Tyre and General Rubber Goods Generic Exposure Scenario

Emission Factor Guidance for Formulation and Industrial Use

[Includes SpERC factsheet for ERC 3 and ERC 6d]

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Introduction

This document provides emission factor guidance for formulation and industrial use in the tyre and general rubber goods (GRG) industry and updates the prior emission factor guidance previously published on the ETRMA website on 16 December 2009. It is anticipated that manufacturer/importer will provide scaling rules as described in Part G: *Extending the SDS* in the REACH CSA TGD to facilitate confirmation of compliance with the exposure scenario forwarded by the registrant at the facility level. To develop plausible exposure estimates for the baseline scenario, guidance on the refinement of the ERC emission factors is provided in this document and in the **ETRMA Scaling Equation Guidance**.

Information is provided on ERC assignment and recommended refined emissions factors for air and water. In addition, specific environmental release categories (SpERC) are defined for ERC 3 and ERC 6d. The SpERC factsheet is included as an attachment to this report (**Attachment A**). The emission factor recommendations in this updated guidance are organized by Tiers as shown in Table 1. The last row indicates the SpERC that has been prepared for ERC 3 and ERC 6d. Tier 0 (screening) estimates are based on the conservative default ERC emission factors. Next, Tier 1 (refined screening) emission factors are derived from EU Technical Guidance Document (TGD) A-tables supported by industry data collection of total zinc and total hydrocarbon data. Finally, Tier 2 (refined data-based) emission factors consists of a large industry wide cross-sectional study design including three substances monitored in water at thirteen tyre production facilities and six general rubber good (GRG) production facilities. Generally, chemical safety assessments (CSAs) should first be prepared with the Tier 0 emission factor and proceed to use of higher tier values if necessary to demonstrate safe use. Therefore, ETRMA recommends that CSAs be prepared with the lowest Tier emission factor necessary to demonstrate safe use.

Table 1: Description of available emission factor estimates.

Emission Factor Estimate	**Source**	**Summary Table in this Guidance**	**Air**	**Water**
Tier 0 (Screening)	ECHA REACH TGD Chapters D and 16 ERC	**Table 2**	ERC 3, ERC 4 and ERC 6d	ERC 3, ERC 4 and ERC 6d
Tier 1 (Refined Screening)	EU TGD A-Tables	**Table 3**	Replaces Tier 0 ERC 3 / 4 / 6d Emission Factors	Replaces Tier 0 ERC 3 / 4 / 6d Emission Factors
Tier 2 (Refined Data-Based Emission Factor for Wastewater)	Industry-wide GRG and Tyre Facility Data Collection	**Table 9**	Not Applicable	Replaces Tier 1 ERC 3 and ERC 6d Emission Factors[a]
SpERC 3/6d (Tier 1 air and Tier 2 wastewater for ERC 3 and ERC 6d)[a]	Tier 1 for Air and Tier 2 for Water	**Attachment A**	Tier 1 Air	Tier 2 Water

[a]See ETRMA SpERC for substance domain in **Attachment A.**

Environmental Release Categories (Tier 0)

The recommended ERCs for tyre production by chemical usage category are provided in **Table 2** in accordance with REACH CSA TGD Appendix D-4. Most tyre chemical TGD use categories are associated with more than one process category (PROC). The most appropriate ERC was selected based on the use of the chemical in the tyre industry and the associated process categories. Substance specific TGD Use Categories can be obtained by request to ETRMA or to the individual tyre industry member companies.

Table 2: Recommended ERC by TGD Use Category (Tier 0 Emission Factor).

TGD Classification	Proc. Cat.	Valid ERC [a]	Process Category Used to Assign ERC	Selected ERC[b]	Default Release to air (Tier 0)	Default release to water (Tier 0)
01 - MASTICATION AGENTS / PEPTISER	(4), 5, 9	2, 3, 6d	(4-batch processes where opportunity for exposure exists) 5-Mixing or blending in batch processes for formulation of articles	6d-Industrial use of process regulators for polymerization processes in production of resins, rubbers, polymers (e.g. vulcanization agents)	35%	0.005%
02 - VULCANISATION AGENTS	(4), 5, 9, 10, 14, 21	1,2,3, 4,5, 6d, 8a, 8c, 8d, 8f	(4-batch processes where opportunity for exposure exists) 5-Mixing or blending in batch processes for formulation of articles 14-Production of articles by tabletting, etc	6d-Industrial use of process regulators for polymerization processes in production of resins, rubbers, polymers (e.g. vulcanization agents)	35%	0.005%
03 - ANTI AGEING AND ANTIFLEX-CRACKING AGENTS / ANTIDEGRADANTS	5, 8b, 9, 10, 14, 21	1,2,3, 4,5, 8a, 8c, 8d, 8f	5-Mixing or blending in batch processes for formulation of articles 14-Production of articles by tabletting, etc.	3- Formulation in materials - resulting in inclusion on a matrix (e.g. additives, fillers, pigments, plasticizers)	30%	0.20%
04 - FILLERS AND PIGMENTS	5, 8b, 9, 10, 14, 21	1,2,3, 4,5, 8a, 8c, 8d, 8f	5-Mixing or blending in batch processes for formulation of articles 14-Production of articles by tabletting, etc.	3- Formulation in materials - resulting in inclusion on a matrix (e.g. additives, fillers, pigments, plasticizers)	30%	0.20%
05 - PLASTICISER	5, 8b, 9, 10, 14, 21	1,2,3, 4,5, 8a, 8c, 8d, 8f	5-Mixing or blending in batch processes for formulation of articles 14-Production of articles by tabletting, etc.	3- Formulation in materials - resulting in inclusion on a matrix (e.g. additives, fillers, pigments, plasticizers)	30%	0.20%
06 - PROCESSING AIDS	5, 9, 14, 21	1,2,3	5-Mixing or blending in batch processes for formulation of articles 14-Production of articles by tabletting, etc.	3- Formulation in materials - resulting in inclusion on a matrix (e.g. additives, fillers, pigments, plasticizers)	30%	0.20%
07 - OTHER AGENTS						
07-5 - Solvents	7, 8b,9, 10	4,5, 8a, 8c, 8d, 8f	7-Spraying in industrial settings 10-Roller or brush application	4-Industial use of processing aids (e.g. solvents, anti-set agents)	95%	100%
07-6 - Emulsifier	7, 9, 10	4,5, 8a, 8c, 8d, 8f	7-Spraying in industrial settings 10-Roller or brush application	4-Industial use of processing aids (e.g. solvents, anti-set agents)	95%	100%
07-7; 07-12 - Hardeners, reinforcing agents	5, 8b, 9, 14	1,2,3	5-Mixing or blending in batch processes for formulation of articles 14-Production of articles by tabletting, etc.	3- Formulation in materials - resulting in inclusion on a matrix (e.g. additives, fillers, pigments, plasticizers)	30%	0.20%
09 - RELEASE AGENTS	7, 8b, 9, 14	1,2,3,4, 5, 8a, 8c, 8d, 8f	7-Spraying in industrial settings	4-Industial use of processing aids (e.g. solvents, anti-set agents)	95%	100%

[a]REACH CSA TGD Appendix D-4.
[b]REACH CSA TGD Table R.16-23.

Tier 1 Emissions Factors for Air and Water based on EU TGD A-Tables

This section provides Tier 1 air and water emission factors for the combined activities of formulation (e.g. filling and weighing) and processing (e.g. extrusion). In some cases, these functions may be performed at separate facilities. As described in the EU Risk Assessment Reports for aniline (2004), zinc metal (2008) and zinc distearate (2008b), the formulation and processing lifecycle stages in the rubber industry are dry processes. However, incidental emissions to water can occur as a result of floor scrubbing, equipment washing/blowdown, compounds cooling or collection of curing press steam condensate. Measurement-based Tier 2 emission factors for the further refinement of wastewater emissions beyond Tier 1 are provided in the next section of this guidance document.

