Gathering and Review of Environmental Emission Scenarios for Biocides

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Appendix 1

Appendix 2

Introduction

This report was initiated and financed by the Federal Environmental Agency, Germany. It has been developed in the framework of the EU project "Gathering, review and development of environmental emission scenarios for biocides" and has been discussed by the concerned EUBEES working group. We would like to thank all members for their comments and helpful information.

An exposition estimation is necessary for the risk assessment of chemical substances. The biocidal products directive 98/8/EU lists the product types, which still lack an environmental exposition estimation as a part of the risk assessment, in appendix V 24. So called emission scenario documents (ESD) are needed for implementation of the EU-biocidal products directive on a national level. The first step in this project is a thorough research of the relevant literature and its applicability for the development of ESDs for the various product types. The life cycle steps are production, formulation, processing, service life, waste treatment and recycling. Production and formulation are outside the scope of the biocide directive.

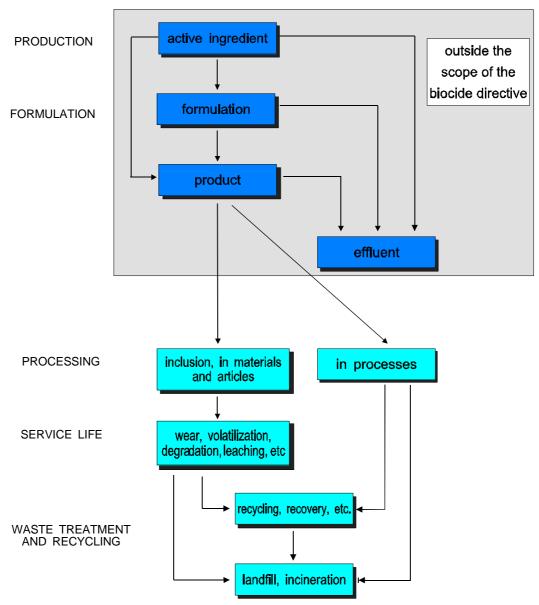
The stage of **processing** is the stage in which the biocide is applied (industrial application or private use). In the case, that the biocide is fixed to a material the **service life** of articles made from these materials is important (e.g. a mothproofing agent on a woollen carpet or a wood preservative in a garden fence). The stage in which waste is disposed off (**waste treatment**) consists of landfill or incineration and reuse or **recycling** of waste streams, and recovery of components.

For performance of ESDs relevant information/data is necessary. In the **processing** stage, data on take up in articles/dose used in processes must be known and will be supplied by the notifier/registrant with the dossier. In addition, data on the relevant processes used is necessary (e.g. amount of articles produced, quantities of water used, abatement techniques, emission factors). Relevant information concerning the **service life** is data about factors such as way of use (indoor, outdoor), leaching rates, degradation rates, product life etc.. Data on relevance of the stage of waste water is e.g. degradation rates in treatment plants, recovery of the biocide and recycling of other components or materials (e.g. paper recycling) where releases of the biocide may occur.

It is necessary to identify the affected environmental compartment (air, water, soil) in all concerned life cycle steps.

The quality of data for the individual product types and the processes involved varies widely. In order to be able to fill the existing data gaps, we formulated a minimum requirement profile for ESDs. These data requirements must be met in order to create a ESD. The quality of the predictions can be improved gradually depending on the data becoming available. For the application of the A and B-tables for example rough market data is necessary. This will not be necessary if product specific information is present, for instance on the quantity applied. In such a case it is possible to calculate a close-to-reality PEC.

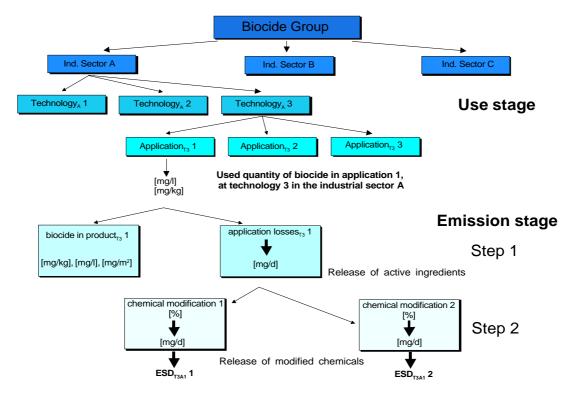
LIFE CICLE STAGE



As more detailed and accurate data is available for all relevant aspects and stages of the life cycle, better ESDs can be generated. This mean less worst case assumptions in the scenario and consequently more realistic PECs. Inaccurate or incomplete data will increase the set of possible negatively evaluating applications.

The processes within a product type may be very inhomogeneous. Slimicides (product type 12) for example may be used in various branches of industry such as sugar production, paper production and oil industry. In paper production they may be applied in an intermittent or a continuous way. Such differences have an implication for the emission scenarios. For one product type several emission scenarios may have to be developed (see figure below), while for some product types emission scenarios of other ESDs may be

used (possibly with a small modification or other default values for some parameters). For human hygiene biocidal products (product type 1) for example, the emission scenario of the ESD for new and existing substances of industrial category 5 "personal/domestic" may usually be used.



We assume, that a biocide group is used in several industrial sectors A, B and C (e.g. for slimicides in the pulp and paper industry, the oil industry and the sugar industry). Three Production technologies are used in the industrial sector A (e.g. paper production from pulp (technology A1) and from recycling paper with a closed water cycle (technology A2) and recycling paper with a semi closed water cycle (technology A3). Within the technology A3 we know 3 application methods (e.g. continuous (application T3 1) or discontinuous dosage (application T3 2). As a result we have the used quantity of biocide in application 1 at technology 3 in the industrial sector A.

Part of the used biocide quantity is fixed in the product (e.g. paper or is active in the water cycle) and another part is lost in the water outflow or overflow. This quantity per day is the release of the active substance and up to now the basis for a PEC/PNEC calculation.

Unfortunately in many cases the lost substance is not identical with the former active biocide-ingredient in the used slimicide product. In our case we had two chemical modifications and only these substances (concerning the biocide sector) are leaving the process and will form the real release for one or several ESDs in that process.

So far, the risk assessment of (new and existing) substances only considers the original substance notified. In the case of biocides the substance notified may not have the biocidal action by itself but one (or more) of the degradation products (normally hydrolysis products) of biocides applied in an aqueous solution. This has implications for the emission scenarios and this problem has to be addressed specifically.

Considering all listed factors we suggest the following structure for an ESD:

- 1. Description of the branches
- 2. Description of technologies/use pattern
- 3. Description of environmental emission routes and received medium a. qualitative
 - b. quantitative
- 4. Present algorithm to calculate emissions (factors)
- 5. Bibliography

A few of the product types are less relevant for environmental emissions and for the development of ESDs than others. This has to be sorted out in a priority ranking procedure to be carried out.

Such product types are e.g.

- 17 Piscicides (known in Norway for special fish farming systems)
- 22 Embalming and taxidermist fluids

We suggest that the following product types are appropriate for the priority ranking of ESDs to be developed:

- In-can Preservatives (product type 6) and film preservatives (product type 7)
- Fibre, leather, rubber and polymerised materials preservatives (product type 9)
- Slimicides (product type 12)
- Rodenticides (product type 14)
- Insecticides, acaricides and products to control other arthropod species (product type 18)
- Antifouling products (product type 21)

1 Human hygiene biocidal products

Introduction

Biocidal products of product type 1 are used for disinfection related to human body hygiene, including antiseptics not covered by the Council Directives concerning medicinal products or cosmetics, which are used in topical application on intact human skin surface to prevent infections.

Product type 1 comprises skin antiseptics, antimicrobial soap, health care products, personnel hand wash products, antiperspirants and deodorants, anti-dandruff shampoos and products to combat acne, whereas preservatives used in cosmetics are not included in this product type. Antiseptics reduce the concentration of transient micro-organisms on intact skin to a certain base-line level. These products contain an antimicrobial chemical substance, with a broad spectrum of activity, rapid action and a certain degree of persistence. (van Dokkum et al., 1998)

The relevant sub-groups are:

- 1.1 Skin antiseptic (professional and non-professional use)
- 1.2 Antimicrobial soap (professional and non-professional use)
- 1.3 Health care personnel hand wash (professional use)
- 1.4 Suntan (non-professional use)

Relevant information data for ESDs

Processing

- Inclusion in materials/articles
- Application in processes

Used quantity of active substances (van Dokkum et al.,1998; Kunz et al.,1986; Balk, 1999)

This product type is characterized by a large number of different products and active substances. Another characteristic of this product type is a strong relation with other legislation, especially cosmetics and medicine legislation. Some examples for products and active substances, which could be covered by product type 1.1 to 1.3, are:

Antiperspirants and deodorants (available as roll-ons, sticks and aerosol sprays): Aluminium salts, triclosan

Anti-dandruff shampoos:

Coal tar, pyrithione zinc, salicylic acid, selenium sulphide, sulphur

Products to combat acne (available as soaps, masks, gels, bars, lotions, etc.): Triclosan, salicylic acid, resorcinol, suphur

Hand and skin disinfection:

Phenols, quaternary ammonium compounds, iodine, alcohols (ethylalcohol, isopropylalcohol, n-propylalcohol), heterocyclic compounds

1.1 Skin antiseptic

During operations: 70-80 % alcohol+0,5 % chlorohexidine (time <4min)

<u>1.2 Antimicrobial soap</u> In soap 0,1-0,15 % chlorohexidine Health care personnel hand wash 70-80 % alcohol, daily, very frequently

Service Life

Waste Treatment

• Waste streams + relevant information (van Dokkum et al., 1998)

The environmental exposure of product type 1 is very diffuse. The products are available as soap bars or liquid soap, sprays, gels, pastes, shampoos or baths, all in small quantities. After application the products will usually be rinsed or washed off and be discharged to the sewage treatment plant or, in exceptional cases, reach the fresh and marine surface water (suntan products). For the environmental compartments fresh surface water and marine surface water emissions are only expected in the bathing season and during the day. During the bathing season, chronic exposure of local ecosystems may be expected and chronic test data is therefore considered as relevant. Substances with a high toxicity are unlikely to be used, as the primary application is on human skin.

The packaging material together with the remnant of the product will enter the municipal waste and be disposed off to a waste dump.

Emission routes for biocides. '+'=relevant; '-' not relevant (van Dokkum et al., 1998, modified)

Produc t type	Applications	Fresh surface water	Marine surface water	Air indoor and outdoor	Soil	Solid Waste	Waste water
1.1	Skin antiseptic (P+N)	-	-	-	-	-	+
1.2	Antimicrobial soap (P+N)	-	-	-	-	-	+
1.3	Health care personnel hand wash (P)	-	-	-	-	-	+
1.4	Suntan products (N)	+	+	-	-	-	+

P: professional use; N: non-professional use

• Recycling/recovery/reuse

Existing and produced emission models

No emission models were found for product type 1. But we suggest the following:

Calculation of the release of disinfectants used for skin antiseptic, antimicrobial soap and hand wash products:

References:

Balk, F., Roorda, A., Rutten, A.L.M., de Kok, M. Th. : "Identification and description of biocidal product types and establishment of scores based on the level of exposure of humans and the environment", Biocides Study DG XI/E2/ETU/980056, Draft final report, June 1999

Kunz, P., Frietsch, G. : "Mikrobizide Stoffe in biologischen Kläranlagen - Immissionen und Prozeßstabilität", Springer Verlag, 1986

van Dokkum, H.P., Bakker, D. J., Scholten, M. C. T. : "Development of a concept for the environmental risk assessment of biocidal products for authorization purposes (BIOEXPO) - Part 2: Release estimation for 23 biocidal product types" TNO MEP Report R97/443, 1998

Wallhäuser, K.H. : "Praxis der Sterilisation, Desinfektion - Konservierung", 5. Völlig überarbeitete Auflage, Georg Thieme Verlag Stuttgart, 1995

2 Private area and public health area disinfectants and other biocidal products

Introduction (van Dokkum et al., 1998)

According to the Biocide Product Directive, this product type includes:

"Products used for disinfection of air, surfaces, materials, equipment and furniture which are not used for direct food or feed contact in private, public and industrial areas, including hospitals, as well as products used as algaecides. Usage areas include, inter alia, swimming pools, aquariums, bathing and other waters; air-conditioning systems, walls and floors in health and other institutions; chemical toilets, waste water, hospital waste, soil or other substrates (in playgrounds)".

All disinfectants not included in one of the other product types belong here. For several sub-groups there is a potential overlap between biocides and medicines legislation. The relevant sub-groups are:

- 2.1 Disinfection of medical equipment (professional use)
- 2.2 Disinfection of swimming pool, aquarium, bathing and other waters (professional and non-professional use), (see also PT 5)
- 2.3 Disinfection of air-conditioning systems (professional use)
- 2.4 Disinfection of accommodation for man (professional and non-professional use), (see also PT 4)
- 2.5 Disinfection of industrial areas (professional use), (see also PT 4, PT 20)
- 2.6 Disinfection of chemical toilets (professional and non-professional use)
- 2.7 Sewage/Waste water disinfection (professional use)
- 2.8 Disinfection of hospital/infectious waste (professional use)
- 2.9 Soil or other substrates disinfection (professional use)
- 2.10 Laundry disinfection (professional and non-professional use)

Relevant information data for ESDs

Processing

- Inclusion in materials/articles
- Application in processes

Active ingredients (van Dokkum 1998, Kunz et al. 1986; Bapp et al. 1995; Rutala 1996, Gartiser et al, 1999; Wallhäuser 1995, Umweltbundesamt 1999, Russel, 1992): In product type 2 a very heterogenous range of products is applied.

2.1 Disinfectants for medical instruments

The choice of disinfectant is based on the risk of infection associated with the use of the item. The quality of disinfection is divided into 3 groups:

High level disinfection: Ethyleneoxide; glutaraldehyde; formaldehyde; chlorine dioxide; hydrogenperoxide; peracetic acid

Intermediate level: ethanol or isopropanol; chlorine compounds; phenolic or iodophore preparations

Low level: quaternary ammonium compounds; iodophores; phenolics (Favero & Bond, 1991, cited in Dokkum et al. 1998).

2.2 Swimming pool disinfectants

Chlorine compounds such as chlorine gas, sodium and calcium hypochlorites, chlorinedioxide in combination with chlorine gas, and chlorinated isocyanates

Elemental liquid bromide, sodium bromide and hypochlorite, organic bromine releasing compounds;

Silver and copper ions;

Hydrogenperoxide in combination with biguanid polymers;

Algaecides based on quaternary ammonium and polyoxyimino compounds, or copperbased Algaecides

2.4 and 2.6 Disinfectants for accommodation for humans (bathrooms, toilets, chemical closets, walls and floors)

Hypochloride; aldehydes; surfactants and quarternary ammonium compounds; alcohols; per-compounds; phenols; guanidines; alkylamines

Formaldehyde is commonly used in room disinfection for hospital rooms.

2.7 Sewage/Waste water disinfectants

Chlorine; hypochlorous acid; chlorine dioxide and ozone

2.8 Hospital/Infectious waste disinfectants

Peroxides; quaternary ammonium compounds; peracetic acid; aldehydes such as glutaraldehyde; phenoles; kationic surfacants; amphoteric surfacants; alcohols

2.10 Laundry disinfectants

Chlorine; peroxide and peracetic acid; aldehydes; phenols; quaternary ammonium compounds; biguanides, halogenated compounds

Used quantity of active substance

2.1 Medical equipment

Sterilization by ethyleneoxide (1200 mg/l) at 50-60°C (0,1 %)

Ethanol 70 %, hypochlorite 1000 ppm (free chl.), jodium 1 % in 70 % alcohol, jodofoor 10 %, o-phenylphenol 2 %, succcinic (10 %) or glutaraldehyde (2 %), chlorohexidine (0,05-4 %), hydrogenperoxide 3-6 %. (Balk, 1999)

2.2 Swimming pool, aquarium, bathing and other waters

No epidemy at > 0,5 mg Cl₂/l; wasted water contains a maximum of 1,4 mg/l free chlorine Swimmers: average contact time: 1 hour, concentration in water $(1,4 \text{ mg/l}=1,4*10^{-4} \text{ %})$ Small swimming pools: biguanides and organo chlorine release compounds Large pools: chlorine and sodium hypochlorite In EU: 80 % of the pools are smaller, private or residential, 10 % in hotels, 5 % in schools, 3 % muncipal pools. (Balk, 1999)

2.4 Accommodation for man

Household hypochlorite preparations are sold at conc. 0,5 to 12,5 % (available Cl-levels), prevalence 3-5 %; typical dilute concentrations for hypochlorite range from 0,01 to 0,5 %; less frequent exposure to conc. Solutions 2,5 to 5 %. (Balk, 1999)

2.7 Sewage/Waste water disinfection

3-10 mg Cl_2/l , 30 to 60 min. contact time

Service Life

Waste Treatment (Dokkum et al. 1998, Luttik 1996)

• Waste streams + relevant information

Due to the large variability in applications within this product type it is not possible to construct just a single emission model.

2.1 Disinfection of medical instruments in hospitals

Aqueous solutions used for the sterilization of instruments will mainly reach the sewer system, whereas gas-disinfectants will be directed to the air.

2.2 Swimming pool disinfectants

The majority of disinfectant agents used for disinfecting swimming pool water will be degraded rapidly, but the remaining active ingredients will be discharged to the sewer system together with the swimming pool water. Emissions of disinfectants to the air have to be taken into consideration as well.

2.3 Disinfectants for air-conditioning systems

The disinfectants will be directed to the air (indoors) when the water is vaporized.

2.4 Disinfectants for accommodations for humans

Since it is assumed that surfaces are rinsed with water after disinfection, the main emission is directed to the sewer system, with emission to the air.

Disinfectants for hospital rooms:

The biocides used for room disinfection will enter the sewage treatment plant, if the room is cleaned with fresh water after disinfection. Also emissions to the air (indoors) have to be taken into consideration.

2.7 Sewage/Waste water disinfectants

In cases where effluent of a sewage treatment plant is discharged into surface water for recreation or growing shell-fish, disinfection prior to the emission to surface water (according to legal provision) can take place. Disinfection is commonly performed by UV-irradiation but chemical disinfection is used as well.

Some active ingredients applied to the water for disinfection will be degraded, but the remaining disinfectant agents will be emitted to the air or transported to the receiving surface water.

2.8 Hospital/Infectious waste disinfectants

The main emission is discharged to the sewer system, but emissions to the air occur as well.

2.9 Disinfectants for soil

There is little information concerning application techniques, but emissions to air (outdoors), soil and to some extent to water can be expected.

2.10 Laundry disinfectants

The waste water from the laundry will enter the sewer system.

Emission routes for biocides. '+'=relevant; '-' not relevant (van Dokkum et al., 1998, modified)

Product type	Applications	Fresh surface water	Marine surface water	Air indoor and outdoo r	Soil	Solid Waste	Waste water
2.1	Disinfection of medical equipment (P)	-	-	+	-	-	+
2.2	Disinfection of swimming pool, aquarium, bathing and other waters (P+N)	-	+*	+	-	-	+
2.3	Disinfection of air- conditioning systems (P)	-	-	+	-	-	+
2.4	Disinfection of accommodation for man (P+N)	-	-	+	-	-	+
2.5	Disinfection of industrial areas (P)	-	-	+	+	+	+
2.6	Disinfection of chemical toilets (P+N)	+	+	-	-	-	+
2.7	Sewage/Waste water disinfection (P)	+	+	+	-	-	-
2.8	Disinfection of hospital/ infectious waste (P)	-	-	+	-	+	+
2.9	Soil or other substrates disinfection (P)	+	-	+	+	+	-
2.10	Laundry disinfection (P+N)	-	-	+	-	-	+

P: professional use; N: non-professional use

*Swimming pool disinfection is not considered relevant for marine bodies of water according to Dokkum. It can be assumed though that hotels and camping grounds which are situated directly at the coast will dispose off of their used swimming pool water directly into the sea (especially in southern countries).

• Recycling/recovery/reuse

Existing and produced emission models

The contribution of disinfectants on geno- and ecotoxic effects in hospital waste water has been evaluated, by compiling the consumption of active substances at 8 hospitals in Germany and by 80 waste water samples. The average specific total consumption of disinfectants (without alcohols) was 4,4 g/(bed*day), corresponding to a waste water concentration of around 9 mg/l. In this addition relevant consumption from kitchen and laundries are taken into account. A disfunktion of muncipal waste water treatment plants through disinfectants from the hospital area is not expected, as both the ecotoxic as well the gentoxic effects of disinfectants were degraded in sewage treatment plants as a rule.(Gartiser, 2000)

2.1 Disinfection of instruments

The following model is designed for calculating the volatization of the disinfectant from water bodies:

- I. Determination of Henry's law constant [Pa + m³ / mol]. The limiting factor of the calculation is Henry's law constant.
- II. If HENRY < 3, then $Elocal_{3, air} = 0$ (end of calculation)

- III. If HENRY \geq 3, the substance is considered to be volatile, determination of the nondimensional Henry's law constant (air-water partition coefficient) Kair-water.
- IV. Calculation of the liquid phase exchange coefficient k_1 (MOLW = molecular weight) $MOLW \le 65$: $k_1 = 5.55 * 10^{-5} * (44 / MOLW)^{1/2}$ MOLW > 65 and WINDSPEED < 1.9 m/sec:

 $k_1 = 6.53 * 10^{-5} + (WATERSPEED^{0.969} / DEPTH_{water}^{0.673}) * (32 / MOLW)^{1/2}$ MOLW > 65 and 1.9 < WINDSPEED < 5 m/sec: $k_1 = 6.53 \ ^* 10^{-5}$ + (WATERSPEED $^{0.969}$ / DEPTH_water $^{0.673}$) * (32 / MOLW) $^{1/2}$ * $e^{0.526} \ ^{(WINDSPEED - 1.9)}$

- V. Calculation of the gas phase exchange coefficient k_g: MOLW < 65: $k_g = 8.33 \times 10^{-3} (18 / MOLW)^{1/2}$ MOLW > 65: $k_g^{"}$ = 3.16 * 10⁻³ (WINDSPEED + WATERSPEED) * (18 / MOLW)^{1/2}
- VI. Calculation of the overall liquid-phase mass transfer coefficient KL: $K_L = (K_{air-water} * k_q * k_1) / (K_{air-water} * k_q + k_1) m/sec$

The following steps for the emission model for the concentration at any time and for the emission scenario are specifically:

VII. Calculation of the concentration after 24 hour (maximum emission on the first day):

 $C_{day2} = C_{day1} * exp (-K_L*T_{day2}/100* DEPTH_{water}) mg/I$

where C_{dav2} = disinfectant concentration at certain time (T_{dav2} in hours)

 C_{dav1} = disinfectant start concentration in refreshed bath,

- T_{dav2} = time in hours
- Calculation of the emission from the difference in concentrations (day 1 -VIII. day 2).

In formula 2 and 3 the limiting factor HENRY is set 3 in the literature. But between 0,03 and 100 a substance is considered as volatile in moderation. Therefore formula 1 and 2 should be modified as follows:

If HENRY <0,03, then $Elocal_{3, air} = 0$ (end of calculation)

If HENRY \geq 0,03, the substance is considered to be volatile, determination of the

nondimensional Henry's law constant (air-water partition coefficient) Kair-water.

Instruments are disinfected in baths, which are regularly disposed off into the sewer.

The following model is used to calculate the maximum emission rate at the day of replacement:

Elocal_{3, water} = Qyear_{disinf} / Temission₃ * (1-f_{red})

where

Qveardisinf = Amount of active substance (kg/year)

Temission₃ = Emission days, i.e. replacements (/y)

= Concentration reduction at replacement, due to dilution, volatization, f_{red} probable decomposition, carry over of the disinfectant

2.2 Disinfection of swimming water (Luttik, 1995 and Luttik, 1996)

Swimming pools are so-called circulating baths. During water treatment the swimming water is supplied with a certain amount of disinfectant.

Discharge of swimming water into the sewage treatment plant (STP)

To calculate the concentration of compounds/metabolites reaching the sewage treatment plant the following model has to be used (Volatilization of the compounds is not taken into consideration, because it is assumed that the concentration of the compounds/metabolites in the waste water of the swimming pools will be low. Therefore the role of volatilisation will be of minor importance.).

The discharge of swimming water into the sewage system can be an acute or chronic situation

- \Rightarrow In the acute case the whole pool is emptied completely into the sewage system (formula 1)
- \Rightarrow In the chronic case a fixed amount of swimming water per visitor is discharged into the sewage system (formula 2)

$$\begin{array}{l} (1) \ C_{surf \ I} = L_{surf} \ast W_{depth} \ast D \ast C_{swimw} \ast (1 - R_{STP}) \ast 10^3 / (Q_{STP1} \ast F_{dilut}) \\ (2) \ C_{surf \ II} = N_{visit} \ast Q_{repl} \ast C_{swimw} \ast (1 - R_{STP}) \ast 10^3 / (Q_{STP2} \ast F_{dilut}) \\ \text{where} \\ C_{surf} = Concentration of compound/metabolite/reaction product in surface water Img/II \\ \end{array}$$

- $L_{surf} = Water surface [m²]$
- W_{depth} = Average depth of water [m]
- D = Discharge to STP (/year)
- C_{swimw} = Concentration of compound/metabolite/reaction product [mg/m³]
- R_{STP} = Fraction removed in the STP [-]
- Q_{STP1} = Quantity of water in the STP [m³/year]
- Q_{STP2} = Quantity of water in the STP [m³/day]
- F_{dilut} = Dilution factor of receiving surface water [-]
- N_{visit} = Number of visitors per day [/day]
- Q_{repl} = Water replaced per visitor [m³]

Discharge of swimming water into the surface water

The concentration of the compound/metabolite/reaction product can be calculated as follows:

 $C_{surf} = C_{swim} / F_{dilut}$

where

- C_{swim} = Concentration of compound in swimming water [mg/l]
- F_{dilut} = Dilution factor of receiving surface water [-]

<u>2.3 and 2.4 Disinfection of rooms, furniture and objects in medical sector</u> (van der Poel, 1999)

Emission scenario for calculating the release of disinfectants used for sanitary purpose in hospitals (The factor 0.1 was not explained in the References.)

 $Elocal_{3, water} = Q_{water1} * C_{disinf1} * 0.1 * F_{3, water} + Q_{water2} * C_{disinf2} * 0.1 * F_{3, water}$ where

 $Elocal_3 = Emission$ rate to waste water (kg/d)

- Q_{water1} = Amount of water with active substance (sanitary purpose) (I/d)
- $C_{disinf1}$ = Concentration at which active substance is used (sanitary purpose)(kg/l)
- $F_{3, water}$ = Fraction released to waste water

 Q_{water2} = Amount of water with active substance (brushes) (I/d)

 $C_{disinf2}$ = Concentration at which active substance is used (brushes)(kg/l)

2.4 Disinfection in accommodation (Luttik 1996)

After use the disinfectants will be discharged into the sewer system.

The concentration of the active ingredient in the receiving surface water (C_{surf}) [mg/l] can be calculated as follows:

 $C_{surf} = X * 10^9 * f_{wwat} * R_{STP} / d * Q_{water} * i_{CO} * F_{dilut}$ where

X = Quantity of active ingredient used in a country [tons/year]

- f_{wwat} = Fraction released to waste water [-]
- R_{STP} = Removal in sewage treatment plant [-]
- d = Number of days disinfectant is used [days/year]
- Q_{water} = Quantity of water used per inhabitant per day [I/day]
- i_{CO} = Number of inhabitants in a country [-]
- F_{dilut} = Dilution factor of the receiving surface water [-]

2.4 and 2.5 Sanitary sector (van der Poel, 1999)

Calculation of the release of disinfectants used for sanitary purpose:

 $Elocal_{,water} = number \ of \ inhabitants \ ^* Q _{product} \ ^* C_{product} \ ^* F_{4,water} \ where$

Elocal = Emission rate to waste water (kg/d)

 $Q_{product}$ = Consumption per capita (I/cap and d)

 $C_{\text{product}} = \text{Active substance in the product (kg/l)}$

 $F_{4,water}$ = Fraction released to waste water (usually 1 as the release to waste water is estimated to be 100%).

2.10 Laundry disinfectants (van der Poel, 1999)

Emission scenario for calculating the release of disinfectants used for doing biologically contaminated laundry from hospitals

Washing street:

 $Elocal_{3,water} = Nm * Cap * V_{product} * C_{didnif1} * (1-f_{red})$

where

Nm = Number of washing tubes (with disinfectant) (-)

Cap = Capacity of washing tube (kg/d)

V_{product} = Amount of disinfectant for laundry (I/kg)

 $C_{disinf1,2}$ = Concentration of active substance in disinfectant (kg/l)

 f_{red} = Concentration reduction in washing process (-)

Tumbler washing machine:

 $Elocal_{3,water} = Nb * Cap * V_{product} * C_{disinf2} * (1-f_{red})$

where

Nb = Number of batches (/d)

Cap = Capacity of washing tube (kg)

V_{product} = Amount of disinfectant for laundry (I/kg)

 $C_{disinf1,2}$ = Concentration of active substance in disinfectant (kg/l)

 f_{red} = Concentration reduction in washing process (-)

Calculation of predicted environmental concentration for sediment

In the emission models only the concentrations for the water phase are calculated, but the impact of the biocides on the sediment can be as important as the impact on the water compartment.

The predicted environmental concentration of biocides in sediment (PEC_{sed}) [g/kg] can be derived from the corresponding water concentration, assuming a thermodynamical equilibrium (Di Toro et al 1991, cited in Luttik 1996)

$$\begin{split} \mathsf{PEC}_{\mathsf{sed}} &= \frac{\Theta_{\mathsf{w}} + \mathsf{K}_{\mathsf{p}(\mathsf{sed})} * \Theta_{\mathsf{s}} * \mathsf{P}_{\mathsf{solid}}}{\mathsf{P}_{\mathsf{sed}}} * \mathsf{PEC}_{\mathsf{aqua}} \\ \text{where} \\ \Theta_{\mathsf{w}} &= \mathsf{volume} \text{ fraction of pore water of moistened sediment [I/I]} \\ \mathsf{K}_{\mathsf{p}(\mathsf{sed})} &= \mathsf{sediment}\text{-water partition coefficient [I/kg]} \\ \Theta_{\mathsf{s}} &= \mathsf{volume} \text{ fraction of solids of moistened sediment [I/I]} \\ \mathsf{P}_{\mathsf{solid}} &= \mathsf{density} \text{ of dry weight solid phase [kg/I]} \\ \mathsf{P}_{\mathsf{sed}} &= \mathsf{density} \text{ of moistened sediment [kg/I]} \end{split}$$

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3 Veterinary hygiene biocidal products

Introduction (van Dokkum et al., 1998; Montfoort et al., 1996)

Biocidal products of product type 3 are used for veterinary hygiene purpose, including products used in areas in which animals are housed, kept or transported in various objectives such as:

Animal health: to prevent animal diseases

Efficiency: to increase the production

Quality: to improve the quality of animal products

The relevant sub-groups are:

- 3.1 Disinfection of animal housings (stables), (professional use)
- 3.2 Disinfection of hatcheries (professional use)
- 3.3 Disinfection in the means of transport (professional use)
- 3.4 Disinfection for veterinary hygiene on non-farm buildings, like e.g. milk extraction systems (professional use)
- 3.5 Disinfection for veterinary hygiene, like footwear and animals' feet (professional use)
- 3.6 Disinfection in fish-farming (professional use)

Relevant information data for ESDs

Processing

- Inclusion in materials/articles
- Application in processes

Used quantity of active substances

(van Dokkum et al.,1998; Kunz et al.,1986; Whistler et al., 1989; Boehm, 1998; Dwyer, 1995; Samberg, 1995; Montfoort et al., 1996; Voeten et al., 1982; GESAMP, 1997; Trenner et al., 1989)

For each application, more than one disinfectant agent can be used.

3.1 Disinfection of stables (animal housings)

Disinfection in animal houses is always a combination between cleaning and disinfection due to the high amount of organic matter present in animal houses. Disinfection is mainly performed by spraying.

The following agents are widely used (Suggestion for concentrations from Montfoort et al. 1996):

Aldehydes (concentration for pig stables 2g/l, poultry 40g/l)

Chlorine compounds (concentration about 0,2 g/l)

Quaternary ammonium salts (concentration 0,5 - 2 g/l)

Hydroxides (concentration about 10,5 g/l)

Phenolic agents, Lyes

3.2 Disinfection in chicken hatching

The concentration of livestock demands a high standard of hygiene in the production, therefore disinfection is widely used. Necessary disinfection measures have to be integrated in the production process. Spraying of egg-shells, or dipping of egg-shells Active ingredients used:

Formaline (concentration about 1.2 g/m³)

Ozone

Quaternary ammonium compounds

3.3 Disinfection of transport vehicles

Disinfection in this area is performed by spraving and the following agents are commonly used:

Chlorine compounds (concentration about 0,2 g/l) Hydroxides (concentration about 10,5 g/l) Lyes

3.4 Disinfection of milking machines In this are the following substances are applied: Hydroxides (concentration about 0,6 g/l) Chlorine compounds (concentration about 0,2 g/l) Lves

Quaternary ammonium compounds

3.5 Disinfection of footwear and paws In this area disinfection baths are applied. Active ingredients used in this subgroup are: Aldehydes (concentration for feet 2 g/l, for footwear 40 g/l) Chlorine compounds (concentration about 0,2 g/l) Quaternary ammonium salts (concentration 0,5-2 g/l) Hydroxides (concentration about 10.5 g/l) Lves

3.6 Disinfection in aquaculture

The most common agent used for the disinfection of pipelines, containers, shoes, hands etc. are:

Halamite, Polyvinyl alcohols, formalin, formol, chloramine, hypochloride, iodophores, ozone, guaternary ammonium compounds and malachite-green.

Service Life

Waste Treatment (van Dokkum et al., 1998)

Waste streams + relevant information •

3.1 Disinfection of stables

The disinfectant is applied by gassing or spraying, emission to the air and to the manure storage tank occur.

3.2 Disinfection in chicken hatcheries

Disinfection in hatcheries is either performed with sprays or with gases. Gases will be mainly directed to the air, sprays will be mainly directed to waste water.

3.3 Disinfection of transport vehicles

As disinfectants are used as a spray, emission to the air occur. If the disinfectant is collected, it is discharged to the sewer or to a manure reception facility. (Lekkerkerk et al. 1994, cited in Dokkum et al. 1998)

3.4 Disinfection of milking machines

Disinfection of milking machines is performed by the CIP-method (Clean In Place), which means that the disinfectant is added to the circulating water.

The active ingredients used for the disinfection of milking machines will be discharged to the sewer.

As milking-machine disinfectants are commonly supplied as powders in large farms, emission to the air (dust) have to be taken into consideration.

3.5 Disinfection of footwear and paws

Disinfection of footwear and paws is applied in baths, which are discharged to manure reception facilities or poured on farmland.

3.6 Disinfection in aquaculture

Depending on the location of the fish farm, the disinfectants will be either directed to the sewage system or to marine or fresh surface water. For volatile agents, emissions to the air may occur as well.

Emission routes for biocides. '+'=relevant; '-' not relevant

(van Dokkum et al., 1998, modified)

Product type	Applications	Fresh surface water	Marine surface water	Air indoor and outdoor	Soil*	Solid Waste	Waste water
3.1	Disinfection of animal housings, stables (P)	+	-	+	+	-	+
3.2	Disinfection of hatcheries (P)	+	-	+	+	-	+
3.3	Disinfection in the means of transport (P)	+	-	+	-	-	-
3.4	Disinfection for veterinary hygiene on non-farm buildings, like e.g. milk extraction systems (P)	-	-	+	+	-	+
3.5	Disinfection for veterinary hygiene, like e.g. footwear and animals' feet (P)	+	-	+	-	-	+
3.6	Disinfection in fish-farming (P)	+	+	+	+	-	+

P: professional use; N: non-professional use

*disposal on manure

• Recycling/recovery/reuse

Existing and produced emission models (Montfoort et al. 1996)

Due to the large variety of applications which belong to this product type it is not possible to create one single disposal scenario for all the products.

3.1 Disinfection of animal housing facilities

The disinfection of animal housing facilities is widely used in poultry and pig farming. The walls and floors are cleaned and often disinfected once all animals have left the building. The quantity of active ingredient $(Q_{a.i.})$ [g] used for the disinfection of a housing facility is calculated as follows:

 $\begin{array}{ll} Q_{a.i.} = C_{a.i.} * Q_{disinfectant} * A_{housing} \\ where \\ C_{a.i} \\ Q_{disinfectant} \\ A_{housing} \end{array} = \begin{array}{ll} Concentration of active ingredient [g/l] \\ = Quantity of disinfectant used per m^2 [l/m^2] \\ = Area of the housing facility [m^2] \end{array}$

The direct emission to the manure storage tank (Edirect_{manure storage}) [kg] is calculated with the following formula:

Edirect_{manure storage} = $Q_{a.i.} \cdot F_{manure storage} / 1000$ where $Q_{a.i.}$ = Quantity of active compound [g]

F_{manure storage} = Fraction released to the manure storage system [-]

The concentration of the active ingredient in the manure storage tank (Cdirect_{manure storage}) [kg/kg] can be calculated if a dilution factor based on the average quantity of manure in the tank is taken. For this model a realistic estimation of half of this maximum amount of manure in the storage is taken as default, assuming that most storage systems have the capacity to store the manure for about 6 month. If relevant: dilution due to cleaning is assumed to be included in the default amount of slurry/manure storage system.

Cdirect _{manure} storage = Edirect _{manure} storage / Q _{manure}				
where				
Edirect _{manure storage}	= Direct emission to the manure storage tank [kg]			
Q _{manure}	= Quantity of manure [kg]			

The concentration of active ingredient in the sludge (C_{sludge}) [kg/kg] depends on the rate of disintegration (which stands for biogradation inclusive hydrolysis and volatilisation together):

C _{sludge} = Cdirect _{manure storage} * (1-F _{dis})					
APPL _{sludge} = Q _{application manure}					
where					
Cdirect _{manure storage}	= Concentration of active ingredient in the storage tank [kg/kg]				
F _{dis}	= Fraction of disintegration in manure [-]				
Qapplication manure	= Application of manure to land				

The dose $[kg/m^2]$ of active ingredient per square meter of pasture and/or arable land is calculated as follows:

 $DOSE = C_{sludge} * T_{emission} / 365 * APPL_{sludge}$

 $T_{emission} = N_{disinfection events}$

where

C _{sludge}	= Concentration of active ingredient in the sludge [kg/kg]
T _{emission}	= Number of days for the emission [d]
APPL _{sludge}	= Quantity of sludge applied to land [kg/m ²]
N _{disinfection events}	= Number of disinfection events [d]

The direct emission to the air (Edirect_{air}) [kg] is calculated with the following formula: Edirect_{air} = $Q_{a.i.} * F_{air} / 1000$ where $Q_{a.i.}$ = Quantity of active compound [g]

 F_{air} = Fraction released to the air [-]

The average annual air concentration (Cdirect_{air}) $[kg/m^3]$ can be calculated using the following formula:

3.1 Model description, parameters/variables and default for the disinfection of animal housing facilities (Montfoort, 1996)

Parameter/variable (unit)	Symbol	Default	C/R/E/O
Input:			
Concentration of active ingredient (g/l)	C _{a.i.}	40	R/E
Quantity of disinfectant used (I/m ²)	Q _{disinfectant}	0,15	Е
Surface of an average housing (m²) - poultry (broilers) or unknown - pigs (fattening) - pigs (breeding)	A _{housing}	4000 390 210	E
Fraction of the emission to the manure storage - spray or unknown - gas or fog	F _{manure} storage	0,65 0,50	E
Fraction of the emission to air - spray or unknown - gas or fog	F _{air}	0,65 0,50	E
Fraction of disintegration in the manure storage	F _{dis}	0	R/E
Quantity of manure in manure storage (kg) - poultry (broilers) or unknown - pigs (fattening) - pigs (breeding)	Q _{manure}	135000 163000 260000	E
Application of manure to land (kg/m²/year) - manure from poultry (broilers) or unknown - manure from pigs (fattening) - manure from pigs (breeding)	Q _{application} manure	0,85 4,45 5,95	E
Number of disinfection events (d) - poultry (broilers) or unknown - pigs (fattening) - pigs (breeding)	N _{disinfection} events	3 2 2	E
Number of days for the emission (d) - poultry (broilers) or unknown - pigs (fattening) - pigs (breeding)	T _{emission}	5 3 2	E
Standard concentration in air at 100 meter from source for a source strength of 1 kg/s (kg/m ³)	Cstd _{air}	24*10 ⁻⁶	С

Output:

Output necessary for c - Direct emission to air - Concentration of a.i. i - Number of days for th - Quantity of sludge ap	from source (kg) in sludge (kg/kg)	Edirect _{air} C _{sludge} T _{emission} APPL _{sludge}
Annual average conce after direct emission (k		Cdirekt _{air}
Dosage of a.i. per squa and or arable land (kg/		DOSE
Model calculations:		
Q _{a.i.}	= C _{a.i.} * Q _{disinfectant} * A _{housing}	
Edirect _{air}	= Q _{a.i.} * F _{air} / 1000	
Edirect _{manure storage}	= Q _{a.i.} * F _{manure storage} / 1000	
Cdirect _{manure storage}	= Edirect _{manure storage} / Q _{manure}	
C _{sludge}	= Cdirect _{manure storage} * (1-F _{dis})	
APPL _{sludge}	= Q _{application} manure	
T _{emission} (in case of air)	= T _{emission} of input part of this table	
$T_{emission}$ (in case of mar	nure) = N _{disinfection events} of input part of this table	
DOSE	= C_{sludge} * $T_{emission}$ / 365 * APPL _{sludge}	
Cdirect _{air}	= Edirect _{air} * T _{emission} / 365 * Cstd _{air}	

C = Constants

 R = (Required) values from the test results in the notification of a biocide

E = Expert estimations (if possible the expert estimations (defaults) are presented)

O = Output from previous modules/calculations

3.2 Disinfection of hatcheries

Disinfection at the hatcheries can take place four times:

Disinfection of the egg before and during the brooding, disinfection of the chicks (and eggshells) and with the cleaning of the rooms of the hatchery.

