]	F_{mwf}	1	0.5	S/D
Fraction of metalworking fluid with chemical of interest in treated volume	[-]	F_{form}	1	0.5	S/D
Fraction of chemical degraded during industrial use	[-]	F_{degr}	0	0	D
Partition coefficient n-octanol/water	[-]	K_{OW}			S
Fraction of elimination of the chemical during physical or chemical treatment – to be discussed	[-]	F_{elim}	see status report Decem-ber 2014	see status report Decem-ber 2014	S
Dilution factor municipal STP-> river	[-]	$D_{STP\text{->}river} = V_{river} \cdot V_{STP}$	100	**10**	D
Overall dilution	[-]	$D_{overall} = D_{company\text{->}\ STP} \cdot D_{STP\text{->}river}$	10000	1000	D

River flow rate	$[m^3\ d^{-1}]$	$V_{river} = CAP_{STP} \cdot D_{STP\text{->}river}$	198000	19800	O
Number of release days (only required for regional concentrations)	[-]	N	300	300	D
Output					
Emission to municipal STP	$[kg\ d^{-1}]$	$E_{local,water} = C_{biocide,dil} \cdot V_{mwf,dil} \cdot F_{form} \cdot (F_{conc/water} \cdot K_{ow}+1) \cdot (1-F_{deg}) \cdot (1-F_{elim})\ F_{mwf}$ $= C_{biocide,dil} \cdot D_{company\text{->}STP} \cdot CAP_{STP} \cdot F_{form} \cdot (F_{conc/water} \cdot K_{ow}+1) \cdot (1-F_{deg}) \cdot (1-F_{elim})\ F_{mwf}$			O
Preservative concentration in municipal STP influent	$[kg\ m^{-3}]$	$PEC_{STP} = E_{loc,water} \cdot CAP_{STP}^{-1}$ $= C_{biocide,dil} \cdot D_{company\text{->}STP} \cdot F_{form} \cdot (F_{conc/water} \cdot K_{ow}+1)^{-1} \cdot (1-F_{deg}) \cdot (1-F_{elim})\ F_{mwf}$			O
Preservative concentration in river water (for further details see standard EUSES algorithm)	$[kg\ m^{-3}]$	$PEC_{freshwater} \approx PEC_{STP} \cdot D_{STP\text{->}river}$			O

Default efficiencies for a number of common waste water treatment techniques as described in the last status report may be applied (“Fraction of elimination of the chemical during physical or chemical treatment”). However, to which extent these values can be implemented in the final ESD has still to be discussed.

APPENDIX D: QUESTIONNAIRE

QUESTIONNAIRE – END-USERS

Background

Currently two different Emission Scenario Documents (ESD) are under discussion for the environmental exposure assessment of biocides in the water phase of water miscible metalworking fluids (wm mwf, emulsifiable and soluble metalworking fluids).

The emission scenario document which is commonly used at the moment in the EU is the EUBEES ESD[40]. There have been questions over the accuracy and reliability of the default values of this ESD. Moreover it has long been recognized that this model will probably not allow any of the existing biocidal substances to pass the environmental risk assessment, thus, its application for exposure estimations is expected to lead to significant restrictions in the metalworking fluids industry sector.

More recently, an OECD document on metalworking fluids has been published (emission scenario document on the use of metalworking fluids, June 2011)[41]. There have been attempts to establish this scenario. However, the OECD document is based only on working practices in the USA and data gathered from the MWF industry in the USA during the mid to late 1990's. Thus there are significant concerns over the relevance of the OECD ESD to European situation and relevance of data gathered in the USA in the 1990's to today's European industry.

Therefore, the Competent Authorities requested data from industry to help inform this ongoing discussion. As result, industry has formed a working group under the umbrella of the "Verband Tegewa e.V." (Frankfurt) in order to provide additional information to the Competent Authorities.

The "TEGEWA MWF Working Group" has agreed to fund a project to investigate the handling and disposal of used metalworking fluids. The project has been placed with the Fraunhofer Institute for Toxicology and Experimental Medicine (Fraunhofer ITEM) and the initial findings of this project are planned to be available for presentation and discussion at the Technical Meeting in June, 2013.

Questionnaire

General

It is intended to gather information about the handling and waste treatment of water miscible metal working fluids (wm mwf). Please give a general description of the situation in your company concerning the use and the discharge of wm mwf. How are your wm mwf handled? Is there any further waste treatment of the used wm mwf?

In the EUBEES scenario document, which is currently in use, a further differentiation of the water based (i.e. water miscible) mwf is made into water soluble and emulsifiable mwf. Different default values are used for both types of mwf. Therefore we will appreciate if you can indicate which type of water miscible metalworking fluids you are

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40 http://ihcp.jrc.ec.europa.eu/our_activities/public-health/risk_assessment_of_Biocides/doc/ESD/ESD_PT

41 http://www.oecd.org/env/ehs/risk-assessment/emissionscenariodocuments.htm

using and describe differences concerning handling and waste treatment, if existent. Otherwise please confirm that both types of mwf are treated together.