Based on a consideration of the available information, the emissions factors for processing/industrial use from the EU TGD A-Tables for the polymer industry (IC-11; Table A3.11) were assigned to each chemical. The A-Table, OECD ESD for the rubber industry and ERC emissions factors are summarized in **Table 3** for the purpose of comparison. Each tyre chemical use category has been assigned to one of four general categories presented in TGD A-Table including additives (I), plasticizers (II), solvent (III) and processing aids (IV). In most cases, the assignment of a general category is straightforward. One exception is vulcanizing agents and chemicals assigned to use category 43 (process regulators). Vulcanizing agents used in the rubber and tyre industry are not explicitly covered in the TGD A-Table and were assigned to Category I, additives where there is an assumed emission to wastewater. This is in contrast to the OECD ESD, where vulcanization agents are assumed to have no emissions to wastewater. TGD A-Table Category V represents 'cross-linking agent' monomers such as styrene or formaldehyde and 'curing agents' such as peroxides used in the plastics industry. Accordingly, the emission factor to air is quite high, ranging from 0.075 to 0.35 and these classes of compounds are not the same as the vulcanization agents used in the rubber industry. Therefore, assignment of Class V as a default emission factor for vulcanization agents is not recommended.

To qualitatively confirm that the A-table emissions factors are representative of average conditions and are inclusive of emissions during the formulation stage, several sources of data supporting the use of the A-table emissions factors were reviewed.

Water

During 2009, screening level wastewater effluent data for total zinc and total hydrocarbon were collected from tyre production facilities representing approximately 40% of total European production (ETRMA, 2009). The purpose of this data collection was to confirm the conservatism of the Tier 1 A-table emission factors and the development of a semi-quantitative emission factor. For Tier 2 emission factor development, a subsequent robust sampling plan was implemented and completed in April 2010.

An aggregate semi-quantitative emission factor for a typical substance used in compounding and mixing was calculated based on the reported production rate and an estimated ZnO consumption rate of 0.015 g ZnO/g tyre. Averaged across all facilities, the emission factor to water was 5×10^{-5} (as Zn). Data was reported for 10 combinations of production rate and Zn emission rate. Among these 10 combinations, the minimum to maximum range of the emission factor to water was 6×10^{-9} to 8×10^{-5}.

In all cases, the A-table emission factor to water of 5×10^{-4} assigned to mastication agents, vulcanization agents, anti-ageing agents, fillers, processing aids, other agents (except solvents) and release agents is greater than that observed for zinc based on facility-specific data. Therefore, the A-table emission factors for water are reasonably conservative (i.e. likely to overestimate true emissions). In addition, the maximum emission factor among the 10 reported combinations of Zn emissions and production volume of 8×10^{-5} is within a factor of 6 of the A-table emissions factors. It is important to note that for some of the data provided, zinc data in influent water was not available to calculate the net emission rate, and therefore, the derived emission factor should be considered an upper bound of average conditions. In addition, other sources of Zn besides ZnO are likely to be present at most facilities and accounting for these other sources would have also lowered the emission factor.

The emission rate for vulcanizing agents suggested in the OECD ESD is zero based on complete reaction of the substance. However, small amounts of vulcanizing agents may be released from the mixing process or during cleaning through incidental spillage and as such become entrained in the plant wastewater. The ZnO EU RAR (2008) suggests that the major source of zinc could be intake of zinc in the influent municipal water. Paired influent and effluent data collected by ETRMA member companies was available for three combinations of production volume and Zn emissions. At these facilities, the effluent load of zinc was about 1.2 to 2.1 times higher than in the influent concentration. In the emission factor presented above, the net Zn emission rate was used for these three facilities. In summary, the Zn data show that very low or negligible emissions of additives used in compounding and mixing occur at some facilities on the order of $< 1 \times 10^{-8}$, but that some facilities are anticipated to have additive (or transformation product) emissions on the order of 1×10^{-4} to 1×10^{-5}.

To supplement the zinc data for other additives such as plasticizers and oils, total hydrocarbon data representing approximately 25% of total European tyre production was also collected from ETRMA members. An overall emission factor for the hydrocarbon fraction used in tyre production was calculated based on the reported production rate and the estimated total hydrocarbon consumption rate of 0.1 g total hydrocarbon/g tyre. Averaged across all facilities, the emission factor to water was 1×10^{-5} after the RMM (oil/water separation). Data was reported for 8 combinations of production rate and total hydrocarbon emission rate. Among these 8 combinations, the minimum to maximum range of the emission factor to water was 7 x 10^{-9} to 3 x 10^{-5} after RMMs (oil/water separation). Based on before- and after-RMM data, the removal efficiency of the RMM (oil/water separation) is approximately 95%. It should be noted that the total hydrocarbon emission factor includes other non-process sources of hydrocarbon, including lubricants and oils utilized in machines and residual hydrocarbons from vehicles. Therefore, the derived emission factor should be considered an upper bound of average conditions.

Based on the results of the total hydrocarbon effluent analysis, the A-table emission factor of 1 x 10^{-3} for plasticizers is likely approximately 2 orders of magnitude higher than the average measured emission factor of 1 x 10^{-5} after oil/water separation. Therefore, consideration of the oil/water separator treatment efficiency in addition to the A-table default value is recommended for plasticizers and oils. When oil/water separation is considered, the overall average emission factor for total hydrocarbon (1 x 10^{-5}) is similar to that derived for total zinc (5 x 10^{-5}).

The OECD ESD for the rubber industry also provides emissions factors for formulation and processing combined, however, the OECD emission factors for water are not recommended for use in the generic exposure scenario. The emission factors for water presented in the OECD ESD for the rubber industry are based on a survey by the Association of the German Rubber Industry in 1999 that collected information on the fraction of various additives remaining after processing. This approach appears to have overestimated the true emission rate to water for many of the use categories including anti ageing agents, fillers, plasticizers, other agents and release agents. For example, in the zinc distearate EU RAR (2008), the OECD ESD emission rate to wastewater for mould release agents of 5% (f_{water} = 0.05) was not considered to be plausible and was replaced by the rapporteur with an emission factor from the TGD A-table (f_{water} = 0.0005).

Air

The EU TGD A-Tables for the polymer industry (IC-11; Table A3.11) are expected to provide reasonable estimates of average emissions to air for formulation and processing. The use of the EU TGD A-Table emissions factors is recommended in the OECD ESD (2004). In addition, the EU RAR (2004) for zinc distearate relied on the A-table emission factor for processing aids.

The assignment of vulcanization agents to the TGD A-table category of additives was evaluated by reviewing the EU RAR for ZnO (2008). Zinc oxide is classified as an accelerator activator under the main category of vulcanizing agents. The RAR indicates the median emission factor to air reported by industry was 5.5 x 10^{-4}. The emission factor that would be assigned using the A-table assignment in Table A3.1 is 5 x 10^{-4} (for vapor pressure < 1 Pa and boiling point > 300 degrees C), which is similar to the median emission factor submitted by industry in the ZnO RAR.

The emission factors for air presented in the OECD ESD (OECD Table 11) are also compiled from the same EU TGD A-Tables as in Table A3.1, however, it should be noted that there are three discrepancies between OECD Table 11 and the TGD A-Table. First, the emission factor for processing aids is a factor of 10 times lower in the OECD document when compared to the values presented in the TGD A-Table. Second, the A-table emissions factor for UC-43 (process regulator) is incorrectly assigned to the category of vulcanizing agents in the OECD document. The OECD air emission factors representing release percentages of 7.5% to 35% are not realistic for vulcanizing agents and correspond to curing agent and cross-linking agents used in the plastics industry. In the plastics industry, cross-linking agents are monomers such as styrene or formaldehyde and 'curing agents' include compounds such as peroxides. The TGD A-Table does not explicitly identify emissions factors for vulcanization agents. Therefore, the emission factors for additives (category I) from the TGD A-Table have been used as a surrogate for the chemical category of vulcanization agents. Finally, the OECD document did not present emissions factors for solvents, but these rates are available in TGD A-Tables.

Table 3: Tier 1 air and water emissions factors for tyre and GRG production.