The quantity of active ingredient $(Q_{a.i.})$ [g] used for one to four disinfections can be calculated using the following formula:

$$Q_{a.i.} = \sum_{n=1}^{4} (Q_{disinfectant n} * (N_{eggs n} / A_{eggs n}))$$

where

Qdisinfectant= Quantity of disinfectant per cubic metre [g/m³]Neggs n= Total amount of eggs disinfected [eggs/day]Aegg n= Amount of eggs per cubic metre [eggs/m³]first disinfection of the eggs (Aeggs 1)other disinfection (Aeggs 2, Aeggs 3, Aeggs 4)

The direct emissions to wastewater (Edirect_{water}) [kg] and air (Edirect_{air}) [kg] are calculated as follows:

 $Edirect_{water} = Q_{a.i.} * F_{water} / 1000$ where

 $Q_{a.i.}$ = Quantity of active ingredient [g]

F_{water} = Fraction of active ingredient to waste water [-]

 $Edirect_{air} = Q_{a.i.}(g) * F_{air}(-) / 1000$

3.2 Model description, parameters/variables and default for the disinfection of hatcheries (Montfoort, 1996)

Parameter/variable (unit)	Symbol	Default	C/R/E/O
Input:			
Quantity of disinfectant used per cubic meter (g/m ³)	Q _{disinfectant}	6,3	R/E
Total amount of eggs disinfected (eggs/day)	N _{eggs}	37000	Е
Amount of eggs per cubic meter (eggs/m ³)	A _{eggs}		Е
- first disinfection of the eggs (A _{eggs1})			1160
- other disinfections of the eggs (A _{eggs2} , A _{eggs3} , A _{eggs4})			1410
Fraction of a.i. to waste water (-)	F _{water}	0,50	Е
Fraction of a.i. to air (-)	F _{air}	0,25	Е
Number of emission days (days/year)	T _{emission}	260	Е

Output:

Output necessary for calculations in USES:	
 Direct emission to water from source (kg/day) 	Edirect _{water}
- Direct emission to air from source (kg/day)	Edirect _{air}
- Number of days for the emission (day/year)	T _{emission}

Model calculations:

Q _{a.i.}	$= Q_{a.i.} = \sum_{n=1}^{4} (Q_{disinfectant n} * (N_{eggs n} / A_{eggs n}))$
	= C _{a.i.} * Q _{disinfectant} * A _{housing}
Edirect _{water}	= Q _{a.i.} * F _{water} / 1000
Edirect _{air}	= Q _{a.i.} * F _{air} / 1000

T_{emission} (days/year) = 260

C = Constants

R = (Required) values from the test results in the notification of a biocide

E = Expert estimations (if possible the expert estimations (defaults) are presented)

O = Output from previous modules/calculations

3.3 Disinfection of means of transport

This area is relevant for pigs and poultry. Pigs are transported just in vehicles, whereas poultry is transported in special boxes.

In the following model only the disinfection of means of transports in slaughter houses is described. In most cases the surplus of disinfectant is discharged to the sewage treatment plant.

To calculate the quantity of active ingredient $(Q_{a.i.})$ [g] the following formula has to be used: $Q_{a.i.} = C_{a.i.} * Q_{disinfectant} * A_{boxes/transport}$

where

 $C_{a.i.}$ = Concentration of active ingredient [g/l]

 $Q_{disinfectant} = Quantity of disinfection used [l/box or l/m²]$

A_{boxes/transport} = Amount of boxes or square metres transport vehicle [- or m²]

The direct emission to water (Edirect_{water}) [kg] is calculated as follows:

 $Edirect_{water} = Q_{a.i.} * F_{water}/1000)$

where

 $Q_{a.i.}$ = Quantity of active ingredient used [g]

 F_{water} = Fraction of active ingredient to waste water [-]

3.3 Model description, parameters/variables and default for the disinfection of means of transport at the slaughterhouse (Montfoort, 1996)

Parameter/variable (unit)	Symbol	Default	C/R/E/O
Input:	Cymbol	Doradit	0,11,2,0
Concentration of active ingredient (g/l)	C _{a.i.}	10,5	R/E
Quantity of disinfectant used (l/box or l/m ²) - poultry or unknown (l/box) - pigs (l/m ²)	Qdisinfectant	2 0,2	E
Amount of boxes or square meters transport (- or m²) - poultry or unknown - pigs (m²)	$A_{boxes/transport}$	2550 12500	E
Fraction of a.i. to waste water	F _{water}	0,75	Е
Number of the emission days (d)	$T_{emission}$	260	Е
Output:			
Output necessary for calculations in USES: - Number of days for the emission (d) - Direct emission to water (kg/day)	T _{emission} Edirect _{water}		
Model calculations:			
$Q_{a.i.} = C_{a.i.} * Q_{disinfectant} * A_{boxes/transport}$			
$Edirect_{water} = Q_{a.i.} * F_{water} / 1000$			
T _{emission} = 260 (days)			

 $\frac{1}{\text{emission}}$

R = (Required) values from the test results in the notification of a biocide

E = Expert estimations (if possible the expert estimations (defaults) are presented)

O = Output from previous modules/calculations

3.4 Disinfection of milk extraction systems

The disinfection of milk extraction systems is relevant for dairy. In 1996 only about 30 % of the farmhouses in the Netherlands have a connection with the sewer. For this model it is assumed that all the active ingredient available for emission is emitted to the manure store. It is expected that the surplus of disinfectant is inactivated in a relatively short time (Monntfoort, 1996).

For calculating the quantity of active ingredient $(Q_{a.i.})$ [g] the following formula should be used:

$$Q_{a.i.} = C_{a.i.} * V_{inst} + C_{a.i.} * V_{tank}$$

where

 $C_{a.i.}$ = Concentration of active ingredient [g/l]

V_{inst} = Amount of disinfectant used for cleaning of the milk installation [l/day]

V_{tank} = Amount of disinfectant used for cleaning the milk storage tank [l/day]

The emission to the manure storage system (Edirect_{manure storage}) depends on the quantity of a.i. used for disinfection of milk extraction systems ($Q_{a.i.}$) and the fraction released to the manure storage ($F_{manure storage}$):

Edirect_{manure storage} = Q_{a.i.} * F_{manure storage} / 1000

The calculation continues analogous to the model for the disinfection of animal houses, but emission to the air is not relevant in the disinfection of milk extraction systems:

Cdirect_{manure storage} = Edirect_{manure storage} / Q_{manure} where:

 $Q_{manure} = (52kg manure + 14,6 kg waste water/cow/day)^{(175 days stalled)^{40} cows Q_{manure} = 466000 kg/storage period$

The concentration of active ingredient in the sludge (C_{sludge}) [kg/kg] depends on the rate of disintegration (which stands for biogradation inclusive hydrolysis and volatilisation together):

 $\begin{array}{ll} C_{sludge} = Cdirect_{manure\ storage}\ *\ (1-F_{dis})\\ APPL_{sludge} = Q_{application\ manure}\\ where\\ Cdirect_{manure\ storage}\\ F_{dis} = Concentration\ of\ active\ ingredient\ in\ the\ storage\ tank\ [kg/kg]\\ = Fraction\ of\ disintegration\ in\ manure\ [-]\\ Q_{application\ manure}\ cows = Application\ of\ manure\ to\ land\ =\ 9\ kg/m^2/year \end{array}$

The dose can be calculated with the following formula:

 $\begin{array}{l} \text{DOSE} = C_{sludge} * T_{emission} / 365 \star \text{APPL}_{sludge} \\ T_{emission} = N_{disinfection \ events} \\ \text{where} \\ T_{emission} = N_{disinfection \ events} = 150 \ days \\ \text{The number of disinfection \ events} \ depends \ on \ the \ amount \ of \ days \ when \ the \ milk \\ \text{tracellation} \ in \ events \ depends \ on \ the \ amount \ of \ days \ when \ the \ milk \ days \ day$

installation is cleaned (twice a day) and when the milk tank is cleaned (once in 3 days): ((365 * 65 * 2) + ((365 / 3) * 45)) / (130 + 45) = 302 days in one year and for the manure storage period of 6 month result about 150 days.

3.4 Model description, parameters/variables and default for the disinfection of animal housing facilities (Montfoort, 1996)

Parameter/variable (unit)	Symbol	Default	C/R/E/O
Input:			
Concentration of active ingredient (g/l)	C _{a.i.}	0,62	R/E
Amount of disinfectant used for cleaning of the milk installation (I/d)	V _{inst}	130	E
Amount of disinfectant used for cleaning of the milk storage tank (I)	V _{tank}	45	E
Fraction of the emission to the manure storage (-)	F _{manure} storage	0,75	E
Fraction of disintegration in the manure storage (-)	F _{dis}	0	R/E
Quantity of manure in manure storage (kg)	Q _{manure}	466000	Е
Application of manure to land (kg/m²/year)	Q _{application manure}	9	Е
Number of disinfection events (d)	N _{disinfection} events	150	Е

Output:

Output necessary for calculations in USES:

- Concentration of a.i. in sludge (kg/kg)
- Number of days for the emission (d)

- Quantity of sludge applied to land (kg/m²/year)

Dosage of a.i. per square meter of pasture and or arable land (kg/m²)

Model calculations: Q_{a.i.} = C_{a.i.} × V_{inst} + C_{a.i.} × V_{tank} Edirect_{manure storage} = Q_{a.i.} × F_{manure storage} / 1000 Cdirect_{manure storage} = Edirect_{manure storage} / Q_{manure} C_{sludge} = Cdirect_{manure storage} × (1-F_{dis}) C_{sludae}

T_{emission} APPL_{sludge}

DOSE

APPL_{sludge} = Q_{application manure}

 $T_{emission} = N_{disinfection events}$

DOSE = C_{sludge} * T_{emission} / 365 * APPL_{sludge}

C = Constants

R = (Required) values from the test results in the notification of a biocide

E = Expert estimations (if possible the expert estimations (defaults) are presented)

O = Output from previous modules/calculations

3.5 Disinfection of footwear or animals' feet

For the disinfection of the farm workers footwear and animals' feet, basins filled with the biocides are used.

The model calculation is the same as described for the disinfection of animal housing facilities with modification of the formula for calculating the quantity of active ingredients (Q_{a.i.}) [g]:

 $Q_{a.i.} = N_{reservoir} * C_{a.i.} * Q_{disinfectant}$

where

N _{reservoir}	= Number of reservoirs [-]
C _{a.i.}	= Concentration of active ingredient [g/l]
Qdisinfectant	= Quantity of disinfectant in one reservoir [l/reservoir]

3.5 Model description, parameters/variables and default for the disinfection of animal housing facilities (Montfoort, 1996)

Parameter/variable (unit)	Symbol	Default	C/R/E/O
Input:			
Concentration of active ingredient (g/l)	C _{a.i.}	40	R/E
Quantity of disinfectant used (l/reservoir) - footwear disinfection (pigs/poultry) or unknown - animal feet disinfection (cows)	Qdisinfectant	10 1000	E
Number of reservoirs (-) - footwear disinfection (pigs/poultry) or unknown - animal feet disinfection (cows)	N _{reservoirs}	2 1	E
Fraction of the emission to the manure storage - footwear disinfection (pigs/poultry) or unknown - animal feet disinfection (cows)	F _{manure} storage	0,75 0,25	E
Fraction of the emission to air - footwear disinfection (negligible) - animal feet disinfection (worst case) or unknown	F _{air}	0 0,50	E
Fraction of disintegration in the manure storage	F _{dis}	0	R/E
Quantity of manure in manure storage (kg) - pigs (fattening) - pigs (breeding) - poultry (broilers) or unknown - cows	Q _{manure}	163000 260000 135000 466000	E
Application of manure to land (kg/m²/year) - manure from pigs (fattening) - manure from pigs (breeding) - manure from poultry (broilers) - manure from cows	Q _{application} manure	4,45 5,95 0,85 9	E
Number of disinfection events (d) - footwear disinfection (pigs/poultry) or unknown - animal feet disinfection (cows)	N _{disinfection} events	52 6	Е

Number of days for the emission (d) Standard concentration in air at 100 meter from source for a source strength of 1 kg/s (kg/m ³)	T _{emission} Cstd _{air}	12 24*10 ⁻⁶	E C
Output: Output necessary for calculations in USES: - Direct emission to air from source (kg)	Edirect _{air}		
 Concentration of a.i. in sludge (kg/kg) Number of days for the emission (d) Quantity of sludge applied to land (kg/m²/year) 	C _{sludge} T _{emission} APPL _{sludge}		
Annual average concentration in the air after direct emission (kg/m ³)	Cdirekt _{air}		
Dosage of a.i. per square meter of pasture and/or arable land (kg/m ²)	DOSE		

Model calculations:

Q _{a.i.} :	= N _{reservoirs} * C _{a.i.} * Q _{disinfectant}
Edirect _{air}	= Q _{a.i.} * F _{air} / 1000
Edirect _{manure storage}	= Q _{a.i.} + F _{manure storage} / 1000
Cdirect _{manure storage} :	= Edirect _{manure storage} / Q _{manure}
C _{sludge}	= Cdirect _{manure storage} * (1-F _{dis})
APPL _{sludge}	= Q _{application manure}
$T_{emission}$ (d) (in case of ai	ir) = T _{emission} of input part of this table
	ure) = N _{disinfection events} of input part of this table
DOSE	= C _{sludge} * T _{emission} / 365 - APPL _{sludge}
Cdirect _{air}	= Edirect _{air *} T _{emission} / 365 • Cstd _{air}
C = Constants	

R = (Required) values from the test results in the notification of a biocide

E = Expert estimations (if possible the expert estimations (defaults) are presented)

O = Output from previous modules/calculations

3.6 Disinfection in aquaculture

The fish waste water is either discharged on surface water or into the STP. M.H.M.M. Montforts shows the following model description, parameters/variables and defaults for the Netherlands.

The scale of fish cultivation for commercial purposes is limited in the Netherlands. In 1994 in total 26 and 10 companies were involved in cultivating eel and catfish, respectively. Rainbow trout is cultivated on a small scale flow-through and in landbased systems, in which the water body fulfils a role in water treatment. Several trout nurseries use flow-through systems: surface water is lead through the fish basin over a settling tank back into the surface water system. Finely, there are occasional projects in the cultivation of tarbot, tilapia and sturgeon. Most nurseries use recirculation systems, that recycle the water after a water treatment (filtration). Catfish nurseries discharge on the Sewage Treatment Plants (STP), but 40 % of the eel nurseries discharge directly on surface water. The number of companies that discharge the fish water untreated is negligible, as most have some way of water treatment (filters, settlement basins, ponds) before the water is discharged. The recycling systems and the settlement tanks before remo0ve virtually all undissolved

particles. Many nurseries collect the sludge from this treatment and sell or use it as fertiliser.

The following scenarios are based on a fish farm that breeds 50 tonnes eel a year, the median production:

continuous treatment; with recirculation/filtration, followed by settlement tank and STP; continuous treatment; without recirculation/filtration, followed by settlement tank;

occasional treatment (≤4 times a year); without recirculation/filtration before discharge on the settlement tank and STP;

occasional treatment (≤4 times a year); without recirculation/filtration before discharge on the settlement tank.

On a yearly basis an eel farm discharges 200-1900 m³ water per tonne fish, depending on the water use. An average 250m³ per tonne fish is used here, resulting in a turnover rate of 35 m³/d. It is assumed the total water volume of the nursery is 70 m³. After the settlement tank the water fraction is discharged, while the sludge (2 % dry matter) in the tank (and filters) is used as soil fertilisier. The load from the settlement tank and recirculation system will be expressed in terms of kg chemical (biocide) per day, and it is assumed that this load is equally spread over 25 days in case of occasional treatment. The recirculation/filtration system and the settlement tank both have an estimated removal efficiency of 50 % of the dose from the water, but this amount is added to the dosage in the sludge used for spreading on the land.

Due to the settlement tank the total amount emitted is equally spread out over 25 days, which of course will have no effect on the surface water concentration in case of continuous treatment. In case of direct discharge on surface water, the $Elocal_{water}$ is used for calculation.

Parameter/variable (unit)	Symbol	Default	C/R/E/O
Input:			<u>.</u>
Dosage product used	Q _{product}		R
Concentration of active ingredient (mg _o /kg)	C _c		R
Volume of waste water discharged (I)	V _{waste water}		
Volume of waste water continuous treatment (I)	Vwaste water, con.	35000	E
Volume of waste water occasional treatment (I)	Vwaste water, occu.	70000	E
Fraction of retention in sludge (-)	F _{ret}		
Fraction of retention in sludge with filtration (-)	Fret, filtration	0,75	E
Fraction of retention in sludge without filtration	F _{ret}	0,50	E
Emission period for discharge to STP (d)	$T_{emission, STP}$	25	
Number of applications in one year (1/yr)	Napplication, year		
Number of applications continuous treatment (1/yr)	Napplication, con.	365	E
Number of applications occasional treatment (1/yr)	N _{application} , occu.	4	E
Intermediate results			
Amount of substance emitted (mg _c /D)	Q _{emitted}		0
Output:			
Emission to waste water during episode (mg _o /d)	Elocal _{water}		0
Number of emission days (d)	T _{emission}		0
Dilution factor for fish waste water reaching the surface water (I/d)			Ō
Dilution factor for fish waste water reaching the surface water,		5	Е
receiving water continuous treatment (-)			
Dilution factor for fish waste water reaching the surface water,	Dilution _{fish. occu.}	3	E
receiving water continuous treatment (-)	non, coca		
Highest initial concentration in surface water (mg _c /l)	$PIEC_{sw, fish}$		0

Model calculations:

 $\begin{array}{l} Q_{emitted} = Q_{product} * C_c * V_{wastewater} \\ Elocal_{water} = Q_{emitted} * (1\text{-}F_{ret}) \ / \ T_{emission, \ STP} \\ T_{emission} = T_{emission, \ STP} * \ N_{application, \ year} \\ * PIEC_{sw, \ fish} = Elocal_{water} \ / \ Dilution_{fish} \end{array}$

C = Constants

R = (Required) values from the test results in the notification of a biocide

E = Expert estimations (if possible the expert estimations (defaults) are presented)

O = Output from previous modules/calculations

*Model for the calculation of the concentration in surface water after direct discharge from fish settlement tank.

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4 Food and feed area disinfectants

Introduction (van Dokkum et al., 1998)

The purpose of applying biocides in the food and feed industry is to reduce the level of potential food pathogens and to minimize the risks of foodborne diseases. Disinfection is also performed in order to avoid spoilage and deterioration of food and feed and to extend the shelf-life.

Hygiene in this area includes cleaning and disinfection.

Disinfection is applied in working areas (e.g. floors, walls, conveyor lines) as well as on food contact surfaces (e.g. pipelines, mixing and storage tanks). Another field of application for disinfectants is aseptic packaging, if disinfection with hot air or steam is not possible.

The relevant subgroups are:

- 4.1 Disinfection of food contact surfaces, environmental areas in food and feed processing (floors, walls and equipment within plants), (professional use)
- 4.2 In-plant chlorination (professional use)
- 4.3 Disinfection of packaging material (aseptic packaging), (professional use)

Relevant information data for ESDs

Processing

- Inclusion in materials/articles
- Application in processes

Used quantity of active substances

(van Dokkum et al., 1998; Kunz et al., 1986; Wallhäußer et al., 1995; Reuter, 1998)

Hypochlorite, concentrated solutions (up to 12,5 %, av. 5 %), used neat or diluted, generelly used by qualified and trained staff.

<u>4.1 Disinfection of floors, walls and equipment within plants</u>
A large variety of different agents is used:
Chlorine compounds (concentration about 1 %)
Iodine compounds
Quaternary ammonium compounds (concentration about 1 %)
Amphotensids (concentration about 1 %)
Polymeric biguanides
Peracetic acid (concentration 0,5 %)
Carboxylic acid and p-hydoxybenzoicacid esters
Inorganic acids and alkalies
Acids and anionic tensides
Alcohols (concentration 80-100 %)
Alkylamin (concentration 1 %)

Disinfection can be performed by the following methods: Low and high pressure spraying Soaking and brushing Fogging CIP (Clean In Place = disinfectant is added to the circulating water) for tools and machines

<u>4.2 In-plant chlorination</u> Chlorine is added to the water supply of the entire plant.

4.3 Disinfection of packaging material

In order to disinfect packaging materials the items are immersed in a bath, containing the disinfection (usually 15 to 35% Hydrogenperoxide)

Service Life

Waste Treatment (van Dokkum et al., 1998)

• Waste streams + relevant information

4.1 Disinfection of floors, walls and equipment within plants

The exposure to environmental compartments depends on the method of disinfection used. During fogging a significant fraction is directed to the air, but due to the fact that the plant is a closed system and the disinfectant agents are highly reactive, significant emission to the air outdoors is not expected.

When disinfectants are applied by soaking, brushing or the CIP method, the main fraction will be washed to the sewage treatment plant. According to Dokkum et al., 1998 direct emission to surface water can occur as well as emission from sewage treatment plants to surface water, if the products are not eliminated.

4.2 In-plant chlorination

The water together with the added disinfectant (hypochlorous acid) is discharged to the sewage system.

4.3 Disinfection of packaging material

The disinfection is performed by immersing the items in a bath at 50 - 60°C followed by drying with hot air. Therefore the disinfectants will be released to the air. If the bath is changed the main fraction will be directed to the sewer system.

Emission routes for biocides. '+'=relevant; '-' not relevant

(van Dokkum et al., 1998, modified)

Product type	Applications	Fresh surface water	Marine surface water	Air indoor and outdoo r	Soil	Solid Waste	Waste water
4.1	Disinfection of food contact surfaces, environmental areas in food and feed processing (floors, walls and equip-ment within plants), (P)	+	-	+	-	-	+
4.2	In-plant chlorination (P)	-	-	-	-	-	+
4.3	Disinfection of packaging material (aseptic packaging), (P)	-	-	+	-	-	-

P: professional use; N: non-professional use

• Recycling/recovery/reuse

Existing and produced emission models

No emission models were found for product type 4. But emission models were assumed to be similar to those of product type 2 (van der Poel 1999).

4.1 Disinfection of floors, walls and equipment within plants

The emission rate to the sewer system from the food and feed sector can be calculated as follows:

Elocal, water = $Q_{water} * C_{disinf} * F_{water}$ where

Elocal = Emission rate to waste water [kg/d]

Q_{water} = Amount of water with active substance [I/d] C_{disinf} = Concentration at which active substance is used [kg/l]

 F_{water} = Fraction released to waste water

For the emission to the air the following formula can be used: Elocal _{air} = $Q_{disinf} * C_{disinf} * F_{air}$ where Elocal _{air} = Emission rate to air [kg/d]

 Q_{disinf} = Amount of disinfectant with active substance [kg/l]

 C_{disinf} = Concentration at which active substance is used [kg/l]

 F_{air} = Fraction released to the air

References:

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5 Drinking water disinfectants

Introduction

The product type 5 includes the biocidal products for the disinfection of drinking water for humans and animals. It does not cover the disinfection for cooling/process water (Product type 11) or disinfection of swimming pools (Product type 2). Drinking water for human consumption has to be disinfected. According to EU legislation, no harmful microorgansims, like coliform or streptococci bacterias are allowed.

The processes which are used for the disinfection of drinking water are:

- boiling
- filtering
- oxidizing agents
- metal ions
- UV-radiation

The processes boiling, filtering and UV-radiation are non chemical techniques, which are not a part of this study. The disinfection with metal ion is rarely used, because the efficiency is very low. This study focuses on the chemicals and biocidal formulations used for oxidizing disinfection.

The product type 5 has no subgroups and there is only professional use.

Relevant information data for ESDs

Processing

- Inclusion in materials/articles
- Application in processes

The main substances used in biocide formulations, which are used for disinfection of drinking water are:

- chlorine compounds
 - o chlorine, gaseous
 - o hypochlorites
 - o chlordioxide
- iodine compounds
- ozone

Used quantity of active substances

Chlorine, Hypochlorites are used in amounts up to 1,2 mg/l, chlordioxide up to 0,4 mg/l and ozone up to 10 mg/l (TVO).

Service Life

Waste Treatment

• Waste streams + relevant information

Emission routes for biocides. '+'=relevant; '-' not relevant

(van Dokkum et al., 1998, modified)

Product type	Applications	Fresh surface water	Marine surface water	Air indoor and outdoor	Soil	Solid Waste	Waste water
05.	Disinfection of drinking water (all products), (P)	+	+	+	+*	-	+

P: professional use; N: non-professional use *If the disinfected water is used for irrigation.

• Recycling/recovery/reuse

Existing and produced emission models

References:

"Verordnung über Trinkwasser und über Wasser für Lebensmittelbetriebe (Trinkwasserverordnung - TrinkwV) in der Fassung vom 5. Dezember 1990", BGBI. I S. 2612; 1991 p. 227; 1993 p. 278; 1998 p. 699

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Katadyn: "Homepage", URL: www.katadyn.net

Sterling-Berkefeld: "Homepage", URL: www.berkefeld.com

6 In-can preservatives

Introduction

Biocidal products of product type 6 are used for the preservation of manufactured products, other than foodstuffs or feeding stuffs, in cans, tanks or other closed containers by control of microbial deterioration to ensure their shelf life.

In-can preservatives are used to prevent e.g.:

- pH-reduction
- loss of viscosity
- evolution of gas
- coagulation
- foul smell (biological degradation)
- colour changes
- breaking of emulsion
- colonies on surface

There is a potential overlap with product type PT 7 (film preservatives) and PT 9 (fibre, leather, rubber and polymerised materials preservation) for products stored in cans and applied in films, such as paints, coatings and glues. Another area of overlap can be the lubricants (product type PT 13).

The relevant sub-groups are:

- 6.1 Washing and cleaning fluids (professional use), human hygienic products and cosmetics (see PT 2), (professional and non-professional use)
- 6.2 Detergents (professional and non-professional use)
- 6.3 Paints and coatings (see PT 7 film preservatives), (professional and non-professional use)
- 6.4 Fluids used in paper-, textile and leather production (see PT 7 film preservatives and PT 9 fibre, leather, rubber and polymerised materials preservation), (professional use)
- 6.5 Lubricants (see PT 13 metal working fluid), (professional use)

In-can preservatives are e.g.:

etheric oils (for example thyme oil, rose oil) alcoholes (for example benzyl alkohol, bronopol) carbonacidesters, -amides (for example 4-hydroxybenzoeacidester, chloracetamide) carbamidacid derivates (for example 3-iod-2-propinyl-buthylcarbamate) dibromdicyanobutane formaldehyde slow-release formaldehydes (for example n-formale, o-formale) isothiazol derivates (for example methylisothiazolinone) mercaptobenzthiazoles organic acid phenol derivates (for example 3-methyl-4-chlor-phenole) quaternary ammonium salts (for example benzalkoniumchloride) 6.1 Washing and cleaning fluids, human hygienic products and cosmetics (see product type 2)

6.2 Detergents

Phosphates, like for example Diethylentriaminpenta-methylenphonacids (DTPMP) are used to stabilize alkalic hydrogeneperoxide solutions. In acidic detergents, citric-, glycolicand lactic acids are used.

In detergents, polycarboxylates, alcoholethoxylates, soda and as a relatively new development, mono- and triisopropylammonium-ethersulfates are used.

6.3 Paints and coatings

Water based or latex paints are typically more prone to contamination and need an antimicrobial or biocide to act as an in-can preservative. In-can microbial growth or degradation most frequently occurs from contaminants, bacteria and yeasts in the raw materials. The same organic paint components act as the microbial food source, causing possible discoloration, gas generation, foul odours, coagulation, rheology changes and can corrosion. A broad spectrum of aktive substance is used to kill a wide variety of bacteria and yeasts that could cause problems either in paint production or in the can during storage.

Typical and the most important in-can preservative chemicals include: isothiazolones, and formaldehyde donors. These preservatives (e.g. 5-Chlor-2-methyl-2,3-dihydroisothiazol-3-on and 2-Methyl-2,3-dihydroisothiazol-3-on (MCI/MI)) are bactericides and their killing action must be quick. Typical in-can preservative dosages are 0,003 % for MIT (2-Methyl-2H-isothiazol-3-on) and also for CIT (5-Chlor-2-methyl-2HH-isothiazol-3-on), (Data from the company THOR, Germany).

Currently there is an upper limit for free formaldehydes in formaldehyde depots of 10 mg/kg in Germany. Due to international pressure (EPA, UBA) a further decrease in the use of these substance groups among the biocides is expected.

Examples of in-can paint preservatives and their recommended use level [%] (Rossmoore, 1995):

4,4-Dimethyloxazolidine (74,7 % ai)	0,05 - 0,3
1,2-Dibromo-2,4-dicyanobutane (25 % ai)	0,10 – 0,3
2[(Hydroxymethyl)-amino]ethanol (100 % ai)	0,10 – 0,3
1-(3-Chlorallyl)-3,5,7-triaza-1-azoniaadamantane chloride (69 % ai)	0,01 – 0,27
1,2-Benzisothiazolin-3-one (19 % ai)	0,04 – 0,125
5-Chloro-2-methyl-4-isothiazolin-3-one (1,15 % ai)	0,05 – 0,167
Hexahydro-1,3,5-triethyl-s-triazine	0,01 – 0,1
2-Hydroxymethyl-2-nitro-1,3-propanediol (50 % ai)	0,02 - 0,3

Application of Zinc Pyrithione Fungicide - Algaecide see PT 7 Film Preservatives. Such Zinc Pyrithiones are used for:

- Dry film and in-can preservative for water-based latexes, emulsions, pigment slurries, paints, caulks, adhesives, sealants, grouts, and patching compounds.
- Dry film preservative for in dry wall and other gypsum, pearlite, plaster-like or mineral-based building materials
- Dry film preservative for SBR and thermoplastic resins intended for use in various applications such as carpet backing and fibre, bath and sink mats, cushion and

mattress foam, tarpaulins and awnings, wire and cable insulation, gaskets and weather stripping materials (see film preservation).

• Dry film preservative for marine antifouling paints (see film preservation)

6.4 Fluids used in paper-, textile and leather production (see PT 7 film preservatives and PT 9 fibre, leather, rubber and polymerised materials preservation)

- 6.5 Lubricants (see PT 13 metal working fluid)
- 6.6 Machine oils

Relevant information data for ESDs

Processing

- Inclusion in materials/articles
- Application in processes

Used quantity of active substances

Preservatives in painting products:

The mount of active biocidal substances in painting products reached about 220 tonnes in 1991 (National Institute of Public Health and Environmental Protection Bilthoven, The Netherlands).

For the quantities of 'Coatings and adhesives' the default values have been generated for the region 'The Netherlands'. For waterborne paints the default value has been set at 210 ktons.yr-1 (VVVF, 1996; 1997), for adhesives with water as a solvent at 25 ktons.yr-1 and for dispersion adhesives at 60 ktons .yr-1 (Selderijk, 1993).

6.1 Washing and cleaning fluids, human hygienic products and cosmetics:

0,1 - 0,5 % by weight in medicine, ointments 0,02 - 0,5 % in creams, shampoos, lotions, hair conditioner (Board et al. 1987; Balk et al, 1999)

6.3 Paints and coatings:

0,5 % by weight of total formulation (1 % by weight in some climates with ideal growth for mildew) 0,05 - 0,2 % by weight typical level of biocides in paints (in can) (Balk et al. 1999)

Service Life

Waste Treatment

• Waste streams + relevant information

Emission routes for biocides '+' relevant; '-' not relevant

(van Dokkum et al., 1998, modified)

Product type	Applications	Fresh surface water	Marine surface water	Air indoor and outdoo r	Soil	Solid Waste	Waste water
6.1	Washing and cleaning fluids (P+N)	-	-	-	-	+	+
6.2	Detergents (P+N)	-	-	-	-	+	+
6.3	Paints and coatings (P+N)	See 21	See 21	+	+	+	+
6.4	Fluids used in paper-, textile and leather production (P)	See 9	-	+	-	See 9	See 9
6.5	Lubricants (P)	-	-	See 13	-	See 13	See 13

P: professional use; N: non-professional use

• Recycling/recovery/reuse

Existing and produced emission models

Default settings for the input parameters of the model for in-can preservatives at **landfilling and incineration** (van der Poel, 1999), region = Netherlands:

Waterborne coatings

F subst-prod	Fraction of preservative in product (by weight) before	applicatio	n: 0,003*
Q reg-prod	Quantity of waterborne coatings in the region [kt/a]:		210
F prod-pres	Fraction of product with a preservative added:		0,8
F penetr	Penetration factor:		0,25
F _{diff}	Fraction lost due to diffuse release:	0,25	
F _{degr}	Fraction lost due to preservative degradation		0,3*
F landfill	Fraction of product waste landfilled:	0,75	
F _{inciner}	Fraction of product waste incinerated:		0,25
Q reg waste	Quantity of total waste in the region [kt/a]:	11880	
F twi	Fraction of total waste landfilled:		0,6

Adhesives with water as a solvent

F subst-prod	Fraction of preservative in product (by weight) bef	ore applicatio	n: 0,003
Q reg-prod	Quantity of adhesives with water as a solvent in th	ne region [kt/a]:25
F prod-pres	Fraction of product with a preservative added:		0,8
F penetr	Penetration factor:		0,25
F _{diff}	Fraction lost due to diffuse release:	0,15	
F _{degr}	Fraction lost due to preservative degradation		0,3*
F landfill	Fraction of product waste landfilled:	0,26	
F inciner	Fraction of product waste incinerated:		0,09
Q reg waste	Quantity of total waste in the region [kt/a]:	11880	
F twi	Fraction of total waste landfilled:		0,6

Dispersion adhesives

F _{subst-prod}	Fraction of preservative in product (by weight) before	applicatio	n [.] 0 003
Q reg-prod	Quantity of dispersion adhesives in the region [kt/a]:	applicatio	60
F prod-pres	Fraction of product with a preservative added:		0,8
F penetr	Penetration factor:		0,25
Fdiff	Fraction lost due to diffuse release:	0,4	
F _{degr}	Fraction lost due to preservative degradation		0,3*
F _{landfill}	Fraction of product waste landfilled:	0,54	
F inciner	Fraction of product waste incinerated:		0,46
Q reg waste	Quantity of total waste in the region [kt/a]:	11880	
F twl	Fraction of total waste landfilled:		0,6
	ompany THOR, Germany		

Calculations:

1. Quantity of biocides (preservatives) in products in total waste [kg/a]:

Q reg subst tw = Q reg-prod * 10^6 * F subst-prod * F prod-pres * F penetr * (1 - F diff - F degr)

2. Concentration of biocides in waste landfill [kg/a]:

C subst-lw = (Q reg subst tw * F landfill) / (Q reg waste * F twl) for any product containing biocides

3. Concentration of biocides in waste incineration [kg/a]:

C subst-iw = (Q reg subst tw * F inciner) / (Q reg waste * (1 - F twl) for any product containing biocides

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7 Film preservatives

Introduction

In many cases the same substance is the active substance in-can as well as in the film. That indicates, that there is a strong correlation to the product type 6 (in-can preservatives).

The relevant sub-groups for film preservatives are in

- 7.1 Paints and coatings (see PT 6 in can preservatives), (professional and non-professional use)
- 7.2 Plastics (see PT 9 fibre, leather, rubber and polymerised materials preservation), (professional use)
- 7.3 Glues and adhesives (professional and non-professional use)
- 7.4 Fluids used in paper-, textile and leather production (see PT 6 in can preservatives and PT 9 fibre, leather, rubber and polymerised materials preservation), (professional use)

The main film preservatives (**zinc pyrithione and iodopropynyl butyl carbamate (IPBC)**) are used in all sub-groups indicated above.

Dry film preservatives that protect the surface coating from mold, mildew and algae growth are typically fungicides. (See conditions that influence the growth of mildew and algae on dry emulsion paint films). The dominant fungal species can vary with environment, climate, and condition of the paint film. Aureobasidium Pullulans is the most predominant fungi in U.S. exterior coatings. Optimum fungal growth conditions include a humid environment, a neutral to acidic environment with an organic food source.

Typical fungicides used in the paint industry for dry film preservation include: chlorothalonil, iodo propynylbutyl carbamate (IPBC), octyl isothiazalone, zinc pyrithione, heterocyclic N.S-compounds and N-haloalkylthio-compounds. Mold and mildew control is typically the focus of paint formulation preservative programs, though algae growth can be a significant problem as well. Algae is sometimes confused with fungi, especially if the algae is black, brown or orange instead of the more common green.

Algal growth requires high humidity, a neutral to alkaline environment, and light, to allow for photosynthetic processes. To facilitate growth, algae also need minerals, which they can find on masonry surfaces. But most fungicides used as dry film preservatives are not good algaecides. Dry film algae protection is a growing trend in the paint industry. One dry film fungicide particularly suited to both fungal and algae protection is **zinc pyrithione**.

Zinc pyrithione though still relatively new to the industry, has been well-received by the industry as both a fungicide and algaecide. During the last 10 years, the industry has not had many choices of new dry-film preservatives. However, zinc pyrithione actually is not a new fungicide -- it has been used for more than 30 years as the fungicide in anti-dandruff shampoos and similar personal care products.

Zinc pyrithione is also known as zinc 2-pyridinethiol-n-oxide. It has a water solubility of 8 ppm at neutral pH. This low solubility makes the zinc pyrithione suitable for use in outdoor products that require protection against micro organisms, because it will not easily leach out of a paint film.

UV degradation of zinc pyrithione in a paint film is gradual, and therefore, efficacy in direct sunlight can be expected for years. Its stability at high temperatures is also very good -- zinc pyrithione can withstand temperatures of 100°C for at least 120 hours, with a decomposition temperature of 240°C. Another concern for fungicides in latex paints is alkaline stability.

Because pyrithione is an excellent chelating agent, zinc pyrithione cannot be used in paints that rely on metal carboxalates for film cure. The metal, particularly cobalt will transchelate with the zinc and lose the ability to catalyze the film curing. Also, in latex paints, if the water supply contains high concentrations of soluble iron, a sequestering agent should be used to preferentially chelate with the iron.

Since zinc pyrithione shows little tendency to yellow in paint films and does not cause acceleration of chalking or fading, the same fungicide can be used for both whites and colours. This reduces inventory and helps formulators avoid the inadvertent addition of the wrong fungicide to a batch of paint.

Zinc pyrithione is also used extensively in adhesive coatings for floorings and for fungal protection of carpet backing, for applications such as dry-film preservation of architectural and industrial paints and coatings, as well as adhesives, sealants and grouts.

lodopropynyl butyl carbamate (IPBC) is a industrial fungicide used in architectural coatings and construction applications (i.e. paints, stains, adhesives, caulks, and sealants), textiles, as well as plastic product applications to prevent dry film fungal growth.

Relevant information data for ESDs

Processing

- Inclusion in materials/articles
- Application in processes

The use of **zinc pyrithione** in a latex paint normally will be in the range of 0.1% to 0.5% of active material on wet paint weight. This range will generally cover the needs of various paints for controlling mildew used in different geographic regions. Zinc pyrithione is exceptional as an algaecide and particularly well suited for use over masonry surfaces. Because of their alkaline nature, masonry and cementitious surfaces usually do not support mildew growth very well. Some fungicides, such as iodopropynyl butyl carbamate will hydrolyze at a pH of 9 and above.

As a consequence, they might badly yellow a white paint. Fresh concrete and Portland cement stucco can have a pH approaching 12. Algae also need trace amounts of minerals to survive, and masonry surfaces provide these minerals. Some tropical countries have recognized the significance of the problem of algal growth on buildings. Singapore has taken the lead in developing test methods to evaluate a coating's ability to fight algae, as well as requiring that standards be met for all governmental buildings. The Singapore Institute for Science and Industrial Research issued a standard (1990 appendix B) that predicts that paint that passes its requirements will remain free of algae for six years. Zinc pyrithione has passed this type of test with a level as low as 0.075 % active on wet paint weight.

Algae will grow almost anywhere where sufficient nutrients and moisture exist. Zinc pyrithione offers the coatings industry a product that is effective against both fungus and algae, without the negative side effects produced by the other commonly used dry-film preservatives.

Such Zinc Pyrithione are used for:

- Dry film and in-can preservative for water-based latexes, emulsions, pigment slurries, paints, caulks, adhesives, sealants, grouts, and patching compounds.
- Dry film preservative for in dry wall and other gypsum, pearlite, plaster-like or mineral-based building materials
- Dry film preservative for SBR and thermoplastic resins intended for use in various applications such as carpet backing and fibre, bath and sink mats, cushion and mattress foam, tarpaulins and awnings, wire and cable insulation, gaskets and weather stripping materials.

• Dry film preservative for marine antifouling paints

In coating applications, 0.3 - 0.5 % of **lodopropynyl butyl carbamate (IPBC)** (active material) in relation to the weight of the total formulation will protect against mildew growth. Where climates are ideal for mildew growth, up to 1.0 % of the active component should be used. White paint formulations should be thoroughly evaluated for yellowing of the dry film, especially those containing resins based on styrenated polymers. Irreversible yellowing of the dry film may occur soon after application. In stains where protection against mold and staining fungi is required, 0.3 - 0.4 % of the active material is recommended.