Details

Questions to end-users of wm mwf:

1. Please indicate if use water soluble or emulsifiable mwf or both. If you differentiate between water soluble and emulsifiable mwf in your company during use and/or waste treatment, please answer all following questions separately for water soluble and emulsifiable mwf. If your company is working at different locations please also answer the questions separately for each site.
2. a. Which overall tonnage of wm mwf concentrate per year does the company consume?

   b. Do you use concentrates which are already treated with biocides? If yes, which fraction of the overall concentrate amount is this?
3. Are there different biocides used for the wm mwf in your company? If yes, please specify if these biocides are used for different application areas (e.g. only for treatment of concentrate, only for a specific process).
4. Which is the maximum fraction for one biocide (e.g. „60% of the overall tonnage are treated with biocide x“)?
5. a. Typical concentration of biocide in wm mwf concentrate and diluted metalworking fluid (overall and/or per biocidal substance, if several biocides were used)?

   b. Typical concentration of biocide in the diluted mwf/ emulsion?
6. Typical fraction of concentrate in ready-to-use wm mwf (please differentiate between different processes if necessary)?
7. Is treatment and disposal in your company organised in a continuous way or are there only some release days per year? How many emission days are there per year (i.e. discharge of used wm mwf)? How many operating days are there?
8. How are the used wm mwf handled?

   a. on-site treatment and internal recycling, disposal into municipal treatment plant or directly into a river or the sea?

   b. are waste emulsions brought to an external waste management company? If yes, please let us now the name and contact data of this company.
9. Flow rate of the river (m^3/day) to which the company or the responsible STP discharges their waste water? Alternatively indicate if the release is into the marine environment.
10. Capacity of STP, if the waste (water) is discharged into a public STP (m^3/day)? Are there restrictions for the discharge into the STP?
11. Which type of on-site waste treatment do you use for your wm mwf (e.g. ultrafiltration, vaporisation of water phase, biological waste water treatment)? Please indicate if and which amount of the waste water is recycled (e.g. evaporation and reuse of water and incineration of remaining chemicals).
12. What is the volume of waste water emitted per day by your company/site?
13. Which kind of chemical analyses do you perform on your wastewater before discharge (e.g. COD, heavy metals)? Do you know in which concentration of

biocide is in your waste water when you release it from your site (to a river, STP, external waste management company)? Which is the efficiency of your on-site waste treatment? Is the major reason for discharge of the fluid the contamination with bacteria and/or fungi?

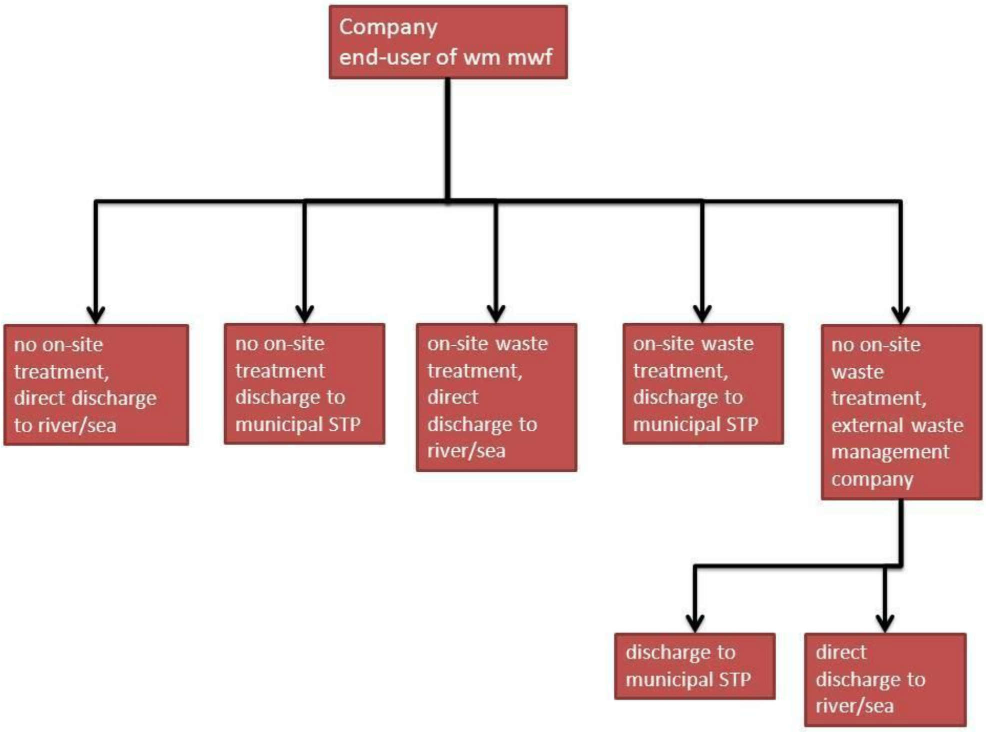

Figure 1: Possible pathways of used wm mwf.

Confidentiality issues

It is suggested that in cases where the relevant information is considered to be confidential it is sent directly to Fraunhofer ITEM:

Contact addresses:

Dr. Susanne Hesse
Fraunhofer Institute for Toxicology and Experimental Medicine ITEM, Chemical Risk Assessment
Nikolai-Fuchs-Strasse 1, 30625 Hannover, Germany
mailto:susanne.hesse@item.fraunhofer.de
Tel.: +49 (0) 5 11/53 50-366
Fax.: +49 (0) 5 11/53 50-335

Dr. Stefan Hahn
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Nikolai-Fuchs-Strasse 1, 30625 Hannover, Germany
mailto:stefan.hahn@item.fraunhofer.de
Tel.: +49 511 5350-326,
Fax: +49 511 5350-335

All information will be treated confidentially and be included into project reports only in anonymised form.

QUESTIONNAIRE – WASTE MANAGEMENT COMPANIES

Background

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In the EUBEES scenario document, which is currently in use, a further differentiation of the water based (i.e. water miscible) mwf is made into water soluble and emulsifiable mwf. Different default values are used for both types of mwf. Therefore we will appreciate if you can indicate which type of water miscible metalworking fluids you are using and describe differences concerning handling and waste treatment, if existent. Otherwise please confirm that both types of mwf are treated together.

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42 http://ihcp.jrc.ec.europa.eu/our_activities/public-health/risk_assessment_of_Biocides/doc/ESD/ESD_PT

43 http://www.oecd.org/env/ehs/risk-assessment/emissionscenariodocuments.htm

Details

Questions to waste management companies

1. Please indicate if you receive water soluble or emulsifiable mwf or both.
   Do you also receive other oil-water-mixtures or other water-mixed liquids? Are the different liquid wastes mixed or separate?