TGD Classification	Use Category	Selected A-Table Category/ Type	Air Emission Factors				Water Emission Factors, F_{water}[a]		
			ERC	TGD A-Table			ERC	OECD ESD for Rubber Industry	TGD A-Table (Tier 1)
				BP (C)	VP (Pa)	F_{air}			
01 - MASTICATION AGENTS / PEPTISER[b]	43 (mastication agent)	Additive (I)	0.35	>300 <300 >300 <300 >300 <300	<1 <1 1-100 1-100 >100 >100	0.0005 0.001 0.001 0.0025 0.005 0.01	5×10^{-5}	0.005	0.0005[c]
02 - VULCANISATION AGENTS[b]	43, 53 (vulcanizing agent)	Additive (I)	0.35	>300 <300 >300 <300 >300 <300	<1 <1 1-100 1-100 >100 >100	0.0005 0.001 0.001 0.0025 0.005 0.01	5×10^{-5}	0	0.0005[c]
03 - ANTI AGEING AND ANTIFLEX-CRACKING AGENTS / ANTIDEGRADANTS	49 (stabilizers)	Additive (I)	0.30	>300 <300 >300 <300 >300 <300	<1 <1 1-100 1-100 >100 >100	0.0005 0.001 0.001 0.0025 0.005 0.01	0.002	0.01	0.0005
04 - FILLERS AND PIGMENTS	20 (filler) 10 (pigment)	Fillers/ Pigments (I)	0.30	>300 <300 >300 <300 >300 <300	<1 <1 1-100 1-100 >100 >100	0.0005 0.001 0.001 0.0025 0.005 0.01	0.002	0.01	0.0005
05 - PLASTICISER	47 (softener)	Plasticizers (II)	0.30	<400 >400	All All	0.01 0.005	0.002	0.05	0.001[d]
06-1- LUBRICANTS	35 (lubricants)	(IV) Processing aids	0.30	>300 <300 >300 <300 >300 <300	<1 <1 1-100 1-100 >100 >100	0.005 0.01 0.01 0.025 0.05 0.1	0.002	0.005	0.0005
06-2- TACKIFIER	2 (adhesive and binding agents)	Additive (I)	0.30	>300 <300 >300 <300 >300 <300	<1 <1 1-100 1-100 >100 >100	0.0005 0.001 0.001 0.0025 0.005 0.01	0.002	0.005	0.0005
06-4- FILLER ACTIVATOR	43 (process regulator)	Additive (I)	0.30	>300 <300 >300 <300 >300 <300	<1 <1 1-100 1-100 >100 >100	0.0005 0.001 0.001 0.0025 0.005 0.01	0.002	0.005	0.0005
06-6- BONDING AGENTS	2 (adhesive and binding agents)	Additive (I)	0.30	>300 <300 >300 <300 >300 <300	<1 <1 1-100 1-100 >100 >100	0.0005 0.001 0.001 0.0025 0.005 0.01	0.002	0.001	0.0005

TGD Classification	Use Category	Selected A-Table Category/ Type	Air Emission Factors				Water Emission Factors, F_{water}[a]		
			ERC	TGD A-Table			ERC	OECD ESD for Rubber Industry	TGD A-Table (Tier 1)
				BP (C)	VP (Pa)	F_{air}			
07-03 – EMUL-SIFIERS	49 (stabilizers)	Additive (I)	0.95	>300 <300 >300 <300 >300 <300	<1 <1 1-100 1-100 >100 >100	0.0005 0.001 0.001 0.0025 0.005 0.01	1	0.05	0.0005
07-12- RE-INFORCING AGENTS	0 (other)	Additive (I)	0.30	>300 <300 >300 <300 >300 <300	<1 <1 1-100 1-100 >100 >100	0.0005 0.001 0.001 0.0025 0.005 0.01	0.002	0.05	0.0005
07-7- HARDENERS	0 (other)	Additive (I)	0.30	>300 <300 >300 <300 >300 <300	<1 <1 1-100 1-100 >100 >100	0.0005 0.001 0.001 0.0025 0.005 0.01	0.002	0.05	0.0005
07 - SOLVENTS	48 (solvents)	Solvent (III)	0.95	All All All All	<100 100-1000 1000-10000 >10000	0.1 0.25 0.5 0.75	1	0.05	0
09 - RELEASE AGENTS	0 (release agents)	(IV) Processing aids	0.95	>300 <300 >300 <300 >300 <300	<1 <1 1-100 1-100 >100 >100	0.005 0.01 0.01 0.025 0.05 0.1	1	0.05	0.0005

[a]TGD emission factors recommended as alternative to ERC emission factors. A survey of ETRMA European facilities in 2009 found that the overall average emission factor to water based on total zinc and total hydrocarbon (after oil/water separation) was 5×10^{-5} and 1×10^{-5}, respectively. Upper bound emission factors were 8×10^{-5} and 3×10^{-5} for total zinc and total hydrocarbon (after RMM), respectively.

[b]A-Table entry for UC 43 does not apply to rubber industry. UC 53 is not covered in A-table. Additive category selected as surrogate.

[c]A-Table emission factor for additives exceeds the ERC emission factor. This occured because ERC 6d relies on an A-Table emission factor not directly applicable to rubber manufacture. TGD A-Table Category V cited by the ERC represents ‘cross-linking agent’ monomers such as styrene or formaldehyde and ‘curing agents’ such as peroxides used in the plastics industry. Accordingly, the emission factor to air is quite high, ranging from 0.075 to 0.35 and these classes of compounds are not the same as the vulcanization agents used in the rubber industry. Vulcanising agents chemicals assigned to use category 43 (process regulators).used in the rubber and tyre industry are not explicitly covered in the TGD A-Table and were assigned to Category I in this table.

[d]Total hydrocarbon data indicates an oil/water separator efficiency of approximately 95%.

Tier 2 Emissions Factors for Air and Water based Measured Data

This section describes the development of Tier 2 wastewater emission factors for the combined activities of formulation (e.g. filling and weighing) and processing (e.g. extrusion). These emission factors are used as the basis for the development of a SpERC replacing ERC 3 and ERC 6d for the manufacture of tyres and general rubber goods. The specific processes covered include storage, weighing, mixing, cement preparation, shaping, curing and final treatment. The domain of substances covered is mastication agents/peptisers, vulcanization agents, anti-ageing agents/antidegradants, fillers and pigments, lubricants, tackifiers, filler activators, bonding agents, reinforcing agents and hardeners.

Data Collection

ETRMA, in participation with the European Rubber Chemicals Association (ERCA), recently conducted a wastewater characterization study for the purpose of emission factor development. The data was collected to develop a refined specific emission factor for ERC 3 – Formulation in materials and ERC 6d - Industrial use of process regulators for polymerisation processes in production of resins, rubbers, polymers for the GRG and tyre manufacturing sectors. The three chemicals monitored (6-PPD, CBS and DPG) were representative of GRG and tyre chemicals assigned to ERC 3 or ERC 6d. General characteristics of the chemicals selected for the wastewater sampling campaign are provided in **Table 4**. For chemicals with appreciable hydrolysis rates (CBS and 6-PPD), the major hydrolysis products were also monitored. The results for these three chemicals were combined into a single dataset because similar fate and transport processes with respect to wastewater are expected for chemicals assigned to ERC 3 or ERC 6d (with the exception of plasticizers) for those process steps where the majority of chemical release is likely to occur. Each of the three chemicals included in the calculation are characterized by low to moderate solubility (0.3 to 475 mg/L) and vapor pressure (< 7×10^{-3} Pa at 25 °C).

A total of 25 plants were included in the original sampling plan and at the completion of the study, information sufficient for emission factor calculation was available from 19 facilities consisting of 13 tyre facilities and 6 GRG facilities. Facilities selection has considered statistical production volumes and location in order to be representative of the EU rubber sector. Prior to data analysis, the analytical results and the responses to the survey were reviewed for completeness and consistency (see **Attachment B**). A total of 50 candidate results were initially considered for subsequent data analysis. Prior to data analysis, cases with non-detect results were reviewed to determine whether the detection limit was sufficiently low for inclusion in the analysis. The detection limit was evaluated by specifying a maximum allowable annual flow to annual mass use ratio based on a target emission factor of 5×10^{-5} for the tyre sector and 5×10^{-4} for GRG sector. These target emission rates were set at a level likely to exceed the true maximum emission factor based on the previous total zinc data collection for the tyre industry and use of the worst case A-table emission factor for the GRG sector, respectively.