Examples of paint film preservatives and their recommended use level [%] (Rossmoore, 1995):

3-lodo-2-propynyl butyl carbamat (100 % ai)	0,1 – 0,5
2-n-Octyl-4-isothiazolin-3-one (45 % ai)	0,1 – 0,3
Diiodomethyl-p-tolylsulphone (95 % ai)	0,2-0,7
N-(Trimethylthio) phthalimide (88 % ai)	1 – 3

Used quantity of active substances

Max. 0,5 % by weight of total formulation (Arch Chemicals, 2000) (1 % by weight in some climates with ideal growth for mildew)
0,25 - 2 % by weight level in dry film of paint products (Balk et al, 1999)
0,02 - 0,5 % by weight level in adhesive or sealant (Haskoning, 1995)

Service Life

Waste Treatment

• Waste streams + relevant information

Existing and produced emission models

Emission routes for biocides. '+'=relevant; '-' not relevant (van Dokkum et al., 1998, modified)

Product type	Products	Fresh surface water	Marine surface water	Air indoor and outdoo r	Soil	Solid Waste	Waste water
7.1	Paints and coatings (P+N)	See 21	See 21	+	+	+	+
7.2	Plastics (P)	See 9	-	+	-	See 9	See 9
7.3	Glues and adhesives (P+N)	-	-	+	-	+	-
7.4	Fluids used in paper-, textile and leather production (P)	See 9	-	+	-	See 9	See 9

P: professional use; N: non-professional use

Recycling/recovery/reuse

Default settings for the input parameters of the model for film preservatives at **landfilling and incineration** (van der Poel, 1999), region = Netherlands:

Paints and coatings

F _{subst-prod}	Fraction of preservative in product (by weight) before ap	plicatior	n:0,02
Q reg-prod	Quantity of waterborne coatings in the region [kt/a]:		310
F prod-pres	Fraction of product with a preservative added:		0,6
F penetr	Penetration factor:		0,25
F _{diff}	Fraction lost due to diffuse release:	0,25	
F _{degr}	Fraction lost due to preservative degradation		0
F landfill	Fraction of product waste landfilled:	0,75	
F _{inciner}	Fraction of product waste incinerated:		0,25
Q reg waste	Quantity of total waste in the region [kt/a]:	11880)
F twl	Fraction of total waste landfilled:		0,6

Adhesives with water as a solvent

F _{subst-prod}	Fraction of preservative in product (by weight) before ap	plication	n: 0,003
Q reg-prod	Quantity of adhesives with water as a solvent in the region	on [kt/a]	:25
F prod-pres	Fraction of product with a preservative added:		0,6
F penetr	Penetration factor:		0,25
F _{diff}	Fraction lost due to diffuse release:	0,15	
F _{degr}	Fraction lost due to preservative degradation		0
F landfill	Fraction of product waste landfilled:	0,26	
F inciner	Fraction of product waste incinerated:		0,09
Q reg waste	Quantity of total waste in the region [kt/a]:	11880	
F twl	Fraction of total waste landfilled:		0,6

Dispersion adhesives

F _{subst-prod}	Fraction of preservative in product (by weight) before ap	plication	n: 0,003
Q reg-prod	Quantity of dispersion adhesives in the region [kt/a]:		60
F prod-pres	Fraction of product with a preservative added:		0,6
F penetr	Penetration factor:		0,25
F _{diff}	Fraction lost due to diffuse release:	0,4	
F _{degr}	Fraction lost due to preservative degradation		0
F landfill	Fraction of product waste landfilled:	0,54	
F inciner	Fraction of product waste incinerated:		0,46
Q reg waste	Quantity of total waste in the region [kt/a]:	11880	
F twl	Fraction of total waste landfilled:		0,6

Calculations:

1. Quantity of biocides (preservatives) in products in total waste [kg/a]: Q reg subst tw = Q reg-prod * 10⁶ * F subst-prod * F prod-pres * F penetr *(1 - F diff - F degr)

2. Concentration of biocides in waste landfill [kg/a]:

 $C_{subst-lw} = (Q_{reg subst tw} * F_{landfill}) / (Q_{reg waste} * F_{twl})$ for any product containing biocides

3. Concentration of biocides in waste incineration [kg/a]: C subst-iw = (Q reg subst tw * F inciner) / (Q reg waste * (1 - F twl) for any product containing biocides

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8 Wood preservatives

The following information are added to this paper from OECD-publication based on the OECD Workshop on Environmental Exposure Assessment to Wood Preservation, Belgirate, Italy, $10^{th} - 12^{th}$ April 2000 (B. Wagner, Umweltbundesamt/UBA, document wag18017.doc). All presented scenarios were discussed and modified at the workshop. For the results see the official OECD-report which has not been published jet. It is planed to gather an OECD-expert group to elaborate OECD-wide emission scenarios for wood preservatives.

II.2 Production and Application [van Dokkum et al. 1998]

Wood is used in a variety of applications, from house fronts to bank revetments. Depending op the type of wood and the type of application (e.g. under water, in houses), it can be affected by insects or moulds. To prevent this, biocides can be used. Biocides can be used either to prevent affection by insects and/or moulds (*preventive use*, on healthy wood) or to combat insects and/or moulds (*curative use*, on affected wood). Both preservatives and curatives are part of product type 8 [EU 1998]. An overview of the applications for preserved wood is presented in Table 3.

Table 3 Applications for preserved wood

Application type	Examples
Indoors	various, roof trusses
Outdoors, no direct contact with soil or	house fronts (claddings)
surface water	roof tiles window frames
	playing tools
	garden houses
	fences
Outdoors, in permanent contact with	landings, wharfs
soil or surface water	bridges
	bank revetment
	sound-proof barriers
	railway sleepers
	telephone poles
	fence poles
	car pools
	wood in gardens

formulations (Boonstra *et al.*, 1991). Coal tar derivatives (creosote oils) and fixating metal salts are the most important from a quantitative point of view. In Table 6 and Table 7, the production volume of biocide products in Germany is summarised.

Table 4 Overview of the preservation and curation of wood with biocides.

Туре	Scale	Preservation process
Preventive	Industrial	Anti-sapstain spraying
		Vacuum pressure
		Pressure
		Immersion (Dipping)
	Sawmills, Joinery	Immersion (Dipping)
		Spraying tunnel
	Manufacturers	Brushing
		Spraying tunnel
		Pills
	Do-it-yourself	Brushing
		Spraying
		Pills
	Professional	Injection in soil
Curative	Professional	Fumigation
	Do-it-yourself	Brushing
		Spraying
		Pills
		Injection

The application of biocides is executed on various scales and with various techniques. An overview is given in Table 4. The individual techniques are described below.

Biocides currently in use include biocides that are available on the market, and biocides that have been available in the (recent) past, because of the long time during which preserved wood is used (up to 50 years). Biocides can be divided into categories based on chemical structure, solvent, conservation process or application range. In Table 5, an overview of biocides is given. Waterborne biocides can be divided in fixating and non-fixating, based on the interactions with the wood. Fixating waterborne biocides are chemically bound to the wood (chemical reaction). An overview of reactions of CCA (copper, chromium, arsenic) salts with wood is presented in Berbee (1989). Non-fixating waterborne biocides have a strong diffusive capacity; wood impregnated with this type of biocides has to be equipped with a paint or lacquer layer, to prevent intensive leaching (Beentjes & Visée, 1994). Oil-borne biocides and coal-tar derivatives do not react with the wood, but are bound by hydrophobic interactions. Emulsions are a relatively new type of biocide

Table 5Biocides used for wood conservation, categorised on solvent type (Boonstra et al., 1991;Beentjes & Visée, 1994)

Туре	Biocides
Waterborne products, fixating	salts, based on chromium, copper, arsenic, borium, fluor and zinc (CCA, CC, CCB, FCB, CCFZ), copper-quat (CQ), copper conazole-boric acid, azaconazole, quat, propiconazole, CuHDO
Waterborne products, non- fixating	bifluorides, boric acid, borium salts
Oil borne products	TBTO, TBTF, PCP, azaconazole, propiconazole, tolylfluanide, dichlofluanide, zincnaphthenate, coppernaphthenate, permethrin, deltamethrin
Coal-tar derivatives	creosote oils, carbolineum
Emulsions	azaconazole, ethylhexanoate, isothiazoline, copperquinolinolate, thiocyanate, quats
Gasses	Methylbromide, phosphine

Table 6 Use of wood conservation biocides in Germany (Brückner & Willeitner, 1992).

	Amount (tons)	Professional use (%)	Do-it-yourself (%)
Salts	11.150	90	10
Other	19.850	55	45
Coal tar derivatives	17.000	60	40 ¹

¹ Now reduced due to chemical legislation

Table 7 Use of wood conservation biocides in Germany, differentiated to purpose (Brückner & Willeitner, 1992).

	Salts (tons)	Coal tar (tons)	Other (tons)
Construction	3.200-5.000	-	5.100-7.600
Outdoors use	3.200-4.300	15.000	3.100-4.300
Others	600-700	-	800-1.100

Another classification of biocide products is based on the conservation technique (Table 8). The use of several biocide substances in wood conservation products is limited because of their strong environmental and health impacts.

Most biocide substances are either insecticides or fungicides, and therefore biocide products usually contain mixtures of substances. Boric acid and arsenic are applicable as both insecticide and fungicide; almost all other substances are specific. Pyrethroids (replacements of lindane) are typical insecticides. Quats and triazoles are typical fungicides. The broad scope of working of creosote is a result of the composition (many different PAH, each with a more or less specific effect).

Table 8Biocides used for wood conservation, categorised in conservation methods (Beentjes &Visée, 1994; Esser & Boonstra, pers. comm.)

Conservation method	Biocides
vacuum/pressure	salts, based on chromium, copper, arsenic, borium, fluor and zinc (CCA, CC, CCB, FCB, CCFZ), copper-quat, quat, creosote, ammonia, CuHDO
dipping	fluor-chromium-borium, bifluorides, quat, CuHDO
spraying, injection (curative: insects)	deltamethrin, permethrin, PCP, lindane, dichlofluanid, tolylfluanid
Spraying, injection, pills (curative: wood moulds)	boric acid, bifluoride, quats, azaconazole

In the past, a number of biocides have been prohibited as wood preservatives. Examples are lindane, PCP, Hg-compounds, and As-compounds (except for CCA salts for vacuum-pressure impregnation).

Because of the low degradability and broad scope of effectiveness of many wood preservation biocides, causing environmental hazard, research is performed to develop alternatives for the currently used biocides. This research is aimed at alternatives for preserved wood (e.g. hard woods), alternative preservation methods (e.g. PLATO-process), alternative formulation methods and improved preservation processes.

II.3 Preventive and Curative Treatment [Garrod 1999]

In order to counter organisms that challenge and destroy it, wood is treated with preservative at either or both of two distinct stages in its "life cycle":

- preventive treatment to stop the occurrence of biological degradation by fungi, bacteria and wood-boring insects (including termites and marine borers); and
- curative treatment (remedial) to remedy infestations once they have occurred.

-

The active substance chosen as the preservative agent needs to be effective against the challenge for a suitable period of time, and also without unacceptable risk to humans or to the environment through emissions to the environment or through contact with non-target organisms.

<u>Preventive treatments</u> are applied to wood before first use. The type of treatment and the active substances applied are made according to the anticipated use of the wood, and the nature of the potential challenge. Protection against degradation in some environments can be controlled through simple surface treatments such as spraying, painting or dipping. Other situations require that the preservative penetrates wood more deeply, so vapour, vacuum or pressure impregnation is appropriate. Good practice means that in most cases, the wood for preservation has been shaped as a "wood product" for later assembly. Sometimes, a period is stipulated for "fixing" the preservative in treated wood.

Subsequent working of treated wood is generally low, being limited to sawing, planing or sanding at the site where it is to be assembled or installed. Factory and construction workers, gardeners and consumers are likely to handle treated wood. Some of the treated wood will be in inaccessible places, some will have decorative finishes applied and some will be accessible and remain undecorated.

<u>Curative treatments (remedial)</u> are applied to wood in-situ. This can involve work in removing decorative coatings, flooring or ceilings to determine the extent of the damage and to apply the remedial treatment where it is needed, as sprays or painted penetrating products. Smokes or furnigant gases without extensive site preparation can treat some insect infestations. Special care must be taken for the protection of bats in attics of churches and ancient buildings, because they are by law-protected animals.

II.4 Fixation [van Dokkum et al. 1998]

After impregnation, the preservative has to be bound firmly to the wood. Metal salts are bound to the wood structure by a chemical reaction. Higher temperature and higher humidity increase the speed of the reaction. A method to increase the speed of the fixation process is to treat the impregnated wood with low-pressure steam (105 °C). Steam treatment is also used after impregnation with creosote, although creosote is bound to the wood structure by lipophilic interactions between wood components and creosote, and not with chemical reactions. Steam treatment of creosoted wood takes place to remove low molecular PAH, to reduce leaching during use.

The amount of biocide released during fixation can be large. Berbee (1989) reports an experiment to determine the loss of metals due to steam fixation. Concentrations of metals in condensate, formed during steam condensation, were compared to initial wood concentrations. The results are presented in Table 9. Losses up to 9 % (w/w) occur. The emissions depend on the treatment of the

steam (condenser) and condensate. When measures are taken, actual emissions can be minimal. Depending on the configuration of the installation, emissions can occur to air (outdoors), surface water, soil, or an STP.

Table 9 Losses (% w/w) of metals during steam fixation (after Berbee, 1989)

	Spruce	Scotch pine
Copper	4.0	1.0
Chromium	9.1	4.2
Arsenic	2.1	2.8

Another technique to fixate the preservative is 'diffusion'. The impregnated wood is covered or sealed in plastic foil, and stored, to facilitate diffusion in the wood.

Providing that climatic conditions allow it, "Natural" fixation by storing the impregnated wood for 4 to 12 weeks (average: 6-8) gives the best fixation results, in terms of reduction of leaching during use (Esser & Boonstra, pers. comm.).

II.5 Storage [van Dokkum et al. 1998]

Emissions in this period are the result of leaching of biocides from the wood. Impregnated wood is stored on open terrain and rainfall causes leaching and transportation of PAH or metals from impregnated wood. On terrain with a paved bottom surface, the water can be collected and treated but on terrain without special bottom protection the water carrying the biocides can penetrate the soil, causing soil contamination and subsequent risks for ground- and surface water.

The TNO Centre for Wood Technology has executed experiments to estimate the amount of preservatives that leaches out of stored wood ("Practise test"; a realistic simulation of the actual storage conditions). Emission factors are included in Table 10 (metals) and Table 11 (PAH).

Table 10 Emission factors (in % of the amount of substance originally present in the wood) for storage (6 weeks) ("Practise test", Boonstra et al., 1991)

Experiment	Copper	Chromium	Arsenic
Scotch pine, Celcure (CC)	1.1	1.3	-
Spruce, Super Wolman salt CO (CCA-type C)	0.41	2.0	0.025

Table 11 Emission factors (in % of the amount of substance originally present in the wood) for storage (10 weeks) ("Practise test", Boonstra et al., 1991).

Experiment	PAH (sum 21 PAH's)
Scotch pine, WEI B1 creosote	0.00012
Spruce, WEI B1 creosote	0.0062

Based on the results of this research and other TNO research, CUWVO (1992) has made an indicative calculation to estimate the total amount of preservatives that leaches out of the storage area of a "standard" impregnation plant (Table 12). The advanced impregnation assumes improved processing techniques and impregnation fluids (modified creosote) and treatment of the impregnated wood (fixation).

Table 12 Results of an indicative calculation of the yearly emissions of impregnation compounds due to leaching during the storage of impregnated wood (CUWVO, 1992).

	Creosote impregnation plant	Metal salt impregnation plant
Production (m ³ wood /a)	20000	3000
Storage area (m ²)	4000	350
Discharge rainwater (m ³ / a)	1200-2000	105-175
Calculated leaching loss (kg/a)		
Conventional impregnation		
PAH	90	
Copper		0.4
Chromium		1.8
Arsenic		0.03
Advanced impregnation		
PAH	0.2	
Copper		0.04
Chromium		0.18
Arsenic		0.003

II.6 Environmental Exposure

Many different processes for impregnation are in use. To assess which emissions and subsequent environmental exposure occurs a detailed description of these processes is provided in *Work Document 2 [A. Garrod, Chapter 2]*. For environmental assessment these processes need to be examined in terms of environmental pathways that lead to emissions and primary environmental compartments into which such emissions are released. For that purpose so-called *Emission*

Scenarios are developed that allow to quantify the emissions in the respective process to air water and soil. According to an agreement in the OECD Organising Committee spills and waste disposal that needs to be authorised are not considered in these scenarios.

These processes and emissions to environmental compartments are presented in the following table for the different impregnation processes. The selection of emission scenarios was made upon importance of the process.

Table 13 Wood preservative applications, environmental compartments that mayreceive emissions, and proposals for Emission Scenario Documents (ESDs)

Application	work doc. 1	ESD No	Environmental compartment exposed			əd		
			soil	ground water	waste water	surfac e water	air	estuary
Preventive application								
sawmill (anti-sapstain) - automated dipping - automated spraying	2.13 2.14	1	Х		Х	Х	Х	
vacuum-pressure processes pressure impregnation	2.15 2.16	2	Х		Х	Х	Х	
thermal impregnation	2.17	no						
vapour process	2.18	no						
double-vacuum process	2.19	no						
deluge/flood process	2.20	no						
dipping process	2.21	3			Х	Х	outdoor	
Spraying	2.22	no						
brush applications of mobile fluids	2.23	no						
curative applications								
low to medium pressure spraying	2.24	4					Indoor/ outdoor	
low pressure spraying	2.25	4					Indoor/ outdoor	
pasting (viscous fluid)	2.26	5	Х			Х		
caulking, plugging and in-situ fumigation	2.27	no						

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wrapping or patching with impregnated fabric	2.28	no				
space fumigation with gases and smokes	2.29	6			outdoor release	

Note: The Breakout Group should consider the environmental relevance of all processes and the need to create further emission scenarios.

Regarding the full scheme of releases to the environment the following scenarios and scales may be considered.

Table 14 Spatial scales of emission estimations of wood preservatives

ADJACENT	LOCAL	REGIONAL
	Production (*)	Production (*)
	Formulation (*)	Formulation (*)
Application: preventive use (soil)	Application: preventive use	Application: preventive use
Application: curative use (soil)	Application: curative use	

(*) Emissions from these two cycles are not considered in the OECD.

II.7 Waste Disposal of Wood Preservatives during Impregnation

Waste disposal is not covered in this paper, because OECD countries have legal requirements. However, it is useful to summarise briefly these legal requirements.

The European Waste Catalogue (EWC) [Commission Decision 94/3/EC of 20 December 1993; OJ No L5, 7.1.1994, p. 15] is presently being replaced and covers the following waste categories concerning wood preservatives. These waste categories are considered as hazardous waste pursuant to Article 1(4) of European Council Directive 91/689/EEC of 12 December 1991 (OJ No. L377, 31.12.1991, p. 20) based upon European Council Directive 75/442/EEC on waste [OJ No. L78, 26.03.1991, p. 32].

Table 15 European Waste Categories for Wood Preservatives

Waste category	Description	
03 02	wood preservation wastes	
03 02 01	non-halogenated organic wood preservatives	
03 02 02	organochlorinated wood preservatives	
03 02 03	organometallic wood preservatives	
03 02 04	inorganic wood preservatives	

[Experts of the other OECD Member countries are requested to provide their waste disposal legislation concerning waste disposal of wood preservatives, in order to amend this paragraph.]

III. EMISSION SCENARIOS: INDUSTRIAL IMPREGNATION PROCESSES

Literature, several recent documents, and instruction manuals describe the industrial impregnation processes well and need not to be repeated here [A. Garrod 1999; UNEP 1994; Bruderman 1999; EPA 1995; Deutsche Gesellschaft für Holzforschung 1991; Ullmann 1996]. Reference is made to work document 2 by Andrew Garrod who describes the preventive and curative wood preservation processes.

In environmental exposure assessment emission need to be quantified. This is best being done through an emission scenario. In this chapter six emission scenarios are presented that represent major impregnation processes in preservative and curative applications. These processes, their potential of environmental releases and pathways into primary compartments are described. The respective emission scenario puts these descriptions into a sequence of equations so that emission rates [Elocal: measured in g/d] and concentrations [Clocal measured in µg/L or µg/kg] in environmental compartments can be calculated. These calculations depend upon default values. Most sensitive are the emission factors (F) that summarise all diffusive emissions at the facility and the storage place. They are set at this stage by expert judgement, based in most cases on research of measured emissions.

Note: These default values and emission factors are subject to discussion by the Workshop.

III.1 Emission Scenario: Sawmill (Anti-sapstain Treatment)

III.1.1 Description [Krygsman 1994]

Freshly cut wood is treated with fungicides to prevent the discoloration caused by blue stain forming fungi. This coloration depreciates the value of the wood in the eyes of buyers. Unlike all other treatment processes sawmill treatment is primarily a short-term treatment. As with the other industrial processes there are a number of different variations in applying preservatives to the wood:

- 1. Dipping
- 2. Green Chain
- Spray.

Dipping and Green Chain are basically the same type of system. The wood is either dipped in a bundle in a treatment vat or fed piece by piece through a treatment vat. The dipping process is usually less than 30 seconds and the treated pieces are usually held over drip areas to collect excess preservative for 30 minutes to an hour. Excess preservative is collected from the drip area and recycled into the process. This process treats wood on the surface. Wood preservatives do not penetrate the wood more than a millimetre. The application rate is measured as kg of wood preservative used per m^2 of treated wood. If a penetration depth of 1 mm is assumed, the application rate can be presented as kg/m³ of treated wood.

Spray systems consist of longitudinal or transversal boxes that apply a diluted preservative to the wood on a continuously moving conveyor belt. Wood logs are fed into the mill and debarked and cut into lengths of various degrees. Workers, called sorters, will inspect the wood pieces either before or after the spray boxes. This is done to eliminate wood that is damaged or has knots, or is already discoloured due to fungi. The wood enters the spray box that applies the preservative to the surface of the wood for a period of 3 - 5 seconds. Splashguards surround the spray boxes to eliminate any droplets of spray from the rest of the mill area. Droplets are large enough to prevent the respiration of preservative solution. Treated wood is stacked or sorted and put into the yard for shipment off-site.

Sapstain treated wood does not remain in storage for long periods of time after treatment. Wood is generally shipped off-site to manufacturers with 2-3 days of treatment.

Preservatives are usually supplied to mills as concentrates that are then diluted - normally with water - to working concentrations at the mill.

In the United States many sawmills have complete recycling and their own water treatment facilities where a list of priority pollutants are screened. In addition, if discharges can occur to surrounding waterways a pollution discharge elimination system permit must be obtained from the water authorities.

Table 16 Characteristic Data for Anti-sapstain Application at the Sawmill

Parameter	Nomenclature	Value	Source
Number of plants in country	Ν	Хх	?
Area of wood impregnated per	AREAwood	xxx m²/d	?
day			
Application rate a.i. per m ²	Afluid	xxx L/m ²	?
Type of solvent and quantity		water: xxx m ³ /a	?
used per year		yyy: m³/a	
Applications per d	APPLICATION	Хх	?
Working days per year	WDAYS	Xx/a	?
Emission factor to waste water	Fwater	Xx	Luttig et al. 1993
Emission factor to air	Fair	Xx	Luttig et al. 1993
Emission factor at storage	Fstorage	Хх	?

Emission factor to spray drift	Fdrift	Хх	
Air release VOC limit value		Xx kg VOC/m ²	?
		impregnated wood	
Air concentration VOC limit		xx mgC/m ² VOC	?
value		impregnated wood	
Storage density	DENSITYwood	$0.76 \text{ m}^3/\text{m}^2$	Luttik et al. 1993
Storage duration	Tstorage	35 d	Luttik et al. 1993

III.1.2 Environmental Release Pathways

The predominant technique used is the spray process with transverse boxes or green chain. Antisapstain chemicals are applied in dilution on a moving assembly line. Spray boxes are relatively contained, and studies have addressed the particle size for the spray preservatives.

Emissions can occur to the air directly after the spray box and from the wet wood as it dries on the belt, in the sorting tray and as it is bundled for stacking at the sorting and stacking areas. Sorting is the process whereby workers will sort the treated wood according to its size and appearance into different stacks where the wood is bundled for placement in the yard. Ventilation in most cases is via fans only.

Mill floors are cemented, so run-off is generally collected and recycled via drip pads. However, unintentional spills, floor cleaning, equipment cleaning and washing waters, tire drag-outs may reach the facility sewer system. The facility sewer is assumed to drain into the public wastewater treatment plant (WWTP).

As a worst case it is assumed that sawmills lie next to surface waters: an adjacent pond and a creek. The pond is burdened by air spray drift depended of its distance to the sawmill. The air spray drift emission factor F_{drift} is taken from the German pesticide assessment practices and may adjusted to OECD countries' practices.

Sorting and storage areas may be uncovered and unpaved, so emissions can occur to surface water and to soil. Releases from storage can occur through rainwater run-off. The emissions origin from a rain event that is assumed to be 20 mm (20 litres) of rain in 24 hrs: i.e. 0.02 m³. It is assumed that one half of the rainwater runs-off directly into the public wastewater treatment plant and the other half seeps into the storage soil. The factor (FAKTOR) takes care of adsorption of the substance to suspended matter, lowering the concentration in the solute aqueous phase [Commission of the European Communities 1997, p. 302].

Note: The following qualitative data should be addressed in this paper (industry input is requested)

- Empty container disposal (legal requirements in countries)?
- Drip collection and drip return process
- Encapsulation of spray tunnels and dripping baths
- Facility waste disposal, e.g. sawmill sludge (legal requirements in countries)
- Sludge disposal (legal requirements in countries)
- Treated wood storage facilities (paved or unpaved surface, rain-water run-off disposal)
- Disposal of waste treated wood (legal requirements in countries).

The following emission pathways at the sawmill are identified, that can be quantified with emission factors:

Table 17 Emission pathways at sawmill

Primary medium	Pathway	Result
Sawmill facility		
Air	direct air emissions from the spray box or dip tank resulting in air emissions per day	Elocalair
Surface water (pond)	air spray drift to adjacent pond	Clocalpond
Surface water	 pathways to the facility sewer system that drains to the public waste water treatment plant (WWTP) leaks from the equipment cleaning water from the mill floor, dip tray, and equipment drag-outs on tyres of vehicles washing water discharges cleaning of empty containers losses at fixation 	Clocalwater- facility
Storage on-site		
Surface water	rain run-off water from unpaved storage into a creek	Clocalwater-run- off
Soil	rain run-off water seeping into unpaved storage soil	Clocalsoil

Table 18 Fraction of air spray drift deposition from sawmill in relation of distance

Distance [m]	Air spray drift = F _{drift}
0	1
5	0.0005
10	0.00005
15	0.00003
20	0.00002
30	0.00001

These fractions of spray drift data come from the German pesticide authorisation performed by Umweltbundesamt and Biologische Bundesanstalt Braunschweig (BBA). The scientific base was elaborated with industry at Umweltbundesamt in 1992.

III.1.3 Emission Scenario No. 1: sawmill

The origin of the data is as follows:

- I input data provided by industry for each authorisation request
- D reasonable defaults or statistically derived default values (90 percentile)
- P value to take from a pick list or table
- M separate calculation
- O output of calculations.

Parameter/variable [unit]	Nomenclature	Value	Origin
Input			
Area of wood impregnated [m ² /d]	AREAwood		Input
Application rate [mL/m ²]	A _{fluid}		Input
Density of product [kg/m ³]	RHO _{product}		Input
Number of applications per day []	APPLICATION		Input
Fraction released to waste water [] solubility in water [mg/m ³]	F _{water}		Default
< 0.25		0.0001	
0.25 – 1		0.0015	
1 - 50		0.003	
50 - 100		0.015	
>100		0.03	

Parameter/variable [unit]	Nomenclature	Value	Origin
Fraction released to air [] vapour pressure at 20 °C	F _{air}		Default
[Pa]		0.001	
<0.005		0.01	
0.005 - 0.05 0.05 - 0.5		0.02 0.075	
0.05 - 0.5		0.075	
1.25 – 2.5		0.25	
>2.5		0.20	
Fraction released at storage after rain	F _{storage}	0.01	Default
event [] Fraction of spray drift deposition in	Fdrift	See Table 18	Default. P
relation to distance []	⊢ drift	See Table 18	Default, P
Distance [m]			
0		1	
5		0.0005	
10		0.00005	
15		0.00003	
20		0.00002	
30 Fraction of substance released in	-	0.00001	N.4
WWTP to receiving surface water []	F _{WWTP}		M SimpleTreat
Pond adjacent: 1 m ² * 0.3 m [m ³]	POND	0.3	Default
Rain event [20 mm] in 24 hr after	RAIN	0.02	Default
storage = 0.02 m^3			
Volume of water in WWTP [m ³ /d]	EFFLUENT	2000	Default
Dilution factor of receiving water	DILUTION	10	Default
Dilution to adjacent creek	DILLUTIONcreek	3	Default
Factor accounting for adsorption on	FACTOR		M
suspended matter in surface water			
(1 + Kp _{susp} * SUSP _{water})	SUSP _{water}	45	TGD
Concentration of suspended matter in the river [mg/L]	SUSP _{water}	15	IGD
Kp _{susp} = 0.1 Koc	Kp _{susp}		М
Soil density [kg/m ³]	DENSITY _{soil}	1700	Default
Soil depth [m]		0.025	Default
Area of storage [m ²]	AREA _{storage}	50	default
Output emissions			
Local emission to air [g/d]	Elocalair		Output
Local emission to pond via spray drift [g/d]	Elocalpond		Output

Parameter/variable [unit]	Nomenclature	Value	Origin
Local emission to waste water [g/d]	Elocal _{water}		Output
Local emission to soil during one storage period [g/d]	Elocal _{storage}		Output
Output concentrations			
	Clocalpond		Output
Local concentration in adjacent pond [µg/L]			
	Clocal _{creek}		Output
Local concentration in creek [µg/L]			
Local influent concentration [µg/L]	Clocal _{infl} .		Output
Local effluent concentration [µg/L]	Clocal _{effl.}		Output
Local concentration in receiving	Clocalwater		Output
surface water [µg/L]			
Local concentration in soil at storage place [µg/kg]	Clocal _{soil}		Output

Facility: Emission to local air from sawmill

Quantity released to air [g/d] Elocal_{air} = AREA_{wood} * A_{fluid} * RHO_{product} * APPLICATION * F_{air}

Facility: Emission to local adjacent pond via air spray drift from sawmill

Quantity released into adjacent pond at distance x meters via air spray drift [g/d] $Elocal_{pond} = AREA_{wood} * A_{fluid} * RHO_{product} * APPLICATION * F_{drift}$

Surface water concentration in adjacent pond [μ g/(L*d)] Clocal_{pond} = Elocal_{pond} / POND

Facility: Emission to receiving surface water via sawmill sewer and public WWTP

Quantity released to waste water [g/d] Elocal_{water} = AREA_{wood} * A_{fluid} * RHO_{product} * APPLICATION * F_{water}

WWTP module

Influent concentration

Elocalwater

Clocal_{infl.} = -----

EFFLUENT

Effluent concentration [mg/L]

Clocal_{effl}. = Clocal_{infl}. * F_{WWTP}

Surface water dilution module

Concentration in surface water [µg/L]

Clocaleffl.

Clocalwater = -----DILUTION * FACTOR

Storage: Emission to local surface water via rainwater run-off from storage [g/d]

Elocal_{storage} = AREA_{wood} * A_{fluid} * RHO_{product} * APPLICATION * F_{storage}

Assumption: One half of Elocal_{storage} is washed by run-off rainwater into a creek, the other half seeps into soil.

0,5 *Elocal_{storage} Clocal_{run-off} = ------RAIN

Clocal_{run-off}

DILUTIONcreek * FACTOR

Storage: Emission to local soil from storage [g/d]

Clocal_{soil} = -----

DENSITYsoil * DEPTHsoil * AREAstorage

All these concentrations are Clocal_{ini}-values.

The continuous releases to pond and surface water while the sawmill is in operation and the episodic releases to soil and creek via rainwater should be considered by breakout Group 4.

III.2 Emission Scenario: Vacuum Pressure and Pressure Processes

III.2.1 Description

Pressure is required to overcome the resistance of wood to deep penetration by preservatives. These heavy-duty processes operate with cylindrical airtight steel pressure/vacuum vessels. Two processes are in operation: the vacuum pressure and the pressure process, both handled in one emission scenario, because the emission pathways are similar. The application rate is measured as kg of wood preservative penetrated into m³ of wood.

Examples for active substances

Two types of preservatives are used in these processes: oil borne and water borne preservatives. Oil-borne preservatives are formulated with solvents or carriers such a mineral spirits and petroleum oils. Solvents influence several properties, including wood colour and paint ability. Examples of oil-borne preservatives are creosote, pentachlorophenol, and copper naphthenate. Water-borne preservatives are used principally to treat wood used in construction, where wood must be clean to handle, odourless, and paintable. Examples for this type of preservatives are chromated copper arsenates (CCA), ammonium copper zinc arsenate (ACZA), copper and boron compounds, sulfur-containing substances such as isothiozolinones and 2-(Thiocyanatomethylthio)benzothiazol (TCMTB).

The preservative is usually delivered to the plant in a form of a concentrate and must be diluted down to a suitable working strength. The degree of dilution will vary depending on the wood species, type of wood product, and anticipated use. Untreated wood is loaded onto small rails or trams cars (bogies) that are pushed into the cylinder using locomotives, forklifts or similar equipment. The cylinder door is sealed via a pressure tight door, either manually with bolts or hydraulically, and a vacuum applied to remove most of the air from the cylinder and the wood cells. Treating solutions are then pumped into the cylinder and the pressure raised. The total treating time and cycles will vary, depending on the species of wood, the commodity being treated, and the desired chemicals retentions, but in all instances the treating process remains a closed system. At the end of the process, the excess solution is pumped out of the cylinder and back to the storage for re-use. The cylinder door is opened, and the trams loaded with treated wood are pulled from the cylinder. At this moment considerable amounts of solvents and creosote can escape into the air.

Table 19	Characteristic	Data for Vacuur	n Pressure Process
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Table 20 Characteristic Data for Pressure Process

Parameter	Nomenclature	Value	Source
Number of plants in country	N	UK: 300	Garrod 1999
		Canada: 60	
		Germany: 420	UBA 1999
Hazard class		3,4,5	
Quantity of wood treated per	Qwood	3 - 58 m ³ /d	Garrod 1999
day		median: 21m ³ /d	
Quantity of a.i. per m ³ wood	Qa.i.	xxx kg/m ³	?
Type of solvent and quantity		water: xxx m ³ /a	?
used per year		other: yyy m ³ /a	
Applications per d	APPLICATION	1 – 3	Garrod 1999
Working days per year	WDAYS	xx/a	?
Emission factor to waste	Fwater	Xx	Luttik et. al. 1993
water			
Emission factor to air	Fair	Xx	Luttik et. al. 1993
Emission factor at storage	Fstorage	Xx	?
Air release VOC limit value		11 kg VOC/m ³	Draft EU Directive
		impregnated wood	1999/13/EC
Air concentration VOC limit		50 mgC/m ³ VOC	Draft EU Directive
value		impregnated wood	1999/13/EC
Storage density	DENSITYwood	0.76 m ³ /m ²	Luttik et al. 1993
Storage duration	Tstorage	35 d	Luttik et al. 1993

Parameter	Nomenclature	Value	Source
creosote			
Type of solvent and quantity used per year per facility		Tar oil: 10 - 20 t/a (Germany)	UBA 2000
Applications per d	APPLICATION	2	Garrod 1999
Working days per year	WDAYS	xx/a	?
Emission factor to waste water	Fwater	Xx	Luttik et. al. 1993
Emission factor to air	Fair	Хх	Luttik et. al. 1993
Emission factor at storage	Fstorage	Хх	?
Air release VOC limit value		5 kg VOC/m ³ impregnated wood	Draft EU Directive 1999/13/EC
Storage density	DENSITYwood	$0.76 \text{ m}^3/\text{m}^2$	Luttik et al. 1993
Storage duration: creosote	Tstorage	70 d	Luttik et al. 1993

Creosote is a critical wood preservative because it contains carcinogenic polyaromatic hydrocarbons (PAHs) with benzo[a]pyren as the lead substance. Likewise, creosotes or tar oils cause VOC emissions that should also be reduced [Draft EU Directive 99/13/EC of 18 February 1999]. EU Member countries are engaged to minimise the risk to creosote wood preservatives by promoting low volatile and low benzo[a]pyren fractions of creosote. Benzo[a]pyren is suggested as lead substance for exposure assessment of creosote. The present limit value for benzo[a]pyren is 50 ppm (EU Directive 94/60/EC] and the EU Commission is considering to lower it because of new scientific knowledge.

Table 21 Classification of Impregnating Oils (Creosote) according to the WEI

Parameter Nomenclature Value Source Number of plants in country UK: 5 Garrod 1999 Ν Canada: ? ---Germany: 20 UBA 2000 Hazard class 4,5 -------? xx m³/d Quantity of wood treated per Qwood median: xx m³/d day Quantity of creosote per m3 Qcreos post: ca. 90 Dt. Ges. für wood [kg/m³] palisades: 45-90 Holzforschung . sheets: 63 1991 sleepers: ca. 63 utility poles: ca. 90 kg/m³ Fraction of benzo[a]pyren in FBaP Χх see Table 21

Technical data	Unit	Method of estimation	WEI Grade A	WEI Grade B	WEI Grade C
Density (20 °C)	g/mL	WEI App.3	1.04-1.15	1.02-1.15	1.03-1.17
water content	Vol %	max. 1	max. 1	max.	max. 1
crystallisation temperature	°C	WIE App.5	max. 23	max. 23	max. 50
water-extract. phenols	Weight %	EN 1014-4	max. 3	max. 3	max. 3
insoluble matter	Weight %	BS 144 App. G	max. 0.4	max. 0.4	max. 0.4
boiling range					

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Technical data	Unit	Method of estimation	WEI Grade A	WEI Grade B	WEI Grade C
 distillate to 235 °C distillate to 300 °C distillate to 335 °C 	vol %	WIE App. 8	max. 10 20-40 55-75	max. 20 40-60 70-90	 max. 10 65-95
Vapour pressure	Ра	?	?	?	?
water solubility	mg/L	?	?	?	?
Benzo[a]pyren	ppm	EN 1014-3	max. 500	max. 50	max. 50
VOC emissions	max %		25	20	2

Source: Rütgers VFT, Frankfurt, September 1999

WEI = West European Institute for Impregnation, Paris

III.2.2 Environmental Release Pathways [van Dokkum et al. 1998]

Emissions during the impregnation are due to contaminated water and due to spills (leakage) of impregnation fluid. During the impregnation process, water vapour is formed during the heating of the impregnation fluid (creosote, not for metals), during the release of the pressure or during vacuum periods. When this water vapour enters condensers, contaminated water will be formed. When no condenser is placed between the impregnation tank and the vacuum pump, contaminated water will be formed within the vacuum pump (several hundreds of litres per day). CUWVO (1986) made an estimation of the water contamination for two "standard" wood conservation companies (vacuum pressure conservation): one using creosote, and one using CCA salts (see Table 22).

Table 22Indication of the water contamination from a "standard" wood impregnation plant
(from: CUWVO, 1986).

Preservation with creosote		Preservation with CCA salt		
Production (wood)	8000 m³/a	Production (wood)	3000 m³/a	
Condensation water	200 m³/a	Condensation water	2 m³/a	
Phenols	200 kg/a	Copper	~1 kg/a	
PAH (19)	40 kg/a	Chromium	~1 kg/a	
PAH (6)	0.8 kg/a	Arsenic	~1 kg/a	
COD	1000 kg/a			
BOD	600 kg/a			

A second source of contamination -next to contaminated water vapour- is leakage of impregnation fluid. After impregnation, the impregnation tank is opened and trollies with impregnated wood are rolled out. From the tank and from the freshly impregnated wood, impregnation fluid is released.

Impregnation companies are equipped with a collection tank for these spills. Rainwater sometimes can also enter these tanks, causing an increase of the volume of contaminated water. The emissions due to this leakage depend on the measures taken at the impregnation plant, to collect and reuse wastewater. Emissions to the atmosphere (evaporation) in this phase can occur.

Assuming that the impregnation plant is fit with collectors to remove water vapour from the air, the main emissions will be directed to a public wastewater treatment plant (WWTP) or to surface water. Depending on the configuration of the plant, spilled impregnation fluid will be emitted to the air (outdoors), to soil or fresh surface water (when the area of the plant is not paved) or to a public WWTP or fresh surface water (when the area is paved).

Releases from storage can occur through rainwater run-off. The emissions origin from a rain event that is assumed to be 20 mm (20 litres) of rain in 24 hrs: i.e. 0.02 m³. It is assumed that one half of the rainwater runs-off directly into the public wastewater treatment plant and the other half seeps into the storage soil. The factor (FAKTOR) takes care of adsorption of the substance to suspended matter, lowering the concentration in the solute aqueous phase [Commission of the European Communities 1997, p. 302].

The mean storage time of impregnated wood is 10 weeks (5 storage events per year per m²) and storage density of the treated wood is 0.76 m³ wood per m² [Luttik et. al 1993].

Table 23 Emission pathways at a vacuum pressure and pressure treatment plant

Primary medium	Pathway	Result
Treatment plant		
Air	 at the vacuum after impregnation (removal of surplus and sticking amounts of creosote), at boiling the creosote, at evaporation following cease of the vacuum, with the vacuum air and replacement air, aerosol air drifts at removal of the wood from the impregnation tank (main release), evaporation losses of solvents can be up to 20% wind dispersal of dried salts 	Elocalair and Clocalair
Surface water	 water discharge of unintentional leaks at equipment (e.g. pumps, condensers, tank loading, on dilution) cleaning water from the floor, the equipment, and drip pad drag-outs on tyres of vehicles washing disposals via the facility sewer and the public waste water treatment system (WWTP) 	Clocalwater

	 contaminated rain water flows out cleaning of empty preservative containers losses at fixation 	
Storage on-site		
Surface water	 rain water from uncovered and unpaved storage area via run-off into the public waste water treatment plant 	Clocalwater
Soil	 rain run-off water seeping into unpaved storage soil 	Clocalsoil

Based on the results of this research and other TNO research, CUWVO (1992) has made an indicative calculation to estimate the total amount of preservatives that leaches out on the storage area of a "standard" impregnation plant (Table). The advanced impregnation assumes improved processing techniques and impregnation fluids (modified creosote) and treatment of the impregnated wood (fixation).

 Table 24
 Results of an indicative calculation of the yearly emissions of impregnation compounds due to leaching during the storage of impregnated wood (CUWVO, 1992).

	Creosote impregnation plant	Metal salt impregnation plant
Production (m ³ wood per year)	20000	3000
Storage area (m ²)	4000	350
Discharge rainwater (m ³ /a)	1200-2000	105-175
Calculated leaching loss (kg/a)		
Conventional impregnation		
PAH	90	
Copper		0.4
Chromium		1.8
Arsenic		0.03
Advanced impregnation		
PAH	0.2	
Copper		0.04
Chromium		0.18
Arsenic		0.003

Quarles van Ufford (1994) calculated total emissions during the vacuum pressure impregnation process (emissions during impregnation, fixation and storage). The results are presented in Table 25. The emissions are based on the assumption that 50% of the process water is recycled, and

that 50% enters the environment. Emissions during storage are based on (CUWVO, 1992). The emissions during the total impregnation process are mainly due to emissions during the storage of wood.