   If you differentiate between water soluble and emulsifiable mwf in your waste management company (concerning general handling and waste treatment) please answer all following questions separately for water soluble and emulsifiable mwf.
2. How much waste is handled (per day, per year)?
3. How much of this is caused by used wm mwf?
4. Which type of waste treatment is your common practice for used wm mwf (e.g. ultrafiltration, vaporisation of water phase, biological waste water treatment)?
5. Which kind of chemical analyses are you doing before your waste water is released (e.g. COD, heavy metals). How efficient is this waste treatment especially for biocides? Are there estimates or measured concentrations for biocides in the water that is released into the environment or a STP?
6. What is the discharge rate of the waste management company (tonnes waste water per day)? Please indicate if the waste water is not discharged but recycled (e.g. by vaporisation of the water and incineration of the remaining waste).
7. Do you discharge your waste water directly to the river/sea or to a public STP?
8. Which is the flow rate of the receiving river (alternatively please indicate if the release is into the marine environment)?
9. Which is the capacity of the STP, if the waste (water) is discharged into a public STP (m^3/day)? Are there restrictions for the discharge into the STP?
10. How many emission days are there per year (i.e. discharge of waste water, ideally only days related to release of waste water from used wm mwf)?
    How many operating days are there?

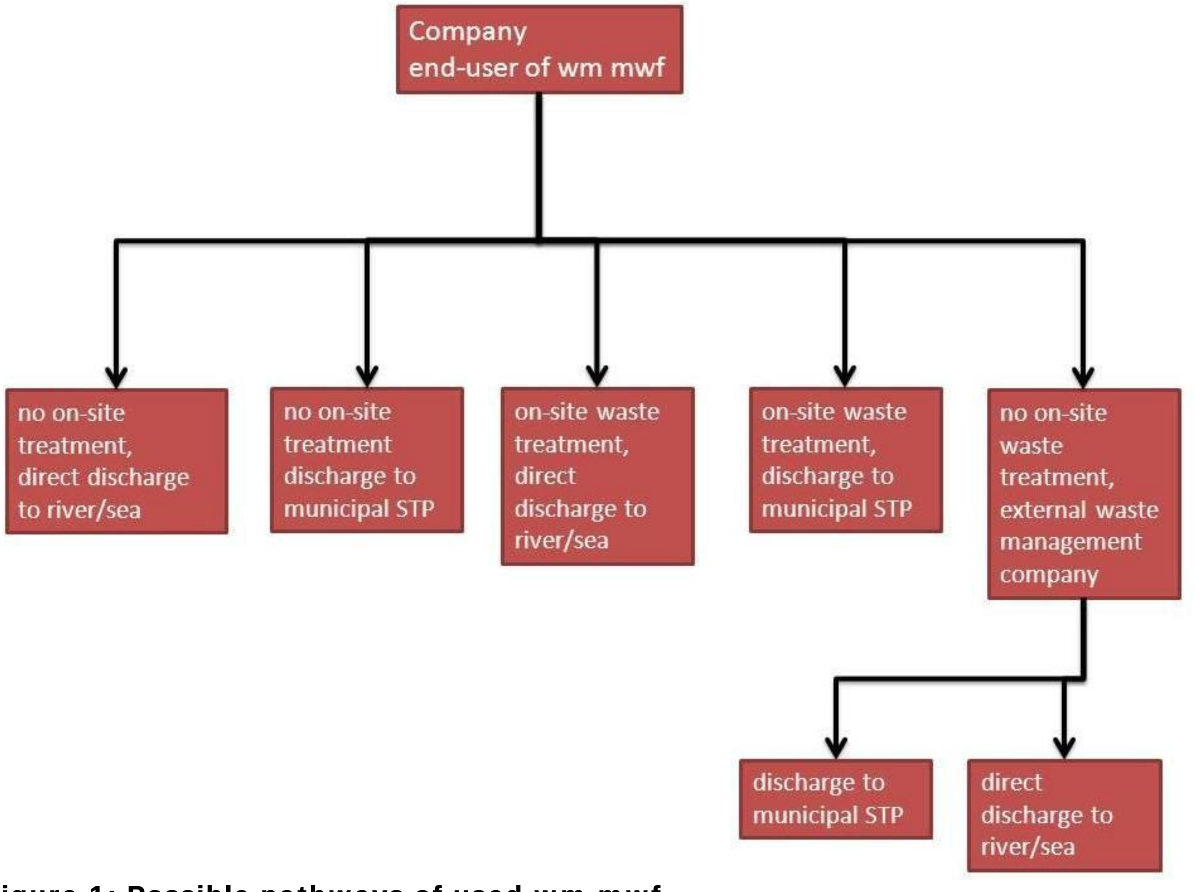

Figure 1: Possible pathways of used wm mwf.

Confidentiality issues

It is suggested that in cases where the relevant information is considered to be confidential it is sent directly to Fraunhofer ITEM:

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All information will be treated confidentially and be included into project reports only in anonymised form.

APPENDIX E: EXCERPT FROM FIRST REPORT "GATHERING OF INFORMATION FOR THE REFINEMENT OF THE ENVIRONMENTAL EMISSION SCENARIO FOR METALWORKING FLUIDS (PT13) UNDER BPD", PRESENTED AT TM II IN 2013

EVALUATION OF EXISTING SCENARIOS FOR METALWORKING FLUIDS: EUBEES ESD, AND OECD ESD NO. 28

SUMMARY AND COMPARISON OF SCENARIOS

In the following paragraphs a general summary and comparison of the EUBEES ESD [6] and the OECD ESD No. 28 [14], which is discussed as an alternative, will be made. The considered release paths will be summarised and relevant defaults be identified. A summary of this comparison and the corresponding parameters can be found in Table 16.