After data review and processing, a total of 45 results defined by chemical substance (i.e. 6-PPD, CBS or DPG) and plant location were available in the final dataset. Summary characteristics of the dataset consisting of 45 results defined by substance and plant location are shown in **Table 5**. Generally, low/moderate scale use (≤100 ton/year/facility) frequencies were close to, but slightly higher than, a value of 220 days per year corresponding to the standard work year. However, large scale (> 100 ton/year) use frequencies were associated with greater than the 300 days per year of use corresponding to default for large tonnage uses. The flow rate at the sample collection points was normal and usage was typically at the normal rate or higher. Some, but not all of the data, include facilities that had pretreatment processes including oil/water separation and/or mechanical pretreatment such as filtration. Additionally, the dataset includes discharges to public STPs as well as direct discharge to rivers.

The effluent data was collected prior to biological wastewater treatment (if present) but after mechanical treatment such as sedimentation or filtration (if present). The samples were collected according to a protocol consistent with that required by the analytical laboratory, Currenta GmbH & Co. OHG Services Analytik (Dormagen, Germany). Sample bottles were filled completely, tightly sealed, kept cool and shielded from light. Personnel responsible for sample collection were required to complete an information survey, confirm compliance with the sampling protocol and maintain chain-of-custody between the plant location and laboratory. Sample collection was performed in the months of April and May, 2010.

Table 4: Chemicals included in the emission factor development study.

Chemical Name	Short Name (CAS No.)	TGD Use Category	Mol. Wt. (g/ mol)	Log K_{ow}	Sol-ubility at 20 to 25 °C (mg/L)	Vapor Pres-sure at 20 to 25 °C (Pa)	Monitored transformation products	
							Monitored transformation products[d] (CAS No.)	Mol. Wt. (g/ mol)
N-(1,3-Dimethylbutyl)-N´-phenyl-1,4-phenylenediamine	6-PPD (793-24-8)	03-Anti-ageing agents / anti-degradants	268	4.68[a]	1[a]	6.85 x 10^{-3}[a]	4-HDPA	185
N-Cyclohexyl benzothiazol-2-sulphenamide	CBS (95-33-0)	02-Vulcan-ization agents	264	4.93[b]	0.32[b]	1.5 x 10^{-6}[b]	BTON (934-34-0) MeSBT (615-22-5) BT (95-16-9) BTSO3H (941-57-1) MeBT (120-75-2) MBT (149-30-4)	151 181 135 215 149 167
1,3-Diphenylguanidine	DPG (102-06-7)	02-Vulcan-ization agents	211	1.6 to 1.8[c]	475	1.7 x 10^{-6}[c]	None[e]	

[a]OECD SIDS 2004b.
[b]EU CBS Final RAR 2008c.
[c]US EPA Risk-Based Prioritization Document 2009.
[d]4-HDPA=4-Hydroxydiphenylamine; BTON=2-Benzothizolone; MeSBT=2-Methylthiobenzothiazole; BT=Benzothiazole; BTSO3H= 2-Benzothiazolesulfonic acid; MeBT=2-Methylbenzothiazole; MBT=2-Mercaptobenzothiazole.
[e]The hydrolysis rate at environmental conditions is expected to be negligible for DPG (US EPA 2009).

Table 5: Characteristics of plants participating in the study. The summary is presented for the dataset of 45 results consisting of 3 substances monitored at 19 facilities.

Attribute	Small/Moderate Scale Use ≤ 100 t/y			Large Scale Use > 100 t/y		
	Metric	**Value**	**Unit**	**Metric**	**Value**	**Unit**
Annual tonnage of substance used at plant	Median Mean Min-Max	8.6 22 0.25-94	ton/year ton/year ton/year	Median Mean Min-Max	337 481 111-1337	ton/year ton/year ton/year
Emission days per year (continuous process)	Median Mean Min-Max	240 232 6-356	days/year days/year days/year	Median Mean Min-Max	334 318 194-365	days/year days/year days/year
Chemical use on the day of sampling[a]	Normal to Maximum	71%	percent	Normal to Maximum	95%	percent
Flow rate on the day of sampling[a]	Normal	87%	percent	Normal	71%	percent
Form of chemical[a]	Pellet or Granule Powder[b]	75% 25%	percent percent	Pellet or Granule Powder[b]	52% 33%	percent percent
Total wastewater flow at plant	Median Mean Min-Max	3.0×10^4 2.2×10^5 3.6×10^3 to 1.9×10^6	m^3/yr m^3/yr m^3/yr	Median Mean Min-Max	3.5×10^5 4.5×10^5 1.8×10^4 to 1.0×10^6	m^3/yr m^3/yr m^3/yr
Total wastewater flow at sample location	Median Mean Min-Max	3.0×10^4 2.1×10^5 1.1×10^3 to 1.9×10^6	m^3/yr m^3/yr m^3/yr	Median Mean Min-Max	2.7×10^5 3.9×10^5 1.8×10^4 to 1.0×10^6	m^3/yr m^3/yr m^3/yr
Pretreatment[a]	Oil/water separator Mechanical pretreat	67% 46%	percent percent	Oil/water separator Mechanical pretreat	76% 52%	percent percent
Other wastewater sources[a]	Sanitary sewer Rain water	33% 66%	percent percent	Sanitary sewer Rain water	43% 43%	percent percent
Discharge fate[a]	Public STP Surface water	75% 21%	percent percent	Public STP Surface water	38% 52%	percent percent

[a]Information was not indicated for at least one result and true percentage in some categories may be higher.
[b]Some respondents may have assigned powder classification to chemicals used in pellet or granule form.

Emission Factor Calculation

A summary of the analytical results reported by the laboratory is presented in **Table 6**. Non-detect results were assigned a value equal to ½ the detection limit. The sensitivity of the calculated emission factor and the specific limit of detection (LOD) assumption used were evaluated in the uncertainty analysis described below. The most frequently detected parent substance was 6-PPD (79%), which is consistent with the low detection limit of 0.1μg/L. DPG, which was infrequently detected, had an appreciably higher detection limit of 10 μg/L. CBS and related benzothiazole accelerators rapidly hydrolyze and accordingly, only the hydrolysis products were detected. The most abundant CBS hydrolysis products were 2-Benzothizolone (BTON) and benzothiazole (BT). **Table 6** also illustrates the conversion of the hydrolysis product to the original concentration of the parent substance using the molecular weight ratios ("As CBS or "As 6-PPD"). The analytical results were used with substance specific information provided on annual flow rate and annual usage to calculate site-specific and overall emission factors.

Table 6: Summary of waste water analytical results.

Analyte[a]	Molecular Weight (g/mol)	n	Detection Fre-quency	Limit of Detection (μg/L)	Average (μg/L)[b]	Average "As CBS" or "As 6-PPD" (μg/L)[b]	75th %-ile (μg/L)	90th %-ile (μg/L)	Maximum Detected (μg/L)
6-PPD	268	19	79%	0.1	41	--	46	144	260
4-HDPA	185	19	42%	1	6	9	2	17	60
CBS	264	16	0%	1	< 1	--	< 1	< 1	Not detected
BTON	151	16	88%	1	7	13	8	10	21
MESBT	181	16	56%	1	3	5	3	6	18
BT	135	16	94%	1	7	13	8	13	35
BTSO3H	215	16	19%	10	13	16	7	27	85
MEBT	149	16	0%	1	< 1	< 2	< 1	< 1	Not detected
MBT	167	16	13%	1	25	40	1	10	380
DPG	211	10	10%	10	10.5	--	5	10.5	60

[a]4-HDPA=4-Hydroxydiphenylamine; BTON=2-Benzothizolone; MeSBT=2-Methylthiobenzothiazole; BT=Benzothiazole; BTSO3H= 2-Benzothiazolesulfonic acid; MeBT=2-Methylbenzothiazole; MBT=2-Mercaptobenzothiazole.
[b]Non-detect results were assigned a value equal to ½ the limit of detection.