		- / /			
Substance	Averag e input (kg.m ⁻³ wood)	Air (kg.m ^{⁻3} wood)	(Process) water (mg.m ⁻³ wood)	Leaching during storage: Range (mg.m ⁻³ wood)	Leaching during storage: 1990 (mg.m ⁻³ wood)
total VOC	20	7			
Naphthalene	8	3	?		300
Fenanthrene	8	0.8	?	3-1000	150
Fluoranthene	4	0.125	50	3-1000	150
Benzo(a)pyren e	0.02	0	<1		1.4
21 PAH	20 (?)	>1	?	10-4500	700
Copper	0.6	0	0	13-130	100
Chromium	1	0	0	60-600	450
Arsenic	0.8	0	0	1-10	8
Zinc		0	0	p.m.	
Fluoride		0	0	p.m.	

Table 25Emissions during impregnation with the vacuum-pressure method (impregnation,
fixation, storage) (Quarles van Ufford, 1994).

III.2.3 Emission scenario No. 2: Pressure Treatment [Luttik et al. 1993, modified]

The origin of the data is as follows:

I input data provided by industry for each authorisation request

D reasonable defaults or statistically derived default values (90 percentile)

P value to take from a pick list or table

M separate calculation

O output of calculations.

Concerning creosote lead substance benzo[a]pyren should be considered in environmental exposure assessment.

Parameter/variable [unit]	Nomenclature	Value	Origin
Input			
Quantity of wood impregnated [m ³ /d]	Q _{wood}		Input

Parameter/variable [unit]	Nomenclature	Value	Origin
Quantity of a.i. per m ³ wood [kg/m ³]	Q _{ai}		Input
Quantity of creosote per m ³ wood [kg/m ³]	Q _{creos}		Input
Fraction of benz[a]pyren in creosote []	F _{BaP}		Input
Number of applications per day []	APPLICATION		Input
Vapour pressure of benz[a]pyren at 20 °C [Pa]		7 * 10 ⁻⁵	Literature
Water solubility of benz[a]pyren at 20 °C [µg/m ³]		4.5	Literature
Fraction released to waste water [] solubility in water [mg/m ³] < 0.25 0.25 - 1 1 - 50 50 - 100 >100	F _{water}	0.0001 0.0015 0.003 0.015 0.03	Default
Fraction released to air [] vapour pressure at 20 °C [Pa] <0.005 0.005 - 0.05 0.05 - 0.5 0.5 - 1.25 1.25 - 2.5 >2.5	F _{air}	0.001 0.01 0.02 0.075 0.15 0.25	Default
Fraction released to soil on storage after rain event []	F _{storage}	0.005	Default
Fraction of substance released in WWTP to receiving surface water []	F _{STP}	calculated	M SimpleTreat
Volume of water in WWTP [m ³ /d]	EFFLUENT	2000	Default
Dilution factor of receiving water	DILUTION	10	Default
Factor accounting for adsorption on suspended matter in surface water [] (1 + Kp _{susp} * SUSP _{water})	FACTOR	calculated	М
Rain event [20 mm] in 24 hr after storage = 0.02 m ³	RAIN	0.02	Default
Storage density of treated wood per m ² [m ³ /m ²]	DENSITYwood	0.76	Default
Soil density [kg/m ³]	DENSITY _{soil}	1700	Default
Soil depth [m]	DEPTH _{soil}	0.025	Default
Outdoor air volume [m ³] Length: 2 x 10 m	V _{air}	4000	default

Parameter/variable [unit]	Nomenclature	Value	Origin
Breath: 2 x 10 m			
Height: 10 m			
Output emissions			
Local emission to air [g/d]	Elocal _{air}		0
Local emission to waste water [g/d]	Elocal _{water}		0
Local emission to soil during one	Elocal _{storage}		0
storage period [g/m ²]	-		
Output concentrations			
	Clocal _{air}		0
Local air concentration [µg/m ³]			
Local influent concentration [µg/L]	Clocal _{infl} .		0
Local effluent concentration [µg/L]	Clocal _{effl.}		0
Local concentration in receiving	Clocalwater		0
surface water [µg/L]			
Local concentration in soil at storage	Clocal _{soil}		0
place [µg/kg]			

Facility: mission to local air

Local air concentration [μ g/m³]: 10 m from impregnation vessel, no dilution Elocal_{air}

Clocal_{air} = -----V_{air}

• all

Facility: Emission to local receiving surface water

Quantity of the substance released with waste water [g/d]salt or organic a.i: Elocal_{water} = $Q_{wood} * Q_{a.i.} * F_{water} * APPLICATION$ or

creosote: Elocal_{water} = $Q_{wood} * Q_{creos} * F_{BaP} * F_{water} * APPLICATION$

Simple Treat Module

Influent concentration Elocal_{water} Clocal_{infi} = ------EFFLUENT

Surface water dilution module Concentration in surface water (Clocal_{water}) Clocal_{water} facility = Clocal_{eff} /(DILUTION * FACTOR)

Storage: Emission to local soil at storage [g/m²]

salt or organic a.i.: Elocal_{storage} = DENSITY_{wood} $^{*}Q_{a.i.} * F_{storage}$ creosote: Elocal_{storage} = DENSITY_{wood} $^{*}Q_{creos} * F_{BaP} * F_{storage}$

Assumption: One half of Elocal_{storage} is washed by run-off rainwater via the facility sewer and the public WWTP into surface water, the other half seeps into soil.

Local soil concentration Clocal_{soil} = 0.5 * Elocal_{storage} / (DENSITY_{soil} * DEPTH_{soil})

Storage: Emission to local surface water via rainwater run-off and public WWTP

Soil emission module salt or organic a.i.: Clocal_{infl.} = 0.5 * Elocal_{storage} / RAIN creosote: Clocal_{infl.} = 0.5 * Elocal_{storage} / RAIN

Effluent concentration Clocal_{effl}. = Clocal_{infl}. * F_{WWTP}

Surface water dilution module Clocal_{water-run-off} = Clocal_{effl} / (DILUTION * FACTOR)

Sum: surface water concentration [µg/L]

Clocal_{water} = Clocal_{water-facility} + C_{localwater-run-off}

III.3 Emission scenario: Dipping [Luttik et al. 1993, modified]

III.3.1 Description

Both mechanised and manual dipping are batch processes, used where the foreseen decay conditions are not severe. Dipping is a surface treatment and not a deep penetration treatment. It involves submerging a pack or single piece of wood into the preservative. Pallets of wood are loaded on automatic equipment (e.g. hydraulic elevator) and lowered into a dipping tank containing preservative. It remains there for a period between a few minutes and an hour. Cold soaking or steeping can extend over several days. The treated wood is held for excess solution to drain for collection of drips, then it is removed to storage. Dipping facilities may be open or encapsulated equipped with vapour trapping and air emission control.

A distinction is made between agents dissolved in water and agents dissolved in organic solvents. Organic solvents evaporate into the air. Estimated storage time of treated wood is 5 weeks, 10 episodes per year and a storage density of $0.50 \text{ m}^3/\text{m}^2$ [Luttik et al. 1993].

Superficial impregnation by dipping is measured in g/m^2 . However, if a penetration of 1 mm is assumed the application rate given in g/m^2 can be transferred into g/m^3 .

Parameter	Nomenclature	Value	Source
Number of plants in country	Ν	UK: ?	R. Peek 2000
		Canada: ?	Work Doc.
		Germany: 3000	
Hazard class		1,2,3	
Quantity of wood treated per	Qwood	xx m²/d	?
day		median: xx m ² /d	
Quantity of a.i. per m2 wood	Qa.i.	xx g/m ²	
Applications per d	APPLICATION	XX	?
Type of solvent and quantity		xxx t/a	
used per year per facility			
Working days per year	WDAYS	xx/a	?
Emission factor to waste	Fwater	Хх	Luttik et. al. 1993
water			
Emission factor to air	Fair	Хх	Luttik et. al. 1993
Emission factor at storage	Fstorage	Xx	
Air release VOC limit value		5 kg VOC/m ³	Draft EU Directive
		impregnated wood	1999/13/EC
Storage density	DENSITYwood	0.50 m ³ /m ²	Luttik et al. 1993
Storage duration	Tstorage	70 d	Luttik et al. 1993

Table 26 Characteristic Data for Dipping Process

III.3.2 Environmental Release Pathways

The open dipping bath can lead to emissions to air by evaporation and co-distillation with water or the solvent. Leaks of the equipment, cleaning and washing waters, tyre drag-out may lead to diffuse aqueous emissions that flow through the facility sewer system to the public waste water treatment plant (WWTP) and to receiving surface waters.

Releases from storage can occur through rainwater wash out. The emissions origin from a rain event that is assumed to be 20 mm (20 litres) of rain in 24 hrs: i.e. 0.02 m³. It is assumed that one half of the rainwater runs-off directly into the public wastewater treatment plant and the other half seeps into the storage soil. The factor (FAKTOR) takes care of adsorption of the substance to suspended matter, lowering the concentration in the solute aqueous phase [Commission of the European Communities 1997, p. 302].

Table 27 Emission pathways at a dipping plant

Primary medium	Pathway	Result
Dipping plant		
Air	 evaporations from open bath co-distillation with solvent wind dispersal of dried salts 	Elocalair and Clocalair
Surface water	 water discharge of unintentional leaks at equipment (e.g. pumps, condensers, tank loading, on dilution) cleaning water from the floor and equipment drag-outs on tyres of vehicles washing water disposals cleaning of empty preservative containers 	Clocalwater
Storage on-site		
Surface water	 rain run-off water from (un)paved storage via the facility sewer and the public waste water treatment system (WWTP) 	Clocalwater
Soil	 rain run-off water seeping into unpaved storage soil 	Clocalsoil

Examples of active substances

Insecticidal components of products include borates, synthetic pyrethroids and creosote, with chromium salts as fixing agent. Fungicidal components include 2-phenylphenol, copper and zinc salts of organic acids, quaternary ammonium compounds, IPBC, carbendazim, tebuconazole, pentachlorophenol and trichlorophenol salts.

III.3.3 Emission Scenario No. 3 for Dipping [Luttik et al. 1993, modified]

The origin of the data is as follows:

- I input data provided by industry for each authorisation request
- D reasonable default or statistically derived default values (90 percentile)
- P value to take from a pick list or table
- M separate calculation
- O output of calculations.

Parameter/variable [unit]	Nomenclature	Value	Origin
Input			
Quantity of wood impregnated [m ³ /d]	Q _{wood}		Input
Quantity of a.i. per m ³ wood [kg/m ³]	Q _{ai}		Input
Number of applications per day []	APPLICATION		Input
Fraction released to waste water [] solubility in water [mg/m ³]	F _{water}		Default
< 0.25		0.0001	
0.25 – 1		0.0015	
1 - 50		0.003	
50 - 100		0.015	
>100		0.03	
Fraction released to air [] vapour pressure at 20 °C	F _{air}		Default
[Pa]		0.001	
<0.005		0.01	
0.005 - 0.05		0.02	
0.05 - 0.5		0.075	
0.5 – 1.25		0.15	
1.25 – 2.5		0.25	
>2.5			
Fraction released at storage after rain event []	F _{storage}	0.01	Default
Fraction of substance released in	F _{WWTP}	calculated	М
WWTP to receiving surface water []			SimpleTreat
Volume of water in WWTP [m ³ /d]	EFFLUENT	2000	Default
Dilution factor of receiving water	DILUTION	10	Default
Factor accounting for adsorption on	FACTOR	calculated	Μ
suspended matter in surface water []			
(1 + Kp _{susp} * SUSP _{water})			
Rain event [20 mm] in 24 hr after	RAIN	20	Default
storage			
Storage density of treated wood per m ² [m ³ /m ²]	DENSITYwood	0.76	Default

Soil density [kg/m ³]	DENSITY _{soil}	1700	Default
Soil depth [m]		0.025	Default
Outdoor air volume [m ³]	V _{air}	4000	default
Length: 2 x 10 m			
Breath: 2 x 10 m			
Height: 10 m			
Output emissions			
Local emission to air [g/d]	Elocal _{air}		Output
Local emission to waste water [g/d]	Elocal _{water}		Output
Local emission to soil during one	Elocal _{storage}		Output
storage period [g/m ²]			
Output concentrations			
	Clocal _{air}		Output
Local air concentration in 10 m next to source [µg/m ³]			
Local influent concentration [mg/L]	Clocal _{infl} .		Output
Local effluent concentration [µg/L]	Clocal _{effl.}		Output
Local concentration in receiving	Clocalwater		Output
surface water [µg/L]			
Local concentration in soil at storage	Clocal _{soil}		Output
place [µg/kg]			

Facility: Emission to local air 10 m vicinity to source [g/d]

Quantity released to air [g/d] Elocal_{air} = $Q_{wood} * Q_{ai} * F_{air} * Application$

Local concentration in air [µg/m³]: 10 m from tank, no dilution Elocal_{air} = -----

Vair

Facility: Emission to local receiving surface water via facility sewer and public WWTP [g/d]

Quantity of the substance released with waste water [g/d] Elocal_{water} = $Q_{wood} * Q_{ai} * F_{water} * APPLICATION$

Simple Treat Module

Influent concentration

Elocal_{water}

EFFLUENT

 $\label{eq:effluent} \begin{array}{l} \mbox{Effluent concentration} \\ \mbox{Clocal}_{\mbox{effl.}} \ = \ \mbox{Clocal}_{\mbox{infl.}} \ ^* \mbox{F}_{\mbox{WWTP}} \end{array}$

Surface water dilution module

Concentration in surface water [µg/L] Clocal_{water-facility} = Clocal_{eff} /(DILUTION * FACTOR)

Storage: Emission to local soil from storage [g/m²]

Elocal_{storage} = DENSITY_{wood} * Q_{ai} * F_{storage}

Assumption: One half of Elocal_{storage} is washed by run-off water into the public wastewater treatment plant, the other half seeps into the local soil.

Local soil concentration [µg/kg] Clocal_{soil} = 0.5 * Elocal_{storage} / (DENSITY_{soil} * DEPTH_{soil})

Storage: Emission to local surface water via rainwater run-off and public WWTP [g/d]

Elocal_{storage} = DENSITY_{wood} * Q_{ai} * F_{storage}

Clocal_{infl.} = Elocal_{storage} / RAIN

Effluent concentration $Clocal_{effl.} = Clocal_{infl.} * F_{STP}$

Surface water dilution module Clocal_{water-run-off} = Clocal_{effi.} / (DILUTION * FACTOR)

Sum: surface water concentration [µg/L]

Clocal_{water} = Clocal_{water-facility} + Clocal_{water-run-off}

IV. EMISSION SCEANRIOS. CURATIVE / REMEDIAL APPLICATIONS

IV.1 Processes [Garrod 1999]

Damage to timber used in construction of buildings can occur through insects and fungi. Especially attics of large churches can be attacked, and remedial work can endanger bats living in these attics. Therefore, special care is taken to protect bats, and a bats emission scenario is proposed (see Emission Scenario nr. 4).

The market for remedial treatment is about 30% of that of the industrial treatment [UBA 1999]. The do-it-yourself market was in 1990/91 about 10% for salts and 45% for organic active substances of the professional market (see Table 6).

Remedial jobs involve considerable structural work to lay bare the extent of areas requiring remedial treatment. Firms with owned or hired equipment perform remedial work. The following techniques may be distinguished [Garrod 1999]:

- low and medium pressure spraying (4 to 7 bar)
- low pressure spraying (1 to 3 bar)
- brush painting (mobile fluids)
- pasting (viscous fluids)
- caulking and plugging
- wrapping or patching with impregnated fabric
- fumigant gases and smokes
- foaming
- injection pills.

Examples for active substances [Garrod 1999]

The insecticidal components include boron compounds, synthetic pyrethroids and pirimiphosmethyl, lindane.

Fungicidal components include copper and zinc salts, zinc salts of organic acids, quaternary ammonium compounds, IPBC, dichlofluanid, flufenoxuron, propiconazole, 2-phenylphenol salts and trichlorophenol salts, azaconazole, carbendazim, diuron, fluoride salts.

Gases: methylbromide, phosphine.

IV.2 Selection of Representative Emission Scenarios

Remedial wood treatment usually relates to limited areas, e.g. attics in houses, garden houses, claddings, wooden barns, bridges, fences, utility poles, furniture, works of art. This wide variety of curative applications necessitates a selection of emission scenarios that are representative and have major environmental emissions. Also, applications and scenarios discussed in the Breakout Group 2 may be considered adequate for remedial applications.

In the brushing method, the biocide product is applied with a brush. It is suited for local preservation. In the spraying method, the biocide is product is applied by spraying under pressure by a professional with spraying equipment. Emissions from spraying will be directed to the local environment via direct release to soil, outdoor or indoor air (spray drift). Emissions from brushing will also be locally to soil, outdoor and indoor air. Water may be contaminated, if spray drift to a nearby surface water occurs.

It is difficult to describe a standard emission scenario for these curative applications, because these applications vary according to the task. Nevertheless, four emission scenarios are selected:

- indoor scenario for remedial timber treatment (Emission Scenario No. 4)
- outdoor scenario for remedial timber treatment (Emission Scenario No. 5)
- indoor scenario for fumigation (Emission Scenario No. 6)
- outdoor utility pole (see Breakout Group 2)
- outdoor house cladding (see Breakout Group 2)

IV.3 Emission Scenario for Indoor Remedial Timber Treatment [Luttik et al. 1993]

IV.3.1 Description

This scenario represents an attic in a building. The Environmental Focus Group defined the dimensions of an attic. [Background Document No 4 "Environmental Exposure Scenarios for Treated Wood"]. Spraying, fogging, and painting are used to fight damage to timber in construction of buildings - especially in attics of large buildings and churches. The product is applied on the surface or immerged into the wood. The application rate is measured in g/m^2 .

Table 28 Characteristic Data for Indoor Timber Treatment

Parameter	Nomenclature	Value	Source
Hazard classes		2	
Area treated of attic	AREAtreated	204.8 m²/d median: xx m²/d	EF-Group Jan. 2000
Application rate of product [g/m ²]	Asolid	xx g/m ²	Input
Or: Application rate of product [mL/m ²]	Afluid	xx mL/m ²	Input
Faction of a.i. in product	Fai		Input
Density of product [kg/m ³]	RHOproduct	xx kg/m ³	Input
Working days per year []	WDAYS	xx/a	?
Emission factor to air[]	Fair	XX	Luttik et. al. 1993
Indoor air volume of attic [m ³]	Vair-indoor	227 m ³	EF-Group Jan. 2000

IV 3.2 Environmental Release Pathways

Figure 8 Emission scenario for indoor remedial timber treatment

The dosage of the active ingredient applied at the surface of the timber expressed in $[g/m^2]$ is used as the exposure concentration for bats. In a worst case situation no degradation and no evaporation from the wood is assumed. The initial indoor air concentration is calculated by assuming a room volume of 227 m³ (generic house). A church attic may be much larger.

Table 29 Emission pathways at indoor remedial timber treatment

Primary medium	Pathway	Result
Attic treatment		
Indoor air	 evaporations from surface of timber depending from vapour pressure of active substance co-distillation with solvent 	Elocalair and Clocalair
Surface water	spray drift by spray application	Not considered so far
Soil	spill by dripping product	To be considered in Brake-out Group 2
Timber surface	Dosage dependent of application rate [g/m ²]	Dosage at surface of treated timber

IV.3.3 Emission scenario No 4 for indoor remedial timber treatments [Luttik et al. 1993]

The origin of the data is as follows:

- I input data provided by industry for each authorisation request
- D reasonable defaults or statistically derived default values (90 percentile)
- P value to take from a pick list or table
- M separate calculation
- O output of calculations.

Parameter/variable [unit]	Nomenclature	Value	Origin
Input			
Fraction of a.i. in product []	F _{ai}		Input
Application rate of solid product [mg/m ²]	A _{solid}		Input
Application rate of liquid product [ml/m ²]	A _{fluid}		Input
Density of product [kg/m ³]	RHO _{product}		Input
Area treated [m ²]	AREA _{treated}		Input
Fraction released to air [] vapour pressure at 20 °C [Pa] <0.005 0.005 - 0.05 0.05 - 0.5 0.5 - 1.25 1.25 - 2.5 >2.5	Fair	0.001 0.01 0.02 0.075 0.15 0.25	Default
Indoor air volume for attic [m ³]	V _{air-indoor}	227	Default
Output dose			
Dosage of a.i. per m ² wood [mg/m ²]	DOSEwood		Output
Output concentrations			
Local indoor air concentration [µg/m ³]	Clocal _{air-indoor}		Output

Indoor scenario: Dosage on wood [mg/m²]

solid product: DOSE_{wood} = A_{solid} * F_{ai}

UBA

Berlin

or

liquid product: DOSE_{wood} = A_{fluid} * RHO_{product} * F_{ai}

Indoor scenario: indoor air concentration [µg/m³]

Clocal_{air_indoor} = DOSE_{wood} * AREA_{treated} * Fair / Vair_indoor

IV.4 Emission Scenario for outdoor Remedial Timber Treatment

IV.4.1 Description

This scenario represents a wooden object, e.g. a fence, cladding, etc, that is exposed to occasional wetting by rain (Hazard Class 3).

Table 30 Characteristic Data for Outdoor Timber Treatment

Parameter	Nomenclature	Value	Source
Hazard classes		3	
Area treated	AREAtreated	200 m ² median: xx m ²	Default
Application rate of product [g/m ²]	Asolid	xx g/m ²	Input
Or: Application rate of product [mL/m ²]	Afluid	xx mL/m ²	Input
Faction of a.i. in product	Fai		Input
Density of product [kg/m ³]	RHOproduct	xx kg/m ³	Input
Working days per year []	WDAYS	xx/a	?
Emission factor for run-off after rain event []	Frun-off	XX	?
Volume ditch [m ³]	DITCH	30	Default
Rain event in 24 hrs [m ³ /m ²]	RAIN	0.02	Default

IV.4.2 Environmental Release Pathways

The treated object may be a fence with the following default dimensions: 50 m long, 2 m high. Rainwater reaches the ground: $0.02 \text{ [m}^3/\text{m}^2\text{]} * 50 \text{ [m]} * 2 \text{ [m]} = 2 \text{ m}^3$. It is assumed that one half of the run-off rain water seeps into the soil and the other half runs into a nearby ditch at 5 m distance. The ditch scenario is taken from the German pesticide authorisation scheme [Kloskowski et al. 1999]. The ditch is 100 m long, 1 m broad, and 0.3 m deep: 30 m³, resulting in 31 m³ after rain event, e.g. a dilution of 1:30. The ditch drains into surface water with a dilution of 1: 25 (default).

It is assumed that one half of the rainwater runs-off directly into the adjacent ditch and the other half seeps into the soil underneath the fence in a distance of 20 cm to both sides of the fence. The factor (FAKTOR) takes care of adsorption of the substance to suspended matter, lowering the concentration in the solute aqueous phase [Commission of the European Communities 1997, p. 302].

Table 31 Emission pathways for outdoor remedial timber treatment

Primary medium	Pathway	Result
Outdoor fence		
Surface water	Rainwater run-off into adjacent ditch	Clocalsurfacewate r
Pond	Spray air drift during spray application	Not considered so far
Soil	Rainwater and preservative seeps into soil	Clocalsoil

IV 4.3 Emission scenario No. 5 for outdoor remedial timber treatment

The origin of the data is as follows:

- I input data provided by industry for each authorisation request
- D reasonable defaults or statistically derived default values (90 percentile)
- P value to take from a pick list or table
- M separate calculation
- O output of calculations.

Parameter/variable [unit]	Nomenclature	Value	Origin
Input			
Fraction of a.i. in product []	F _{ai}		Input
Application rate of solid product [mg/m ²]	A _{solid}		Input
Application rate of liquid product [ml/m ²]	A _{fluid}		Input
Density of product [kg/m ³]	RHO _{product}		Input
Area treated [m ²]	AREA _{treated}		Input
Surface under treated object burdened by a.i. after rain event at 20 cm of both sides of treated object [m ²]	AREA _{soil}		Input
Fraction released after rain event []	F _{run-off}	0.01	Default
Rain event [20 mm] in 24 hrs after application = 0.02 m^3	RAIN	20	Default
Ditch [m ³] Long: 100 m Broad: 1 m Deep: 0.3 m	DITCH	30	Default
Dilution ditch to surface water []	DILUTION	25	Default
Soil density [kg/m ³]	DENSITY	1700	Default
Soil depth [m]	DEPTH _{soil}	0.025	Default
Factor accounting for adsorption on suspended matter in surface water [] (1 + Kp _{susp} * SUSP _{water})	FACTOR	Calculated	М
Output dose			
Dosage of a.i. per m ² wood [mg/m ²]	DOSEwood		Output

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Output concentrations		
Local surface water concentration [µg/L]	Clocal _{surfacewater}	Output
Local soil concentration [µg/kg]	Clocal _{soil}	Output

Dose [g/m²]

DOSE_{wood} = A_{fluid} * RHO_{product} * F_{ai}

Assumption: One half of $Elocal_{run-off}$ is washed by run-off rainwater into the ditch, the other half seeps into soil.

Local surface concentration[µg/L]

Clocal_{surfacewater} = -----

DITCH * DILUTION_{ditch} * FACTOR

0.5 * Elocal_{rup-off}

Local soil concentration[µg/kg]

Clocal_{soil} = -----

DENSITY_{soil} * DEPTH_{soil} * AREA_{soil}

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9 Fibre, leather, rubber and polymerised materials preservatives

Introduction

The purpose of applying biocides in fibre, leather, rubber and polymerised materials is to control of microbiological deterioration and to preserve fibrous or polymerised materials. The relevant sub-groups are:

- 9.1 Fibre (Textile and fabrics (wood, cotton)), (professional use)
- 9.2 Leather and Hides (professional use)
- 9.3 Rubber, Plastics and polymerised material (professional use)
- 9.4 Paper and cardboard (professional use)

9.1 Fibre

For textiles and fabrics some information, concerning emission scenarios for waste treatment, is available (van der Poel, July 1999).

For cellulose fibres, preservatives are mainly applied to prevent rot and mildew. They are often applied in the finishing process of the fabrics, where biocides are added together with antistatics, water repellents, dyes, etc. They are applied in aquaeous solutions of 0,25 - 1% in baths through which the fabric is transported (van Dokkum, 1998). 70 - 80% of the biocides are adsorbed by the fabric. The fixation is very high (up to almost 100 %), if the insect proofing agents are applied in a bath process where the liquor ratio influences the degree of fixation (e.g. in dyeing baths).

Typical biocides used in the textile industry (Rossmoore, 1995):

2,2'Dihydroxy-5,5'-dichloro-diphenylmethane 2-Phenylphenol Quartenary ammonium salts Copper-8-quinolinolate Dichlorophen Zinc naphthenate Thiobendazole Organotin 2,4 Dichlorobenzyl alcohol 2 Bromo-2-nitropropane-1,3-diol Sodium-2-phenyl-phenolate

9.2 Leather and hides

General data:

Tanneries in Europe (IPPC, 1999):

Country	No of tanneries	Production [1.000m ³] (1997)	Disposal route for solid wastes
Austria	7	5011	
Belgium	7	2226	66 % landfill 17 % Incineration 17 % agriculture
Denmark	2	1330	
Finland	9	1841	
France	113	12300	95 % landfill 5 % agriculture
Germany	37	10800	100 % landfill
Greece	150	4600	
Ireland	4	4250	60 % landfill 40 % agriculture
Italy	2400	194500	100 % landfill
Netherlands	14	3617	100 % landfill
Norway	3	1140	100 % landfill
Portugal	110	10680	
Spain	255	47165	90 % landfill 10 % agriculture
Sweden	4	2200	100 % landfill
Switzerland	4	5528	
United Kingdom	55	13500	90 % landfill 10 % agriculture

Biocides can be applied prior to or during several stages of the tanning process as preservatives, disinfectants, or as pesticides. Some biocides may also be incorporated in proprietary products, such as dyes and casein finishes. Furthermore, raw hides and skins may contain biocides, which have been applied to the animal to protect it from diseases during its life.

As preservatives they prevent microbial destruction of rawhides and skins, intermediate, and finished products, as disinfectants they reduce germs in the production plant. Preservatives and disinfectants are added at various stages of the process, e.g., curing, soaking, after tanning. As pesticides they prevent animal pest, fly infection, moth larvae damage, and beetle attack so that they cannot damage hides and skins prior to slaughtering or in the raw state, of intermediate and finished products particularly if the hides and skins are intended for long transport.

Sheep are dipped in pesticides (e.g. synthetic pyrethroids like cypermethrin and permethrin, organophosphates like diazinon, chlorphenvinphos, phosmet and fenthion) on a regular basis to protect them from diseases, whereas bovine animals are not. Currently there is a trend to substitute organophosphates with synthetic pyrethroids. However in addition to the fact, that synthetic pyrethroids are reported to be more toxic to aquatic life than organophosphates, both groups of pesticides have also been reported to have endicrine disrupter effects. Synthetic pyrethroids and organophosphates survive the aggressive chemical conditions in the tanning processes and are consequently found in significant quantities with respect to environmental quality standards in the waste water effluents.

For the wetblue-conservation (conservation of cured skins) the following substances are used:

- Phenoles para-Chlormetakresol (CMK) Trichlorphenol ortho-Phenylphenol (oPP)
- Heterocyclic substances
 2-Tricyanatomethylthiobenzothiazol (TCMTB)
 2-n-Octylisothiazolin-3-on (OITZ)
 2-Benzimidazolymethylcarbamat (BCM)
- Diiodmethyltolylsulfon (DIMTS)
- In many countries the use of halogenated phenoles is not allowed.

Even when using non-halogenated phenoles it must be observed that for example no sodiumchlorid is used immediately prior in the tannery since this might cause the production of chlorated phenoles during the process. Such a production can be discovered by monitoring the AOX-values in the waste water.

Normally active substances are added in a quantity of 1 - 2 % (of the salt weight) to salt. Although salt is an excellent preservative, halophilic or halotolerant bacteria may grow on the cured hide. After tanning, biocides are used in finishing operations to prevent microorganisms. In this stage e.g.

- p-nitrophenol is used in a quantity of 0,3 % of the weight of the leather) (van Dokkum, 1998)
- 2-chloro-4-nitrophenol
- tetrachlorohydroquinone
- bis (4-nitrophenyl)carbonate
- bis(2-chloro-4-nitrophenyl)carbonate
- 5,6-dichloro-2-benzoxazolinone

are used.

There are also some insecticides in use to protect leather against beetles.

9.3 Rubber, Plastics and polymerised material

To prevent the rubber and plastics from bio deterioration biocides have to be applied on the surface of the products. They must be able to diffuse to the surface, but must not leach out (e.g. by water). In some cases the biocide is incorporated into the plasticizer. For plastic formulations mercury- and other metal-containing compounds are used, sulphur-, quaternary ammonium- and halogenated compounds.

Salicylaldehydes, Dihydroxychlor-diphenyl-methanederivates Thiurames and Zincdithiocarbamates are used as antimicrobic substances. Furyldithiocarbamates have virtually disappeared from the market due to their allergizating effect.

Latex-products contain caseine- and hemoglobine-solutions which can create fouling-processes, potassium-o-phenylphenolate is used as preservative (Baumann et al, 1998).

9.4 Paper and cardboard

General data:

Paper production in Europe (packaging papers, sanitary and houshold, graphic papers) (IPPC, 2000):

Country	Production [Mio. t] (1996)
Austria	3,6
Belgium	1,2
Denmark	0,3
Finland	10,1
France	8,2
Germany	13,3
Greece	0,4
Ireland	-
Italy	6,6
Netherlands	3,1
Norway	2,1
Portugal	1,1
Spain	3,5
Sweden	8,8
United Kingdom	5,8

Biocides are used as preservatives of paper and as slimicides for the preservation of pulp (see product type 12).

Biocides used for paper preservation are:

Ascorbic acid

Sodium-, potassium-, calcium- and magnesium ascorbates

Benzoic acid

Sodiumbenzoate

Formic acid

Hydrobenzoic acid ethylester (adduct of 70 % benzylalcohol and 30 % formaldehyde) Glutardialdehyde

2,2-Dibrom-3-nitril-propionamide (DBNPA)

2-Brome-2-nitroproandiole (BNPD)

Methylendithiocyanate (MBT)

Isothiazolone

1,2-Benzisothiazolin-3-one (BIT)

3,5-Dimethyl-tetrahydro-1,3,5,2H-thiazdiazine-2-thione

There is a lack of information about the quantity applied in use. Realistic values are 0,1 - 1 % as application on the surface of the paper and 0,1 to 4 % in the paper mass (dry weight). We calculate with a release of 80 % in the paper. There is no or extremely low air emission < 1 % (IPPC, 2000) of the applied quantity.

In the paper industry, additives in aqueous often contain biocides to guarantee a safe storage (Geller, 1995). Some common ground exists with product type 6 (in-can biocides).

Conservation	Use in	Filler-	Starch-	Starch-	Starch-	Painton	Disper-	Dextrin-
substances	ppm	slurry	slurry	solution	glues	colours	sions	glues
Benzisothiazolone	50-200				х	Х	х	
Brom-nitropropandiol	10-100	х	Х	Х	х	Х	Х	
Dibromnitrilopropion- amide	10-250		X	Х	x	х		
Dimethyltetrahydro- thiodiazinthione	500- 2500						x	х
Formaldehyd and Formaldehyd producers	250- 5000		x	X	x		x	
Isothiazolinone	5-50	х	Х	Х	х	Х	х	
Quarternere compounds	20-800				x	х		х
Org. Sulphur compounds	200- 4000	x						
o-Phenylphenol	100- 1000			Х	x	х	x	х
Tetramethylthiuram- disulfid	5-1000			Х	x	х	x	x

Relevant information data for ESDs

9.1 Fibre

Processing

- Inclusion in materials/articles
- Application in processes

Total amount of textile-biocides per year: 20 t/a Netherlands (organochlorines), (Heuvelmann et al 1993)

Used quantity of active substances

- 0,25 1 % by weight copper fungicides (e.g. copper naphthalenate) and other organometal compounds (van der Poel, 1999)
- 0,035 0,5 % by weight to textile or fibre during impregnation by solvent or emulsion (Balk, 1999). Permethrin: 0,02 %, Carbendazim: 0,03 0,2 % (Worthing and Hance, 1991), Organometallics: 1 5 %, TBTO: 0,05 % (Board et al, 1987)

Service Life

Waste Treatment

- Waste streams + relevant information
- Recycling/recovery/reuse

Release on textile biocides into the aquatic system:

Up to 50 g/l measured in untreated waste water (CUWVO, 1993)

Existing or produced emission models

Model for Textile industry

Parameter/variable (unit)	Symbol	Default	C/R/E/O
Input:			
Quantity of material treated per day (kg/day)	Q _{mater}	1000	R/E
Quantity of active ingredient per kg material (mg/kg)	Q _{a.i.}	5000	R/E
Fraction fixed to material (-)	F _{fixat}	0,8	R/E
Fraction of i.a. transferred to wash water (-)	F _{washw}	0,001	R/E
Quantity of waste water in STP (m ³ /day)	Q _{STP}	1800	С
Fraction removed in STP (-)			
(calculation by standard module of USES)	R _{STP}		0
Dilution factor of receiving surface water (-)	F_{dilut}	32	С
Output:			
Concentration of a.i. in receiving surface water (mg/l)	C _{surf}		

Model calculations

 L_{wwb} = Quantity of a.i. released from bath (kg/day)

= $Q_{mater} * Q_{a.i.} * (1-f_{fixat}) * 10^{-6}$

L_{www} = Quantity of a.i. released from wash out (kg/day)

= $Q_{mater} * Q_{a.i.} * f_{fixat} * f_{washw} * 10^{-6}$

L_{wwt} = Quantity of a.i. totally released with waste water (kg/day)

 $= L_{wwb} + L_{www}$

 $R_{\mbox{\scriptsize STP}}$ Calculations by standard module of USES

$$C_{surf} = L_{wwt} / Q_{STP} * R_{STP} / F_{dilut} * 10^{3}$$

9.2 Leather

Processing

- Inclusion in materials/articles
- Application in processes

General data:

Volume produced in EC-tanneries:

bovine: 800.000 t/a (IPTS, 1999)
sheep, goats: 300.000 t/a (IPTS, 1999)

Water consumption in EC-tanneries:

- bovine: 32 -
- sheep, goats:

32 - 40 Mio. m³/a or 40 - 50 m³/t 21 - 24 Mio. m³/a or 70 - 80 m³/t

Volume of raw hides processed as fresh hides

(no biocides during curing, storing and soaking):

- Germany 60 % (Umweltbundesamt, 1998)
- Germany 60 70 % (IPTS, 1999)
- Austria 60 70 % (IPTS, 1999)
- South America 75 % (IPTS, 1999)

Average value, used for PEC-calculations: 60 % (curing, storing and soaking)

	100 % (pickling, tanning and drying)				
Number of working days/a:	220 (Böhm et al. 1999)				
Production quantity per day [t/d]:	15 (Böhm et al. 1999)				
Specific water consumption:	20 – 30 m ³ /t from raw hide to wet blue				
Specific water consumption:	15 - 30 m ³ /t from wetblue to crust				
Specific waste water quantity [l/kg]:	2 – 4 m ³ /t Curing and Storing/Soaking				
where biocides are used in the process					

Relevant process stages for the use of biocides:

- Curing & storing
- Soaking (15 25 % of the total water consumption, conventional process for bovine salted hides and chrome tanning) (Zimpel, 1997)
 There are different References-sources for water consumption in this process unit:
 IPTS, 1999: 4 15 m³/t hide and skins
 Umweltbundesamt, 1998: 2 3 m³/t hide and skins
- Pickling and Tanning (fungicides), water consumption: 0,5 3 m³/t wetblue
- Drying (a finishing stage with biocides), water consumption: $2 6 \text{ m}^3/\text{t}$ crust

Water consumption in various process units for a conventional process for bovine salted hides and chrome tanning (IPTS, 1999):

Process unit	Water consumption [%] (rough average)
Soaking	15 – 25
Liming, rinsing	23 – 27
Deliming, batinmg, rinsing	10 – 15
BEAMHOUSE SUM	50 – 65
Pickling, tanning, rinsing after tanning, neutralisation, rinsing	10
Retanning, dyeing, fatliquoring, rinsing	30
POST-TANNING OPERATIONS SUM	30 – 40
Finishing	10
TOTAL	100

UBA

Berlin

Used quantity of active substances

0.3% p-nitrophenole (of the weight of the leather)

Service Life

Waste Treatment

- Waste streams + relevant information
- Recycling, recovery, reuse

Existing and produced emission models

PEC-calculation for a **leather production** location including **on-site sewage treatment** (according to Böhm et al, 1999):

Produced raw hides/day: Specific biocide quantity: Fixation:	W1 = 15 t/day W2 = 0,1 kg/t (1 % biocides in 10 kg/t dye) F = 95 %		
Quantity of the daily production treated with biocides : Volume of the sewage treatment plant: Untreated/ non-degraded part of the	A = 100 % 2000 m³/d		
used biocide quantity: Dilution factor:	e.g. 90 % in STP 10		
Emission per day:	W1 x W2 x (1-F) x A 15 t/d x 0,1 kg/t (1- 0,95) x 1 = 75 g/d		
Concentration of biocides at the sewage treatment plant inflow:	75 [g/d] / 2000 m ³ /d = 37,5 μg/l		
Concentration of biocides at the sewage treatment plant outflow:	37,5 μg/l x 0,9 = 33,75 μg/l (10 % reduction)		
Concentration of biocides in surface water (PEC): 33,75	$[\mu g/l] / 10$ (dilution factor) = 3,4 $\mu g/l$		
 (150 mg/kg). 95 % of the substance offered are ads skin, 7,5 mg/kg or 7,5 kg/l Biozid enter During the rinsing and finishing (toget the rinsing water, 128,3 mg/kg remain 	(15 % ai) charge with 1,5 kg active substance per 10 t skin obed by the skin, i.e. 142,5 mg/kg remain on the r the tanning flotilla (75 g in 10 t flotilla). her 3,8 m ³) 10 % of the substance (14,3 g) enter in the skin. ostance enter 32 m ³ waste water per t leather		

If we assume that 80 % of the substance are removed in the sewage disposal plant, 80 % are adsorbed into the waste water sludge and a thinning to 10 % takes place in the effluent, the PEC for the outfall is calculated 0,011mg/l.

When comparing the two calculations, please note that the degradation rate in the sewage disposal plant in one case is 10% (adsorbed on flocs) and 80% in the second case (Neuber, 1998). If we assumed only a 10% reduction in the sewage treatment plant, we would have a PEC value of 2,26 mg/l. This calculated PEC is 200 times as high as that calculated by Neuber. The comparison of these examples demonstrates the interpretation potential inherent in the calculation of an emission scenario.