Wording and definitions:

The considered emission scenarios (EUBEES ESD and OECD ESD No. 28) both describe the handling and waste treatment of used water miscible metalworking fluids (wm mwf, coolant lubricants). However, further differentiation and wording varies between the different ESDs:

- In the EUBEES ESD it is differentiated between two types of water miscible metalworking fluids: water soluble and emulsifiable metalworking fluids. Default values for both types of metalworking fluids are different.
- In the OECD ESD No. 28 differentiates only between straight oils, conventional soluble oils, semi-synthetic and synthetic fluids. Different default concentrations for the different ingredients of the mwf concentrate are given, however, the rest of the algorithm and default values are identical for the different types of mwf.
- It should further be kept in mind that in the OECD ESD No. 28 the undiluted mwf is referred to as "neat metalworking fluid", while it is called "concentrate" in the EUBEES scenario document.

Table 16: Comparison of OECD ESD No. 28 and EUBEES ESD

	OECD ESD No. 28	EUBEES ESD	
basic defaults	water miscible	emulsifiable	water soluble
type of treatment	on-site treatment of waste assessed (mwf from one end-user treated and released, mass balance model)	external waste treatment assessed (UBA, 2001) (emulsions from different end-users received, treated and released)	
amount of mwf concentrate per year	***maximum of 45 t/year neat metal working fluid*** ***minimum 8 t/year neat metal working fluid*** ***(undiluted concentrate)***	200 m^3/day diluted mwf for emulsifiable mwf ➔ ***maximum 12000 t/year mwf concentrate (20% mwf concentrate assumed as worst case)*** ➔ ***minimum 3000 t/year mwf concentrate (5% mwf concentrate assumed)***	40 m^3/day (estimated from market share of water soluble metalworking fluids[44]) ➔ ***maximum 2400 t/year mwf concentrate (20% concentrate in water assumed as worst case)*** ➔ ***minimum 600 t/year mwf (5% concentrate in water assumed as worst case)***
concentration of mwf concentrate in water	3-10% (process dependent, 10% suggested as default)	5-20% (process dependent)	
concentration of biocide (bactericide) in mwf concentrate	2 %	5 %	4 %
fungicide	0.1 %	0.1 %	0.1 %

44 based on market share of water soluble mwf (~20%)

	OECD ESD No. 28	EUBEES ESD	
number of operating days and number of release days	247 working days -> 247 release days	300 working days -> 300 release days	
→Resulting release of biocide per day	***worst case: 0.9 t/a bactericide*** ***best case: 0.32 t/a bactericide***	***worst case: 600 t/a bactericide*** ***best case: 150 t/a bactericide***	***worst case: 96 t/a bactericide*** ***best case: 24 t/a bactericide***
Release paths:			
Release 1: Container residue.	Substance is filled from IBC containers into target machine. A part of the mwf is lost due to incomplete draining of the container. $E_{cont.res.} = V_{cont}$ $_{chem.neat}$ * $F_{cont.res.}$ *1 container/site if $N_{container}$ < number of working days $Eloc_{cont.res.} = Q_{chem.site.day} * F_{cont.res.}$ if $N_{container}$ > number of working days $Eloc_{cont.res.}$: local release due to container residue V_{cont}: Volume of container □□: density of mwf | $F_{chem.neat}$: Fraction of chemical of interest $F_{cont.res.}$: Fraction of mwf that stays in the container $N_{container}$: number of containers per site $Q_{chem.site.day}$: Daily tonnage of chemical at site Default: $F_{cont.res.} = 0.03$ Release medium: water/land/incineration	This release part assumed to be negligible ➔ Default: $F_{cont.res.} = 0$	

	OECD ESD No. 28	EUBEES ESD	
Release 2: Drag out-losses (losses due to adsorption of mwf on work pieces and metal shavings)	$E_{loc\ drag\ out} = Q_{chem.site.day} * (1 - F_{cont.res.}) * F_{drag\ out\ loss}$ $E_{loc\ drag\ out}$: Local release due to drag out losses $F_{dragoutloss}$: Fraction of chemical released due to drag out losses Default: $F_{dragoutloss} = 0.11$ Release medium: water	Is assumed to be negligible Default: $F_{dragoutloss} = 0$	
Release 3: Waste due to recycling of mwf, e.g. filter material which will be incinerated	$E_{loc\ recycle} = Q_{chem.site.day} * (1 - F_{cont.res.}) * F_{recycle}$ Default: $F_{recycle} = 0.36$ Release medium: water/land/incineration	Is assumed to be negligible Default: $F_{recycle} = 0$	
Release 4: Discharge of used cooling lubricant	Residue of chemical after all other release paths: $E_{loc\ discharge} = Q_{chem.site.day} * (1 - F_{cont.res.}) * (1 - F_{dragoutloss} - F_{recycle})$ ➔ $F_{discharge} = 0.51$	Main release path $E_{loc,discharge} = c_{proc,emul} * F_{conc/water} * V_{mwf,dil} * c_{mwf,dil} * F_{form} * (F_{conc/water} * K_{ow} + 1)^{-1} * (1 - F_{deg}) * (1 - F_{elim})$[45] $= Q_{chem,site,day} * F_{discharge} * (1 - F_{deg}) * (1 - F_{elim})$	Main release path $E_{loc,discharge} = c_{proc,sol} * V_{mwf,dil} * c_{mwf,dil} * F_{form} * F_{conc/water} * (1 - F_{deg}) * (1 - F_{elim})$ $= Q_{chem,site,day} * F_{discharge} * (1 - F_{deg}) * (1 - F_{elim})$ $c_{proc,sol}$: Concentration of biocide in the mwf concentrate

45 Mistake in official EUBEES ESD:

Equation shown in EUBEES ESD: $E_{loc,discharge} = c_{proc,emul} * V_{mwf,dil} * c_{mwf,dil} * F_{form} * (F_{conc/water} * K_{ow} + 1)^{-1} * (1 - F_{deg}) * (1 - F_{elim})$ → $F_{conc/water}$ is missing. This factor is needed as the equation uses the concentration in mwf concentrate and not in the diluted mwf. It converts the concentration of the biocide in the mwf concentrate into the concentration in the diluted mixture.