It should be noted that in addition to 6-PPD and CBS, there are other sources of the quantified hydrolysis products. To correct for other sources of the hydrolysis products, a market share adjustment was applied to the measured hydrolysis concentration. In Western Europe, the annual demand for CBS among all benzothiazole-type accelerators is 54% (EU CBS RAR 2008). For 6-PPD, the worldwide market share is 90% among all PPDs (OECD SIDS 2004). Based on these market shares, it was assumed the 54% of the benzothiazole hydrolysis products and 90% of the hydrolysis product 4-HDPA originated from CBS and 6-PPD, respectively

The emission factor is calculated using the measured concentration in water, annual flow rate, annual use and molar ratios for hydrolysis products. Separate equations were used to calculate the emission factor at individual facilities and overall aggregate emission factors within subcategories. The equation used to calculate the emission factor for plant *i* and substance *j* was:

$$EF_{i,j} = \frac{M_{i,j}}{A_{i,j}} \qquad \text{Equation 1}$$

$$M_{i,j} = Q_i \times CF \times \sum_{k=1}^{N} (C_{i,j,k} \times f_k \times r_k) \qquad \text{Equation 2}$$

where:

i	= index number of plant (e.g. 1=Plant 1,2=Plant 2, etc.)
j	= index number of test substance (e.g. 1=6-PPD, 2=CBS, 3=DPG)
k	= index number of analyte (e.g. 1=6-PPD, 2=4-HDPA, etc.)
N	= number of analytes for substance *j* where the number of hydrolysis products is equal to N-1
$EF_{i,j}$	= emission factor for substance *j* at plant *i* (kg/kg)
Σ	= sum of adjusted concentration for formulated substance and hydrolysis products
$A_{i,j}$	= annual mass used of substance *j* at plant *i* (ton/year)
$M_{i,j}$	= annual mass of substance *j* released in wastewater at plant *i* (ton/year)
Q_i	= annual flow rate at sample collection point of plant *i* (m^3/y)
$C_{i,j,k}$	= result for analyte *k* of substance *j* where *k* =1 is the parent substance and *k*=2 to N are the hydrolysis or transformation product(s) (µg/L)
f_k	= fraction of analyte *k* from target source substance
r_k	= molecular weight ratio for analyte *k* (=$MW_{parentl}/MW_{product}$)
CF	= conversion factor = 1×10^{-12} ton/µg x 10^3 L/m^3

To derive a reliable estimate of the emission factor based on critical determinants of environmental release, aggregate emission factors summing across multiple chemicals and plants were developed. The equation for the aggregate emission factor is:

$$EF_c = \frac{\sum_{i=1}^{P_c} \sum_{j=1}^{3} M_{i,j}}{\sum_{i=1}^{P_c} \sum_{j=1}^{3} A_{i,j}} \qquad \text{Equation 3}$$

c	= index number of sub-category (e.g. 1=Greater than 100 ton/year use, etc.)
i	= index number of plant (e.g. 1=Plant 1,2=Plant 2, etc.)
j	= index number of test substance (e.g. 1=6-PPD, 2=CBS, 3=DPG)
EF_c	= emission factor for sub-category *c*
$M_{i,j}$	= annual mass of substance *j* released in wastewater at plant *i* (ton/year) as defined in Equation 2 (ton/year)
$A_{i,j}$	= annual mass used of substance *j* at plant *i* (ton/year)
P_c	= number of plants in sub-category *c*

Results

The dataset was evaluated to determine the critical determinants of the aggregate emission factor. The determinants of exposure evaluated included:

- Scale of substance use (≤100 ton/year or < 100 ton/year);
- Sector (Tyre or GRG);
- Substance (6-PPD, CBS or DPG);

- Physical form (Powder, Granule or Pellet);
- Release fate (Surface water or STP); and
- Pretreatment (Oil water separation or mechanical treatment).

A critical determinant of the aggregate emission factor was the scale of use as shown in **Table 7**. When all the data is considered, the overall aggregate emission factor was 2 x 10^{-5} based on a dataset of 45 results summing to a mass used of 10611 tons per year and mass release of 194 kg/'year. On average, the individual substance release was about 4 kg/yr/facility. When the data is segregated by sector and tonnage use, an order of magnitude difference is observed by tonnage, but no appreciable difference is observed by sector. For local uses less than or equal to 100 tons/year, the aggregate emission factor was 1 x 10^{-4} based on a set of 24 results summing to a mass used of 519 tons per year and mass release of 66 kg/year. Similarly, the aggregate emission factor for substance uses greater than 100 ton per year was 1 x 10^{-5} based on annual mass use of 10092 tons per year and annual mass release of 128 kg/year. The release per facility on average is 2.8 kg/year and 6.1 kg/year for substance uses ≤ 100 tons/year/facility and > 100 tons/year/facility, respectively. These average emission rates are representative of an upper bound weighted higher by the data points with higher than average values. Accordingly, the annual mass release associated with the aggregate emission factor represents approximately the 80th percentile of individual substance emission factors by rank.

Table 7: Summary of preliminary calculated aggregate emission factor by sub-category.

Tonnage Used (ton/year/ facility)	Sector	Number of Results	Sum of Mass Used (total tons/year)	Sum of Mass Released (total kg/y)	Aggregate Emission Factor (unitless)	Median Emission Factor	90th Percentile Emission Factor
All (Regional)	GRG+Tyre	45	10611	194	2E-05	3E-05	6E-04
≤ 100 (Local)	GRG+Tyre	24	519	66	1E-04	1E-04	3E-03
	GRG	13	39	9	2E-04	1E-04	3E-03
	Tyre	11	480	57	1E-04	9E-05	7E-04
> 100 (Local)	GRG	--	--	--	--	--	--
	Tyre	21	10092	128	1E-05	9E-06	4E-05

For completeness, the median and 90th percentile emission factors are also shown in **Table 7**. However, as discussed in more detail in the uncertainty section, the best estimate of the sector emission factor is the aggregate factor that considers data from many different plants. The median and 90th percentile metrics are not independent metrics because they are each associated with a specific annual usage rate. For example, a 90th percentile emission factor could result in a much lower percentile annual release in kg/year because annual release is the product of annual use multiplied by the emission factor. In short, the emission factor is not an independent value with respect to annual usage rate, and the two values must be considered together to understand true environmental release. Incorrect conclusions can be drawn when point estimates of the emission factor are evaluated without consideration of the associated annual use rate. In contrast, the aggregate emission factor shown in Table 7 considers the both the total mass used, as well as the total mass released in each sub-category.

The remaining facility characteristics were also evaluated to identify other important determinants of exposure. For substance identification (i.e. 6-PPD, CBS or PPD) and release fate (i.e. surface water or STP), there was approximately a factor of 2 difference between the highest and lowest aggregate emission, which is within the range of experimental variability expected in a cross-section study of this type when no true difference exists. For physical form, the emission factor for the pellet form appeared to be lower than that of other types, but there were too few sample results in some categories to quantify the effect.

The effect of pre-treatment was assessed by scale of use. For large scale uses, defined as a process with optimization for efficient raw materials use (>100 t/y substance use), there was a negligible effect of pretreatment with approximately a factor of 1.2 to 2.1 difference with and without an oil/water separator or mechanical pretreatment. However for small/moderate scale processes with efficient raw material use (≤100 t/y substance use), there was an effect of pretreatment observed with approximately a factor of 3 difference with and without mechanical pretreatment. There was a negligible effect difference with and without an oil/water separator.

Based on the above results, three final categories of emission factors were assigned:

- Process with efficient raw material use (≤100 t/y substance use);
- Process with efficient raw material use and mechanical pre-treatment (≤100 t/y substance use); and
- Process with optimization for efficient raw materials use (>100 t/y substance use).

Each of these categories was assigned a specific ERC (SpERC) identification code (Table 8). Processes with optimization for efficient raw material use were defined as those processes with state of art, optimized and/or automated systems for the transport and handling of raw materials, that minimize overall exposure levels and incidental spills. As discussed previously, the recommended emission factor is the aggregate emission factor, but the median and 90th percentile of individual emission factors have been presented for information only. **Table 8** provides recommendations for local release factors. Generally, total regional emission should be calculated by taking into account the fraction of small/moderate scale uses and large scale uses or by selecting the most common scale of use. In the absence of this information or as a check on the final result, the regional emission combining small/moderate and large scale uses can be applied.

The Tier 2 emission factors recommended based on the emission factor study conducted in April and May 2010 at Tyre and GRG formulation and processing facilities are presented in **Table 9**. The SpERC factsheet for ERC 3 and ERC 6d are presented in **Attachment A**. These emission factor recommendations apply to all substances in ERC 3 or ERC 6d with the exception of plasticizers. For plasticizers, the A-table emission factor is 0.001, however, the Tier 1 total hydrocarbon data collection effort supports an emission factor of 0.00001 when an oil/water separator is included as a risk management measure.

Table 8: Summary of final aggregate emission factor by sub-category and assignment of ETRMA SpERC category.