9.3 Rubber and Plastics

Processing

- Inclusion in materials/articles
- Application in processes

Used quantity of active substances

Service Life

Waste Treatment

- Waste streams + relevant information
- Recycling/recovery/reuse

Existing or produced emission models

9.4 Paper and cardboard

Processi*ng*

- Inclusion in materials/articles
- Application in processes

Specific water consumption:

14 l/kg (medium value) (Geller, 1995)

Used quantity of active substances:

1 % by weight as surface preservative (dry paper weight)

4 % by weight as mass preservative (dry paper weight)

Service Life

Waste Treatment

- Waste streams + relevant information
- Recycling, recovery, reuse

Release of biocides into the aquatic system:

20 % of the used quantity into waste water

Existing or produced emission models

Model for paper and cardboard industry and default values for parameters

Parameter/variable (unit)	Symbol	Default	C/R/E/O
Input:			
Quantity of water discharged per day (m ³ /day)	Q _{water}	3000	R/E
Concentration of a.i. in process water discharged (mg/l)	C _{a.i.}		R
Quantity of water in STP (m ³ /day)	Q_{STP}	3000	R/E
Dilution factor of receiving surface water (-)*	F_{dilut}	10	E(D)
Output:			
Concentration of a.i. in receiving surface water (mg/l)	C_{surf}		
* Dilution factors of 3 for stagnant waters (e.g. lakes), 10 for semi-stagna for large rivers. As effluent from several factories is discharged to semi-s 10 is used as a default value [Luttik., 1993]			

Model calculations

L_{wwt} = Quantity of a.i. totally released with waste water (kg/day)

 $= Q_{water} * Q_{a.i.} * 10^3$

 $R_{\mbox{\scriptsize STP}}$ Calculations by standard module of USES

 $C_{surf} = L_{wwt} / Q_{STP} * R_{STP} / F_{dilut} * 10^3$

Emission routes for biocides. '+'=relevant; '-' not relevant (van Dokkum et al., 1998, modified) [weight %]

Product type	Applications	Fresh surface water	Marine surface water	Air indoor and outdoo r	Soil	Solid Waste	Waste water
9.1	Textile (P)	+	-	-	-	+	Up to 50g/l
9.2	Leather (P)	+	-	-	-	+	+
9.3	Rubber, Plastics (P)	+	-	-	-	+	+
9.4	Paper and cardboard (P)	+	-	-	-	+	20 %

P: professional use; N: non-professional use

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10 Masonry preservatives

The relevant sub-groups are:

- 10.1 Coating systems (professional use)
- 10.2 Injection agents (professional use)
- 10.3 Plasters (professional use)
- 10.4 Screed (professional use)
- 10.5 Concrete additives (professional use)

Introduction

In the following text the product type protective agents for masonry is briefly described. The main focus is on those substances employed as biocides. Since there are several substances in use which have a biocidal effect as a secondary function, these will be listed under their primary function. The sub-group products are used in professional fields.

<u>10.1</u> <u>Coating systems</u> (e.g. coating systems of plaster bound with artificial resins, elastic, crack covering coats, base coat, silicon colour systems, building proofing and –restoration, special plasters, glue/resins)

10.2 Injection agents (Drainage of masonry with silicon-emulsions)

Depending on the absorption rate and the wall thickness, rows of drill holes are placed in the wall. A pump introduces the injection agent, which will quickly spread throughout the masonry and form a permanent protective layer against rising dampness, in short impulses over infusion pipes (which remain in the wall) and tubes. In addition to this, defective and salt loaded plaster coats are removed and the open masonry cleaned.

<u>10.3 Plasters</u> (e.g. mineral plaster systems, front plaster systems for frame houses, front plaster systems, scratch coat pretreatment, sanitating plaster systems, special mortar, heat insulation plaster systems)

Sanitating plasters differ significantly from traditional plasters in grain fom and -type and the type and / or amount of binding agents, additives and loading material. On critical or salt heavy ground, the masonry to be dried must be covered with a sanitary plaster system made up of several layers. The evaporation zone of the salt loaded capillary water is moved from the surface of the masonry to the sanitary plaster layer. The salts will now crystalize in the pores of the sanitary plaster layer without causing damage (buffer layer). The hydrophobic system prevents a hydroscopic dampening of the salt loaded masonry as well as any dampening from the air.

<u>10.4</u> <u>Screeds</u> (e.g. ground coats, screed additives, mortar, filler, impregnation/sealing, injection resins, protective coats for oil rooms, glueing/jointing)

10.5 Concrete additives

Concrete additives are preservatives, antifoaming agents, liquefiers, inhibitors, accelerators, air-entraining agents, recycling agents and some other product types.

Antifoaming agents are used to reduce the production of foam during packing and dosage of the concrete additives as well as reducing the uncontrolled formation of air bubbles in the concrete through the additive. With regard to the desired stability of the concrete, this is a very important function. Preservatives protect the additives from a biological infestation. They insure stability during storage and keeping quality even under difficult conditions. With regard to the toxicological and ecotoxicological evaluation of the concrete additives, the concentration of these additives has to be taken into account. One example: A solvent contains an additive with 0,5 weight- %. This solvent is used in a dosage of 2 % - in relation to the concrete weight – for example in a concrete of the hardness class B 35 with 320 kg concrete/m². The final hard concrete will contain 0,0014 % of this additive.

Tributylphosphates and silicon-organic compounds are mainly used as antifoaming agents. A concrete addive ususally contains less than 0,5 % tributylphosphate.

Preservatives are added to the concrete, plasters and so on, to provide temporary protection. Most formulations of preservatives used are from the following substance groups:

- I. Formaldehyde and formaldehyde-producing compounds
- II. Phenolic compounds
- III. Isothiazolinon preparates

In the market, formaldehyde producing compounds are most common. The concentration is about 0,1 weight% of the product to be conserved. The use of slow release formaldehyde substances is especially suitable because due to the low volatility of the slow-release substances and the gradual release of formaldehyde, there is only a low concentration of formaldehyde in the gaseous phase. The second interesting substance group is made up by phenolic compunds. The concentrations used here vary between 0,2 weight% and 0,5 weight% - in relation to the total product weight. Due to the low effective concentrations, the declaration of the concrete addive is not affected by the conservation substance.

Concrete liquefiers (CL) are used to reduce the amout of water needed or to increase the plasticity. Concrete liquefiers are usually supplied in fluid form. The concentration of the active substances is between 10 and 40 weight%. The usual dosage of concrete **liquefiers** is between 0,2 and 0,5 weight percent in relation to the cement weight.

Solvents (SL) are used to reduce the amount of water needeed, to improve the plasticity. They are used to create concrete with a fluid consistency (fluid concrete).

The concentration of the active substances is also between 10 and 40 weight%. The most common dosage of solvents is between 0,8 weight% and 2 weight% in relation to the cement weight.

The raw materials mainly used for CL and SL e.g. in Germany are:

- I. Lignosulphonate
- II. Melaminesulphonate
- III. Naphthalenesulphonate
- IV. Polycarboxylate

All raw materials are watery solutions, meaning, they are free of organic solvents. Usually the polycondensationproducts of melamine and naphtaline contain traces of free formaldehyde as a result of the production process. These usually fall below the limit value for an identification obligation. The melaminesulphonates used are sulfid modified melamine-formaldehyde-condensation products. This raw material is especially suited for fluid concrete and is well suited for use with cement.

A solvent dosage of 2 weight % of a 40% solution in relation to the cement weight results in 0,1 % active substance in the final hard concrete. According to current knowledge the usual raw materials of concrete liquefiers and solvents will sorb at the border between cement particles and water shortly after the additive has been added. This quickly reduces the concentration of the active substances in the watery phase. Sorbtion experiments with calciumligninsulfonate, sodiummelaminsulfonate and sodiumnaphtalinesulfonate have shown that these substances will be bound to the cement stone to 90 % within seven days. Analysis of the pore water extracted from 28 days old cement stone under high pressure (up to 5000 bar) verified the results of these sorption experiments. After a hydration period of 28 days, the concentration of, for example calciumligninsulfonat in the pore water was only about 10 % of the amount originally added to the water. This means that, considering a hydration degree of about 80 % for this cement stone (w/z = 0,40), about 95 % of the effective substance have been sorbed to the cement.

For an evaluation of the environmental effect and recyclability of concretes which were produced with additives, the possible release of components from the additives is relevant, not the sorption behaviour. Since additives for concrete are usually not very volatile, it can be assumed that those small amounts dissolved in the pore water as a result of chemical balances will mainly be released to the environment as a result of natural duffusion processes in the fluid phase. This amounts to a leaching of less than 5% of the original substance amount. For sealed structure components as are commonly used, this diffusion process is very slow. Eluation experiments on unbroken cementstone cylinders (w/z = 0,40, diameter and height 100 mm) in the vat procedure showed that less than 0,5 % of the substance amount introduced were eluated within 24 hours. This release rate decreased further with time. Consequently the ususally damp exterior building elements show very low leaching rates. Lechings are not possible for dry interior building elements. Therefore tests for the suitability of concrete liquefiers and solvents for the construction of drinking water installations reach the following conclusions:

- 1. The United States Environmental Protection Agency (EPA) states than an addition of 4,5 weight % Melment L10/20% of the cement weight is uncritical for concrete in contact with drinking water.
- 2. Examination of mortar prisms with 2 weight % Melmet L 10/20 % according to the Belgian norm NBNS 29.004 showed, that the concrete, the fly ash and the solvent L 10/20 % fulfilled this norm and may be used for the coating of containers intended for the long term storage of drinking water since the amounts of leached fomaldehyde and melaminsulfonates were well below the limiting value of the norm.
- 3. Examination of mortar prisma with 14 ml melaminsulfonat-solution per kg cement or 14 ml naphtalinsulfonat-solution per kg cement or 4 ml sodium-ligninsulfonat-solution showed, that the tested mortars fulfilled the requirements for drinking water containers and -coats.

Therefore the additives mentioned above may be used in concretes for these purposes in Germany. Several everyday-use related test results are currently available concerning the possible emission of gaseous substances from concretes containing additives:

- a) During an examination of a plymetal sheet produced with floatings and repair plaster containing melment, a formaldehyde balancing concentration of 0,01 ppm was measured. This conforms to the blind value of the chamber.
- b) During an examination of 28 days old concrete sheets which had been produced with the highest legal dose of 32 ml/kg cement Melment L 10/20 %, a formaldehyde concentration of 0,03 ppm was measured after 120 hours in the 1m³ test chamber. The ammonia release of this concrete sheet was determined as 0,02 ppm in the 1m³ chamber. 2 year old concrete sheets with a similar content of melment resulted in a formaldehyde concentration of 0.01 ppm after a test period of 192 hours. Under similar conditions, naphtalinsulfonat (40 % solution) in a dosage of 14 ml/kg cement produced a formaldehyde concentration of 0,01 ppm after 28 days. These formaldehyde concentrations are well below the guidance value of 0,1 ppm recommended for the indoor air-formaldehyde concentration for inhabited rooms
- c) In addition to the tests on hardened concrete sheets in the 1m³ testing chamber, the formaldehyde emission of fresh concrete with solvents based on naphtalineand melaminsulfonates was measured under normal construction conditions on construction sites, in concrete transport installations, in installations for the production of ready made concrete parts and in a concrete. All these examinations resulted in formaldehyde emissions between not-measurable to 0,0245 mg/m³ air.

Due to these results we can assume that according to current knowledge, concrete with concrete liquefiers and solvents does not pose a danger for humans and environment as a result of released volatile substances.

Further additives used in concrete are

- I. stabilizing agents (restoration agents)
- II. sealing agents (restoration agents)

- III. injection agents (restoration agents)
- IV. recycling agents
- V. chromate reducers

Restoration agents (Concrete restoration, overground workings, bridges/surface protection, front protection and –restoration, joint restoration systems, hydrophobic impregnation, cleaning, stabilizing)

Some vertabrates can play a role in the deterioration of masonry. Insecticides are used against these organisms (see also product type 18: insecticides, acaricides and products to control other arthropods).

Biocides used on monuments and their efficacy to several fouling organisms (van Dokkum, 1998)

Biocide	Application mode	Algea	Lichens	Mosses	Weeds
Hydrogen peroxide	Spray	+++	++	+	+/-
НСНО	Spray	+++	+++	++	+
H ₂ COCH ₂	Spray	++++	++++	++++	++++
Pentachlorphenolate	Spray, brush	++	++	-	-
Di-isobutyl phenoxy-ethoxyethyl dimethyl benzyl ammonium chloride	Spray, brush	+++	++	+	+/-
Fluorometuron	Spray, pack	+++	+	++	++
Hexazinone	Spray, injection	++	+	+++	+++

A process that sees increasing use is **concrete recycling**. Old concrete is broken up and used as stand alone material for street building or as filler material for fresh concrete. Due to the immobility of the fixed substances bound in the CA, there are probably no difficulties concerning the use of old concrete. Preliminary results in the basic reserch of this area confirm the good experiences form everyday work.

Recycling agents for rinsing water enable the reusing of rinsing water collected during the cleaning of mixing vehicles and mixers. Recycling agents for concrete remains enable a reuse of concrete remains up to a storage time of 72 hours. The raw materials used in rinsing water and concrete remains are watery mixes made of phosphon acids and fruit acids. Phosphon acids used in recycling agents are organic derivates of phosphon acid which have a P-C-link. 2-phosphanobutan-1, 2, 4-tricarbonacid (PBTC) are preferredly used for the production of recycling agents. Fruit acids have an anitmicrobiological effect. Common substances are citric acid, wine acid, glucon acid, lactic acid and malic acid. They are hydroxycarbonic acids and have an inhibiting effect in concrete (see for example gluconates). Citric acid is preferably used for the production of recycling agents. The substance concentration is between 10 and 20 weight%. Like for example concrete liquefiers and -inhibitors, recycling agents are adsorbed on the surface of the hydration products of the cement and bound into the cement matrix during the cement hydration. There is currently no data available concerning their eluation behaviour. According to current knowledge, there is no danger to the environment or new concrete when reusing old concrete with recycling agents.

Relevant information data for ESDs

Processing

- Inclusion in materials/articles
- Application in processes

Used quantity of active substances

10.5 Concrete additives

The used concentration of **formaldehyde producers** is about 0,1 weight% of the product to be conserved.

A second group of substances are **phenolic compounds**. The used concentration here are between 0,2 weight% and 0,5 weight% - relative to the total product weight.

Isothialozinic formulations (for example chlormethylisothiazolinon/Methylisothiazolinon) as a third product type of the conservation agents are used in concentrations of 0,02 weight% to 0,2 weight%.

Emissions into the environment

10.5 Concrete additives

According to current knowledge the commonly used substances for concrete liquefiers and solvents are sorbed to the interface between cement particles and water immediately after their addition to the mixture, therefore the concentration in the watery phase drops quickly. Sorption experiments with calciumligninsulphonat, sodiummelaminsulphonat and sodiumnaphtalinsulphonate indicated, that these substances were bound to the cement stone to 90 % within seven days.

Used substance amount:

0,5 weight% relative to the finished product

Service Life

10.5 Concrete additives

Since concrete additives are usually involatile substances it can be assumed that those percentages which are dissolved in the pore water of the cement stone as a result of the chemical balance will be released to the environment mainly through natural duffusion processes. This amounts to a leaching of less than 5 % of the original substance amount. This process is slow for sealed construction objects, as used in everyday construction. Eluation experiments on unbroken cement stone cylinders (w/z = 0,40, diameter and height 100 mm) by the tub procedure indicated, that less than 0,5 % of the effective substance amount are eluated within 24 hours. This eluation rate drops further with time. Consequently the diffusion processes in commonly damp exterior building elements result in very small eluation rates. Dry interior building elements do not have any eluation at all. Experiments with 28 days old concrete sheets which had been produced with the highest legal dosage of 32 ml/kg cement melment L 10/20 %, a formaldehyde concentration of 0.03 ppm was measured in the 1 m³ test chamber after a testing period of 120 hours. The ammonia release of this concrete sheet in the 1m³ test chamber was determined at 0,02 ppm. 2 year old concrete sheets with similar concentrations of melment resulted in a fomaldehyde concentration of 0,01 ppm after a testing period of 192 hours. Naphtalenesulphonate (40 % solution) in a dosage of 14ml/kg cement indicated a formaldehyde concentration of 0,01 ppm after 28 days under the same conditions.

Biocide loss into the aquatic system:

10 % of the effective substance (0,05 % of the finished product or 0,5 kg/t finished product)

Waste Treatment

• Waste streams + relevant information

Emission routes for biocides. '+'=relevant; '-' not relevant (van Dokkum et al., 1998, modified)

Product type	Applications	Fresh surface water	Marine surfac e water*	Air indoor and outdoor	Soil	Solid waste	Waste water*
10.1	Coating systems (P)	+	-	+	+	+	-
10.2	Injection agents (P)	+	-	+	+	+	-
10.3	Plasters (P)	+	-	-	+	+	-
10.4	Screeds (P)	-	-	-	+	+	-
10.5	Concrete additives (P)	+	-	+	+	+	-

P: professional use; N: non-professional use

* For special proposes there is a use of coating systems, plasters, screeds etc also for marine systems. For those applications marine surface water will be affected.

** An effect to waste water is possible during formulation and disposal stage

• Recycling/recovery/reuse

Existing and produced emission models

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Product information of the company Deitermann

Product information of the company Sakret

Product information of the company Remmers

11 Preservatives for liquid-cooling and processing systems

Introduction

The product type 11 focuses on the biocides used in cooling and process water systems in different industrial sectors. The cooling and process water systems can be divided into three relevant sub-groups (Dokkum 1998):

- 11.1 Flow-through cooling (professional use)
- 11.2 Open recirculating cooling systems (professional use)
- 11.3 Closed recirculating cooling systems (see 7 film preservatives), (professional use)

11.1 Flow-through cooling

Water is extracted from a river, canal or lake transported to the heat-exchange module and then discharged to the surface water. According to legislation the temperature of the cooling water must not differ more than 18 °C from the temperature of the recipient waterbody. Hence cooling towers are used to reduce the temperature of the cooling water before discharge. In the cooling tower a part of the cooling water is evaporated.

11.2 Open recirculating cooling systems

In open recirculating cooling systems, the water is cooled in cooling towers, and reused for cooling. The amount of water which evaporates, must be replenished with fresh water. This amounts to about 1-3 % of the water flow of a flow-through cooling system with the same cooling capacity (Van Donk, 1996).

11.3 Closed recirculating cooling systems

In closed recirculating cooling systems, the cooling water is not discharged after cooling. To decrease the temperature of the used cooling water, it is brought into contact with air by a fine-maze system of tubes. The cooling effect comes from air ventilators. The amount of cooling water discharged is very small (<2%)(Assink, 1991).

The intake of cooling water comes from surface water or ground water. Depending on the type of the cooling system, the water is discharged immediately or after regulating the temperature. Biocides are used in the pre-treatment of the fresh water. Biocides for cooling water are used to prevent the growth of microorganism in cooling water systems. Different bacteria, fungi, algae etc. may cause problems with the function of the cooling system. The biological problems can be split into four groups:

- development of biological biofilm
- plugging and fouling
- deteroriation of wood
- microbiologically induced corrosion

Relevant information data for ESDs

Processing

- Inclusion in materials/articles
- Application in processes

Biocides are emitted trough the spray and wind drift in the cooling towers (<0,2 % of the recirculating water volume, <0,01 % in modern towers). The cooling water in recirculating systems is removed once a year. The used water is collected and treated by special companies.

Used quantity of active substances

Hence the different subgroups for cooling systems, the biocides are also subdivided into different groups

11.1 Flow-through cooling systems

The most common biocide is chlorine (like 10 ppm sodium hypochlorite) in a discontinuous treatment. Other oxidizing agents are also used. (Table 1)

11.2 Open recirculating cooling systems

For open recirculating systems oxidizing and non-oxidizing biocides are used. The range of the concentrations from non-oxidizing biocides goes from 1-50 mg/l, the concentration of oxidizing agents is much lower. (0,1-02 mg/l).

11.3 Closed recirculating cooling systems

The biocides used in closed systems are mostly organic compounds. For the Netherlands registered biocides for cooling systems are listed in Table 1. (Baltus, 1996 and additional data)

Туре	Active substance	Concentration in cooling water (mg/l)
Oxidizing	Sodium hypochlorite	0,1 – 0,2 (active chlorine)
	Chlorine dioxide	0,2
	1-bromo-3-chloro-5,5-dimethylhydantoine	2 - 7
	sodium bromide	n.d.
	Ozone	0,015 - 0,2
	Hydrogenperoxid	n.d.
Isothiazolins	2-methyl-4-isothiazolin-3-on	1 – 5 (isothiazolins)
	5-chloroo-2-methyl-4-isothiazolin-3on	
Quats	Alkyldimethylbenzylammoniumchloride	3 – 50 (quats)
	Alkyldimethylethylbenzylammoniumchloride	
	Didecycldimethylammoniumchloride	
	Poly(oxyethylene-(dimethyliminio)-ethylene- (dimethyliminio)-ethylenedichloride)	
Others	-bromo- nitrostyrene	1 – 5
	2-bromo-2-nitro-(1,3)-propanediol (bronopol)	1 – 25
	2,2-dibromo-3-nitriloproprionamide	4 – 10
	Glutaraldehyde	25 – 50
	Methylenebisbenzamide	2 – 6
	2,2-dithiobisbenzamide	n.d.
	1,2-benzoisothiazolin-3-on	n.d.

Table 1.:	Biocides used for cooling systems in the Netherlands (n.d. = no data) (Donk,
1996)	

Service Life

Waste Treatment

Waste streams + relevant information •

Emission routes for biocides. '+'=relevant; '-' not relevant (van Dokkum et al., 1998, modified)

Produc t type	Applications	Fresh surface water	Marine surface water	Air indoor and outdoor	Soil	Solid waste	Waste water
11.1	Flow-through cooling systems (P)	+	+	+	+*	-	-
11.2	Open recirculating cooling systems (P)	+	+	+	+*	-	+
11.3	Closed recirculating cooling systems (P)	-	-	+	-	-	+

P: professional use; N: non-professional use

*Contamination through Winddrift

• Recycling/recovery/reuse

Existing and produced emission models

A scenario exists for open recirculating cooling systems (Luttik et al., 1993). The parameter and model calculations are described below. The default for the losses due spray and wind drift is 0,025 %.

Parameter/variable (unit)	Symbol	Default	C/R/E/O
Input:			
Dilution factor in receiving surface water (-)	F _{dilut}	3	Е
Or:			
Quantity of water discharged per day (m ³ /day)	Q _{water}		R
Surface water flow (m ³ /day)	Q _{surf}		R
And:			
Concentration of a.i. in cooling water (mg/l)	C _{a.i.}	0,5	R/E
Only circulation systems:			
Quantity of water in circulation per day (m ³ /day)	Q_{circ}	10000	R/E
Fraction of water lost due to spray and wind drift (-)	W_{depos}	0,00025	R/E
Soil surface where deposition occurs (m ²)	A _{soil}	100	R/E
Output:			
If flow water discharged and receiving water are input	F _{dilut}		
Concentration of a.i. in receiving surface water (mg/l)	C _{surf}		
Daily dosage of 1 m 2 soil surface with a.i. (mg/m ² *day)	D _{soil}		

=Constant (if possible the constants are presented) С

=(Required) values from the test results in the notification of a biocide R

=Expert estimations (if possible the expert estimations (defaults) are presented)

E =Expert estimations (if possible the corporation O =Output from previous modules/calculations

Model calculations:

 $F_{dilut} = (Q_{water} + Q_{surf}) / Q_{water}$ $C_{surf} = C_{a.i.} / F_{dilut}$ $D_{soil} = Q_{circ} * C_{a.i.} * W_{depos} / A_{soil} * 10^{3}$

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12 Slimicides

Introduction

Slimicides are biocides used to control slime-producing microorganisms in industrial processes (Eriksson et al., 1996), mostly in water circuits. Slimicides are used in large quantities in different industrial sectors, examples are:

- Pulp and paper industry
- Oil industry
- Sugar industry
- Textile industry
- Leather industry

For information for active substances used in the Textile and Leather industry, see product type 9. So the product type 12 "Slimicides" can be subdivided in the following relevant subgroups:

- 12.1 Pulp and Paper industry (professional use)
- 12.2 Oil industry (professional use)
- 12.3 Sugar industry (professional use)

Depending on the focus, there is a potential overlap with cooling water biocides and in can preservations. Slimicides are used in industrial process fluids, in cases were slime formation might cause hampering of the process-operation, or deterioration of intermediate or end products.

12.1 Paper industry

The materials used in the pulp and paper industry offer a favourable environment for the growth of microorganisms. Microorganisms can be harmful by producing slime, which can interfere with the processing. Other organism produces sulphite through the anaerobic reduction of sulphur compounds or sulphuric acid through aerobic oxidation, which causes corrosion. Each pulp has its own specific environment, and therefore biocidal treatment of slime is very difficult. A variety of active substances are in use. The main function of the slimicides is to suppress the microbial growth of the microorganism. This can be achieved by a continuous supply of a biostatic or by a single or repeated shock treatment with elevated doses. A good housekeeping supports these measures.

Slimicides used in the paper industry include aldehydes, phenol derivates, heterocyclic N, S compounds, thiocarbamates and thiocyanates. (Baumann et al., 1993)

12.2 Oil industry

In oil and gas production, biocides are used for many different applications. They are used in formulations for the preservation of drilling muds, work over fluids, fracturing fluids, hydraulic fluids and in great amounts for the preservation of injection water.

The use of injection water is necessary when the pressure of the reservoir is not high enough to drive the oil out the reservoir automatically. Therefore seawater is pumped into the well to drive out the oil. The mixture of water and oil is separated on the production platform, and the water is injected again. In the well, anaerobic, reducing conditions predominate. The presence of microorganism causes different problems, such as corrosion, the formation of HOS gas or they produce slime, which can clog filters. (Paulus, 1993)

12.3 Sugar Industry (Luttik, 1993)

In the sugar industry biocides are used in cooling water treatment and for the desinfection of the extraction units. For information about cooling water treatment see productgroup 11 "Preservation for liquid cooling and processing systems". The process and cooling water in the sugar industry is reycled largely and the the waste water finally discharged into the sewer for treatmentin a STP amounts 400-650 litres per ton of beets.

Relevant information data for ESDs

Processing

- Inclusion in materials
- Application in processes

Used quantity of active substances

12.1 Slimicides in paper industry

The amount of slimicide products used is 20-200 grams per ton produced paper. The fraction of active substance in the products is app. 25%. (Baumann et al., 1993). Other amounts are listed in Haskoning (Haskoning, 1995):

50-1000 grams per ton dry fibre

0,25 to 150 ppm in process water

12.2 Slimicides for secondary oil recovery

The main substances used in biocide formulations, which are used in the oil industry, are (Herbert, 1995):

- · aldehydes (acrolein, glutaraldehyd, formaldehyd)
- biguanides (esp. cationic polymeric biguanides)
- isothiazolines
- · quaterny ammonuim compounds, diamines and amine acetate salts

Against sulphate reducing bacteria in off-shore industry:

100 mg/l CTAB (cetyltrimethyl-ammonium bromide, glutaraldehyd) (Board et al., 1987)

30-100 mg/l against planktonic SRB 50-800 mg/l sessile SRB

12.3 Sugar industry (professional use), (Luttik, 1993)

The main active substances used for the desinfection of extraction units is a formaldehyde solution (40 % formalin). In the Netherlands the average capacity of a sugar factory is 250 – 550 tons of sugar beets per hour. Per tonne of sugar beets 50 –75 grams of formaldehyde is applied. The production process is carried out continuously over 3 months up to 4,5 months.

Service Life

Waste Treatment

• Waste streams + relevant information

Emission routes for biocides. '+'=relevant; '-' not relevant

(van Dokkum et al., 1998, modified)

Product type	Applications	Fresh surface water	Marine surface water	Air indoor and outdoor	Soil	Solid waste	Waste water
12.1	Slimicides in paper industry (P)	+	+	-	-	-	+
12.2	Slimicides for secondary oil recovery (P)	-	+	-	-	-	-
12.3	Slimicides in sugar industry (P)	+	+	-	-	-	+

P: professional use; N: non-professional use

• Recycling/recovery/reuse

Existing and produced emission models

12.1 Paper/cardboard (Luttik et al., 1993)

From Luttik et al. a model was developed for the Netherlands paper and cardboard industry. The production volume lies between 20.000 and 200.000 tons per year. In many cases paper and cardboard producers have their own STP.

In the scenario an industrial STP is used, because the water consumption lies between $800 \text{ m}^3 - 11.000 \text{ m}^3$ per day. The default value of the flow equal to the waste quantities is 3000 m^3 per day.

Parameter/variable (unit)	Symbol	Default	C/R/E/O
Input:			
Quantity of water discharged per day (m ³ /day)	Q _{water}	3000	R/E
Concentration of a.i. in process water discharged (mg/l)	C _{a.i.}		R
Quantity of water in STP (m ³ /day)	Q_{STP}	3000	R/E
Dilution factor of receiving surface water (-)	F _{dilut}	10	E(D)
Output:			
Concentration of a.i. receiving surface water (mg/l)	C_{surf}		

Model calculations:

L_{wwt} Quantity of a.i. totally released w. waste water (kg/day)

 $= Q_{water} * C_{a.i.} * 10^{-3}$

R_{STP}: Fraction removed by STP Calculation by standard module of USES

 $\frac{C_{surf}}{C = Constant (if possible the contents are presented)} = \frac{L_{wwt} / Q_{STP} * R_{STP} / F_{dilut} * 10^{-3}}{C = Constant (if possible the contents are presented)}$

R = (Required) values from the test results in the notification of a biocide

E = Expert estimations (if possible the expert estimations (defaults) are presented)

O = Output from previous modules/calculations

12.1 Paper/cardboard (Eriksson, 1995)

To compare the different slimicidal active substances the Swedish National Chemicals Inspectorate has performed calculations of predicted environmental concentrations according to three different scenarios, which are summarize below.

	Fine paper mill (scenario 1)	Newspaper Mill (scenario 2)	Newspaper Mill (scenario 3)
Water consumption	5000m ³ /d	25000 m ³ /d	28000 m ³ /d
volume white water circuit	300 m ³	10000 m ³ /d	300 m ³ /d
Dosage	15 min every 12 h	15 min every 12 h	15 min every 12 h
average retention time white water	40 min at 50°C and pH 4,5	60 min at 50°C and pH 4,5	20 min at 50°C and pH 4,5
average retention time clarifier (sedimentation & chemical precipation)	20 hours at 35°C and pH 7	12 hours at 35°C and pH 7 (only sedimentation)	5 hours at 35°C and pH 7 (only sedimentation)
average retention time aerated basin		20 hours at 30°C and pH 7	12 hours at 30°C and pH 7
average retention time secondary clarifier (sedimentation & chemical precipation)		15 hours at 25°C and pH 7	5 hours at 25°C and pH 7

The distribution to sludge is estimated from results of USES.

12.1 Paper/cardboard (Finish Environmental Institute)

The Finish Environmental Institute used different scenarios for calculations of predicted environmental concentrations, PEC, for the slimicides in the Finnish paper mill industry

The Equations presented here are used in the Excel-spreadsheet-based model to compute the concentrations of slimicides in the paper making process, sewage treatment plant and environment.

The properties of the active ingredient

Here are given the DT50 for hydrolysis at pH 5 and 7, photolysis and biodegradation in water/sediment system and in the activated sludge. If DT50 is not measured for the activated sludge, as a conservative estimate it is assumed that the biodegradation in activated sludge occurs twice as fast as in water or a water/sediment system and thus the DT50 for activated sludge is DT50 for water/sediment is divided by 2. On the basis of DT50, the rate constant is calculated from the formula:

Rate constant (d-1) k=ln 2/DT50 (d)

Scenario (mill) 1

The mill produces 540 tons of paper a day. The waste water volume is higher than normally, 800 m³/h. (Note: Average effluent discharge of a Finnish paper mill is 20 000 m³/d. The average number of yearly emission days of a Finnish paper mill is almost 365 days.) The pH is 5 and temperature 55-60 °C during the process. The retention time of water in the process is half an hour. In the waste water treatment plant (WWTP) the pH is adjusted to 7 and the temperature is 35°C. The retention time for the three treatment methods at minimum are the following:

Preliminary settling and chemical/mechanical treatment 4 h.

Activated sludge unit treatment 4 h and subsequent secondary settling 4 h.

Biological treatment with the long retention time 48 h (including secondary settling).

The preliminary settling always precedes the activated sludge and other biological treatments.

Concentrations in the process water before the waste water treatment plant

The concentrations during the process (retention time 30 min):

Before any degradation (theoretical)	C=(conc _{a.i} ./Waste Water volume) x (Daily
production/24 h)	

Hydrolysis	$C_{h}=C \times e^{(-khydr5 \times 0,5/24)}$
Biodegradation	$C_{b}=C \times e^{(-kbiol \times 0,5/24)}$

Average concentrations at the waste water treatment plant

After preliminary settling (retention time 4 h):

Hydrolysis	C _{preh} =C _h x e ^(-khydr x 4/24)
Biodegradation	$C_{\text{pre}} = C_{\text{b}} \times e^{(-\text{kbiol} \times 4/24)}$

In the activated sludge unit (short retention time, 4 h): PEC (to compare with the PNEC for microorganisms) The average concentration is calculated in the middle of the r

The average concentration is calculated in the middle of the retention time in the STP (assuming homogenous mixing in the aeration tank), thus the retention time x 0.5

Hydrolysis	$C_{eah}=C_{preh} \times e^{(-khydr \times (4+4)/24)}$
Biodegradation	$C_a = C_{\text{pre}} \times e^{(-\text{kasl} \times 4 \times 0, 5/24)}$

In the biological treatment with retention time of 48 h (=long retention time): PEC (to compare with the PNEC for microorganisms)

The average concentration is calculated in the middle of the retention time in the STP (assuming homogenous mixing in the aeration basin), thus the retention time x 0.5

Hydrolysis

$$C_{\text{bih}} = C_{\text{preh}} \times e^{(-\text{khydr} \times 48 \times 0, 5/24)}$$

Photolysis (which is assumed to include also hydrolysis); the photolysis is presumed to occur under day time (i.e. half of time)

 $C_{bif} = C_{preh} \times e^{(-kphotol \times 48 \times 0.5 \times 0.5/24)}$

Biodegradation (which is assumed to include also hydrolysis) $C_{\text{bib}}=C_{\text{preb}} \times e^{(\text{-kbiol} \times 48 \times 0,5/24)}$

Biodegradation and photolysis (assuming that photolysis and biodegradation are two independent processes which both follow first order kinetics, and that photolysis occurs before biodegradation)

C_{bib+f}=C_{preb}-(C_{preb}-C_{bf})-(C_{preb}-C_{bb}) x [C_{preb}-(C_{preb}-C_{bf})/C_{preb}]

<u>Environmental concentrations after the waste water treatment plant</u> (to compare with the PNEC for aquatic organisms and considering an appropriate dilution factor)

After chemical/mechanical treatment (retention time 4 h): PEC (same as the concentration after the preliminary settling)

 $\begin{array}{ll} \mbox{Hydrolysis} & C_{eah} = C_{preh} \; x \; e^{(-khydr \; x \; (4+4)/24)} \\ \mbox{Biodegradation} & C_{em} = C_b \; x \; e^{(-kbiol \; x \; 4/24)} \end{array}$

After the activated sludge unit (retention time 4 + 4 h): PEC

Hydrolysis	$C_{eah} = C_{preh} \times e^{(-khydr \times (4+4)/24)}$
Biodegradation	$C_{ea} = C^{pre} \times e^{(-kasl \times 4/24)} \times e^{(-kbiol \times 4/24)}$

After the biological treatment with long retention time (48 h): PEC

Hydrolysis

 $C_{ebih} = C_{preh} \times e^{(-khydr \times 48/24)}$

Hydrolysis and photolysis; the photolysis is assumed to occur under day time (half of time) $C_{ebif}=C_{preh} \times e^{(-kphotol \times 48 \times 0,5/24)}$

Biodegradation

Cebi=Cpre x e^(-kbiol x 48/24)

Biodegradation and photolysis (assuming that photolysis and biodegradation are two independent processes which both follow first order kinetics, and that photolysis occurs before biodegradation)

Cebib+f=Cpreb-(Cpreb-Cebf)-(Cpreb-Cebb) x [Cpreb-(Cpreb-Cebf)/Cpreb]

Scenario (mill) 2

The mill produces waste water 8740 m³ d-1, of which 60 % is from the short circulation of the wire part in the paper machine. (Note: Average effluent discharge of a Finnish paper mill is 20 000 m³/d. The average number of yearly emission days of a Finnish paper mill is almost 365 days.) The pH is 5 and temperature 55-60 °C during the process. The retention time of water in the process is half an hour. In the waste water treatment plant (WWTP) the pH is adjusted to 7 and the temperature is 35 °C. The retention time for the three treatment methods at minimum are the following:

- Preliminary settling and chemical/mechanical treatment 4 h
- Activated sludge treatment 4 h and subsequent secondary settling 4 h
- Biological treatment with the long retention time 48 h (including secondary settling)

The preliminary settling always precedes the activated sludge and biological pond treatments.

Daily average and maximum concentrations in the process water before the waste water treatment plant

The concentrations during the process (retention time 30 min):

The average daily concentration in the wire part

C=((additions x length of addition/24) x conc_{a.i.} x WWvol x 60 %)/(WWvol x 60 %)

The average daily concentration after the dilution in the wire part

Caverage=(additions x length of addition/24 x conca.i. x WWvol x 60 %)/WWvol

The concentration before the waste water treatment plant

Hydrolysis, average $C_h=C_{average} \times e^{(-khydr5 \times 0.5/24)}$ Biodegradation, max. conc. $C_b=C_{average} \times e^{(-kbiol \times 0.5/24)}$ Biodegradation, average $C_b=C_{average} \times e^{(-kbiol \times 0.5/24)}$	Hydrolysis, max. conc.	$C_{hmax} = (conc_{a.i.}/(100/60)) \times e^{(-khydr5 \times 0.5/24)}$
Biodegradation, max. conc. $C_{bmax}=(Conc_{a.i}/(100/60)) \times e^{-kbiol \times 0.5/24}$	Hydrolysis, average	$C_{h} = C_{\text{average}} \times e^{(-kn) d(5 \times 0.5/24)}$
	Biodegradation, max. conc.	$C_{bmax} = (CONC_{a.i.}/(100/60)) \times e^{-Kbiol \times 0.5/24}$

Daily average and maximum concentrations at the waste water treatment plant

After the preliminary settling (retention time 4 h):

Hydrolysis, max. conc.	$C_{\text{prehmax}}=(C_{\text{hmax}} \times \text{length of add./4}) \times e^{(-khydr \times 4/24)}$
Hvdrolvsis, average	$C_{\text{preh}} = C_h \times e_{(kh)(dr \times 4/24)}$
Biodegradation, max. conc.	$\begin{array}{l} C_{\text{prebmax}}=(C_{\text{bmax}} \times \text{length of add./4}) \times e^{(-kbiol \times 4/24)} \\ C_{\text{preb}}=C_b \times e^{(-kbiol \times 4/24)} \end{array}$
Biodegradation, average	$C_{\text{preb}} = C_b \times e^{(-Kbiol \times 4/24)}$

In the activated sludge unit (short retention time, 4 h): PEC (to compare with the PNEC for microorganisms) The concentration is computed in the middle of the retention time in the STP (assuming homogenous mixing in the aeration tank), thus retention time x 0.5

In the biological treatment with long retention time of (48 h): PEC

(to compare with the PNEC for microorganisms)

The concentration is computed in the middle of the retention time in the STP (assuming homogenous mixing in the aeration basin), thus retention time x 0.5

Hydrolysis, average conc. $C_{\text{bih}}{=}C_{\text{preh}} \mathrel{x} e^{(\text{-khydr} \mathrel{x} 48 \mathrel{x} 0,5/24)}$

Photolysis, average conc. (which is assumed to include also hydrolysis); photolysis is assumed to occur under day time (i.e. half of time) $C_{\text{bif}}=C_{\text{preh}} \times e^{(-kphotol \times 48 \times 0.5 \times 0.5/24)}$

Biodegradation, average conc. (which is assumed to include also hydrolysis) $C_{bib} = C_{preb} \times e_{(-kbiol \times 48 \times 0.5/24)}$

Biodegradation and photolysis (assuming that photolysis and biodegradation are two independent processes which both follow first order kinetics, and that photolysis occurs before biodegradation)

 $C_{\text{bib+f}} = C_{\text{preb}} - (C_{\text{preb}} - C_{\text{bf}}) - (C_{\text{preb}} - C_{\text{bb}}) \times [C_{\text{preb}} - (C_{\text{preb}} - C_{\text{bf}})/C_{\text{preb}}]$

Environmental concentrations after the waste water treatment plant (to compare with the PNEC for aquatic organisms and considering an appropriate dilution factor)

After chemical/mechanical treatment (retention time 4 h): PEC =C_{pre max}= Biodegradation (b) or hydrolysis (h), maximum concentration after preliminary settling

Hydrolysis, max. conc.	$C_{emh}=(C_{hmax} \times length of addition/4) \times e^{(-khydr \times 4/24)}$
Biodegradation, max. conc.	$C_{emb} = (C_{bmax} \times length of add./4) \times e^{(-kbiol \times 4/24)}$

After the activated sludge treatment (retention time 4 + 4 h): PEC

Hydrolysis, max. conc.	$C_{eah} = C_{preh} \times e^{(-khydr \times (4+4)/24)}$
Biodegradation, max. conc.	$C_{eab} = C_{prebmax} \times e^{(-kasl \times 4/24)} \times e^{(-kbiol \times 4/24)}$

After the biological treatment with long retention time (48 h): PEC

Hydrolysis, average

 $C_{\text{ebih}} = C_{\text{preh}} \; x \; e^{(\text{-khydr} \; x \; 48/24)}$

Hydrolysis and photolysis; the photolysis is assumed to occur under day-time (half of time) $C_{ebif} = C_{preh} \times e^{(-kphotol \times 48 \times 0.5/24)}$

Biodegradation, average

$$C_{ebib} = C_{preb} \times e^{(-kbiol \times 48/24)}$$

Biodegradation and photolysis (assuming that photolysis and biodegradation are two independent processes which both follow first order kinetics, and that photolysis occurs before biodegradation)

C_{ebib+f}=C_{preb}-(C_{preb}-C_{ebf})-(C_{preb}-C_{ebib}) x [C_{preb}-(C_{preb}-C_{ebf})/C_{preb}]

Abbreviations:

C h f	concentration hydrolysis photolysis
b	biodegradation
pre	preliminary settling
а	activated sludge unit (short retention time, 4 + 4 h)
bi	biological treatment with retention time of 48 h (=long retention time)
е	environment
m	chemical/mechanical

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13 Metalworking-fluid preservatives

Introduction

The metal industry could be divided into different working sectors. These are

- blast furnaces
- iron foundry
- rolling mills
- metal forming
- metal cutting
- galvanic industry

Metalworking fluids are used only in the sectors metal forming/cutting and galvanic industry. The greatest amounts of metalworking fluids are used in the metal cutting industry. No biocides are used in the modern galvanic industry. The exceptions are some metal degreasing procedures.

13.1 Metal forming/cutting

Metalworking fluids are used in a small amounts in the metal forming industry. No biocides are used in the fluid employed here.