It is furthermore noticed that EUSES 2.1.2, the officially supported exposure estimation tool for the environment uses a different equation. Instead of the factor $F_{conc} = V_{conc}/V_{water}$ it uses the fraction of concentrate in the mixture, i.e. $V_{conc}/(V_{conc}+V_{water})$. This does not affect the result very much for low concentrations, however for larger fractions of concentrate EUSES will produce lower exposure estimates than the official EUBEES ESD.

	OECD ESD No. 28	EUBEES ESD	
		$F_{conc/water}$: volume ration between mwf concentrate and water $F_{discharge}$: Fraction of chemical that stays in the waste water after the ultrafiltration and splitting of emulsions. $E_{loc,discharge}$: released biocide $c_{proc,emul}$: Concentration of biocide in the mwf concentrate F_{form}: fraction of mwf with chemical of interest. F_{deg}: fraction of chemical that is degraded during use. F_{elim}: fraction eliminated during PC treatment.	
	Optional: Waste water treatment of water from drag out-losses or other water based releases ultrafiltration: 70% efficiency [46] oil/water separation: 50% efficiency [46] chemical precipitation: 0% efficiency Release medium: Rest/sludge etc. incineration treated water POTW	Defaults: $F_{deg} = 0$ $F_{form} = 1$ $F_{elim} = 0$ Release medium: Water, POTW	Defaults: $F_{deg} = 0$ $F_{form} = 1$ $F_{elim} = 0.8$ [47] Release medium: Water, POTW

46 not applicable for water soluble biocides

47 EUBEES about different F_{elim}: „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, by example, reversed osmosis.“

General approach

Both scenarios represent completely different approaches: While the EUBEES ESD considers only the waste water treatment and handling of used metalworking fluids to be of relevance, the OECD ESD No. 28 scenario considers all use stages and summarises the release into four main steps.

It should be noted that there exists another OECD document; OECD ESD No. 10 (lubricants and lubricant additives) already described a scenario for the release of biocides due to the use of water based metalworking fluids. This scenario is partly based on the same equations as the EUBEES ESD and differs in several points from the later published OECD ESD No. 28. It is considered to be important to be aware of this doubling and the resulting contradictions. For example the OECD ESD No. 10 also uses the default release of 200 and 40 m^3 per day for emulsifiable (water miscible) and soluble (synthetic) metalworking fluids which is based on German waste management companies in the 1990s instead of the defaults introduced later in the OECD ESD No. 28 which are based on small companies in the US. Moreover the document states that the treated volume of 45 000 t/year suggested for a typical treatment plant are not only emulsions but may contain up to ~50% other wastes [7, 15].[48]

Default values

The OECD ESD No. 28 suggests default values for tonnages per site which are based on measured data of small companies during the late 1990s in the US [16][49]; see also Table 17) while the EUBEES ESD tonnage is based on data from Germany, also collected during the 1990s. Thus, both underlying datasets are approximately 15 years old. However, the OECD relies in addition on datasets from outside the EU, which makes it questionable if the default will be representable for EU sites.

The EUBEES ESD approach of 200 m^3 release of metalworking fluid is based on the assumption that metalworking fluid end-users will refer to an external waste management company, i.e. the 200 m^3 suggested for emulsifiable metalworking fluids are not intended to represent the release of a single company but of an external recycling or waste management facility (max capacity for emulsions is 45 000 m^3 per year for a German treatment plant).

Furthermore the volume of used water soluble metalworking fluid per day (40 m^3) is based on the market share of water soluble fluids in relation to the emulsifiable amount and not on any measured release volumes. This market share was around 20% for water soluble mwf when the document was published. Current information indicates that the market share decreased.[50]

On the other hand this fairly high volume is assumed to be released into a standard EU sewage treatment plant of 2000 m^3 (resulting dilution factor of 10). It is already recognised in the ESD document itself that this approach should be revised.

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[48] "Around 50% of this is made up of separable emulsions, with other wastes forming the remaining 50%. A daily treatment rate of 200 m^3 of this type of fluid is considered representative."
OECD ESD No. 10, see also original UBA scenario.

[49] Study on 79 small metalworking shops conducted in 1997 and 1998. Mean result 4260 gallons, 90th percentile result 12000 gallons neat mwf per site. The amount that should be used for exposure assessments depends on the types of exposure which shall be assessed (see Table 17).

[50] M. Scholz, personal communication: Market share of 10 % for water soluble metalworking fluids.

Table 17: Tonnage of wm mwf per site (OECD ESD No. 28)

	Volume neat mwf; gal concentrate /site/year	Number of mwf per site	volume neat mwf: L per site and year	for one mwf (m /site and year); volume of neat mwf	diluted volume (m /site and year)
water based or unknown; occupational and environmental exposure are a concern (based on page 33: use rate)	4260	2	16126	8.06	161.262 (based on maximum concentration suggested in OECD ESD No. 28: 5% concentrate in prepared mwf)
water based or unknown; only environmental exposure is a concern (based on page 33: use rate)	12000	1	45425	45.42	908.50
According to table on page 44: Releases of Dilute Metalworking Fluid from Metal Shaping Operations	-	-	6960 (based on maximum concentration suggested in OECD ESD No. 28: 5% concentrate in prepared mwf) (machining 4610, grinding 1280)	6.96 (based on maximum concentration suggested in OECD ESD No. 28: 5% concentrate in prepared mwf) (machining 4.61, grinding 12.8)	average 2.898 t/machine and year; together with the suggested default of 48 machines per site this leads to 139.1 t/year diluted metalworking fluid (machining 92.2, grinding 256.8)

In contrast to this volume based approach in the EUBEES ESD, the OECD ESD No. 28 a mass balance model of consumed (tonnages) metalworking fluids in the metalworking industry. Certain percentages are assumed to be released due to cleaning of containers, during use, filtration operations and after the treatment of used metalworking fluid. However, not all exposure paths of the OECD ESD No. 28 will necessarily lead to release into (waste) water, as residues from filtration or sedimentation operations may also be incinerated or – as a worst case – be released to landfill as a consequence of regular disposal without cleaning.