ETRMA SpERC	**Environmental Release Factor Sub-Category**	**Number of Results**	**Sum of Mass Used (total tons/ year)**	**Sum of Mass Released (total kg/y)**	**Aggregate Emission Factor (unitless)**	**Median Emission Factor**	**90th Percentile Emission Factor**
Regional	Regional	45	10611	194	**2E-05**	3E-05	6E-04
ETRMA SPERC 3/6d.1 v.1	Process with efficient raw material use (local use ≤100 ton/year/ substance)	13	172	39	**2E-04**	4E-04	3E-03
ETRMA SPERC 3/6d.2 v.1	Process with efficient raw material use and mechanical pre-treatment (local use ≤100 ton/year)	11	347	27	**8E-05**	7E-04	3E-03
ETRMA SPERC 3/6d.3 v.1	Process with optimization for efficient raw materials use (local use >100 ton/year)[a]	21	10092	128	**1E-05**	9E-06	4E-05

[a]Processes with optimization for efficient raw material use (ETRMA SPERC 3/6d.3) include state of art, optimized and/or automated systems for the transport and handling of raw materials, that minimize overall exposure levels and incidental spills.

Table 9: Tier 2 Water Emissions Factors for Tyre and GRG Production.

TGD Classification	ERC	SPERC[a]	Water Emission Factors, F_{water}[a]				
			Tier 1	Tier 2			
			TGD A-Table	Local Emission Factor[b]			Regional Emission Factor (all use scales)[c]
				ETRMA 3/6d.1 Process with efficient raw material use (local use ≤100 ton/year/ substance)	**ETRMA 3/6d.2** Process with efficient raw material use and mechanical pre-treatment (local use ≤100 ton/year/ substance)	**ETRMA 3/6d.3** Process with optimization for efficient raw materials use (local use >100 ton/year)	
01 - MASTICATION AGENTS / PEPTISER	6d	ETRMA 3/6d.x v.1	0.0005	0.0002	0.00008	0.00001	0.00002
02 - VULCANISATION AGENTS	6d	ETRMA 3/6d.x v.1	0.0005	0.0002	0.00008	0.00001	0.00002
03 - ANTI AGEING AND ANTIFLEX-CRACKING AGENTS / ANTI DEGRADANTS	3	ETRMA 3/6d.x v.1	0.0005	0.0002	0.00008	0.00001	0.00002
04 - FILLERS AND PIGMENTS	3	ETRMA 3/6d.x v.1	0.0005	0.0002	0.00008	0.00001	0.00002
05 - PLASTICISER	3	N/A	0.001[c]	N/A	N/A	N/A	N/A
06-1- LUBRICANTS	3	ETRMA 3/6d.x v.1	0.0005	0.0002	0.00008	0.00001	0.00002
06-2- TACKIFIER	3	ETRMA 3/6d.x v.1	0.0005	0.0002	0.00008	0.00001	0.00002
06-4- FILLER ACTIVATOR	3	ETRMA 3/6d.x v.1	0.0005	0.0002	0.00008	0.00001	0.00002
06-6- BONDING AGENTS	3	ETRMA 3/6d.x v.1	0.0005	0.0002	0.00008	0.00001	0.00002
07-03 – EMUL-SIFIERS	4	N/A	0.0005	N/A	N/A	N/A	N/A
07-12- RE-INFORCING AGENTS	3	ETRMA 3/6d.x v.1	0.0005	0.0002	0.00008	0.00001	0.00002
07-7- HARDENERS	3	ETRMA 3/6d.x v.1	0.0005	0.0002	0.00008	0.00001	0.00002
07 - SOLVENTS	4	N/A	0	N/A	N/A	N/A	N/A
09 - RELEASE AGENTS	4	N/A	0.0005	N/A	N/A	N/A	N/A

Note: N/A indicates not applicable.
[a]ETRMA 3/6d.x v.1 where 3/6d indicates ERC 3 or ERC 6d, x = 1 (≤100 t/y use), 2 (≤100 t/y use with pretreatment) or 3 (>100 t/y) and v.1 indicates Version 1.
[b]Small/moderate scale uses are defined as annual uses ≤100 t/y. Large scale uses are defined as annual uses < 100 t/y.
[c]Substance-specific emissions should be calculated based on the typical scale of the use (small/moderate versus large scale uses). A regional emission factor is presented here to provide a bounding estimate for substance with both small/moderate scale and large scale uses.

Uncertainty Assessment

The Tier 2 emission factors recommended in **Table 9** and **Attachment A** are not without uncertainty. There are several factors which contribute variability and uncertainty to the quantification of industrial environmental release rates to wastewater. A strength of this cross-sectional study is that a large number of facilities have been included that are representative of the release conditions expected at both GRG and tyre facilities in small/moderate scale and large scale uses. As such, the chemical-specific release rates at each facility are point estimates of the emission factor *intra*-facility variability has not been characterized. To account for this, additional analyses were completed to evaluate the plausible upper bound emission factor, taking into account that only point estimates were available. A second strength of the study is that low detection limits were available, for example, the detection limit for 6-PPD was 100 ng/L or 0.1 µg/L. However, the detection limits for some substances were higher and for CBS, some results consisted of the sum of several non-detect values. This section describes additional calculations completed to characterize an upper bound exposure factor and a second analysis to evaluate limit of detection assumptions for non-detect results. Uncertainty attributable to the use of hydrolysis products in the quantification of emission factor is also addressed qualitatively. Finally, the results of this assessment are compared to the prior total zinc and hydrocarbon assessment.

Evaluation of Upper Bound Exposure Factor

To best characterize the true emission factor, an aggregate emission factor (defined as the total sum of the mass of substance released divided by the total sum of the mass of substance used) approach has been used for each of three critical subcategories defined by tonnage and, for small/moderate scale uses, the presence or absence of mechanical pre-treatment. The aggregate emission factor is considered to be a reliable estimate of the emission factor for small/moderate scale and large scale uses of ERC 3 or ERC 6d substances in the Tyre and GRG sector. This metric is recommended because of the large number of individual data points included in each category including 24 for small/moderate scale uses and 21 for large scale uses. In addition, this metric includes the contribution of facilities with higher emission rates, whereas other metrics such the median or geometric mean capture only central tendency emission rates. However, additional evaluation is needed to characterize the certainty in the true emission factor. Accordingly, additional analysis has been completed to derive an estimate of upper bound emission factor taking into account that only point estimates are available for each facility where data was collected.

Environmental release is determined by the product of the usage amount multiplied by the emission factor. Therefore, a high emission factor does not necessarily indicate a high environmental release. To develop an unbiased upper bound estimate of the emission factor taking into account both mass used and the mass released, each data point was ranked by mass release (kg/year) within each of the three main categories. Upper bound emission factors were then calculated by taking into account only the 80^{th} or higher percentile environmental releases in kg/year in each category.

As shown on **Table 10**, the upper bound estimate of emission factor is within the same order magnitude as the aggregate estimate (best estimate). On average, the upper bound emission factor is about a factor of 2 times higher than the aggregate estimate which is within the margin of error expected for a large cross-sectional study of environmental release. This analysis shows that an appreciably higher emission factor would not have been calculated if only the facilities with the highest environmental releases were considered.

This analysis also shows that overall regional emissions are sensitive to the relatively higher emission rate at a few facilities as compared to typical rates for the majority of facility and substance combinations. The upper bound emission factor includes only 20% of the data points in the dataset (n=10 of 45 total), but represents over 75% of total emissions of 6-PPD, CBS and DPG in this set (148 kg/year ÷ 195 kg/year x 100% = 76%). As a result, both the aggegate and upper bound estimates overestimate the true emission factor at a typical or 'median' facility.

The best estimate of the emission factor at a central tendency or midpoint facility can be approximated by the emission rate for 50^{th} percentile mass release in kg/year. For example, when the 40^{th} to 60^{th} percentile annual release in kg/year is considered (i.e. 0.8 to 2 kg/year), the overall emission factor (i.e. sum of release divided by sum of use) is 5×10^{-6}. Therefore, emissions at a 'typical' facility can be considered to be about a factor of 10 times lower than that represented by either the best or upper bound estimate of emission factor.