The main fraction of metalworking fluids are used in the metal cutting industry for their cooling and lubricating abilities. Cooling lubricants are used during manufacture and production in the metal working industry. Water-miscible and non-water miscible cooling lubricants are used in metal working to reduce the friction, to remove arising heat and to sweep away metal chips from the cutting place. For water-miscible cooling lubricants. A cooling lubricant is composed of many different substances, these influence, among other things the workmanship, the surface finish, the corrosive behaviour, the productivity and the tool wear. Water miscible lubricants are delivered as concentrates, which are diluted with water before use. In many cases water based cooling lubricants are often used in circulation systems, to increase the emulsion lifetime and for the suppression of unwanted odours, biocides are used in water-miscible cooling lubricants. (Margoni, 1997)

Relevant information data for ESDs:

Processing

- Inclusion in materials/articles
- Application in processes

It is not normaly economic to recover water based coolants from swarf, so dragout on swarf is the major exit route for the cutting fluid from the process, except in the case where more frequent changes are necessary due poor standard of housekeeping and fluid maintance. The table below summarises the losses of water based coolants and the emission to the environment. (Margoni, 1997)

Losses/annum	Emission to
Misting/evaporation 5%	Air
Overalls 2%	Water
Leaks 3%	Waste oil/water
Dragout-swarf 87%	90% oxidised oil to air
	10 % to landfill
Dragout-workpiece 3 %	Water 1 %
	Chemical waste – alkaline degreasant 2%

Used quantity of active substances

The main substances used as biocides in metalworking fluids are (Baumann, 1996):

- aldehydes (like triazine, oxazolidine)
- fatty acid ester
- heterocyclic substances with N,O,S (benzotrialzole, thiazole)
- boron compounds

Typically a concentration of 1-5 % of biocide is contained in the concentrated oil by the formulator to give a concentration of about 0,15 % in the working solution (Haskoning 1995)

Service Life

Waste Treatment

• Waste streams + relevant information

Emission routes for biocides. '+'=relevant; '-' not relevant

(van Dokkum et al., 1998, modified)

Produc t type	Applications	Fresh surfac e water	Marine surface water	Air indoor and outdoor	Soil	Solid waste	Waste water
13.	Metalworking-fluid preservation (P)	-	-	25-60 weight %	-	5-20 weight %	(+)

P: professional use; N: non-professional use

• Recycling/recovery/reuse

Waste emulsion from large machine shops is split before disposal. The whole system would be replenished at intervals of between 1 and 6 month depending on th ability of the operator to maintain the oil in good condition by proper houskeeping, (Margoni, 1997).

Existing and produced emission models

Luttik et al. (Luttik et al., 1993) presented a scenario, which is based on van der Poel and Ros (1987). The biocides emission is calculated, but according to EU-legislation there is no emission into wastewater during the processing step. The only emission into wastewater is the emission during waste/recovery treatment.

The ESD IC8 (Metal Processing) described the discharge into the compartment water from two types of water miscible cooling lubricants during the waste/recovery treatment. The two types are:

- Cooling lubricant emulsion
- Aqueous cooling lubricant solutions

Cooling lubricant emulsion

An estimation of the release of a covered cooling lubricant additive in the watery phase is done with the aid of the Nernst distribution law. Therefore to determine the release of a substance or the appropriate cooling lubricant additive, specific substance data has to be available. In addition to this, the capacity of the point source is required.

If the substance is not part of the whole fraction to be disposed off, the default value f=1 can be lowered if appropriate information is provided by the notifier or the industry about the relevance of the substance. If a chemical or physical treatment takes place the fraction of elimination can be considered.

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

$$C_{wp} = C_{CLE} \cdot \frac{f \cdot (m+1)}{\left(m \cdot K_{OW} + +1\right)} \cdot (1 - El) \qquad \text{and} \qquad V_W = \frac{V_{CLE}}{m+1}$$

the release is calculated as follows:

$$Elocal_{water} = C_{CLE} \cdot V_{CLE} \cdot \frac{f}{\left(m \cdot K_{OW} + 1\right)} \cdot (1 - El)$$

Symbols: symbol explanation Unit default C/R/E/O $[kg d^{-1}]$ **Elocal**_{water} emission per day $[mg l^{-1}]$ concentration of the Cwp chemical in the untreated sewage water phase of the lubricant $[kg m^{-3}]$ R CLIF concentration of the chemical in the cooling lubricant $[m^3 d^{-1}]$ VCLF treated volume of 200 m³d- E cooling lubricant per day 1 (average) $[m^3 d^{-1}]$ Vw volume of the treated water phase

m	volume ratio oil phase / water phase	[-]	1:20	R
K _{ow}	partition coefficient between n-octanol and water (KOW=10log KOW)	[-]		R
EI	fraction of elimination of the chemical during physical or chemical treatment	[-]	0	R
f	factor of relevance	[-]	1	R
C =Constant (if possible the constants are presented)			

R =(Required) values from the test results in the notification of a biocide

E =Expert estimations (if possible the expert estimations (defaults) are presented)

O =Output from previous modules/calculations

Aqueous cooling lubricant solutions

For water-soluble cooling lubricants the concentration of the chemical in the untreated water phase of the lubricant is similar to the concentration of the substance in the lubricant solution that is either given by notifier, industry or calculated from the lubricant to water mixture ratio.

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

The release is calculated as follows:

 $Elocal_{water} = C_{ACL} \cdot V_{ACL} \cdot m \cdot (1 - El) \cdot f$

Symbols:					
symbol	Explanation	unit	default		C/R/E/O
Elocal _{water}	emission per day	[kg d-1]			
C _{ACL}	concentration of the	[kg m-3]		R	
	chemical in the				
	aqueous cooling lubricant				
V _{ACL}	treated volume	[m³ d-1]	40	Е	
m	volume ratio oil phase/	[-]	1:20	R	
	water phase				
EI	fraction of elimination	[-]	0,8	R	
	of the chemical during				
	physical or chemical				
	treatment				
f	factor of relevance	[-]	1	R	

C =Constant (if possible the constants are presented)

R =(Required) values from the test results in the notification of a biocide

E =Expert estimations (if posssible the expert estimations (defaults) are presented)

O =Output from previous modules/calculations

Margoni et al. (Margoni, 1997) describes a example release calculation for an corrosion inhibitor in an semi-synthetic metalworking fluid. The results of the calculation with a biocide concentration are presented below.

Total EU usage = 100 tonnes Concentration in fluid = 2 %

Thus the total amount of fluid containing biocide is 5000 t/year

Local release during use at a large metalworking plant

Size of holding tank	= 10 000	litres
Amount of biocide*	= 200	kg
Loss of biocide to air =5 %	= 10	kg/year
Loss of biocide to water (overalls) =2 %	= 4	kg/year
Loss of biocide to water (leaks) = 3 %	= 6	kg/year
Loss of biocide to waste =2 %	= 4	kg/year
Loss to water from workpiece dragout =1 %	= 2	kg/year
Loss of biocide on swarf dragout =87 %	= 174	kg/year

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14 Rodenticides

Introduction

Rodenticides are biocidal products used to control rodents such as different types of mice, rats, moles and other small rodents. Their non-agricultural use is in and around homes, commercial and industrial sites, lawns, golf courses, highway medians, etc.

In order of the relevance of the different industrial sectors, the product type 14 "Rodenticide" can be subdivided depending on the application technique and the location in the following subgroups:

- 14.1 Fumigation products used outdoors (professional use)
- 14.2 Fumigation products used with fumigation installation (professional use)
- 14.3 Fumigation products for indoor-use, products used on skin (indoors), (professional use)
- 14.4 Pest control products for powder application, powders, dust, powder concentrates and tracking powders (contact powders) used in closed spaces (professional and non-professional use)
- 14.5 Baits used in outdoors (professional and non-professional use)
- 14.6 Baits used in sewer systems (professional and non-professional use)
- 14.7 Baits used in closed spaces and animal housings (professional and non-professional use)

Rodenticides are applied indoors and outdoors by professionals and are also used for doit-yourself purposes. The application range for rodenticides range includes in and around public buildings, in industrial areas, for transport facilities, in animal housings, in and private ground, on water banks, in and around sewer systems, around waste disposal and waste dump (Balk, 1998).

The rodenticide formulations include baits (ready-to-use baits (liquid or solid), liquid concentrates to prepare baits) and tracking powders (contact powders). Gasses or gas- or smoke forming biocides are applied by professionals only in closed spaces. The main formulation for outdoor use is baits, for example wax blocks. Fumigation can be used outdoors to combat rats in their burrows.

The rodenticides can be classified into inorganic compounds including arsenic, thallium, phosphorus, barium carbonate, zinc phosphine and inorganic compounds including sodium fluoroacetate, alpha-naphthyl-thiourea, anticoagulants and strychnine.

The most important active ingredients among the rodenticides are the anticoagulants like the hydrocoumarins Warfarin, Warficide, Bromadiolone, Brodifacoum, Diphenadione, Coumachlor, Coumafuryl, Fumasol, Prolin and the indandiones like Valone as well as Pindone (Meulenbelt, 1996). They are chronic poisons and usually applied in baits. Several feedings are required to accumulate lethal amounts, which reduces the risk for non-target animals. Other acute working poisons are hydrogen cyanide and phosphine (fumigation).

In Germany, 51 products are used as rodenticides, which may contain the 9 following active substances: Hydrogen cyanide, Brodifacoum, Bromadiolon, Chlorphacinon, Difenacoum, Difeethialon, Flocoumafen, Warafin and Zinc phosphide. The most important rodenticides are Warfarin, Diphacinone and Zinc phosphide.

Warfarin (coumafene, zoocoumarin) is an anti-clotting pesticide that causes internal bleeding after ingestion. It is used for controlling rats and house mice. Formulations of Warfarin are ready-to-use bait, concentrate, powder, liquid concentrate, nylon pouch coated talc and dust formulations. In the Netherlands it has not been allowed since 1994, because of problems of resistance against Warfarin.

Diphacinone is an anticoagulent rodenticide bait for the control of rats, mice, voles and other rodents. It is available as meal, pellet, wax block, liquid bait, tracking powder and concentrate formulations.

Zinc phosphide is an inorganic biocide for control of rats, mice, voles, ground squirrels, musk-rats and other rodents. Because of its non-agricultural use it is applied to lawn, golf courses, highway medians and as tracking powder for control of house mice. Zinc phosphide is formulated as grain based baits, scrap bait or paste.

Relevant information data for ESDs

Processing

- Inclusion in materials/articles
- Application in processes

Used quantity of active substances

Substances used as rodenticides are: Multidose substance: doses 0,005 - 0,01 % (Haskoning, 1995) alpha-naphthyl-thiourea

Antu: 0,5 – 2 % Powder and liquid concentrate (Scholl, 18/96) Arsenic Barium carbonate Brodifacoum: 0,005 % a.i. feed poison in preparated, pourable baits; I (BgVV) 0,005 % a.i. pourable baits; I (BgVV) 0,005 % a.i. ready use wax block bait; I (BgVV) Bromadiolon: 0,0046 % a.i. feed poison in preparated, pourable baits; I (BgVV) 0,005 % a.i. pourable baits; O, I (BgVV) bait (50 mg/kg), single dose, formulation for preparation of bait: 0,25 g/l of dry powder (van Dokkum, 1998) Bromethalin: 0.005 % bait (Scholl, 18/96) 0,1 % and 2 % concentrate (Scholl, 18/96) Chloralose: \leq 40 g/kg bait against mice, trained personal (ed. Tomlin, 1997) Chlorphacinon: (old fashion) 50 – 250 mg/kg bait (van Dokkum, 1998) Cholecalciferol: 0,75 % pellets, grains (Scholl, 18/96) Coumachlor: 1 % bait concentrate (Scholl, 18/96) Coumafuryl: 1 % bait concentrate (Scholl, 18/96) Coumatetralyl: 0,04 % a.i. pourable baits; O, I (BgVV) 0,0015 % a.i. feed poison in preparated, pourable baits; O, I (BgVV) Crimidin: 0,5 % pellets (Scholl, 18/96) 0,1 % grain baits (Scholl, 18/96) Difenacoum: 0,005 % a.i. pourable baits; I (BgVV)

0,005 % a.i. feed poison in preparated, pourable baits; I (BgVV) 0,005 % a.i. ready use Form baits (ratbait); I (BgVV) Difethialon: 0,0025 % a.i. pourable baits; O, I (BgVV) 0,0025 % a.i. paste as ready use bait; I (BgVV) Diphenadione Flocoumafen: 0,005 % a.i. pourable Form baits); I (BgVV) Fumasol Hydrogen cyanide: 9 % for gassing; I (BgVV) fumigating enclosed spaces (stored grain in warehouses, glasshouses, rabbit burrows, rat runs (trained personal) Formulations packed in metal containers; also absorbed on porous material, formulation 400 g a.i./kg (water soluble powder), (ed. Tomlin, 1997) Methylbromide Norbromid: 0,5 % baits (Scholl, 18/96) Phosphine Phosphorus Pindone: 0,025 baits (Scholl, 18/96) 0,5-2 % powder concentrate (Scholl, 18/96) Prolin Scillirosid: 0,015-0,05 % baits (Scholl, 18/96) Sodium flouroacetamide Sodium flouroacetate Strychnine: 0,5-1,8 % concentrate powder Thalliumsulfat: 2 % grain baits (Scholl, 18/96) Valone Warfarin: 0,04 % (granule); 0,055 % (ready use bait); 0,079 % (ready use bait); 0,08 % (ready use bait) a.i. pourable baits; O, I) (BgVV) 0,055 % (ratring); 0,075 % (ratdiscs) a.i. ready use Form baits; O, I (BgVV) 0.048 % a.i. stomach poison in preparated, pourable baits; O, I (BgVV) 0,045 % a.i. stomach poison in preparated, pourable baits; O, I (BgVV) 0,079 % a.i. stomach poison in preparated, pourable baits; O, I (BgVV) 0,047 % a.i. stomach poison in preparated, pourable baits; O, I (BgVV) Warficide Zinc phosphide: [well known rodenticide against rats on landfills, application rate in agriculture 8-10 lb/A (Scholl, 18/96)] 80-95 % concentrate (Scholl, 18/96) 0,5-3 % baits (Scholl, 18/96) 5-10 % paste (Scholl, 18/96) 10 % powder (Scholl, 18/96)

I - used indoors, O - used outdoors

Service Life

Waste Treatment

• Waste streams + relevant information

Emission routes for biocides. '+'=relevant; '-' not relevant

(van Dokkum et al., 1998, modified) [weight %]

Product type	Applications	Fresh surface water	Marine surface water	Air indoor and outdoo r	Soil	Solid Waste	Waste water
14.1	Fumigation products used outdoors (P)	-	-	+	+	-	-
14.2	Fumigation products used with fumigation installation (P)	-	-	50 %	-	50 %	-
14.3	Fumigation products for indoor-use, products used on skin (indoors), (P)	-	-	+	-	-	-
14.4	Pest control products for powder application, powders, dust, powder concentrates and tracking powders (contact powders) used in closed spaces (P+N)	-	-	+	-	+	+
14.5	Baits used outdoors (P+N)	+	-	-	+	+	-
14.6	Baits used in sewer systems (P+N)	-	-	-	-	-	+
14.6	Baits used in closed spaces and animal housings (P+N)	-	-	+	-	+	+

P: professional use; N: non-professional use

• Recycling/recovery/reuse

Existing and produced emission models

Regional water suppliers were asked, but their information is treated as confidential and therefore could not be supplied to us.

A regional producer told us that special buckets are used on waste dumps near the rat holes. The closed buckets have two holes for the rats to enter and the center of the bucket contains a fixed bait. In this manner the environmental campartments are not exposed. A regional waste management organisation was ask but their information is treated as confidential and therefore could not be supplied to us.

14.3 Fumigation products for indoor-use

One of the application methods of rodenticides is fogging, in which the product is applied gaseously. R. Luttik shows a model for calculating release to the air for compounds used for fumigation of buildings, silos, etc. (Luttik, 1995).

Parameter/variable(unit)	Symbol	Default	C/R/E/O
Input:			
Amount used (kg)	Q _{subst}		R
Fraction of retention in goods (-)	F _{ret}	0,02	E
Fraction of disintegration (-)	F _{desin}	0,001	Е
Output:			
Emission to the air at degassing (kg)	Q _{emis}		
Model calculations:			
Q _{emis} = Q _{subst} * (1 - F _{ret}) *(1 - F _{desin})			
$Q_{emis} = Q_{subst} * (1 - 0.02) * (1 - 0.001)$			
$Q_{emis} = Q_{subst} * (0,979 \text{ kg})$			
C =Constant (if possible the constants are presented)			
P -(Paguirad) values from the test results in the patification of a biaside			

R =(Required) values from the test results in the notification of a biocide

E =Expert estimations (if posssible the expert estimations (defaults) are presented)

O =Output from previous modules/calculations

14.5, 14.6 and 14.7 application of baits

Loss to the environment: baits should be recovered but it is estimated that the loss during rodent control is 20% (Balk, 1998).

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15 Avicides

Introduction

Avicides are biocidal products used to control nuisance birds. Their non-agricultural use is predominantly against pigeons and sparrows around and in public buildings to prevent fouling of building exteriors by droppings and for health and hygiene reasons (Allsopp and Seal, 1986). They are also used against various birds in and around livestock feeding pens and food stores to prevent eating and fouling. Avicides are excepted from mutual recognition by the member states (van Dokkum, 1998).

The product type 15 "Avicide" can be subdivided depending on the application technique and the location in the following subgroups:

- 15.1 Fumigation products for indoor-use (professional use)
- 15.2 Baits used in outdoors (professional use)
- 15.3 Baits used in animal housings and closed spaces (professional use)
- 15.4 Contact pastes used outdoors (professional use)

Avicides are applied in and around buildings as well as in animal housings mainly by professionals. In NL birds are not controlled by avicides. In other EU MS doves and starlings may be controlled by narcotics or sticking materials (polybutylene). In Africa avicides against weaver finch were applied. The avicides are mainly formulated as ready-to-use baits (pellets) and as liquid concentrates to prepare baits. In special situations either gas is employed in closed spaces in form of fogging/fumigation or contact paste is appointed in roosting areas (van Dokkum, 1998).

The insecticide Fenthion has a high toxicity to birds, therefore it is used in various parts of the world for weaver finch control and also to control pigeons around public buildings. Fenthion is applied as a paste to roosting areas (van Dokkum, 1998).

Relevant information data for ESDs

Processing

- Inclusion in materials/articles
- Application in processes

Used quantity of active substances

Chloralose bait 15 g a.i./kg grain against birds, trained personal (ed. Tomlin, 1997) Anthraquinone: 800 g/kg, used as powder for bird repellent (seed treatment), (ed. Tomlin, 1997)

Service Life

Waste Treatment

• Waste streams + relevant information

Emission routes for biocides. '+'=relevant; '-' not relevant (van Dokkum et al., 1998, modified) [weight %]

Product type	Applications	Fresh surface water	Marine surface water	Air indoor and outdoo r	Soil	Solid Waste	Waste water
15.1	Fumigation products for indoor-use (P)	-	-	+	-	-	-
15.2	Baits used outdoors (P)	+	-	-	+	+	-
15.3	Baits used in animal housings and closed spaces (P)	-	-	+	-	+	+
15.4	Contact pastes used outdoors (P)	-	-	-	+	+	-

P: professional use; N: non-professional use

• Recycling/recovery/reuse

Existing and produced emission models

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16 Molluscicides

Introduction

Molluscicides are biocidal products for the control of molluscs, snails and slugs. Their nonagriculture use is among other things to avoid contamination of international cargo with foreign pests. Several states of the USA including Alabama, Arkansas, Louisiana, Mississippi, Oregon, Tennessee, Virginia and Florida have imposed strict quarantine regulations to prevent the accidental introduction of molluscs. In this product type the use of molluscicides which combat molluscs in aquatic systems (marine or freshwater), is not accounted for. They are described under either product type 11 (Preservatives for liquidcooling and processing systems) or product type 21 (Antifouling products). Molluscicides are not used by professionals in the EU, but non-professional use is in gardens. In the EU they are not used in the aquatic environment (van Dokkum , 1999).

In order of the relevance of the different industrial sectors, the product type 16 "Molluscicides" can be subdivided depending on the application technique and the location in the following subgroups:

16.1 Pest control products for wet surface application, powders, and other products used outdoors (non-professional use)

[Products for wet surface application includes the application techniques in which a liquid product or an available product by dilution of addition of a solvent and/or water.]

- 16.2 Baits used in outdoors (non-professional use)
- 16.3 Baits used in closed spaces and animal housings (professional and non-professional use)
- 16.4 Powders used outdoors (non-professional use)
- 16.5 Powders used in closed spaces (non-professional use)

Snails and slugs are considered pests because they can cause damage to stored food and can induce diseases. Molluscicides are employed in buildings (houses, industrial and public buildings, food and feed preparation as well as storage, veterinary purpose) and outdoors (gardens, roads, open spaces). The Molluscicides for use against slugs and snails are formulated as baits (stomach poison in form of pellets, granules and powders) and also other forms like contact poison in form of wettable powders, aqueous solutions/dispersions/suspensions for application.

The most important molluscicides are methaldehyd and methiocarb others are 3,4-dichloro BNT, 3,5-dichloro, azinphosmethyl, aluminium sulfate, carbamate, carbaryl (Sevin), complexone, cooper chloride, Cooper sulfat, dimethylaminoaniline, deltamethrin (Decis), MGK-264, N-tritylmorpholine, niclosamide, organophosphorus pesticides ROGOR, piperonyl butoxide, propoxur, pyrethroid and sulfoxid (Luttik, 1995; Dreyfuss et al, 1996; Young, 1996; Hata, 1997).

Organophosphate, carbamate and pyrethroid pesticides are also used to control snails. According to the literature, synergists like piperonyl butoxide (PB), sulfoxid (SU), dimethylaminoaniline (DAA) and MGK-264 increase the molluscicidal activity of synthetic pesticide like organophosphate, carbamate and pyrethroid. Methylaldehyd acts toxic in the stomach after ingestion and is available in form of granules, sprays and pelleted baits (Tripathi, 1997; Panigrahi, 1998; Singh, 1998; Tripathi, 1998).

Cabaryl is a wide-spectrum carbamate insecticide that is also used as a molluscicide. It's both a contact and a stomach poison and it's available in many types of formulation including baits, dusts, wettable powders, granules, aqueous dispersions and suspensions (van Dokkum, 1998).

Cooper sulfate is mainly appointed as fungicide, but it is also used as molluscicide in form of dust, wettable powders and fluid concentrates (van Dokkum, 1998).

Propoxur is a non-systemic insecticide that also acts as molluscicide and exists in many application forms like ready-to-use liquids and aerosols, emulsifiable concentrates, wettable powders, granular baits and dusts (van Dokkum, 1998).

Azinphosmethyl is a non-systemic broad spectrum insecticide that is also appointed as molluscicide and belongs to the groups of organophosphates. It operates as contact and stomach poison. The main application types of azinphosmethyl are emulsifiable liquid, flowable liquid, ultra-low-volume liquid and wettable powder formulations (van Dokkum, 1998).

Complexone a chelate is widely used as source of iron trace-element mixes and acts as contact poison (Young, 1996).

Most toxic compounds are also repellent and the interaction of toxicity with repulsion prevents the ingestion of sufficient poison to kill the mollusc.

Relevant information data for ESDs

Processing

- Inclusion in materials/articles
- Application in processes

Used quantity of active substances

16. The following substances are used as molluscicides:
3,4-dichloro BNT (0,13 mg/l for toxicity tests), (Dreyfuss et al, 1996)
3,5-dichloro BNT (0,15mg/l for toxicity tests), (Dreyfuss et al, 1996)
Complexone (6-12 % by weight)
Metaldehyde: bait for slug control 50 – 60 g/kg (pellets), (van Dokkum, 1998)
Metaldehyd-formulation 2-7,5 % by weight (www.gifte.de; Hata, 1997)
Methiocarb: bait 10 – 40 g/kg for slug control, used in pellets 200 g a.i. per ha against slugs and snails and bird repellent (seed treatment), (ed. Tomlin, 1997; Hata, 1997)
Methiocarb-formulation 2-6 % by weight (Hata, 1997)
Niclosamide (0,1-1 mg/l for toxicity tests),), (Dreyfuss et al, 1996)
Organophosphorus Pesticides ROGOR (0,10-0,35 ml/l for toxicity tests), (Panigrahi, 1998)

Service Life

Waste Treatment

• Waste streams + relevant information

Emission routes for biocides. '+'=relevant; '-' not relevant

(van Dokkum et al., 1998, modified)

Product type	Applications	Fresh surface water	Marine surface water	Air indoor and outdoo r	Soil	Solid Waste	Waste water
16.1	Pest control products for wet surface application used outdoors (N)	+	-	+	+	+	+
16.2	Baits used in outdoors (N)	+	-	-	+	+	-
16.3	Baits used in closed spaces and animal housings (N)	-	-	+	-	+	+
16.4	Powders used outdoors (N)	+	-	+	+	+	-
16.5	Powders used in closed spaces (N)	-	-	+	-	+	+

P: professional use; N: non-professional use

• Recycling/recovery/reuse

Existing and produced emission models

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17 Piscicides

Introduction

Piscicides are biocidal products used to control or reduce fish populations in bodies of water. These may have become contaminated with undesirable fish, there may be a disrupted predator-prey balance or some species may have become overabundant and stunted (van Dokkum, 1998). Piscicides are excepted from mutual recognition by member states. In order of the relevance of the different industrial sectors, the product type 17 "Piscicides" can be subdivided depending on the application technique and the location in the following subgroups:

17.1 Baits used in outdoors (professional and non-professional use)

17.2 Liquids used in outdoors (professional and non-professional use)

In Scandinavia piscicides are inserted into the fish farm ponds after harvesting the fish, so that newly introduced young fish are not eaten by the remaining grown fish (Schmidt-Sonnenschein, 2000).

In aquariums only those young fish are killed, which show a crippling and degenerated appearance (Anon.).

The application of piscicides is limited to fish culture. The applications are the use of baits (e.g. pellets) and the use of liquids (van Dokkum, 1998).

Antimycin and Rotenone, is a botanical, selective, non-specific insecticide which is also used for fish elimination as a part of water body management. These products are registered piscicides in the USA (Dawson, 1998; Schnick, 1992).

3-trifluoromethyl-4-nitrophenol (TFM) and Bayluscide are used and registrated as lampricideand in the USA (Dawson, 1998; Schnick, 1992).

Trician (MS 222) is used as a toxic narcotic for breeding- and toy fishes (Anon.).

5-Hydroxy-2-methyl-1,4-naphthoquinone is present in plant of plumbago and diospyros and is used as piscicide in Okinawa (Japan).

The combination of commercial bleaching powder and urea with equal proportion has been used in India as piscicide.

Relevant information data for ESDs

Processing

- Inclusion in materials/articles
- Application in processes

Batch application: Emission factor = 100 % Dilution factor= 10 Effected compartments: sea and fresh water (sweet water - or salt water fish)

Used quantity of active substances

Trician: 250-500 mg/l (depending on the (breeding or toy) fish species) TFM: 36 % active ingredient (for toxicity tests) Antimycin: 99 % active ingredient (for toxicity tests) Rotenone: 2,5 % (for toxicity tests)

Service Life

Waste Treatment

• Waste streams + relevant information

Emission routes for biocides. '+'=relevant; '-' not relevant (van Dokkum et al., 1998, modified)

Product type	Applications	Fresh surface water	Marine surface water	Air indoor and outdoo r	Soil	Solid Waste	Waste water
17.1	Baits used in outdoors (P+N)	+	+	-	-	-	-
17.2	Liquids used in outdoors (P+N)	+	+	-	-	-	-

P: professional use; N: non-professional use

• Recycling/recovery/reuse

Existing and produced emission models

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18 Insecticides, acaricides and products to control other arthropod species

Introduction

Insecticides are biocides for controlling insects like scapers, cockroachs, bugs, flies, gnats, mosquitoes, ants, silverfish, moths, beetles, plant louse, aphid, greenfly, scale lice, lice, fleas of dogs and cats, ticks, katydid, grass hoppers, cicadas and other insects in non-agricultural settings. Insects are parasites or vector (reservoir) systems and cause severe diseases to human and/or to domestic animals. Acaricides are biocides toxic to spider mites and mites. Furthermore, biocides used to control other arthropod species are included in this product type. The non-agricultural use of both groups of biocides includes controlling insects in and around domestic, public and industrial buildings, control of animal parasites (pets) and controlling insects in food stores.

mice, rats, moles and other small animals. Their non-agricultural use is in and around homes, commercial and industrial sites, lawns, golf courses, highway medians, etc.

In order of the relevance of the different industrial sectors, the product type 18 "Insecticides" can be subdivided depending on the application technique and the location in the following subgroups:

- 18.1 Aerosol/Fumigation products used outdoors (professional and non-professional use)
- 18.2 Aerosol/Fumigation products used with fumigation installation (professional and nonprofessional use)
- 18.3 Aerosol/Fumigation products for indoor-use, products used on skin (indoors), (professional and non-professional use)
- 18.4 Pest control products for wet surface application and other products used outdoors (professional and non-professional use)
 [Products for wet surface application includes the application techniques in which a liquid product or an available product by dilution of addition of a solvent and/or water.]
- 18.5 Pest control products for wet surface application, powders, and other products used in closed spaces (professional and non-professional use)
- 18.6 Pest control products for wet surface application, powders, and other products used in animal housings (professional and non-professional use)
- 18.7 Baits used outdoors (professional and non-professional use)
- 18.8 Baits used in sewer systems (not used in Germany; professional and nonprofessional use)
- 18.9 Baits used in closed spaces and animal housings (professional and non-professional use)
- 18.10 Pest control products used on skin (outdoors) (professional and non-professional use)

Insecticides are used in many different applications. They are used indoors in buildings, outdoors, in sewer systems and for veterinary purposes in animal housings. The use indoors in buildings includes houses (do-it-yourself and professional), public buildings (for example schools, hospitals), museums, various industries (e.g., food production, cosmetics, leather and textile industries) and the transport sector. The use outdoors includes public places, waste disposal sites, gardens, water banks and surface waters. Insecticides (including acaricides) are applied in housings for pets and domestic animals, and in slaughter houses. Furthermore, insecticides are used in sewers, water treatment plants and pumping stations.

The formulations used are also very diverse. The formulations include products for spraying (e.g., aerosols, solutions, suspensions, emulsions), for pouring, for brushing, dusts, granulates, baits, contact pesticides (pastes, gels, foam), fogs, mists, smoke and

fumigants. Furthermore, materials can be impregnated with the insecticide (e.g., strips, balls, nets).

Insecticides are used both as do-it-yourself and professional products. An indication of the relative amounts is reported by Liebisch et al., (1992) (percentages based on the number of products available; German situation):

- 1. Do-it-yourself products for pest control ("Household" insecticides): app. 32 %
- 2. Do-it-yourself products used in relation to pets: app. 8 %
- 3. Products used on farms for pest control: app. 20 %
- 4. Products used for professional pest control: app. 40 %

For storage pest control, the two main biocides are methyl bromide and phosphine, both applied as gasses. In the Netherlands, the consumption of these gasses was 40 tons of methyl bromide and 0.1 tons of phosphine in 1992 (VROM, 1994). The average of methylbromide per fumigation was 28,7 kg in 1993 (netherlands). From this data, it could be calculated that on 27 locations on average 100 kg or more is used, the highest average on 1 location was 617,9 kg. As realistic worse case approach for the use of methylbromide an amount of 100 kg per event seems reasonable. No data on the size of the space treated was available (Luttik, 1995).

Storage pest control products include both biocides (e.g., food and feed storage) and plant protection products (e.g., storage of raw materials such as grain).

In the sixties, mainly phosphoracidesters like E605, Dichlorvos, Trichlorfon and Lindan were used as insecticides in the agricultural sector. In the seventies chlorinated hydrocarbones with phosphoracidesters were the most commonly used insecticides in the agricultural sector all around the world.

Active Substances/	Biocide		Application rate	Formulation
Literature	type			type
Acephate	Insecticide	Organophosphorus		GR;
				SP;
Tomlin;				WP;
				CG;
				AE;
Acetamiprid	Insecticide			GR;
				SP;
Tomlin;				WP;
				FU;
Acrinathrin	Acaricide,	Pyrethroid		EC;
	Insecticide			SC;
Tomlin;				WP;
				EW;
AKD-2023	Acaricide	Acequinocyl		SC;
Tomlin;				
Alanycarb	Insecticide	Oxime carbamate		WP;
				EC;
Tomlin;				
Aldicarb	Insecticide,	Oxime carbamate		GR;
	Acaricide,			
Tomlin;	Nematicide			
Allethrin	Insecticide	Pyrethroid		AE;
				EC;
Tomlin;				DP;
				WP;
Amitraz	Acaricide	Amidine		EC;
				WP;
Tomlin;				PO;
Anthelmintic			(against worms) in animal feeds	

Active Substances/ Literature	Biocide type		Application rate	Formulation type
Balk, 1999			EC 500-1000 g/l, Granules 5 g/kg, liquid 200-1000 g/l.	
Azadirachtin Tomlin;	Insecticide	Extracted from neem tree		EC;
Azamethiphos Tomlin;	Insecticide	Organophosphorus		WP; AE;
Azinphos-ethyl	Insecticide, Acaricide	Organophosphorus	Trade name : Gusathion K forte (33,3 %)	EC; WP;
Tomlin; Rebmann; Azinphos-methyl Tomlin; Rebmann;	Insecticide	Organophosphorus	Trade names: Gusathion-Spray dust (25 %), Gusathion MS (25 %) combined with Demeton-S- methylsulfon (7,5 %), Multapon (25 %) combined with Demeton- S-methyl (7,5 %), Rhodiatox Kombi (25 %) combined with Demeton-S-methylsulfon (7,5 %), Rospin (25 %) combined with Demeton-S-methyl (7,5 %)	UL; WP; EC; DP; SC;
Azocyclotin Tomlin;	Acaricide	Organotin	• • • •	WP;
Bendiocarb Tomlin; Rebmann;	Insecticide	Carbamate	Trade names: Ant spray Spiess- Urania (0,5 %); Antdust (1 %); Ant-Stop (1 %); Faicam W (80 %); Fisons Ant-Spray (0,5 %); Fisons Ant-Dust (1 %); Garvoxin 3 G (3 %); Garvoxin 20 WP (20 %); maiblü Ant-Spray (0,5 %); Multamat (80 %); Multamat 3 G (3 %); Seedoxin (80 %); Seedoxin FHL (500 g/l); Insect- Spray Nexa Lotte Special (2 %) combined with Neopynamin (0,1 %), Piperonylbutoxyd (0,05 %).	AE; DP; FS; GR; SC; UL; WP;
Benfuracarb Tomlin;	Insecticide	Carbamate	Applied mainly as soil treatment 0,5-2,0 kg a.i./ha for maize; 1,0- 2,5 kg/ha for vegetables; for seed treatment 0,4-1,5 kg/100 kg seed; applied as foilar spray 0,3-1,0 kg/ha	EC; GR; WP; SC;
Bensultap Tomlin;	Insecticide		Typical application rate 0,25-1,5 kg a.i./ha	WP; GR; DP;
Benzoximate Tomlin;	Acaricide			EC;
Bifenthrin Tomlin;	Insecticide, Acaricide	Pyrethroid	Application rates rang from 5 g a.i./ha to 45 g/ha	EC; SC; WP; UL; GR;
Bioallethrin	Insecticide	Pyrethroid		EC;

Active Substances/ Literature	Biocide type		Application rate	Formulation type
				TC;
Tomlin;				AE;
				VP;
				OL;
				Oil;
				Coil;
Bioresmethrin	Insecticide	Pyrethroid		AE;
				EC;
Tomlin;				OL;
				SL;
Bromopropylate	Acaricide	Benzilate		EC;
Tomlin;				
Buprofezin	Insecticide,			WP;
	Acaricide			DP;
Tomlin;				GR;
				SC;
Butocarboxim	Insecticide	Oxime carbamate		EC;
Datocarboxim	modulut			AE;
Tomlini				SL;
Tomlin;				SL,
Butayaarbayim	Incontinido	Oxime carbamate		Cardboard
Butoycarboxim	Insecticide,	Oxime carbamate		
T l' .	Acaricide			sticks
Tomlin;				
Cadusafos	Nematicide,	Organophosphorus	3-10 kg/ha	GR;
	Insecticide			EW;
Tomlin;				
Carbaryl	Insecticide	Carbamate	0,25-2,0 kg a.i./ha	TK;
				WP;
Tomlin;				DP;
				RB;
				SC;
				GR;
				OF;
Carbofuran	Insecticide,	Carbamate		SC;
	nematicide			GR;
Tomlin;				WP;
,				FS;
				,
Carbosulfan	Insecticide	Carbamate		GR;
				EC;
Tomlin;				WP;
i olimit,				DP;
				UL;
				CS;
				00,
Cartap	Insecticide	2-dimethylamino-	0,4-1,0 kg/ha	SP;
Janap	machicide	propane-1,3-dithiol	0, 1 -1,0 kg/11a	DP;
Tomlin;				GR;
CGA 50 439	Acaricide		>01021/	EC;
CGA 30 439	Acancide		>0,1 g a.i./l	EU,
Tamlini				
Tomlin;		Quality		
Chlordane	Insecticide	Cyclodiene		EC;
L		organochlorine		GR;
Tomlin;				DP;
	1	1	1	WP;

Active Substances/ Literature	Biocide type		Application rate	Formulation type
				Oil;
Chlorethoxyfos	Insecticide	Organophosphorus		GR;
Tomlin;				50
Chlorfenapyr	Insecticide, Acaricide	Pyrazole		EC; SC;
Tomlin;				0.5
Chlorfenvinphos Tomlin; Rebmann	Insecticide, Acaricide	Organophosphorus	Trade names: Birlane-Fluid (240 g/l), Birlane Granulat (10 %), Sapecron fluid (240 g/l), Sapecron-Granulat (10 %)	GR; EC;
Chlorfluazuron	Insecticide	Benzoylurea		EC;
Tomlin;				SC; UL;
Chlormephos	Insecticide	Organophosphorus	2-4 kg a.i./ha	GR;
Tomlin;		e iganophiciphici de		
Chloropicrin	Insecticide,			TC;
' Tomlin;	Nematicide			TB; OL;
Chlorpyrifos Tomlin; Rebmann; Balk;	Insecticide	Organophosphorus	Trade names: Chlorpyrifos 480 E.C. (480 g/l), Chlorpyrifos pur. (99 %); CD-forte Concentrate (18 %) combined with Naled (2 %), Pyrethrum (8 %); Contra- Insect against Ants (1 %); Detmol-dur (120,7 g/l) combined with Dichlor-vos (48,2 g/l), Pyrethrum-Extrakt 25 % (27 g/l); Detmol-laque (4,1 %); Detmol- laque Spray can (2 %); Detmol- tex (10 g/l) combined with Methoxychlor (30 g/l); Dursban fluid (480 g/l); Dursban Spray dust (25 %); Gesektin K (480 g/l); Loxiran Ant-spreading- und pouring agent (1 %); Loxiran spreading agent (1 %); Moth protection Nexa Lotte (2,7 %) combined with Empenthrin (0,9 %); Salut (278 g/l) combined with Dimethoat (222 g/l); SchwabEX-ban (3 %); SchwabEX-ban (3 %); SchwabEX-fluid (5 g/l) combined with Dichlorvos (5 g/l), Pyrethrum-Extrakt 25 % (1,8 g/l); SchwabEX-spray (0,67 %) combined with Dichlorvos (0,5 %), Pyrethrum-Extract 25 % (0,2 %); Insect-bait Nexa Lotte Special (0,5 %) Demeton-S- methyl, Emulsifiable	GR; EC; WP; DP; UL;

Active Substances/ Literature	Biocide type		Application rate	Formulation type
			ultralow volume liquid 25 g/l, in soil, on foilage, against household pests, ectoparasites on cattle and sheep: granules 60-150 g/kg, wettable powder 250 g/kg, 240-1200 g a.i./ha for EC and 500-2500 g/ha for GR	
Chlorpyrifos-methyl Tomlin;	Insecticide, Acaricicde	Organophosphorus		EC; UL; Fogging
Clofentezine	Acaricide	Tetrazine		concentrate; WP; SC;
Tomlin;				,
Coumaphos Tomlin;	Insecticide	Organophosphorus		Powder; Spray; Liquid;
Cryrolite	Insecticide		5-30 kg/ha	WP;
Tomlin;				
Cyanophos Tomlin;	Insecticide	Organophosphorus	25-50 g a.i./hl	DP; EC; UL; WP;
Cycloprothrin	Insecticide	Pyrethroid		GR; DP;
Tomlin;				EC;
Cyfluthrin Tomlin;	Insecticide	Pyrethroid		AE; EC; EO; ES; EW; UL; WP; GR; Oilspray;
Cyhalothrin	Insecticide	Pyrethroid		EC;
Tomlin;				WP;
Cyhexatin	Acaricide	Organotin		WP; SC;
Tomlin; Cypermethrin	Insecticide	Pyrethroid		EC;
Tomlin;	INSECUCIUE			EC, GR; WP; UL;
Cyphenothrin Tomlin;	Insecticide	Pyrethroid		AE; EC; UL; WP;
Cyromazine	Insecticide			WF, HN; SC;

Active Substances/ Literature	Biocide type		Application rate	Formulation type
Tomlin;				SP; SG; SL; WP;
D2341 bifenazate Tomlin;	Acaricide		0,25-0,75 kg/ha	SC; WG; WP;
DDT Tomlin;	Insecticide	Organochlorine	Used as a mosquito vector for the eradication of malaria	EC; WP; DP; GR; Aerosol;
Deltamethrin Tomlin;	Insecticide	Pyrethroid	Against indoor insects (12,5 mg/m²); dip or spray 12,5-75 mg/l	PO; SL; EC; WP; UL; SC; GR; DP; HN; EG;
Demeton-S-methyl Tomlin;	Insecticide, Acaricide	Organophosphorus		EC;
Diafenthiuron	Insecticide, Acaricide			SC; WP;
Diazinon Tomlin;	Insecticide, Acaricide	Organophosphorus		SO; GR; WP; EC; DP; DS; FT; CS; KN;
Dichlorvos Tomlin; Rebmann; Balk;	Insecticide, Acaricide	Organophosphorus	Trade names: Baygon-Insect strip (6,25-25 g); Blattanex- Special-Spray (0,5 %) combined with Propoxur (2 %); Detia- Pflanzol-Spray (0,192 %) combined with Pyrethrum (0,05%), Piperonylbutoxid (0,225%); Detmol-dur (48,2 g/l) combined with Chlorpyrifos (120 g/l), Pyrethrum-Extrakt (27 g/l); Detmol-fum (3,5 %) combined with Piper-onylbutoxid (0,32 %), Pyrethrum-Extrakt (0,32 %); Detmolin F (35 g/l) combined with Piperonyl-butoxid (0,64 g/l), Pyrethrum-Extrakt (1,3 g/l); Detmolin M (10 g/l) combined with Malathion (75 g/l); Flystrip Blattanex (für 10 m ² : 6,25 g/	SL; EC; AE; GR; HN; KN; OL; Impregnated Strip;