The concentration of mwf concentrate in water differs slightly between the two ESDs with the EUBEES scenario providing higher estimates. OECD values are based on information provided by the metal lubricants company in 1997 while the EUBEES default relies on Baumann and Herberg-Liedtke [17].

The same applies to the concentration of biocide in the mwf concentrate, which is around 2 percent according to the OECD ESD No. 28 and 4 or 5 % according to the ESD. The

OECD value is based on information provided in 2005 by ILMA (independent lubricant manufacturers association) while the EUBEES default is again based on Baumann and Herberg-Liedtke [17], i.e. while the OECD value may be more up to date it has still to be evaluated if it also applies to European standards.

For fungicides a concentration of 0.1% is assumed in the UBA scenario while they are not mentioned in OECD ESD No. 28.

Both ESDs apply high numbers of release days (247 for the OECD ESD No. 28, 300 for the EUBEES ESD). However, while the OECD document spreads the annual tonnage of mwf - which is based on measured data - evenly over these 247 days, the EUBEES realises that the "turnover in a central supply unit is about 1 month. This means that within one month, the complete content has been exchanged once, this is also called diffuse overflow or spooning share. " (original reference [18]) but however combines 300 emission days with the release volume corresponding to one complete month. This is explained by the assumption that a representative company using metalworking fluids is expected to refer to external waste management companies which will have high volumes and high numbers of release days. Further experimental data to support the reliability of this approach and the chosen default values are not given.

Both scenarios assume no degradation during use as a default. However, if specific data is available degradation may be considered.

In the EUBEES ESD physical chemical treatment is not considered to be a regular part of the water/oil separation for emulsions, however, for water soluble cooling lubricants it is expected that other techniques (osmosis) will be used which will lead to a reduction of the biocide concentration.

The OECD document on the other hand recommends efficiencies for certain treatment techniques. However it is not discussed if the given efficiencies are applicable for all substances. It is expected that the values are only appropriate for the oil content. The same applies to default values set for container residues etc.

Some parameters that are needed for the OECD ESD No. 28 exposure assessment (e.g. number of machines per facility, container residue) are not reflected in the EUBEES ESD due to the completely different approach, i.e. considering only the release from specialised waste management companies.

GENERAL PLAUSABILITY CHECK

In this chapter it is intended to check the general plausibility of the EUBEES ESD and to do some basic comparisons of tonnages per year and number of sites per year with values as they would arise from the EUBEES ESD.

OECD ESD No. 28 and the EUBEES ESD both assume no degradation during use as a default. This may more or less represent reality if only the degradation processes during use are considered as redosing of biocide is often practiced to ensure a constant biocide concentration that will prevent bacterial contamination before it appears. However, in some cases waste water is stored before being treated or collected by waste management companies and in these cases there will certainly be degradation of the biocidal substances over time.

The default fraction for one biocidal substance is assumed to be 1 in the EUBEES ESD. As this scenario is intended to reflect the situation in a typical waste management company this means that all treated emulsions in one waste management company are related to wm mwf and have been conserved with the same biocidal substance although it could be expected that the used metal working solutions are delivered from different metalworking companies. This assumption refers to a very worst case and is not supported by experimental data.

The OECD ESD No. 28 recommends efficiencies for certain waste water treatment techniques but does not discuss if these are applicable for all substances. E.g. for ultrafiltration an efficiency of 70% is suggested. Ultrafiltration usually separates particles > 0.01 µm (for mwf usually 20- 200 kD cut off, see [19] and [20]; 1000 – 500000 g/mol [1, 2]). Therefore the efficiency value of 70% is questionable for common biocidal substances due to their comparably small molecular mass (see Chapter 0). Instead they are expected to distribute between oil and water phase according to their hydrophilic characteristics. The resulting removal efficiency can for example be described by including the partition coefficient Kow into the scenario equations, like it is done in the EUBEES scenario. On the other hand there may be a small amount of oil remaining in the water phase which would lead to underestimations of exposure when the biocide is dissolved mainly in the oil phase.

Moreover it is not clear if the defaults for removal due to container residues or adsorption to shavings will also apply to biocides as adsorption properties will not necessarily be the same for the water and the oil content of a water-oil-mixture used as metalworking fluid. Depending on the physical chemical properties of the chemical of interest there may be some substances where less is adsorbed on work pieces than would be expected from to the reported default removal rates. Moreover, some contact persons from the metalworking sector who sent replies to our survey suggested different default losses during the application processes (see also Chapter 0): End user 3 from survey: 30 %; Stimular [21] 80-95%; RIVM rapportnummer 738620001: 75-80%.[51]

SUMMARY

The following main differences between the two ESDs could be extracted:

- OECD ESD No. 28 refers to release directly from the end-user while the EUBEES ESD refers to external waste treatment companies. However, this information is not clearly mentioned in the EUBEES ESD itself and it has to be extracted from the original UBA document [7].
- Additional differences occur due to the different default values implemented in both models. However, both sets of defaults are based on datasets from the 1990s (in case of the tonnages) and in some cases on assumptions or simplifications without further experimental background or differentiation concerning the applicability to certain ingredients of water miscible metalworking fluids (biocides vs. oil part).
- OECD No. 28 tonnages are based on US data while EUBEES ESD tonnage defaults are based on German data.