Limit of Detection

In this assessment, the conventional assumption of replacing non-detect values with ½ the limit of detection (LOD) has been used. Although more sophisticated approaches are available, the most robust approach is to explicitly evaluate whether the calculated result is sensitive to the LOD assumption by varying the imputed value from 0 to the LOD and checking the effect on the result (e.g. Murbach et al. 2008). As shown in **Table 11**, there was a negligible effect of the LOD assumption for non-detect analytical results on the calculated emission factor. This indicates that appropriate analytical techniques with sufficiently LODs were used in this study. As supported by the relatively high detection frequencies shown on **Table 6**, the emission factors in this study were calculated based on confirmed detections of the substances of interest and not sensitive to assumptions when non-detect results occurred. As expected, there was no effect for 6-PPD, which had the lowest detection limit of 0.1 µg/L and the largest effect was observed for DPG, which had the highest detection limit of 10 µg/L.

Hydrolysis Products

Two of the three substances (6-PPD and CBS) included in the study hydrolyze rapidly enough that monitoring of the hydrolysis products was necessary to calculate the emission factor. Each of the hydrolysis products monitored has other sources in the rubber industry in addition to 6-PPD and CBS. A quantitative correction was performed to account for these other sources. It should be noted that while this correction will result in a reliable overall emission factor, the emission factor at individual facilities may include a contribution of other sources that has not been fully corrected. For example, at one facility the detection of moderate to high BTSO3H levels and low BT could indicate possible a MBTS source. For each substance the primary hydrolysis products were selected based on a review of the literature. Some minor products, such as 4-Aminodiphenylamine (4-ADPA) for 6-PPD were not quantified, but these minor products are not expected to have had a major contribution to the total emission factor.

Comparison to Prior Data Collection of Zinc and Total Hydrocarbon

Previously in 2009, an overall semi-quantitative emission factor for a typical substance used in compounding and mixing was calculated based on the reported production rate and an estimated ZnO consumption rate of 0.015 g ZnO/g tyre. Averaged across all facilities, the emission factor to water was 5×10^{-5} (as Zn). Similarly, an overall emission factor for the hydrocarbon fraction used in tyre production was calculated based on the reported production rate and the estimated total hydrocarbon consumption rate of 0.1 g total hydrocarbon/g tyre. Averaged across all facilities, the emission factor to water was 1×10^{-5} after the RMM (oil/water separation). As shown in **Table 12**, the quantitative emission factor developed in this study compares favorably to the prior data collection effort. The slightly higher apparent emission factor for zinc is attributable to two factors including other substance sources of zinc in addition to ZnO and the failure to account for influent zinc at many of the sites in that dataset.

Table 10: Comparison of best estimate emission factor to upper bound estimate emission factor.

Emission Factor Category	Aggregate Estimate of Emission Factor (Best Estimate)				Upper Bound Emission Factor[a]			
	Number of Estimates (n)	Sum of Annual Release (kg/year)	Sum of Mass Used (ton/ year)	Emission Factor (kg/kg)	Number of Estimates (n)	Sum of Annual Release (kg/ year)	Sum of Mass Used (ton/ year)	Emission Factor (kg/kg)
Small or moderate scale use with no pretreatment (≤100 t/y)	**6-PPD**: n=4 **CBS**: n=5 **DPG**: n=4	39	172	0.0002	**CBS**: n=2 **DPG**: n=1	35	134	0.0003
Small or moderate scale use with pretreatment (≤100 t/y)	**6-PPD**: n=4 **CBS**: n=5 **DPG**: n=2	27	347	0.00008	**CBS**: n=2 **6-PPD**: n=1	17	127	0.0001
Large scale use (>100 t/y)	**6-PPD**: n=11 **CBS**: n=6 **DPG**: n=4	128	10092	0.00001	**CBS**: n=5 **6-PPD**: n=1	101	3432	0.00003
Regional (all data)	**6-PPD**: n=19 **CBS**: n=16 **DPG**: n=10	194	10611	0.00002	**6-PPD**: n=2 **CBS**: n=6 **DPG**: n=2	148	3735	0.00004

[a]Upper bound emission factor calculated using plants with 80th percentile or higher annual release in kg/year.

Table 11: Evaluation of the change in overall emission factor when the assumption for non-detect results is changed.

Substance	Overall Emission Factor		
	Non-Detect Results Set Equal to LOD	Non-Detect Results Set Equal to ½ LOD	Non-Detect Results Set Equal to 0
6-PPD	1E-05	1E-05	1E-05
DPG	3E-05	2E-05	1E-05
CBS	3E-05	3E-05	2E-05
Combined	**2.1E-05**	**1.8E-05**	**1.4E-05**

Table 12: Comparison of substance specific emission factors developed in the Tier 2 study to the semi-quantitative emission factors developed to support the Tier 1 use of the A-table emission factors.

Substance	Tier	Overall Emission Factor	
		n	Non-Detect Results Set Equal to ½ LOD
Total Zn	1	10	5E-05[a]
Total Hydrocarbon	1	8	1E-05
6-PPD+DPG+CBS	2	45	2E-05
6-PPD only	2	19	1E-05
DPG only	2	10	2E-05
CBS only	2	16	3E-05

[a]Some data points in Zn set did not account for zinc in the influent water supply. The substance use rate was estimated based on only on ZnO consumption.

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Attachment A

SPERC Fact Sheet

ERC 3 and ERC 6d

Date: 04 August 2010
Ref: ETRMA 3/6d.x v.1

REACH SpERC (Specific Emission Release Category)

Formulation and Industrial Use of Materials Resulting in Inclusion on a Matrix (ERC 3) in the General Rubber Good and Tyre Industries

Characteristics of specific ERC		Type of Input Information	Processing of Input Information
Title of specific ERC	Formulation and industrial use of materials resulting in inclusion on a matrix	None	None
Applicable ERC	3 – Formulation in materials	ERC	None
Responsible	ETRMA	None	None
Version	Version 1 [4 August 2010]	None	None
SpERC Code	ETRMA SPERC 3/6d.1 v.1 Small or moderate scale use (≤100 t/y) with no-pretreatment ETRMA SPERC 3/6d.2 v.1 Small or moderate scale use (≤100 t/y) with pretreatment ETRMA SPERC 3/6d.3 v.1 Large scale use (>100 t/y)	Tonnage	None
	Covers the whole process of formulation (e.g. filling and weighing) and processing (e.g. extrusion) that occurs in the manufacture of tyres and general rubber goods. The specific processes covered include storage, weighing, mixing, cement preparation, shaping, curing and final treatment. The domain of substances covered is listed below.	None	None
	<u>Code</u> – <u>Description</u> 01 – Mastication agents/peptiser 02 – Vulcanization agents 03 – Anti-ageing agents / antidegradants 04 – Fillers and pigments 06-1 – Lubricants 06-2 – Tackifiers 06-4 – Filler activators 06-6 – Bonding agents 07-12 – Reinforcing agents 07-7 – Hardeners	TGD Use Classification	None
Coverage	Process Categories: 5, 7, 8b, 9, 10, 13, 14, 21	None	None

<table>
<tr><th colspan="3">Characteristics of specific ERC</th><th>Type of Input Information</th><th>Processing of Input Information</th></tr>
<tr><td rowspan="3">Operational Conditions</td><td>ETRMA SPERC 3/6d.1 v.1</td><td>Process with efficient raw material use (M_{SPERC} ≤100 ton/year substance use)</td><td rowspan="3">Classification of formulation and processing facilities.</td><td rowspan="3"><u>Default</u>
$M_{SPERC} = M_{SITE} \times R \times (W \div 100 \text{ phr}) \div F$

where:
$M_{SITE,TYRE}$ = 52400 ton/year tyre (see ETRMA Production Rate Guidance)
$M_{SITE,GRG}$ = 5000 ton/year rubber (OECD, 2004)
R_{TYRE} = rubber compound fraction in tyre = 0.85
R_{GRG} = rubber compound fraction in GRG = 1
W = weight content of additive in phr or wt%
F_{phr} = recipe factor = 2 when W in phr
$F_{\%}$ = recipe factor = 1 when W in wt%

<u>Example</u>
W=2 phr = 1% (for example, vulcanization accelerator)

$M_{SPERC,TYRE}$ = 52400 x 0.85 x (2÷100)÷2 = 450 ton/year = 1500 kg/day for 300 day/year → Use ETRMA SPERC 3/6d.3 v.1