Active Substances/ Literature	Biocide type		Application rate	Formulation type
			Strip); Fog 2 (35 g/l) combined with Piperonylbu-toxid (0,64 g/l), Pyrethrum-Extrakt (1,5 g/l); Geo plantspray (0,49 %); Mafu Nebelautomat (50 g/400 ml Dose); Nogos-plantspray (0,49 %); Paral Insect-Strip (27 %); SchwabEx-fluid (5 g/l) combined with Chlor-pyrifos (5 g/l), Pyrethrum-Extract (1,8 g/l); Schwab-Ex-spray (0,5 %) combined with Chlorpyrifos (0,67 %), Pyrethrum-Extract (0,2 %), as fumigant to protect stored products at 0.5 to 1 g a.i./100m ³	
Dicofol Tomlin;	Acaricide	Organochlorine	0,50-2,0 kg a.i./ha	EC; WP; DP; SC;
Dicrotophos Tomlin;	Insecticide, Acaricide	Organophosphorus		SL; UL; EC;
Dicyclanil Tomlin;	Insecticide			
Dienochlor	Acaricide	Organochlorine		WP; EW;
Tomlin; Diflubenzuron Tomlin;	Insecticide	Benzoylurea	Against fly larvae in animal housings 0,5-1 g a.i./m ² surface; 25-75 g a.i./ha against insects in forestry	WP; UL; GR; HN; OF; SC; WG;
Dimethoate Tomlin; Rebmann;	Insecticide, Acaricide	Organophosphorus	Trade names: Aadimethoat (400 g/l); Blattlaus Spray (0,1 %); CFM Dimethoat 40 (400 g/l); Cindy (0,1 %); Dehner gardenspray (0,1 %); Dehner gardenspray NEW (0,1 %); Dimethoat ICI (400 g/l); Etisso combi-fertilizersticks (0,4 %); Etisso plant protection- suppositories (0,4 %); Euflor- Plantprotection (0,1 %); Gabi Plantspray (0,1 %); Gärtners Saft+Kraft Plantprotection-Spray (0,1 %); Insekticid-Sticks (0,5 %); IT-Insekten Gieß- und Spritzmittel (400 g/l); IT- Plantspray (0,1 %); maiblü plant louse- und plantspray (0,1 %);	EC; WP; UL; GR; Aerosol;

Active Substances/ Literature	Biocide		Application rate	Formulation
Literature	type		Maxima plantprotection (0,1 %); Mestro (0,1 %); Perfekthion (400 g/l); Perfekthion plantspray (0,1 %); Perfekthion plantspray new (0,1 %); Poly-Plant Combi- Plantprotection-Fertilizersticks (0,4 %); recozit plantspray (0,1 %); Rogor (404 g/l); Rogor 40 I (400 g/l); Roxion (400 g/l); Salut (222 g/l) combined with Chlorpyrifos (278 g/l); Substral plantprotectionspray (0,1 %); Substral plant protection sticks (0,4 %)	type
Dimethylvinphos	Insecticide	Organophosphorus	0,6-0,8 kg a.i./ha	2% dust
Tomlin;				
Dinobuton Tomlin;	Acaricide		50 g a.i./100 l	EC;
Diofenolan	Insecticide	Diphenyl ether		EC;
Tomlin;	line estimist	Organische eine		
Disulfoton Tomlin;	Insecticide, Acaricide	Organophosphorus		GR; EC; DS;
DNOC	Insecticide,	Dinitrophenol		SC;
Tomlin;	Acaricide			PA; SL; WP;
DPX-JW062 and DPX-MP062	Insecticide	Indoxacarb	12,5-70 g/ha	Under Development!
Tomlin;				
Empenthrin	Insecticide	Pyrethroid		Aerosol; Impregnated
Tomlin; Endosulfan	Insecticide,	Cyclodiene		material; EC;
Tomlin;	Acaricide	organochlorine		WP; DP; GR; UL; SC; Powder concentrate;
EPN (JMAF)	Insecticide, Acaricide	Organophosphorus	0,5-1,0 kg a.i./ha	DP; EC;
Tomlin; Esfenvalerate	Insecticide	Pyrethroid	5-25 g a.i./ha	EC;
Tomlin;	msecucide	r yreunolu	5-25 y a.i./iia	SC; UL;
Ethiofencarb	Insecticide	Carbamate		EW;
Tomlin;		Carbamate		GR; EC;
Ethion	Acaricide,	Organophosphorus		WP;

Active Substances/ Literature	Biocide type		Application rate	Formulation type
Tomlin;	Insecticide			EC; DP; GR; Seed
Ethoprophos Tomlin;	Nematicide, insecticide	Organophosphorus	1,6-6,6 kg a.i./ha	GR; EC;
Ethylene dibromide	Nematicide, insecticide			Oil;
Tomlin; Ethylene dichloride	insecticide			Fumigant;
Tomlin; Etofenprox	Insecticide	Non-ester pyrethroid		EC;
Tomlin;				WP; GR; DP; EW; CS; SL; UL;
Etoxazole	Acaricide		50 g/ha	SC;
<u>Tomlin;</u> Etrimfos Tomlin;	Acaricide, Insecticide	Organophosphorus	250-750 g a.i./ha	DP; EC; GR; LS; UL;
Famphur	Acaricide, Insecticide	Organophosphorus		PO; DP;
Tomlin; Fenazaquin	Acaricide		10-25 g/hl	EC; SC;
Tomlin; Fenbutatin oxide	Acaricide	Organotin		WP; SC;
Tomlin; Fenitrothion Tomlin;	Insecticide	Organophosphorus		EC; WP; GR; DP; UL; AE;
Fenobucarb	Insecticide	Carbamate		EC; DP;
Tomlin; Fenothiocarb	Acaricide			UL; EC;
Tomlin; Fenoxycarb	Insecticide			WP;
Tomlin;				RB; EC;

Active Substances/ Literature	Biocide type		Application rate	Formulation type
Fenpropathrin	Acaricide,	Pyrethroid		ÉĊ;
	insecticide			SC;
Tomlin;				WP;
				UL;
Fenpyroximate	Acaricide	Pyrazole		SC;
Tomlin;				
Fenthion	Insecticide	Organophosphorus		EC;
Tanalia				WP;
Tomlin;				UL; GR;
				DP;
				HN;
				PO;
Fenvalerate	Insecticide,	Pyrethroid		EC;
- "	Acaricide			UL;
Tomlin;				SC;
				WP;
Fipronil	Insecticide	Phenylpyrazole	10-80 g/ha foilar application	SC;
1 promi	mocellelae			GR;
Tomlin;				FS;
				EC;
				WG;
				UL;
Flucycloxuron	Acaricide, insecticide	Benzoylurea	0,01-0,015 % a.i.	DC;
Tomlin; Flucythrinate	Insecticide	Pyrethroid		EC;
Flucytinnate	Insecticide	Fyletinolu		WP;
Tomlin;				WG;
Flufenoxuron	Insecticide,	Benzoylurea		CG;
	Acaricide			EC;
Tomlin;				DC;
Flufenprox	Insecticide	Non-ester pyrethroid		AL;
				GR;
Tomlin;				EW;
Flumethrin	Insecticide	Pyrethroid		EC;
riameann	Insecticide	Fyreimold		
Tomlin;				
Fluvalinate	Insecticide,	Pyrethroid		EC;
Tomlini	Acaricide			EW;
Tomlin; Fonofos	Insecticide	Organophosphorus	1,0-1,5 kg a.i./ha	ULV; GR;
	msecticide	organophosphorus	1,0-1,0 NY a.i./IId	MG;
Tomlin;				EC;
				SC;
				CS;
				Seed
Farmer (Oration 1		treatment;
Formetanate	Acaricide,	Carbamate		SP;
Tomlin;	insecticide			
	1			

Active Substances/ Literature	Biocide type		Application rate	Formulation type
	Acaricide			ÚL;
Tomlin;				
Furathiocarb	Insecticide	Carbamate		DS;
				GR;
Tomlin;				EC;
Halfenprox	Acaricide	Non-ester pyrethroid		EC;
Tomlin;				CS;
Halofenozide	Insecticide	Diacylhydrazine	0,5-2,0 lb/A	SC; GR;
Tomlin;				Urt,
HCH;	Insecticide	Organochlorine	300-400 g/kg; pellets 18 g/kg;	SC;
Lindane		- 3	Lindane combined with	EC;
			dichlorphos and S 421 as spray	FU;
Tomlin; Haskoning;			agent 25 ml/m ²	LS;
Balk; bgVV				WP;
				GR;
				DP;
Line (and 1		Qualert		UL;
Heptachlor	Insecticide	Cyclodiene		WP;
Tomlini		organochlorine		EC;
Tomlin;				DP; GR;
				Seed
				treatment;
Heptenophos	Insecticide	Organophosphorus	Trade name: Hostaquick (550	EC;
	Insecticide	Organophosphorus	g/l)	
Tomlin; Rebmann; Hexaflumuron	Insecticide	hanzouluroo		EC;
	Insecticide	benzoylurea		SC;
Tomlin;				
Hexythiazox	Acaricide			WP;
Tomlin;				EC; FU;
Hydramethylnon	Insecticide			PA;
				RB;
Tomlin; Hydrogen cyanide	Insecticide,			GA;
	Rodenticide			GE;
Tomlin;				
Hydroprene	Insecticide	Juvenile hormone		EC;
Tanalia		mimic		KN;
Tomlin;	Incentiaista			Aerosol;
Imidacloprid	Insecticide			DP;
Tomlin;				GR; SC;
ronnin,				WG;
				WB;
				WF, WS;
				FS;
				SL;
Imiprothrin	Insecticide	Pyrethroid		AE;
Tomlin;				
Isazofos	Insecticide,	Organophosphorus		EC;

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Berlin

Active Substances/ Literature	Biocide type		Application rate	Formulation type
	nematicide			GR;
Tomlin;				
Isofenphos	Insecticide	Organophosphorus		GR;
				EC;
Tomlin;				WP;
				DS;
Isoprocarb	Insecticide	Carbamate		WP;
				DP;
Tomlin;				EC;
				GR;
				HN;
Isoxathion	Insecticide	Organophosphorus	500-1000 g a.i./ha	EC;
			-	WP;
Tomlin;				MG;
				DP;
Lufenuron	Insecticide,	Benzoylurea		EC;
	Acaricide	-		
Tomlin;				
Malathion	Insecticide,	Organophosphorus		EC;
	Acaricide			WP;
Tomlin;				DP;
,				UL;
				- 1
Mecarbam	Insecticide,	Organophosphorus		EC;
	Acaricide			,
Tomlin;				
Methacrifos	Insecticide,	Organophosphorus		DP;
moundomed	Acaricide	organophoophorad		EC;
Tomlin;				_0,
Methamidophos	Insecticide,	Organophosphorus	0,5-1,0 kg/ha	SL;
	Acaricide	e.geepepe		- ,
Tomlin;				
Methidathion	Insecticide,	Organophosphorus	Trade names: Ultracid 40 Ciba-	EC;
	Acaricide	organophoophorad	Geigy (40 %), Ultracid 200 Ciba-	WP;
Tomlin; Rebmann;	/ tourioido		Geigy (195 g/l), Ultracid 400	UL;
			Ciba-Geigy (420 g/l), Ultracron	01,
			(225 g/l) combined with	
			Dicrotophos (225 g/l) combined	
			with Dicrotophos (225 g/l)	
Methomyl	Insecticide,	Oxime carbamate	Trade names: Lannate 20 L (200	WP;
	Acaricide		g/l); Lannate 25 WP (25,7 %)	SL;
Tomlin; Rebmann;				SP;
Methoprene	Insecticide	Juvenile hormone		AE;
		mimic		SC;
Tomlin;				EC;
				BR;
				SL;
				CB;
Methoxychlor	Insecticide			AE;
				WP;
Tomlin;				EC;
				DP;
				GR;
Metolcarb	Insecticide	Carbamate		DP;
Melucan	Insecticide	Carbamate		EC;
Tomlin;				EC, MG;
romin,		1		wið,

Active Substances/ Literature	Biocide type		Application rate	Formulation type
				WP;
Mevinphos	Insecticde, Acaricide	Organophosphorus	Trade names: Shell Phosdrin 50 (525 g/l)	EC; SL;
Tomlin; Rebmann;				
Milbemectin	Acaricide, Insecticide			EC;
Tomlin;				
Monocrotophos	Insecticde, Acaricide	Organophosphorus		SL; UL;
Tomlin;				
Naled	Insecticde, Acaricide	Organophosphorus		EC; DP;
Tomlin;	la e e eticiale			UL;
Nicotine Tomlin;	Insecticide			DP; SL; Fumigant;
NP(Less effectes			0.0
Nitenpyram Tomlin;	Insecticide			SP; GR;
Nithiazine	Insecticide			
	Insecticide			
Tomlin; Novaluron	Insecticide	Banzoviluraa		EC.
	Insecticide	Benzoylurea		EC; SC;
Tomlin; Omethoate	Incontinido	Organanhaanharus		Δ.Ε.
	Insecticide, Acaricide	Organophosphorus		AE; EC;
Tomlin;				SL; UL;
Oxamyl	Insecticde, Acaricide	Oxime carbamate	Trade names: Vydate L (245 g/l)	GR; SL;
Tomlin; Rebmann;	, louineide			01,
Oxymedemeton- methyl	Insecticide	Organophosphorus	Trade names: Dipterex MR (200 g/l) combined with Trichlorfon	EC; SL;
Tomlin; Rebmann;			(392 g/l), Ecombi (200 g/l) combined with Parathion (175 g/l), Metasystox R (250 g/l),	
			Metasystox R special (100 g/l)	
Parathion (E605) Tomlin; Rebmann;	Insecticide, Acaraicide	Organophosphorus	Trade names: Ecombi (175 g/l) combined with Oxydemeton- methyl (200 g/l), E 605 forte	WP; EC; GR;
			(500 g/l), Eftol-Oil (100 g/l), Folidol-Oil (100 g/l), Parathion forte (500 g/l), Parathion-P-O-X konzentriert (500 g/l)	DP; CS; Aerosol;
Parathion-methyl	Insecticide	Organophosphorus	Trade name: ME 605-Spray dust (40 %)	WP; EC;
Tomlin; Rebmann;				DP; UL; CS;
Pentachlorophenol	Insecticide			GP; WP;
Tomlin;				OL;
Permethrin	Insecticide	Pyrethriod	control of biting flies in animal	EC;

Active Substances/ Literature	Biocide type		Application rate	Formulation type
Tomlin;			housing at 30- 200 mg a.i./m ² wall (Emulsifiable concentrate, wettable powder)	WP; UL;
thrin	Insecticide	Pyrethriod		ol; EC; OL;
, Phenthoate	Insecticide, Acaricide	Organophosphorus		EC; DP;
Tomlin; Phorate	Insecticide, Acaricide	Organophosphorus		GR;
Tomlin; Phosalone	Insecticide, Acaricide	Organophosphorus		EC; WP;
Tomlin; Phosmet	Insecticide, Acaricide	Organophosphorus	0,5-1,0 kg a.i./ha	SC; WP; EC;
Tomlin;				DP; SL;
Phosphamidon Tomlin; Rebmann;	Insecticide, Acaricide	Organophosphorus	Trade names: Detia Dimecron (200 g/l), Dimecron 20 (200 g/l)	SL; SC; EC; UL;
Phosphine Tomlin;	Insecticide, Rodenticide			GE; Fumigant;
Phoxim Tomlin;	Insecticide, Acaricide	Organophosphorus	5 kg/ha	EC; KN; GR; DP; UL; WP; Seed treatment;
Piperonyl butoxid Tomlin;	Insecticide synergist			Aerosol; Emulsion; Oil;
Pirimicarb Tomlin;	Insecticide	Carbamate		AE; WP; WG; FU; EC; DP;
Pirimiphos-ethyl Tomlin;	Insecticide	Organophosphorus		DS; EC; GR; CG;
Pirimiphos-methyl Tomlin;	Insecticide, Acaricide	Organophosphorus		AE; DP; EC; FU;

Active Substances/ Literature	Biocide type		Application rate	Formulation type
				UL;
				HN;
				LS;
				SG;
				KN;
Prallethrin	Insecticide	Pyrethriod		AE;
				EC;
Tomlin;				EW;
				KN;
Ductouctor	luce estimiste	Ormananhaanhamus		Oil;
Profenofos	Insecticide, Acaricide	Organophosphorus		EC;
Tomlin;	Acancide			UL;
Propaphos	Insecticide	Organophosphorus		GR;
Гюрарноз	msecticide	Organophosphorus		DP;
Tomlin;				D 1,
Propargite	Acaricide		0,75-1,8 kg/ha	WP;
				EC;
Tomlin;				EW;
Propetamphos	Insecticide,	Organophosphorus	Trade names: Antagent New (2	WP;
	Acaricide		%), Antagent (Spreading agent)	EC;
Tomlin; Rebmann;			(2 %), Delu Antdust (2 %),	DP;
			Detmol-Concentrate PRO (250	LA;
			g/l) combined with Pyrethrum	EW;
			(64 g/l), maiblü Antdust (2 %),	Aerosol;
			Safrotin 50 EC (582 g/l)	
Propoxur	Insecticide	Carbamate		AE;
				WP;
Tomlin;				EC;
				DP;
				FU;
				RB; UL;
				GR;
				SL;
				Oilspray;
Prothiofos	Insecticide	Organophosphorus		WP;
i rounoios	mocoliolae	organophosphoras		EC;
Tomlin;				20,
Pymetrozine	Insecticide	Azomethine		WP;
,				,
Tomlin;				
Pyraclofos	Insecticide	Organophosphorus	0,25-1,5 kg a.i./ha	EC;
				WP;
Tomlin;				GR;
Pyrethrins	Insecticide,		1000-300 kg/ha	AE;
T l' .	Acaricide			DP;
Tomlin;				EC;
				WP;
				UL; Eogging
				Fogging
Pyridaben	Insecticide,		5-20 g/hl	concentrate;
i ynuauen	Acaricide		J-20 g/m	EC;
Tomlin;	Acanciue			WP;
				SC;
Pyridaphenthion	Insecticide,	Organophosphorus		EC;

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Active Substances/	Biocide		Application rate	Formulation
Literature	type			type
- "	Acaricide			WP;
Tomlin;				UL;
Pyrimidifen	Acaricide,			DP; WP;
rymmunen	Insecticide			SC;
Tomlin;	mocolioide			00,
Pyriproxyfen	Insecticide	Juvenile hormone		EC;
		mimic		GR;
Tomlin;				WG;
Quinalphos	Insecticide,	Organophosphorus	250-500 g a.i./ha of EC; 0,75-1,0	EC;
Tomline	Acaricide		kg a.i./ha of Gr	GR;
Tomlin;				DP; UL;
				EW;
Resmethrin	Insecticide	Pyrethroid		AE;
		, , , , , , , , , , , , , , , , , , ,		EC;
Tomlin;				UL;
				WP;
Rotenone	Insecticide,			DP;
T P .	Piscicide			EC;
Tomlin; Silafluofen	Insecticide	Non-ester		WP;
Shahuoren	Insecticide	Pyrethroid		EO; EC;
Tomlin;		T yroanold		DP;
, chinh,				WP;
Sodium fluoride	Insecticide			Used in insect
Tomlin;				baits
Sodium	Insecticide	Inorganic fluoride	1 kg a.i./ha	RB;
hexafluorosilicate				
Tomlini				
Tomlin; Sulcofuron-sodium	Insecticide			High
Sucolulon-Socialit	msecticide			concentrate;
Tomlin;				Liquid;
Sulfluramid	Insecticide			RB;
Tomlin;				
Sulfotep	Insecticide,	Organophosphorus		Fumigant;
Tomline	Acaricide			VP;
Tomlin; Sulfuryl fluoride	Insecticide			Fumigant;
	mseclicide			r uniyanı,
Tomlin;				
Sulprofos	Insecticide	1		EC;
				UL;
Tomlin;				
SZI-121	Acaricide	Tetrazine	60-100 g/ha	SC;
Tomlin				
Tomlin; Tebufenozide	Insecticide	Diacylhydrazine		WP;
	msecticide			SC;
Tomlin;				SU;
				DP;
				GR;
Tebufenpyrad	Acaricide	Pyrazole	3,3-10 g a.i./100 l	EC;
				WP;

Active Substances/ Literature	Biocide type		Application rate	Formulation type
Tomlin;				EW;
Tabaa islaata	Less et al de	O		WG;
Tebupirimfos	Insecticide	Organophosphorus		GR;
Tomlin;				
Teflubenzuron	Insecticide	Benzoylurea		SC;
Tomlin;				UL;
Tefluthrin	Insecticide	Pyrethroid		GR;
				EC;
Tomlin;				CS;
Temephos	Insecticide	Organophosphorus		EC;
Tomlin;				MG; GR;
romin,				DP;
				SG;
				RB;
				KN;
Taulaufaa		Orean and a sub-arrive		Fumigants;
Terbufos	Insecticide	Organophosphorus	0,25-2,0 kg a.i./ha	GR;
Tomlin;				
Tetrachlorvinphos	Insecticide,	Organophosphorus		WP;
	Acaricide			EC;
Tomlin;				DP;
Tetradifon	Acaricide		150-300 g a.i./ha	SC; EC;
Tomlin;	Acancide		150-500 g a.i./iia	20,
Tetramethrin	Insecticide	Pyrethroid		AE;
				EC;
Tomlin;				DP;
				OF; UL;
				EW;
				Oil;
Thiocyclam	Insecticide			WP;
				SP;
Tomlin;				GR;
				Dust;
Thiodicarb	Insecticide	Oxime Carbamate	200-1000 g/ha	SC;
			U C	WP;
Tomlin;				SG;
				DP;
				RB;
				GB; WG;
				Dust;
Thiofanox	Insecticide, Acaricide	Oxime Carbamate	0,4-3 kg/ha	GR;
Tomlin;				
Thiometon	Insecticide,	Organophosphorus		EC;
	Acaricide			UL;
Tomlin;				
Toxaphen			Feed-/contactinsekticide, a	
			substance mixture made from	

Active Substances/ Literature	Biocide type		Application rate	Formulation type
			chlorinated camphen which contains up to 69 % Chlor	
Tralomethrin Tomlin;	Insecticide	Pyrethroid	7,5-20 g a.i./ha	EC; SC; WP;
Transflumethrin Tomlin;	Insecticide	Pyrethroid	Transflumethrin is effective against hygiene-, health- and material-damaging insects in the household like flies, mosquitoes and cockroaches as a contact and breathable poison.	VP; AL; FU; XX; Spaying cans; Vapouriser liquid; Mosquito coils;
Triazamate	Insecticide		35-280 g/ha	EW; WP;
Tomlin; Triazophos Tomlin; Rebmann;	Insecticide, Acaricide	Organophosphorus	Trade name: Hostathion (420 g/l)	EC; UL;
Trichlorphon Tomlin; Rebmann;	Insecticide	Organophosphorus	Trade names: Dipterex MR (393 g/l), Dipterex SL (50 %), Loxiran Anttraps (0,15 %)	SL; WP; SP; DP; GR; UL; PO; SC; GB;
Triflumuron Tomlin;	Insecticide	Benzoylurea		SC; WP; EC; OF; UL;
Trimethacarb Tomlin;	Insecticide, Mollus- cicide	Carbamate		GR; WP;
Vamidothion Tomlin;	Insecticide, Acaricide	Organophosphorus	37-50 g a.i./hl	EC;
XDE-105 Tomlin;	Insecticide	Spinosyn	50-100 g/ha	SC; WG; under Development!
XMC Tomlin;	Insecticide	Carbamate		DP; WP; EC; MG;
Xylylcarb Tomlin;	Insecticide	Carbamate		EC; WP; DP; MG;

- AE: Aerosol dispenser
- AL: Other liquids to be applied undiluted
- BR: Briquette
- CB: Bait concentrate
- CG: Encapsulated granule
- CS: Capsule suspension
- DC: Dispersible concentrate
- DP: Dispersible powder
- DS: Powder for dry seed treatment
- EC: Emulsifiable concentrate
- EG: Emulsifiable granule
- EO: Emulsion, oil in water
- ES: Emulsion for seed treatment
- EW: Emulsion, oil in water
- FS: Flowable concentrate for seed treatment
- FT: Smoke tablet
- FU: Smoke generator
- GA: Gas
- GB: Granular bait
- GE: Gas generation product
- GP: Flo-dust
- GR: Granule
- HN: Hot fogging concentrate
- KN: Cold fogging concentrate
- LA: Lacquer
- LS: Solution for seed treatment
- MG: Microgranule
- OF: Oil miscible concentrate
- OL: Oil miscible liquid
- PA: Paste
- PO: Pour-on
- RB: Bait (ready to use)
- SC: Suspension concentrate (=flowable concentrate)
- SG: Water soluble granules
- SL: Soluble concentrate
- SO: Spreading Oil
- SP: Water soluble powder
- SU: Ultra-low volume (ULV) suspension
- TB: Tablet
- TC: Technical material
- TK: Technical concentrate
- UL: Ultra-low volume liquid
- ULV: Ultra-low volume
- VP: Vapour releasing product
- WG: Water dispersible granules
- WP: Wettable powder
- WS: Water dispersible powder for slurry treatment
- XX: Others

Relevant information data for ESDs

Processing

- Inclusion in materials/articles
- Application in processes

Used quantity of active substances

Product type 18: Insecticides, acaricides and products to control other arthropods Substances used as insecticides are CHLORINATED HYDROCARBONS like Aldrin, Chlordan, DDT (DDT is a chlorinatedd aromatic hydrocarbon that acts as a nerve toxin by modifying the kinetics of voltage-dependent ion channels associated with the neurolemma and it is forbidden in Germany since 1974.), Dieldrin, Endosulfan (Commonly offered on the Market in combination with TBTO as Mergal IB 45 and Mergal IB50.), Endrin, Heptachlor, Lindane, Methoxychlor, Toxaphen (feed-/contact insecticide, a substance chlorinated camphen, mixture made form containing up to 69% chlor.) (Wissenschaftsladen) CARBAMATES like Aldicarb, Bendiocarb, Cabaryl, Carbofuran, Ethiofencarb, Isolan, Methomyl, Oxamyl, Propoxur (a contact- and feed poison which prompts the insects to leave their hiding places after application and thus expose themselves to the insecticide and which has a good effect against insects resistant to chlorinated hydrocarbon andphosphoric acid) (Wissenschaftsladen; Bayer AG;) ORGANOPHOSPHATES are also called alkylphosphates. The organophosphates also include Azinphosmethyl, Chlorfenvinphos, Chlorpyrifos, Diazinon, Dichlorvos, Dimethoat, Fenthion, Heptenophos, Malathion, Methidathion, Mevinphos, Oxymedemeton-methyl, Parathion (E605), Parathion-methyl, Phoxim, Phosphamidon, Propetamphos, Triazophos, Trichlorphon (Wissenschaftsladen).

PYRETHROIDS are synthetic esther compounds related to natural pyrethrum, an active substance made from chrysantemum flowers, and are counted among the most common household insecticides. Pyrethroides target the nerve cells of the insects directly, therefore only small amounts are necessary. The pyrethroids include: Bioallethrin, Cinerin, Dekamethrin, Fluvalinate, Jasmolon, Permethrin, Resmethrin, Cyfluthrin, Cypermethrin, Deltamethrin, Fenvalerate, Flumethrin, Transflumethrin (Wissenschaftsladen; ratiopharm).

Service Life

Waste Treatment

• Waste streams + relevant information

Regional water suppliers were asked, but their information is treated as confidential and could not be provided to us. A regional producer told us, that insecticides are not used in sewer systems.

Emission routes for biocides. '+'=relevant; '-' not relevant (van Dokkum et al., 1998, modified) [weight %]

Product type	Applications	Fresh surface water	Marine surface water	Air indoor and outdoo r	Soil	Solid Waste	Waste water
18.1	Aerosol/Fumigation products used outdoors (P+N)	+	+	+	-	-	-
18.2	Aerosol/Fumigation products used with fumigation installation (P+N)	-	-	50 %	-	50 %	-
18.3	Aerosol/Fumigation products for indoor-use (P+N)	-	-	100 %	-	-	-

18.4	Pest control products for wet surface application and other products used outdoors (P+N)	+	-	+	+	+	-
18.5	Pest control products for wet surface application, powders, and other products used in closed spaces (P+N)	-	-	+	-	+	+
18.6	Pest control products for wet surface application, powders, and other products used in animal housings (P+N)	-	-	+	-	+	+
18.7	Baits used outdoors (P+N)	+	-	-	+	+	-
18.8	Baits used in sewer systems (P+N)	-	-	-	-	-	+
18.9	Baits used in closed spaces and animal housings	-	-	+	-	+	+
18.10	Pest control products used on skin (outdoors), (P+N)	-	-	+	-	-	-

P: professional use; N: non-professional use

• Recycling/recovery/reuse

Existing or produced emission models

18.3 Fumigation products for indoor-use

One of the application methods of insecticides is fogging, in which the product is applied gaseously. R. Luttik shows a model for calculating release to the air for compounds used for fumigation of buildings, silos, etc. (Luttik, 1995).

Parameter/variable(unit)	Symbol	Default	C/R/E/O
Input:			
Amount used (kg)	Q _{subst}		R
Fraction of retention in goods (-)	F _{ret}	0,02	E
Fraction of disintegration (-)	F _{desin}	0,001	E
Output:			
Emission to the air at degassing (kg)	Q _{emis}		
•	Q _{emis}		
$Q_{emis} = Q_{subst *} (1 - F_{ret}) * (1 - F_{desin})$			
$Q_{emis} = Q_{subst} * (1 - 0.02) * (1 - 0.001)$			

C = Constant (if possible the contants are presented)

R = (Required) values from the test results in the notification of a biocide

E = Expert estimations (if possible the expert estimations (defaults) are presented)

O = Output from previous modules/calculations

 $Q_{emis} = Q_{subst} * (0,979 \text{ kg})$

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19 Repellents and attractants

Introduction

Repellents and attractants are biocides that are not intended to directly affect organisms, but to control harmful organisms by repelling or attracting them (sometimes in combination with an insecticide). Some repellents for example Autan are used in human hygiene, therefore is here an overlap with product type 1. Repellents are also used for the protection of the goods/materials for example like spray on storage cases etc. In order of the relevance of the different industrial sectors, the product type 19 "Repellents and attractants" can be subdivided depending on the application technique and the location in the following subgroups:

- 19.1 Aerosol/Fumigation products used outdoors (professional and non-professional use)
- 19.2 Pest control products for wet surface application, powders, and other products used outdoors (professional and non-professional use)
 [Products for wet surface application includes the application techniques in which a liquid product or an available product by dilution of addition of a solvent and/or water.]
- 19.3 Pest control products for wet surface application, powders, and other products used in closed spaces (professional and non-professional use)
- 19.4 Pest control products for wet surface application, powders, and other products used in animal housings (professional and non-professional use)
- 19.5 Baits used outdoors (professional and non-professional use)
- 19.6 Baits used in closed spaces and animal housings (professional and non-professional use)
- 19.7 Skin application used in outdoors (professional and non-professional use)
- 19.8 Skin application used in closed spaces (professional and non-professional use)
- 19.9 Skin application used in animal housings (professional and non-professional use)

Repellents stimulate an oriented movement from a source. Attractants include sex attractants (pheromones, to attract males), oviposition lures (against females) or food lures (both males and females). Repellents and attractants can be used in many applications. Repellents are formulations, which keep ectoparasites from the skin and used dermally and prevent mosquitoes, ticks, stinging insects and others from settling on the skin. They are used indoors like private houses, public and industrial buildings, transport sector, textile- and leather industry, food and feed industry, for veterinary purposes (animal housings, abattoirs, corpses), for sewer systems (sewage water treatment, cooling water systems) and outdoors (e.g., public places, private and public gardens).

Some general repellents are smoke, plant extracts like oil of citronella (geraniol, citronellol, terpenes). Natural repellents are oils of anise, bay leaf, caraway, cardamon, clove, coriander, cumin, fennel, garlic, jasmine, lavender, mace, nutmeg, thyme, perilla, pimento, peppermint, rosemary, sage, white pepper, capsicum oleoresin and vanilla oleoresin and demonstrate a proven repelling effect against mosquitoes and moths.

N,N-diethyl-m-toluamide and dimethylphthalate repel flying mosquitoes, they are both used for skin preparation and dimethylphthalate acts additionally for impregnation of clothes. Naphthalene and paradichlorobenzene are used in mothballs.

Ziram, renardine and methyl-anthranilate proved successful in preventing voles recolonizing areas under mulch mats placed around newly planted trees as weed control barriers.

Ortho-, meta- and para-aminoacetophenone, meta- and para-methoxyacetophenone, ortho-, meta- and parahydroxyacetophenone, methyl anthranilate, 2-amino-4',5'- methoxyacetophenone, veratyl amine were tested as vertebrate repellents for rodents.

Relevant information data for ESDs

Processing

- Inclusion in materials/articles ٠
- Application in processes •

Used quantity of active substances Substances used as attractants and repellents are:

Vertebrates/ Literature	Type of pesticide	Effective substance	Concentration	Application type
Bats	Repellent	Naphthalene	100 %	Flakes
	Repellent	Naphinalene	100 %	FIGKES
Jacobs, 1994 Beavers	Repellent	Denatonium	0,065 % (also contains	Liquid
Jacobs, 1994	Repellent	saccharide	0,035 % Thymol)	Liquid
Deer & Elk	Repellent	Ammonium Soaps	15 %	Liquid
Jacobs, 1994	Kepellent	of Higher Fatty Acids (Hinder)	13 76	Concentrate
	Repellent	Bonetar Oil (Magic	93,75 %	Liquid
Jacobs, 1994	Repellent	Circle)	33,73 78	Concentrate
000000, 1001	Repellent	Capsaicin (Hot	2,5 %	Liquid
Jacobs, 1994		Sauce)	2,0 /0	Concentrate
Jacobs, 1994	Repellent	Denatonium saccharide (Ro-pel)	0,065 % (also contains 0,035 % Thymol)	Liquid
	Repellent	Egg Solids,	36 %	Powder
		Putrescent Whole	37 %	Liquid
Jacobs, 1994		(Deer- Away)		concentrates
Jacobs, 1994	Repellent	Thiram	7-42 %	Liquid
Dogs & Cats	Repellent	Anise, Oil of	1,6 %	Liquid
Jacobs, 1994				
Jacobs, 1994	Repellent	d-Limonene	4,015 % (also contains 0,049 % dihydro-5-heptyl- 2(3H)-furanone and 0,024 % dihydro-5-pentyl- 2(3H)-furanone)	Granular
000003, 1004	Repellent	Methylnonyl-ketone	0,08-1,9 %, 1,8 %,	Granulars, "Water
			1,9 %,	crystals",
			47,5-95 % (Methylnonylketone products also contain compounds "related" to methylnonylketone at an aggregate concentration of about 5 % of the concentra- tion declared for me- thylnonylketone)	sprays, concentrates/ technicals
Jacobs, 1994				
Jacobs, 1994	Repellent	Naphthalene	15 % (also contains 5,0 % dried blood, 4,0 % Thiram, and 0,5 % Nicotine	Granular
	Repellent	Tobacco dust	70 % (also contains 15 %	Dry mixtures

Vertebrates/ Literature	Type of pesticide	Effective substance	Concentration	Application type
Jacobs, 1994			dried blood and 15 % Naphthalene)	
Jacobs, 1994	No-Chew Product	Bitrex	0,065 % (also contains 1,3 % Thymol, and 1,3 % essential oils	Spray
Jacobs, 1994	Attack Repellent	Capsaicin (Oleoresin of Capsicum)	0,35-1,0 %	Spray
Jacobs, 1994	Attack Repellent	Denatonium saccharide	0,065 % (also contains 0,035 % Thymol)	Liquid
Insects Tomlin, 1997	Pheromone; Control of codling moth	Codlemone		Vapour releasing product
Tomlin, 1997	Pheromone; Control of oriental fruit moth	Dodec-8-en-1-yl acetate		Vapour releasing product
Tomlin, 1997	Pheromone; Control of the European grapevine moth	Dodeca-7,9-dien-1- yl acetate		Vapour releasing product
Tomlin,1997	Pheromone; Used as a mating disruptant and in combination with an insect to attract and kill	Gossyplure		Granules, Beads, Flakes, Hollow fibre, Rope, Pvc strips
Tomlin, 1997	Pheromone; Control of housefly; mainly used in combination with an insecticide to attract and kill	Muscalure		Granular bait
Tomlin, 1997	Pheromone	Tetradec-11-en-1- yl acetate		Tubes
Tomlin, 1997	Pheromone ; Control of tomato pinworm	Tridec-4-en-1-yl acetate		Microencaps ulated
Tomlin, 1997	Its chief use is as a repellent to Blattodea at 1 g a.i./m ²	2-(octylthio) ethanol		Emulsifiable concentrate ; Oil miscible powder
Chark, 1997	Repellent	Diethyltoluamide (Deet)	12 to 15 % ; 5-95 % formulated in ethylalcohol	Aerosol, lotion, pump spray, roll-on stick
Chark, 1997	Repellent	Di-n-propyl isocynchomero- nate (MGK R-326)	2,5 to 4,5 %	Aerosol, lotion, pump spray, roll-on stick
Chark, 1997	Repellent	N-octyl bicycloheptene dicarbooximide (MGK 264)	2,5 to 4,5 %	Aerosol, lotion, pump spray, roll-on, stick
Rabbits	Repellent	Ammonium Soaps Of Higher Fatty	15 %	Liquids
Jacobs, 1994		Acids (Hinder)		

UBA

Berlin

Vertebrates/ Literature	Type of pesticide	Effective substance	Concentration	Application type
Jacobs, 1994	Repellent	Capsaicin	2,5 %	Liquid
Jacobs, 1994	Repellent	Thiram	7-42 %	Liquid
Jacobs, 1994	Repellent	Tobacco Dust	70 % (also contains 15 % dried blood and 15 % Naphthalene)	Dry mixtures
Jacobs, 1994	Repellent	Ziram	23 %	Dust (to be applied as is or to be mixed and sprayed)
Tree Squirrels Jacobs, 1994	Repellent	Capsaicin	2.5 %	Liquid concentrate
Jacobs, 1994	Repellent	Denatonium saccharide (Ro-pel)	0,065 %	Liquid
Jacobs, 1994	Repellent	Naphthalene	100 %	Flakes
Jacobs, 1994	Repellent	Polybutenes	90 %	Tacky gel

Service Life

Waste Treatment

• Waste streams + relevant information

Emission routes for biocides. '+'=relevant; '-' not relevant

(van Dokkum et al., 1998, modified)

Product type	Applications	Fresh surface water	Marine surface water	Air indoor and outdoo r	Soil	Solid Waste	Waste water
19.1	Aerosol/Fumigation products used outdoors (P+N)	+	+	+	-	-	-
19.2	Pest control products for wet surface application, powders, and other products used outdoors (P+N)	+	-	+	+	+	-
19.3	Pest control products for wet surface application, powders, and other products used in closed spaces (P+N)	-	-	+	+	+	+
19.4	Pest control products for wet surface application, powders, and other products used in animal housings (P+N)	-	-	+		+	+
19.5	Baits used outdoors (P+N)	+	-	-	+	+	-
19.6	Baits used in closed spaces and animal housings (P+N)	-	-	+	-	+	+
19.7	Skin application used in outdoors (P+N)	+	-	+	-	+	-
19.8	Skin application used in closed spaces (P+N)	-	-	+	-	-	+
19.9	Skin application used in animal housings (P+N) (see also PT 3)	-	-	+	-	(+)	+

P: professional use; N: non-professional use

• Recycling/recovery/reuse

Existing and produced emission models

Skin application

Calculation of the release of disinfectants used for skin application: Elocal,_{water} = number of inhabitants $*Q_{product} * C_{product} * F_{water}$

where

- Elocal = Emission rate to waste water (kg/d)
- Q_{product} = Consumption per capita (I/cap and d)
- $C_{product}$ = Active substance in the product (kg/l)

 F_{water} = Fraction released to waste water (usually 1 as the release to waste water is estimated to be 100 %).

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20 Preservatives for food or feedstocks

Introduction

This product type is interpreted as biocides used in rooms were prepaired food or feedstock is stored.

- The relevant sub-groups are:
- 20.1 Products added to the food or feedstock (professional and non-professional use)
- 20.2 Products used for the treatment of food surface coatings (professional and nonprofessional use)

The effect of preservatives relies on the removal of water (for example during pickling, salting, sweetening), the removal of oxygen while adding antimicrobial gasses (for example carbon dioxide, nitrogen), or lowering the ph-value through acidizing agents (for example acetic acid, lactic acid) or by adding chemical compounds which directly affect the metabolism of the microorganisms (for example Nisin).

In most cases the preservatives are added directly to the food- or feedstuff. Exceptions are pickling, smoking as well as surface treatments of citrus fruits and cheese products. There are three different processes for pickling which each use a salt mixture with a low content (0,4-0,5 %) of potassium- or sodiumnitrat or –nitrit. During dry pickling, the salt mixture is rubbed onto the product which is then stored for several weeks in a cool environment while the product is stored for several days in a 15-20 % pickling salt solution during wet pickling. The injection pickling finally relies on a direct injection of the pickling salt solution into the product. (http://wbtd15.biozentrum.uni-wuerzburg.de/projekte/biotech/food/lz/lz8/lz8apoek.htm; ROEMPP).