[51] RIVM rapport number 738620001 (cited in personal communication) indicated 75-80 % loss (referring to the late 1980s; Vapour/mist: 15-42%; Leakage/ splash/ spillage: 14-21%; Drag-out 10-12%; Drag-out 4-12%; total 60-70, i.e. System cleaning leads to a release of 40-30% of which 90% end up in waste treatment)
Stimular 1997 (cited in personal communication by Joost Bakker, referring to the 1990s and four small companies with 850-16250 l/a emulsion) indicated that without proper control/management about 80-95 % of the used metal working fluid would be lost to the environment due to or via spray, splash, evaporation, drag out, leakage and spillage and only 5-20% will be collected and disposed of as waste (25-60% spray, vapour; 20-25% splash, leakage, spill; 15-20% drag out via work piece; 5-20% drag out via chips and shavings)

- OECD No. 28 does not differentiate between emulsifiable and water soluble mwf in contrast to the EUBEES ESD
- In the OECD ESD No. 28 some of the chemical is already removed before the discharge of used metalworking fluid. As long as this also will be released into water, this different basis is not expected to change the outcome significantly. However, some of the chemical may be incinerated together with sludge or filter material and would then not attribute to the release into waste water (and the corresponding intoxication of the sewage treatment plant and the water body it is connected to).

Further comparison with collected data will be shown in Chapter 0.

APPENDIX F: DILUTION FACTORS FOR END-USERS ($D_{COMPANY \rightarrow STP}$): SUPPORTING INFORMATION

In this section some statistical considerations concerning mwf based waste water releases from end-users will be made. This data may not be sufficient to be used without the datasets collected via questionnaires, however, it can be used as supporting information in order to evaluate, if Germany (of which the majority of end-user questionnaires was received) can be seen as representative or even worst case when compared to other EU countries.

In Table 18 the average number of enterprises, relative financial output related to the metalworking sector and average persons per enterprise are summarised for each member state (see Ref. [9] [52]) . These data have been amended by average STP capacities as documented in the EU wide STP database[53].
It is now assumed that the relative financial output related to metal articles correlates with the mwf consumption in the corresponding country

To evaluate common enterprise sizes the relative output can be divided by the number of enterprises. Results of this procedure indicate that in Germany comparably large companies are located which have a high output of metal articles. Only for Ireland the output per enterprise is higher than in Germany. That means as a consequence, that waste water release due to used wm mwf per enterprise is comparably high in Germany. This indicates also a comparably high tendency to refer to on-site treatment (instead of external waste treatment companies), as this is usually only practiced for larger companies.

This average output per enterprise is now combined with average STP capacities for each country. The numbers shown in this column give an indication on the probability, that in this country a high waste water volume resulting from wm mwf is released into a small municipal sewage treatment plant.

If all member states are compared it is obvious, that Germany is again close to the upper border of the displayed range. In other words, dilution factors for the step end-user → municipal STP are comparably low in Germany.

The only exception is Ireland, which shows a clearly higher output per enterprise and STP capacity.

These results are also consistent with the company size as indicated by the average number of persons per enterprise: Only Ireland, Luxembourg and Slovakia[54] show comparable or higher numbers of person per enterprise, with Ireland being the only one showing STP volumes in a clearly smaller order of magnitude than Germany.

As a consequence, an in-depth analysis of potential end-users with of wm mwf with on-site treatment in Ireland has been performed using information stored in the PRTR (see Table 19, for evaluation strategy of PRTR see also Appendix C).

It can be summarised, that this industry sector is clearly not very relevant in Ireland (see also Table 18), as only a limited number of companies was located in the selected

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http://ec.europa.eu/enterprise/sectors/mechanical/files/metalworking/mma_final_report_181109_final_en.pdf
[52] http://ec.europa.eu/enterprise/sectors/mechanical/files/metalworking/mma_final_report_181109_final_en.pdf

[53] http://www.eea.europa.eu/data-and-maps/data/waterbase-uwwtd-urban-waste-water-treatment-directive-3

[54] comment: In addition, one dataset is available within the collection of end-user questionnaires, representing a

large end-user on-site with on-site treatment in Slovakia.

industry areas of which some are not actually involved in metal processing. Of the remaining enterprises, some probably only store their waste and do not treat it on-site or release wastewater themselves. However, as a worst case all companies have been taken in to account which may be involved in the use of mwf. It can be seen that all derived dilution factors are more than a factor of 10 above the suggested default of 100 (see section 4.1.4), i.e. even if some uncertainty concerning the number of release days may be present, a risk related to lower dilutions from the company to the responsible sewage treatment plant is considered to be very unlikely for release from end-users in Ireland.

Overall it can therefore be summarised that mwf end-users in Germany show comparably low dilution factors (average STP volumes combined with comparably high outputs per enterprise) and are therefore probably a worst case.