$M_{SPERC,GRG}$ = 5000 x 1 x (2÷100)÷2 = 50 ton/year = 227 kg/day for 220 day/year → Use ETRMA SPERC 3/6d.2 v.1 (with pretreatment) or ETRMA SPERC 3/6d.3 v.1 (with or without pretreatment)</td></tr>
<tr><td>ETRMA SPERC 3/6d.2 v.1</td><td>Process with efficient raw material use and mechanical pre-treatment (M_{SPERC} ≤100 ton/year substance use)</td></tr>
<tr><td>ETRMA SPERC 3/6d.3 v.1</td><td>Process with optimization* for efficient raw materials use (M_{SPERC} >100 ton/year substance use)

* Processes with optimization for efficient raw material use (ETRMA SPERC 3/6d.3) include state of art, optimized and/or automated systems for the transport and handling of raw materials, that minimize overall exposure levels and incidental spills.</td></tr>
<tr><td rowspan="3">Days Emitting</td><td>ETRMA SPERC 3/6d.1 v.1</td><td>220 days/year</td><td rowspan="3">Classification of formulation and processing facilities.</td><td rowspan="3">Conservative default values assigned based on survey of facilities used to derive emission factor. The average days of release for ≤100 ton/year substances in the ETRMA survey was 232 days per year. The average days of release for > 100 tons/year of use was 318 days per year.</td></tr>
<tr><td>ETRMA SPERC 3/6d.2 v.1</td><td>220 days/year</td></tr>
<tr><td>ETRMA SPERC 3/6d.3 v.1</td><td>300 days/year</td></tr>
<tr><td>Environmental Parameters for Fate Calculation</td><td colspan="2">Dilution factor of 10 for freshwater and 100 for marine water.</td><td>REACH TGD Default.</td><td>None, but can be scaled with site specific data,</td></tr>
</table>

Characteristics of specific ERC					**Type of Input Information**	**Processing of Input Information**
Emission fraction to air (f_{AIR})	**Process classification**	**BP (C)**	**VP (Pa)**	**F_{AIR*}**	Substance physical properties including vapor pressure (VP in Pa) and boiling point (BP in °C)	Default values from EU TGD A-Tables for the polymer industry (IC-11; Table A3.11). *Note: Air (F_{AIR} emission factors for processing aids (IV) are a factor 10 times higher. This includes lubricants and release agents.
	ETRMA SPERC 3/6d.x v.1 where x =1, 2 or 3	>300	<1	0.0005		
		<300	<1	0.001		
		>300	1-100	0.001		
		<300	1-100	0.0025		
		>300	>100	0.005		
		<300	>100	0.01		
Emission fraction to water (F_{WATER})	**Process classification**	**F_{WATER}**			Classification of formulation and processing facilities.	Default values from ETRMA wastewater effluent data collection and survey for 6-PPD, CBS and DPG conducted in April and May 2010. The stated emission factors are before biological treatment at a public or other STP.
	ETRMA SPERC 3/6d.1 v.1	0.0002				
	ETRMA SPERC 3/6d.2 v.1	0.00008				
	ETRMA SPERC 3/6d.3 v.1	0.00001				
Type of RMM	Typical environmental risk management measures by production phase are described in detail in the GRG and Tyre Generic Exposure Scenario available from the ETRMA website.				None	None

Characteristics of specific ERC		Type of Input Information	Processing of Input Information
Narrative description of / justification for specific ERC	Formulation and processing activities in the GRG and tyre industries are designed to minimize the loss of raw materials for economic efficiency. Processes for substances with large scale local use (>100 tons/year) are highly optimized for raw material use and recovery. The formulation and processing lifecycle stages in the rubber industry are dry processes. However, incidental emissions to water can occur as a result of floor scrubbing, equipment washing/blowdown or collection of curing press steam condensate. The specific processes covered include storage, weighing, mixing, cement preparation, shaping, curing and final treatment. The emission factors to air are based on the conservative A-Table emission values, as recommended in the Emission Scenario Document for the Rubber Industry. The emission factors for water are based on a large data collection effort in April and May 2010 of 13 tyre facilities and 6 GRG facilities. The emission factor estimates were based on measured concentrations of 6-PPD, CBS and DPG in water, annual wastewater flow rate, annual chemical usage and the source contribution of hydrolysis products. The study is documented in the **ETRMA Emission Factor Guidance for Formulation and Industrial Use Version 2.0** dated 4 August 2010.	None	None
Safe Use	Downstream users (DU) are required to confirm compliance with the exposure scenario forwarded by registrant. Because of the diversity of OCs and RMMs among tyre production facilities, ETRMA expects that the manufacturer/importer will provide scaling rules as described in *Part G: Extending the SDS* in the REACH CSA TGD. This may include the inclusion of a scaling equation in the eSDS annex, identification of valid linear relationships for key determinants of exposure or preparation of a spreadsheet model. The scaling equation allows DUs to combine OCs and RMMs differently than in the ES prepared by the registrant to confirm compliance with the ES at the facility level. The scaling approach allows the DU to make an independent determination of whether a specific facility has achieved control of risk within the boundaries of the ES. The calculation or determination is performed by the DU user after receipt of the eSDS and does not affect the CSA prepared by the supplier. The scaling equation approach is not required when control of risk can be demonstrated for worst case parameter selections, such as the ERC emission factors.	Key exposure determinants.	See also **ETRMA Scaling Equation Guidance** (most current Version 1.0 dated 16 December 2009).

Attachment B

Detection Limit Evaluation

Attachment B: Detection Limit Evaluation

Maximum target emission factors of 5 x 10^{-4} and 5 x 10^{-5} were selected for GRG and Tyre uses, respectively. For each non-detect result, a value of ½ the detection limit was assigned. These targets was selected as a reasonable maximum emission factor based on prior information collection for zinc and total hydrocarbon, as well as the default A-table emission factors. For each entry in the database that consisted entirely of non-detect results for the parent substance and all transformation products, the ratio of Q/M was calculated and compared to Q/M_{max} calculated for the target emission factors. Results where all Q/M exceeded Q/M_{max} and all results were non-detect were eliminated from the dataset. The equation for Q/M_{max} is:

$$(Q/M)_{max} = \frac{EF_{max,target}}{CF \times \sum(\frac{1}{2} LOD_k \times f_k \times r_k)} \quad \text{Equation B.1}$$

where:

$EF_{max,target}$	= maximum target emission factor (kg/kg)
Σ	= sum of formulated chemical and hydrolysis products
M	= annual mass used (ton/year)
Q	= annual flow rate (m^3/y)
LOD_k	= limit of detection for analyte *k* (µg/L)
f_k	= fraction of analyte k from target source substance
r_k	= molecular weight ratio for analyte *k* (=$MW_{parentl}/MW_{product}$)
CF	= conversion factor = 1 x 10^{-12} ton/µg x 10^3 L/m^3

The acceptance criteria for non-detect sample results is shown in Table B.1. The samples removed from the dataset because the result was non-detect and the calculated emission factor exceeded the maximum target emission factor are listed in Table B.2 below.

Table B.1: Acceptance criteria for non-detect results.

Chemical	**Number of Analytes Including Hydrolysis Products**	**½ LOD (µg/L)**	$f_{hyd\text{-}rolysis}$	$r_{hydrolysis}$	$(Q/M)_{max}$ **EF=0.05% (m^3/t)** [GRG]	$(Q/M)_{max}$ **EF=0.005% (m^3/t)** [Tyre]
6-PPD	2	0.05 to 0.5	0.9	1.4	722000	72200
CBS	7	0.5 to 5	0.54	1.2 to 2	81800	8180
DPG	1	5	--	--	100000	10000

Table B.2: Non-detect samples removed from the analysis because the detection limit exceeded the level required to meet the maximum target emission factor.

Chemical	**Sector**	**Q/M (m^3/t)**	**Any analyte or hydrolysis product detected?**	**Emission Factor Using ½ Limit of Detection for Non-Detect Result**
DPG	Tyre	23818	No	1.2 x 10^{-4}
CBS	Tyre	111765	No	6.8 x 10^{-4}
DPG	Tyre	475000	No	2.4x10^{-3}
DPG	GRG	289474	No	1.4x10^{-3}
DPG	GRG	104167	No	5.2x10^{-4}