Table 18: Detailed geographic overview of the MMA sector in 2006 (excerpt from Table 2.5 of [9] amended by information concerning STP capacities)

	number of enterprises (% of EU27)	relative financial output (% of EU27)	Average persons per enterprise	Average sewage treatment plant capacity (m /day, based on EU database)	Relative output per enterprise	relative output per enterprise and m STP capacity
Belgium	1.6	2.5	11	3637	1.56	4.E-04
Bulgaria	0.9	0.2	12	1738	0.22	1.E-04
Czech Rep.	8.5	2.1	5	3931	0.25	6.E-05
Denmark	1.1	1.3	11	5710	1.18	2.E-04
Germany	9.5	24.6	22	6815	2.59	4.E-04
Estonia	0.2	0.2	16	6527	1.00	2.E-04
Ireland	0.1	0.4	23	2473	4.00	2.E-03
Greece	3.6	0.9	3	11656	0.25	2.E-05
Spain	10.8	9.4	9	7696	0.87	1.E-04
France	7.5	13	15	5118	1.73	3.E-04
Italy	24.1	19.7	8	3103	0.82	3.E-04
Cyprus	0.3	0.1	4	11687	0.33	3.E-05
Latvia	0.2	0.1	15	8308	0.50	6.E-05
Lithuania	0.4	0.1	13	5804	0.25	4.E-05
Luxembourg	0[55]	0.2	22	5634	2.00	4.E-04
Hungary	2.4	0.8	8	4208	0.33	8.E-05
Netherlands	2	3.6	13	11369	1.80	2.E-04
Austria	1.1	2.6	18	6586	2.36	4.E-04
Poland	7.5	3	10	8383	0.40	5.E-05
Portugal	4.4	1	5	6264	0.23	4.E-05
Romania	1.6	0.6	17	8828	0.38	4.E-05
Slovenia	1.1	0.6	8	5282	0.55	1.E-04
Slovakia	0.3	0.4	27	5789	1.33	2.E-04
Finland	1.2	1.4	10	no information	1.17	
Sweden	2.9	2.5	8	no information	0.86	

[55] 0.1 assumed for estimation of output per enterprise and output per enterprise and STP.

	number of enterprises (% of EU27)	relative financial output (% of EU27)	Average persons per enterprise	Average sewage treatment plant capacity (m /day, based on EU database)	Relative output per enterprise	relative output per enterprise and m STP capacity
UK	6.9	8.8	12	9191	1.28	1.E-04
EU overall				**6531**		

Table 19: PRTR datasets for Ireland related to mwf relevant industry areas ("Surface treatment“ and “production and processing of metals”)

Facility Name	URL	transferred hazardous waste (domestic) t/a	waste water m /day (300 days and 95% water assumed)	STP	STP capacity (m /day, according to EU database)	Dcompany-STP
Industrial Activity	2 Production and processing of metals					
Andersen Ireland Limited	http://prtr.ec.europa.eu//PopupFacilityDetails.aspx?FacilityReportId=809075	only transboundary transfer to UK and Germany				
Basta Parsons Limited	http://prtr.ec.europa.eu//PopupFacilityDetails.aspx?FacilityReportId=808891	only transboundary transfer to Belgium				
C & F Automotive Limited	http://prtr.ec.europa.eu//PopupFacilityDetails.aspx?FacilityReportId=808902	292	0.92	Mullingar	11000	11896
Dublin Aerospace Limited	http://prtr.ec.europa.eu//PopupFacilityDetails.aspx?FacilityReportId=809011	37	0.12	Ringsend	328000	2799431
Galco (Waterford) Limited	http://prtr.ec.europa.eu//PopupFacilityDetails.aspx?FacilityReportId=809098	25.7	0.081	Ringsend	328000	4030309
Galvotech (International) Limited	http://prtr.ec.europa.eu//PopupFacilityDetails.aspx?FacilityReportId=809077	8.6	0.027	Claremorris	1067	39179
Hewlett Packard (Manufacturing) Limited	http://prtr.ec.europa.eu//PopupFacilityDetails.aspx?FacilityReportId=809024	41	0.13	Leixlip Waste Water Treatment Plant	16000	123235
Loredo Limited	http://prtr.ec.europa.eu//PopupFacilityDetails.aspx?FacilityReportId=809020	nothing reported				
Lufthansa Technik	http://prtr.ec.europa.eu//PopupFacilityDetails.aspx?FacilityReportId=80900	109	0.35	Ringsend	328000	950266

Facility Name	URL	transferred hazardous waste (domestic) t/a	waste water m /day (300 days and 95% water assumed)	STP	STP capacity (m /day, according to EU database)	$D_{company-STP}$
Airmotive Ireland Limited	6					
Molex Ireland Limited	http://prtr.ec.europa.eu//PopupFacilityDetails.aspx?FacilityReportId=809076	42	0.13	Claremorris	1067	8023
Moy Isover Limited	http://prtr.ec.europa.eu//PopupFacilityDetails.aspx?FacilityReportId=809137	26.3	0.083	Clonmel Waste Water Treatment Plant	16000	192115
Ossian Limited	http://prtr.ec.europa.eu//PopupFacilityDetails.aspx?FacilityReportId=809168	1	0.0032	Macroom U.D.C. Waste Water Treatment Plant	1060	334739
Industrial Activity	9.(c) Surface treatment of substances objects or products using organic solvents					
Alkermes Pharma Ireland Limited	http://prtr.ec.europa.eu//PopupFacilityDetails.aspx?FacilityReportId=808942	manufacture of pharmaceutical preparations, not mwf relevant				
Intel Ireland Limited	http://prtr.ec.europa.eu/FacilityDetails.aspx?FacilityId=9642&ReportingYear=2012	electronic components, not mwf relevant				
Johnson & Johnson Vision Care (Ireland) Limited	http://prtr.ec.europa.eu//PopupFacilityDetails.aspx?FacilityReportId=809079	Manufacture of medical and dental instruments and supplies, 11t/a transferred hazardous waste	0.035	Limerick	26000	746411

Facility Name	URL	transferred hazardous waste (domestic) t/a	waste water m /day (300 days and 95% water assumed)	STP	STP capacity (m /day, according to EU database)	$D_{company-STP}$
Merck Millipore Limited	http://prtr.ec.europa.eu//PopupFacilityDetails.aspx?FacilityReportId=809199	Manufacture of plastic plates, sheets, tubes and proiles				
Pfizer Ireland Pharmaceuticals	http://prtr.ec.europa.eu/FacilityDetails.aspx?FacilityId=49003&ReportingYear=2012	Manufacture of basic pharmaceutical products, not mwf relevant				

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