The principle of smoking relies on the treatment of the product with gasses from the incomplete combustion of plant products (wood, peat etc.). Many components of the smoke are absolved by the product and cause a biocidal effect (ROEMPP).

The surface treatment of citrus fruits is done by applying a 0,1-2 % thiabendazol layer or by dunking the fruit in a 0,5-2 % orthophenylphenole solution and rinsing with clear water after that. Instead of this direct treatment, an indirect treatment with bi- or diphenyl may take place. In this case the substances are slowly released to the air from previously treated boxes or packing material and are absorbed by the fruit peel. The substances used for surface treatment do not enter the product or, in the case of cheese treatment with natamycin only penetrate to a depth of 0,5mm (<u>http://wbtd15.biozentrum.uni-wuerzburg.de/projekte/biotech/food/lz/lz8/lz8apoek.htm</u>).

Foodstuffs are preserved on a large scale biologically (silage, lactic acid fermentation) or by adding propion acid (http://www.uni-hohenheim.de/i3v/00217110/00677441.htm).

Examples of food or feedstock preservatives and their recommended use level:

The highest amount of conservation agent is calculated with the formula:

ADI-value x average body weight/estimated dayly dosage of the foodstuff

The ADI-value (Accepted Dayly Intake) is determined by the amount of the substance (in mg/kg body weight) shown to be harmless as dayly consumption in animal tests and divided by a safety factor of 100.

Relevant information data for ESDs

Processing

- Inclusion in materials/articles
- Application in processes

Used quantity of active substances

Preservation in vegetable products:

- 250 mg/kg benzoic acid or derivates
- 50 100 mg/kg SO₂ or related
- 550 2500 mg/kg SO₂ on dehydrated products
- Feedstocks (preservation of crops, e.g. hay, silage, high moisture grain):
- 2-6 % by weight (dry matter) urea
- Prepacking (on farm):
 - Acetic acid-solution: 5 7 % (2 minutes dipping)
 - Organic acids and esters: 100 5000 mg/kg food (medium: 1000 mg/kg)
- Preservation of cheese: 2,5 mg/kg nisin (antibiotic)

Preservation of meat: 1 - 50 mg/kg nisin (antibiotic)

Preservation of drinks: 2,5 – 25 mg/l nisin (antibiotic), 5 – 18 % ethanol, 0,01 – 1 % antioxidantia (Russe and Gould, 1991)

Service Life

Waste Treatment

• Waste streams + relevant information

Release on biocides into air

During food-production: loss of VOC (e.g. alcohol) to air

Release on biocides into waste water

During food-production: 10 % loss to waste water

Emission routes for biocides. '+'=relevant; '-' not relevant

(van Dokkum et al., 1998, modified)

Product type	Products	Fresh surface water	Marine surface water	Air indoor and outdoo r	Soil	Solid Waste	Waste water
20.1	Products used for the treatment of food surface coatings (P+N)	-	-	+	+	+	+

• Recycling/recovery/reuse

Existing and produced emission models

References:

van Dokkum, H.P., et al. : "Development of a concept for environmental risk assessment of biocidal products for authorization purposes (BIOEXPO).", Umweltbundesamt (UBA): Umweltforschungsplan. UFOPLAN 106 01 065. Berlin, 1998, p. 213

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21 Antifouling Products

Introduction

The relevant sub-groups are:

- 21.01 Professional use on inland craft >25 m
- 21.02 Non-professional use on inland craft < 25 m
- 21.03 Professional use on commercial craft
- 21.04 Professional use on seagoing craft
- 21.05 Aquaculture equipment and other immersed structure

Fouling is not a new problem. Ancient mariners used lead and later copper sheathing to protect the hulls of wooden ships. Today, copper is still used in the form of coprous oxide and remains the marine industry's antifoulant of choice for control of barnacles, algae and other hard fouling organisms. Cooper is a good algaecide.

In the 1970s, tributyltin (TBT) compounds, which were effective against both soft (e.g., algae), and hard fouling organisms, were introduced. For antifouling agents like copper and tin compounds to be effective, they must be continuously released from a hull's surface at some minimum rate. However, released TBT is persistent in the environment and has adversely affected populations of non-target organisms. The toxicity of released copper appears not to be rapidly neutralized in an aquatic environment by complexation, adsorption and other naturally occurring. Copper is only partially complexed or adsorbed in the aquatic environment. The remaining section remains in solution and can affect further toxically aquatic organisms. Dependent on the chemico-physical conditions copper can also again be desorbed and complexes can be resolved.

Marine fouling on the bottom of ships is a real problem from both a cost and performance point of view. The increased friction caused by uncontrolled growth of marine fouling organisms reduces the speed of a vessel and causes an increase in fuel consumption. Since man first ventured into the sea, he has searched for solutions to this problem. The key has been finding a material that will disrupt the life cycle of these organisms, and thus prevent their accumulation and growth on the protected surfaces while not impacting the environment. Long-term self polishing antifouling paints have become the preferred solution for the marine fouling problem as they prevent biofouling on ships between drydocking intervals. By protecting against fouling, these paints lower a ship's drag, thereby reducing the operating cost suffered by vessels with fouling.

Historically, tributyltin (TBT) has been the agent most often used in this application. Tributyltin is effective against both soft and hard fouling organisms. However, in spite of its performance, the negative impact of tributyltin compounds on the marine environment and its long half life in the environment, have prompted marine paint manufacturers to look for a nonpersistent alternative.

At the 21st session of the International Maritime Organization (IMO) assembly in London in November 1998, a resolution was approved that calls for the elimination of organotin biocides by 2003. The resolution language bans the application of tin biocides as antifouling agents on ships by January 1, 2003 and prohibits the presence of tin biocides by January 1, 2008. The IMO also called for a diplomatic conference in 2001 to approve a legally binding instrument that will be completed by their Marine Environment Protection Committee in its next three meetings prior to the conference.

The negative impact of TBT has led to usage restrictions by many governments and to an intense search for alternatives. One approach is using a co-biocide (algaecide), which is effective against soft fouling organisms, in combination with cuprous oxide, which is effective against hard fouling organisms. The ideal co-biocide must have broad spectrum activity since many organisms contribute to fouling, low water solubility for performance longevity, a history of safe usage, and environmentally acceptable properties, i.e., must not adversely affect non-target populations. Since the environmental risk is directly related to the environmental concentration, the successful antifoulant must be non-persistent when released into the aquatic environment. Zinc pyrithione (ZPT) and copper pyrithione (CuPT) are two of several pyrithione compounds that have these properties.

To substitute TBTO extensive environmental tests were made to find a environmentally safe alternative. 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one was chosen as a substance with a half life of one day in seawater and a very rapid degradation in sediment (half life 1 hour), but the metabolites are persistent in sediment (information of UBA, Berlin). TBTO has a half life time of nine days in seawater and respectively nine months in sediment. TBTO has widespread chronic toxicity, thus the maximum allowable environmental concentration of TBTO is 0.002 ppb, that of 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one is 0,63 ppb (EPA, 1999).

Environmental Risk of some Antifouling Biocides

Several studies of zinc and copper pyrithione were conducted to assess environmental fate, persistence and impact. These studies include leach rates, abiotic hydrolysis and photolysis, aerobic and anaerobic aquatic metabolism, adsorption/desorption, and dieaway studies.

Leach Rates

The main route of entry for antifouling agents into the aquatic environment is by leaching from painted hulls. The leach rates of zinc and copper pyrithione have been determined for several ablative and self-polishing coatings. The steady state, 21 to 45 day leach rate was 2,3 (µg/cm²/day), (Rexrode, M., Spatz, D. (1997)). CuPT has a lower leach rate in the same formulation reflecting its lower water solubility.

In the Netherlands, the concentration of tributyltin has been measured in two yacht-basins with stagnant water (Evers et al., 1993). For calculation of the equilibrium dissolved concentration of tributyltin in the yacht basin water the following input was used:

Mean flux of compound:

 $2,5 \,\mu g/cm^2/day$ First order degradation rate for biodegradation in water: 0,041/day Log pOW 3.8

The calculated concentration of tributyltin in the model yacht-basin is 8,08 µg/l. This concentration is comparable with measured concentrations $(1,4-7,2 \mu g/l)$.

Swedish calculations, measurements and models also use leaching rates of 2,5 µg/l for different antifouling substances. TBTO leaching may not exceed 4 µg/cm²/day. For Cuproducts. Sweden defined a maximum release of 75 µg Cu/cm² in the first 14 days (Johnson et al., 1996).

Hydrolysis and Photolysis

ZPT and CuPT hydrolysis and photolysis were studied in sterile synthetic seawater and freshwater. Whereas the half life for hydrolysis of pyrithiones in dark sterile water ranged from 7 to more than 90 days, the photolysis half life ranged from 15 to 30 min. Environmental photolysis rates for compounds with high quantum yields, e.g., the pyrithiones, depend upon various factors including angle and intensity of incident surface solar radiation, water depth and clarity, presence of photosensitizers and particulate matter, and wave action. It is clear, however, that radiation in the 300 to 355 nm range, which causes photo degradation of pyrithione, can penetrate to significant depths under

favourable conditions (Smith, 1976). Therefore, it is likely that photochemical processes play an important role in the environmental degradation of pyrithiones.

Aquatic Metabolism

Biotic degradation of ZPT and CuPT were studied under dark, aerobic and anaerobic conditions. Anaerobic degradation was very rapid. The first and second half-lives (75% disappearance) appear to occur in less than one hour, while sorbed pyrithione shows a slower, although still rapid, degradation. Aerobic aquatic metabolism show a similar bimodal degradation. The first half-life occurs very rapidly with subsequent half-lives following a slower kinetic process.

Relevant information data for ESDs

Processing

- Inclusion in materials/articles
- Application in processes

Four different type of antfouling paints are mainly used:

- 1. Conventional, soluble matrix antifouling: in those paints, the biocide is released together with the soluble binder of the matrix; **the lifetime is about one year**.
- 2. Advanced, insoluble matrix antifouling: in these products the binder is no longer soluble in sea water; biocides and other soluble ingredients dissolve from the surface layer; **the useful lifetime is abut two years**.
- 3. Self-polishing antifouling: these products are based on a matrix, e.g. organotin polymer, of remarkable mechanical strength, which allows the build-up of a very thick layer. **The time of release is about 5 years**.
- 4. Polishing/ablative antifouling: these products are based around the same principles as self-polishing antifouling and works with a polishing/ablation mechanism, offering the best performance without the use of organo-tin components.

Used quantity of active substances

The concentration of antifouling agents in paints of a.i. (active ingredient): Traditional paints: up to 80 % copper (I)oxide (Haskoning, 1995) Modern paints: around 25 % copper (I)oxide) (Balk, 1999) Insoluble antifouling coatings: 10 - 12 % anorganotin (Balk, 1999) Self-polishing antifoulings: 10 - 30 % tributyltinoxide (Balk (1999)

Release on biocides into air:

The release into air depends on the application technique (CUWVO, 1991):

Brush or roller, indoor halls	0 – 5 %
Brush or roller, outdoor	2 – 5 %
Airless spraying	5 – 45 %
Pneumatic spraying	50 – 60 %

Service Life

Release on biocides into the aquatic system:

During use, 65 % by weight is lost to the aquatic environment, 30 % by weight remains as film on the ship, 5 % by weight is removed during remedial treatments and disposed off as chemical waste (Balk, 1999)

Leaching rates of TBT from antifouling paints: Sailing: 2,3 (μ g/cm²/day), (Rexrode, M.; Spatz, D. (1997) Sailing (self polishing coatings): 4 – 5 (μ g/cm²/day), (Willemsen et al., 1992) Sailing (matrix/ablative coatings): 5 (μ g/cm²/day), (Willemsen et al., 1992) Mooring (matrix/ablative coatings): 2-3 (μ g/cm²/day), (Willemsen et al., 1992)

Erosion rates:

self polishing coatings: 0,1 μm/day (16 – 18 knots, 25 °C) 120 – 160 sailing days and a thickness of the coating is between 50 to 150 μm → the paint is to be renewed every 5 years.

The maximum allowable environmental concentration of: TBTO: 0,002 ppb (EPA, 1999) 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one: 0,63 ppb (EPA, 1999)

The following values are used as default leaching rates in the MAM-PEC model [CEPE, 1999]:

Copper	50	µg/cm²/day
ТВТ	4	µg/cm²/day
Other biocides	2,5	µg/cm²/day

Emissions from yachts in marinas

Typical settings for emission estimation in pleasure boat marina [CEPE, 1999]

Input Parameter Emission estimation	Unit	Marina-1 Dutch Marina	Marina-2 Golfe Juan	Marina-3 Antibes
Nr of berths	-	250	841	1230
Ships at berth ¹	-	89	299	437
Ships moving	-	0	0	0
antifouled area per ship ²	m²/ship	5	22,5	25,5
application factor ³	%	100	20	20
leaching rate ⁴	µg/cm²/day	2,5	2,5	2,5

This is derived in the models of Johnson and Luttik (1994) and Bauer and Jacobsen (1997) from the year-averaged fraction of boat slips used (100 % in summer, 25 % in winter; overall 50%) and the average fraction of yachts present in the harbour (71 %), i.e. not sailing or dry docked.

Values taken from Bauer and Jacobsen (1997) set as 50 % of boat deck area.

³ In model of Bauer and Jacobsen (1997) default value for application set at 20 %

⁴ Default value as in Johnson and Luttik (1994) and Bauer and Jacobsen (1997),

Waste Treatment

• Waste streams + relevant information

Emission routes for biocides. '+'=relevant; '-' not relevant [weight %] (van Dokkum et al., 1998, modified)

Product type	Products*	Fresh surface water	Marine surface water	Air indoor and outdoor	Soil***	Solid Waste	Waste water
21.1	Antifouling products on inland craft > 25 m (P)	65 %	-	0 - 40 % (Appli- cation, Overspray)	-	5 %	+
21.2	Antifouling products on inland craft < 25 m (P+N)	65 %	-	0 - 60 % (Appli- cation, Overspray)	-	5 %	+
21.3	Antifouling products on commercial craft (P)	+	+	0 – 40 % (Appli- cation, Overspray)	-	5 %	+
21.4	Antifouling products on seagoing craft (P+N)	-	65 %	0 - 40 % (Appli- cation, Overspray)	-	5 %	+
21.5	Aquaculture equipment and other immersed structure (P)	65 %	See fresh surface water**	0 - 40 % (Appli- cation, Overspray)	-	5 %	+

* for conventional , soluble matrix antifouling paints

** if the use is affecting marine surface water

*** possible effects on sediments (settling and partitioning)

P: professional use; N: non-professional use

Release of biocides into solid waste:

5 % by weight, during remedial treatments (Balk, 1999)

Release on biocides into waste water:

5 %, if the removed amount is not properly disposed off as chemical solid waste

• Recycling/recovery/reuse

Existing or produced emission models

Predicted Environmental Concentration (PEC)

A general study on the estimation of biomagnification potential for the marine environment was presented by Vega et al. (Vega et al, 1999)

Data from the following studies can be used to predict environmental concentration, fate and persistence of zinc and copper pyrithione in harbors and lakes. Using U.S. EPA software (EXAMS2.97, Burns, 1996), the PECs in the water column and in the sediment were calculated for different environments, including a worst case harbour, which was simulated by using actual measured concentrations of persistent antifoulants (Scarlett, 1997; Rexrode et al., 1997). In a harbor where a persistent antifoulant would have a PEC of 400 ppt, the pyrithiones are calculated to have a PEC of ~15 ppt in the water column and less than 1 ppt in the sediment. EXAMS predicts that the major degradation pathways for pyrithione are photolysis and biodegradation. These predictions are supported by recent harbour monitoring studies carried out in southern England where pyrithione could not be detected (Thomas, 1999).

Risk Assessments

Tin and copper compounds are often combined in antifouling biocide products. In reference to Dokkum et al.,1998 antifouling systems can be divided into seven categories:

- 1. Soluble matrix type
- 2. Insoluble matrix type
- 3. Ablative or polishing tin free paints
- 4. Self-polishing organotin paints
- 5. Non-stick coatings (synonyms silicon coatings, foul release coatings, low-surface energy coatings)
- 6. Coal tar
- 7. others

The substances not bound to a matrix diffuse through the paint layer and are released into the water. The initial release rate will be very high, but after some time the release rate will be too slow to prevent fouling.

The most promising coating without biocides is the non stick coating (most are on a silica basis). The top layer of this coating is formed with very low surface tension, which gives fouling organisms no (or very low) opportunities to attach firmly.

Around 80 % of all seagoing ships are protected by a selfpolishing organotin paint. Other systems for seagoing ships are ablative and matrix types.

Coal tar is only used on freshwater ships, where fouling is not as strong as in salt water. The active substances are polycyclic aromatic hydrocarbons (PAH).

The major question in assessing the risk of using a biocide in an application is: Will the environmental concentration reach the toxicity threshold for non-target organisms? The LC50s of pyrithiones range from 2,6 to 400 ug/L for aquatic organisms. A worst case PEC for the pyrithiones is ~0,015 ug/l. An indicator of the risk is the risk quotient: RQ = PEC/LC50 = 0,015/2,6 = 0.006.

A further estimate of the emissions of antifouling substances into the marine environment was presented by Isensee (Isensee, B. et al., 1994). In a first step the total amout of biocides used is determined. This is done on the basis of the complete ship hull area of a fleet in contact with sea water. Using the amount of biocid in the antifouling agents, the complete amount of biocides used can be calculated.

Parameter/variable(unit)	Symbol	Default	C/R/E/O
Input			
wetted surface (m ²)	WS		E
Concentration of a.i. in product (kg/m ³)	C _{a.i.}		R/E
thickness of antifouling coating (µm)	S	150	R/E
Output			
Biocides applied [g]	VB		0

Model calculations

$$VB = \frac{WS * C_{a.i.} * s}{1000}$$

C =Constant (if possible the constants are presented)

- R =(Required) values from the test results in the notification of a biocide
- E =Expert estimations (if posssible the expert estimations (defaults) are presented)
- O =Output from previous modules/calculations

A coating of antifouling agent protects the hull of a ship for about 3 to 5 years. During this time 80-90 % of the biocide are emitted into the water. Therefore the emission per day can be calculated as shown below:

$$E\left[\frac{kg}{d}\right] = \frac{VB*0.9}{1000}$$

In a project of the European Commission from 1996, an inventory was made of currently available antifouling products and their active ingredients. Additionally, a computer model was developed to calculate predicted environmental concentrations (PEC) for the active substances in various typical marine environments. The computer model, called "Marine Antifoulant Model to Predict Environmental Concentrations" (MAM-PEC) was developed by the Institute for Environmental Studies (Amsterdam) and WL Delft Hydraulics (Delft) (CEPE, 1999).

The objectives of the study were:

- to provide a concise and critical review of relevant chemical fate models for contaminants currently used in marine risk assessment;
- to specify the requirements and specifications for a simple model for the prediction of antifouling products;
- to develop, refine and present a working 1D-computer model suitable for a set of predefined typical marine environments;
- to validate the model with existing monitoring data for a selected number of compounds.

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22 Embalming and taxidermist fluids

Introduction

Embalming is the preservation of a human or an animal corpse.

Thanatopraxis is the temporary preservation of a human corpse. The objective is to obtain short-term preservation for transport or preservation objectives. A fluid (in most cases formalin) is injected into the body, while blood is removed. The concentration of formalin is much lower than that for embalming.

Taxidermy includes all methods of reproducing a life-like three dimensional representation of an animal for permanent display. In some cases the skin is preserved and mounted on an artificial armature.

The relevant sub-groups are:

- 22.1 Embalming chemicals (professional use)
- 22.2 Taxidermist chemicals (professional use)

Applications

There are three different procedures:

- Surface disinfection (soaps)
- Fluids for arterial injection to substitute body fluids
- Cavity fluids (e.g. torax)

The main biocide and fixative is formaline (37 % formaldehyde). Others are Isopropylalcohol, liquefied phenol, phenolic acids, inositols, castor oil (phorbyol), DL-camphor and glyoxal (oxaldehyde) (van Dokkum, 1998; Mejanelle, 1997).

Relevant information data for ESDs

Processing

- Inclusion in materials/articles
- Application in processes

Used quantity of active substances

Quantities of a.i.:

- Embalming for a long-term-conservation: 3,6 to 15 % Formaline, 2 to 6 liter per human corpse
- For delay funeral: 0,2 % formaline

Service Life

Emission during service life is 100 % a.i. The impact of embalming range between some month and thousands of years

Waste Treatment

• Waste streams + relevant information

Emission routes for biocides. '+'=relevant; '-' not relevant (van Dokkum et al., 1998, modified)

Product type	Products	Fresh surface water	Marine surface water	Air indoor and outdoor	Soil	Solid Waste	Waste water
22.1	Embalming chemicals (P)	-	-	+	+*	-	+***
22.2	Taxidermist chemicals (P)	-	-	+	-	+**	+***

* if the embalmed body is buried

** if the preserved specimen are disposed off at solid waste disposal site

*** during processing

P: professional use; N: non-professional use

Release on biocides into air:

Volatile organic chemicals, like formaldehyde are used for embalming. This will create air emissions.

Release on biocides into waste water:

During embalming biocides will be emitted to the sewer system.

• Recycling/recovery/reuse

Existing or produced emission models

References:

van Dokkum, H.P., Scholten, M.C.T. Bakker, D.J. : "Development of a concept for environmental risk assessment of biocidal products for authorisation purposes (BIOEXPO)" , TNO MEP Report R97/443, 1998

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23 Control of other Vertebrates

Introduction

This product type shows a large similarity with rodenticides, as target animals and application techniques are comparable. Rodenticides aim to kill species of the order of *Rodentia*, such as rats, mice, squirrels, groundsquirrels, lemmings and voles, whereas this product type is aimed at all other groups of vertebrae pests. The most important non-rodent pests are probably rabbits and hares (order: *Lagomorpha*). In order of the relevance of the different industrial sectors, the product type 23 "Control of other Vertebrates" can be subdivided depending on the application technique and the location in the following subgroups:

- 23.1 Fumigants for control of other vertebrates, used outdoors (P+N) (professional and non-professional use)
- 23.2 Baits for control of other vertebrates, used outdoors (professional and nonprofessional use)
- 23.3 Baits for control of other vertebrates, used in animal housings) (professional and nonprofessional use)

Application

The application techniques are essentially the same as for rodenticides. However, the application areas 'Closed Spaces' and 'Sewer Systems' are not relevant for this product type, as biocides for controlling (other) vertebrates are not used in these areas. The biocides of this product type are used outdoors and (possibly) in animal housings. Application techniques are fumigation and baits.

Relevant information data for ESDs:

Processing

- Inclusion in materials/articles
- Application in processes

Used quantity of active substances [weight %]:

Multidose substance: doses 0,005 - 0,01 % (Haskoning 1995) Bromadialon: bait (50 mg/kg), single dose, formulation for preparation of bait: 0,25 g/l of dry powder

Chlorofacinon (old fashion) 50 - 250 mg/kg bait

Chloralose \leq 40 g/kg bait against mice, trained personnel (Tomlin, 1997)

Hydrogen cyanide: fumigating enclosed spaces (stored grain in warehouses, glasshouses, rabbit burrows, rat runs (trained personnel)

Formulations packed in metal containers; also absorbed on porous material, formulation 400 g a.i./kg (water soluble powder), (Tomlin, 1997)

Pesticides federally registered to control [weight %] (Jacobs, 1994):

Vertebrates	Type of pesticide	Effective substance	Concentration	Application type
Ground Squirrels	Toxicant	Zinc Phosphide	1,0-2,0 %	Dry baits
	Fumigants	Aluminium Phosphide (Phostoxin)	55-60 %	Tablets, pellets, bags
		Gas Cartridges	Various concentration	Ignitable cartridges
Moles	Toxicants	Strychnine Alkaloid	0,5 %	Dry bait
	Fumigants	Aluminium Phosphide (Phostoxin)	55-60 %	Tablets, pellets, or bags
		Gas Cartridges (many active ingredients)	Various concentration	Ignitable cartridges
Foxes	Toxicants	Sodiumcyanide	89 %-91 %	Powder packed in capsules

Service Life

Waste Treatment

• Waste streams + relevant information

The environmental compartments exposed to other vertebrates depend on the application technique and the location where the product is applied is shown in the following table.

Emission routes for biocides. '+'=relevant; '-' not relevant (van Dokkum et al., 1998, modified)

Product type	Products	Fresh surface water	Marine surface water	Air indoor and outdoor	Soil	Solid Waste	Waste water
23.1	Fumigants for control of other vertebrates, used outdoors (P+N)	-	-	+	+	+	-
23.2	Baits for control of other vertebrates, used outdoors (P+N)	+	-	-	+	+	-
23.3	Baits for control of other vertebrates, used in animal housings (P+N)		-	+	+	+	+-

P: professional use; N: non-professional use ,* disposal on manure

• Recycling/recovery/reuse

Existing or produced emission models

References:

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Cooperating Organisations

- Agriculture, Fisheries and Forestry, Australia
- Austria Research Centre in Selbersdorf, Austria
- Chemical Manufacturers Association (CM)
- Council of Europe, France
- CTBA Technical Centre for Wood and Furniture, France
- DESOWAG GmbH, Germany
- Dutch ministry of Health, Welfare and Sport, Netherlands
- Environmental Administration, Finland
- EPA Environmental Protection Agency, USA
- Federal Agency for Consumer Health Protection and Veterinary Medicine, Germany
- Federal Agency for Material Quality and -control, Germany
- Federal Environmental Agency, Forest and Agriculture, Germany
- Food and Agriculture Organisation of the United Nations, USA
- Ghent University, Switzerland
- Government Ireland
- Government New Zealand
- Health Canada
- Hickson International PLC, Great Britain
- Imperial College of Science, Technology and Medicine London, Great Britain
- Instituto Recupero Crediti, Italy
- Johnson & Johnson
- Kemikalieinspektionen KEMI National Chemicals Inspectorate, Sweden
- Ministerium van Sociale Zaken en Werkgelegenheid, Netherlands
- Ministry of Heath, Spain
- Ministry of Housing, Spatial Planning and the Environment, Netherlands
- Ministry of Middleclass and Agriculture, Belgium
- National Institute of Agricultural Science and Technology (NIAST), Korea
- National Institute of Public Health and the Environment, Netherlands
- Organisation for Economic Co-operation and Development, France
- OSMOSE, INC., USA
- Rohm and Haas Deutschland GmbH, Germany
- SLOVENIAN STATE INSTITUTIONS, Slovenia
- SP Swedish National Testing and Research Institute, Sweden
- The Italian National Institute of Health (ISS), Italy
- TNO Building and Construction Research, Netherlands
- TNO Voeding, Netherlands

Product type	1 Human hygiene biocidal products	2 Private area and public health area disinfectants and other biocidal products	3 Veterinary hygiene biocidal products	4 Food and feed area disinfectants	5 Drinking Water	6 In-can Preservatives	7 Film Preservatives
Areas of application	anti-dandruff shampoos, antimicrobial soap, antiperspirants and deodorants, health care products, personal hand wash products, products to combat acne, skin antiseptics	Products for disinfection of air, water and materials in private, public and industrial areas, including hospitals, chemical toilets, waste water, waste, soil or other substrates	Disinfection of animal housing, footwear and animals' feet, milk extraction systems, means of transport, hatcheries Disinfection in fish-farming	Disinfection of floors, walls and equipment within plants, In- plant chlorination on food contact surfaces, Disinfection of packaging material	Drinking water	Human hygienic products and cosmetics, detergents, paints and coatings, Fluids used in paper-, textile and leather production, lubricants, machine oils	Paint coating (paint, spray, dunk/dive) (on plastics/ synthetic materials, metals, leather, wood, stone, concrete etc.), Adhesive coating, Paper coating
Market data							
 Product quantities for areas of application European-wide- -sample country 	0	0	0	0	0	0	0
 Product quantities by product categories 	0	0	0	0	0	++	++
Percentage of products, which are equipped with biocides	0	0	0	0	+	+++	+++
Biocide quantities in products	+	+	+	+	++	+++	+++
Use							
Quantities applied EG [g/m ²]	0	0	0	0	0	0	0
Emissions at application	0	0	0	0	0	0	0
Emissions during service life	+	+	+	+	0	0	0
Emissions at waste treatment	-	0	0	0	-		
Emissions at landfill and incineration	-	0	0	0	-	++	++

Product type	9 Fibre, leather, rubber and polymerized materials preservation	10 Protective Agents for Masonry	11 Preservatives for liquid- cooling	12 Slimicides	13 Metalworking fluids	14 Rodenticides	15 Avicide
Areas of application	Fibre (Textile and fabrics (wood, cotton), leather and hides, rubber plastics, paper	coating systems, injection agents	flow-through cooling, open recirculating cooling systems, closed recirculating cooling systems	Pulp and Paper industry, oil Industry, textile industry, leather industry, sugar industry	Metal cutting	In houses, industrial and public buildings, food and feed preparation as well as storage, veterinary purpose, outdoors, competitive application	Ready-to-use- baits (in and around buildings, in and around livestocking feeding pens, in food stores), liquids to prepare baits, gas, contact paste
Market data							
 Product quantities for areas of application European-wide- -sample country 	++	0	0	0	+	0	0
Product quantities by product categories		0	0	0	0	0	0
Percentage of products, which are equipped with biocides		0	0	0	0	0	0
Biocide quantities in products	++	++	+	+	+	++	++
Use							
Quantities applied EG [g/m ²]	0	+	+	0	+	0	0
Emissions at application	++	+	0	0	0	0	0
Emissions during service life	0	+++	0	0	0	+	+
Emissions at waste treatment	0	0	0	0	0	-	-
Emissions at landfill and incineration	0	0	0	0	0	-	-

Product type	16 Molluscicides	17 Piscicide	18 Insecticides, Acaricides	19 Repellents	20 Preservatives for food or feedstock	21 Antifouling Products	22 Embalming and taxidermist fluids	23 Other Vertebrates
Areas of application	In houses, industrial and public buildings, food and feed preparation as well as storage, veterinary purpose, outdoors	Baits e.g. pellets (spread as solid product) (in seas, rivers, ponds, ditches), liquids (admitted) (in seas, rivers, ponds, ditches, fish tanks	In and aroand domestic houses, industrial and public buildings, control of animal parasites (pets), controlling insects	indoors like private houses, public and industrial buildings for veterinary purposes, for sewer systems, cooling water systems, transport sector, outdoors	Spraying (e.g., aerosols, solutions, suspensions, emulsions), pump sprays, lotion,crème, milk	Surface coatings of food, ingredients of feed- and foodstuff	Surface disinfection (soaps) Fluids for arterial injection to substitute body fluids Cavity fluids (e.g. torax)	In houses, industrial and public buildings, food and feed preparation as well as storage, veterinary purpose, outdoors
Market data								
 Product quantities for areas of application European-wide- -sample country 	0	0	0	0	0	0	0	0
Product quantities by product categories	0	0	0	0	0	0	0	0
Percentage of products, which are equipped with biocides	0	+++	0	0	-	0	+++	0
Biocide quantities in products	++	+	++	+	+++	+	0	++
Use								
Quantities applied EG [g/m ²]	0	0	0	0	0	0	++	0
Emissions at application	0	0	0	0	0	+	0	0
Emissions during service life	0	+++	+	+	0	+	0	+
Emissions at waste treatment	-	-	-	-	0	0	-	-
Emissions at landfill and incineration	-	-	-	-	0	0	-	-

Product type	1 Human hygiene biocidal products	Assessment of existing data	Comments
Areas of application	 Skin antiseptic (professional and non- professional use) Antimicrobial soap (professional and non- professional use) Health care personnel hand wash (professional use) Suntan (non-professional use) Competitive applications 	-	An ESD has to be executed for every application, because the expected emissions depend on the type of coating, the contact intensity with environmental mediums, the mechanical, chemical, and biological strain, etc.
Market data			
 Product quantities for areas of application -european-wide -sample country 		0	No European market data available. No European-wide and country specific data for the quantities of single/individual areas of application available.
Product quantities by product categories		0	No European market data available. No European-wide and country specific data for the quantities of single/individual areas of application available.
Percentage of products, which are equipped with biocides		0	No European market data available. No European-wide and country specific data for the quantities of single/individual areas of application available.
Biocide quantities in products	 alcohol 70-80 %+0,5 % chlorohexidine alcohols (ethylalcohol, isopropyl-alcohol, n-propylalcohol) aluminium salts coal tar heterocyclic compounds iodine phenols pyrithione, quaternary ammonium compounds resorcinol salicylic acid, selenium sulphide triclosan 	+	
Use			
Application techniques	used as liquid product like baths, liquid soap,	-	

Product type	1 Human hygiene biocidal products	Assessment of existing	Comments
	shampoos • used as solid product like soap bars • spray • pastes • gels	<u>data</u>	
Quantities applied EG [g/m ²] [g/l], g/kg]	 used as liquid product used as solid product spray pastes gels 	0	Data needs to be elaborated
Emissions at application	 used as solid/liquid product water Spray (gas) air used as paste water used as gel water 	0	Data needs to be elaborated
Emissions during service life	Spray (gas) 100% into air	+	Data needs to be elaborated
Emissions at waste treatment	Not relevant	-	
Emissions at landfill and incineration	Not relevant	-	

Product type	2 Private area and public health	Assessment	Comments
	area disinfectants and other biocidal	of existing	
	products	data	
Areas of application	 2.1 Disinfection of medical equipment (professional use) 2.2 Disinfection of swimming pool, aquarium, bathing and other waters (professional and non-professional use), (see also PG 5) 2.3 Disinfection of air-conditioning systems (professional use) 2.4 Disinfection of accommodation for man (professional and non-professional use), (see also PG 4) 2.5 Disinfection of industrial areas (professional use), (see also PG 4, PG 20) 2.6 Disinfection of chemical toilets (professional and non-professional use) 2.7 Sewage/Waste water disinfection (professional use) 2.8 Disinfection of hospital/infectious waste (professional use) 2.9 Soil or other substrates disinfection (professional use) 2.10 Laundry disinfection (professional and non- professional use) Competitive applications 	-	An ESD has to be executed for every application, because the expected emissions depend on the type of coating, the contact intensity with environmental mediums, the mechanical, chemical, and biological strain, etc.
Market data			
 Product quantities for areas of application -european-wide -sample country 		0	No European market data available. No European-wide and country specific data for the quantities of single/individual areas of application available.
 Product quantities by product categories 		0	No European market data available. No European-wide and country specific data for the quantities of single/individual areas of application available.
 Percentage of products, which are equipped with biocides 		0	No European market data available. No European-wide and country specific data for the quantities of single/individual areas of application available.
 Biocide quantities in products 	 alcohols aldehydes algaecides based on copper	+	

Product type	2 Private area and public health	Assessment	Comments
	area disinfectants and other biocidal	of existing	
	products	data	
	algaecides based on polyoxyimino compounds		
	 algicides based on quaternary ammonium 		
	alkylamines		
	biguanides		
	 bromide (elemental liquid) 		
	 bromide (sodium) 		
	 bromine organic releasing compounds 		
	chlorine		
	No epidemy at >0,5 mg Cl ₂ /I Swimming pool,		
	aquarium, bathing and other waters		
	wasted water contains a maximum of 1,4 mg/l		
	free chlorine Wasto water disinfection: 2 10 mg Cl /l 20 to 60		
	Waste water disinfection: 3-10 mg Cl ₂ /l, 30 to 60 min. contact time		
	 chlorinedioxide 		
	 chlorinedioxide in combination with chlorine gas 		
	 chlorine gas 		
	chlorohexidine		
	0,05-4 % for medical equipment sterilization		
	copper ions		
	ethanol		
	70 % for medical equipment sterilization		
	ethyleneoxide		
	for medical equipment sterilization 1200 mg/l at		
	50-60°C		
	Formaldehyde		
	glutaricaldehyde		
	2 % for medical equipment sterilization		
	• guanidines		
	hydrogenperoxide		
	3-6 % for medical equipment sterilization		
	hydrogenperoxide in combination with biguanid networks		
	polymers		
	 hypochlorites (sodium and calcium) hypochlorite 1000 ppm (free chl.) for medical 		
	equipment sterilization		
	0,5 to 12,5 % (available CI-levels; Household		
	hypochlorite preparations), prevalence 3-5 %;		

Product type	2 Private area and public health	Assessment	Comments
	area disinfectants and other biocidal	of existing	
	products	data	
	 typical dilute concentrations for hypochlorite range from 0,01 to 0,5 %; less frequent exposure to conc. Solutions 2,5 to 5 % () hypochlorous acid iodophore preparations jodium 1 % in 70 % alcohol or jodofoor 10 % for medical equipment sterilization isocyanates (chlorinated) isopropanol ozone peracetic acid Phenols o-phenylphenol 2 % for medical equipment sterilization quaternary ammonium compounds silver ions succcinic 10 % for medical equipment sterilization 		
	 surfactants 		
Use			
Application techniques	liquid productsolid productgas	-	
Quantities applied EG [g/m ²] [g/l], g/kg]	 used as liquid product used as solid product gas 	0	Data needs to be elaborated
Emissions at application	 used as solid/liquid product water gas air 	0	Data needs to be elaborated
Emissions during service life	• spray (gas) 100% into air	+	Data needs to be elaborated
Emissions at waste treatment		0	Data needs to be elaborated
Emissions at landfill and incineration		0	Data needs to be elaborated

Product type	3 Veterinary hygiene biocidal products	Assessment of existing data	Comments
Areas of application	 3.1 Disinfection of animal housings (stables), (professional use) 3.2 Disinfection of hatcheries (professional use) 3.3 Disinfection in the means of transport (professional use) 3.4 Disinfection for veterinary hygiene on non-farm buildings, like e.g. milk extraction systems (professional use) 3.5 Disinfection for veterinary hygiene, like footwear and animals' feet (professional use) 3.6 Disinfection in fish-farming (professional use) Competitive applications 	-	An ESD has to be executed for every application, because the expected emissions depend on the type of coating, the contact intensity with environmental mediums, the mechanical, chemical, and biological strain, etc.
Market data			
 Product quantities for areas of application -european-wide -sample country 		0	No European market data available. No European-wide and country specific data for the quantities of single/individual areas of application available.
Product quantities by product categories		0	No European market data available. No European-wide and country specific data for the quantities of single/individual areas of application available.
Percentage of products, which are equipped with biocides		0	No European market data available. No European-wide and country specific data for the quantities of single/individual areas of application available.
Biocide quantities in products	 Aldehydes concentration for feet 2 g/l, for footwear 40 g/l concentration for pig stables 2g/l, poultry 40g/l Chloramine for Disinfection in aquaculture Chlorine compounds concentration for Disinfection of footwear and paws about 0,2 g/l concentration for Disinfection of transport vehicles about 0,2 g/l concentration for Disinfection of milking machines about 0,2 g/l concentration for disinfection of stables about 0,2 g/l 	+	

Product type	3 Veterinary hygiene biocidal	Assessment	Comments
	products	of existing	
	•	data	
	Formaline		
	for disinfection in aquaculture		
	concentration disinfection in chicken hatchery		
	about 1,2 g/m ³		
	Formol		
	for Disinfection in aquaculture		
	Hydroxides		
	concentration for Disinfection of footwear and		
	paws about 10,5 g/l		
	concentration for Disinfection of transport		
	vehicles about 10,5 g/l		
	concentration for Disinfection of milking machines about 0,6 g/l		
	concentration for disinfection of stables about		
	10,5 g/l		
	Hypochloride		
	for Disinfection in aquaculture		
	Iodophores		
	for Disinfection in aquaculture		
	malachite-green		
	for Disinfection in aquaculture		
	• ozone		
	for Disinfection in aquaculture		
	for Disinfection in chicken hatchery		
	Phenolic agents for disinfection of stables		
	for disinfection of stables Polyvinyl alcohols 		
	for Disinfection in aquaculture		
	 quaternary ammonium compounds 		
	for Disinfection in aquaculture		
	for Disinfection in chicken hatchery		
	for Disinfection of milking machines		
	Quaternary ammonium salts		
	concentration Disinfection of footwear and paws		
	0,5-2 g/l		
	concentration for disinfection of stables 0,5 - 2 g/l)		
Use			
Application techniques	 used as liquid product for bathes, dipping, 	-	
	pouring		

Product type	3 Veterinary hygiene biocidal	Assessment	Comments
	products	of existing	
		data	
	 supplied as powders 		
	 spraying 		
	• gassing		
	clean in place-method		
Quantities applied EG [g/m ²] [g/l], g/kg]	used as liquid product	0	Data needs to be elaborated
	 used as powder product 		
	• gas		
	• spray		
	clean in place		
Emissions at application	 used as solid/liquid product 	0	Data needs to be elaborated
	- water		
	• gas		
	- air		
	• spray - air		
	clean in place - water		
Emissions during service life	Spray (gas) 100% into air	+	Data needs to be elaborated
Emissions at waste treatment		0	Data needs to be elaborated
Emissions at landfill and incineration		0	Data needs to be elaborated

Product type	4 Food and feed area disinfectants	Assessment of existing data	Comments
Areas of application	 4.1 Disinfection of food contact surfaces, environmental areas in food and feed processing (floors, walls and equipment within plants), (professional use) 4.2 In-plant chlorination (professional use) 4.3 Disinfection of packaging material (aseptic packaging), (professional use) Competitive applications 	-	An ESD has to be executed for every application, because the expected emissions depend on the type of coating, the contact intensity with environmental mediums, the mechanical, chemical, and biological strain, etc.
Market data			
 Product quantities for areas of application european-wide sample country 		0	No European market data available. No European-wide and country specific data for the quantities of single/individual areas of application available.
Product quantities by product categories		0	No European market data available. No European-wide and country specific data for the quantities of single/individual areas of application available.
Percentage of products, which are equipped with biocides		0	No European market data available. No European-wide and country specific data for the quantities of single/individual areas of application available.
Biocide quantities in products	 Acids and anionic tensides Alcohols (concentration 80-100%) Alkylamin (concentration 1%) Amphotensids (concentration about 1%) Chlorine compounds (concentration about 1%) Hypochlorite, concentrated solutions (up to 12,5%, av. 5%), used neat or diluted, generally used by qualified and trained staff Inorganic acids and alkalies Iodine compounds Polymeric biguanides Peracetic acid (concentration 0,5%)Carboxylic acid and p-hydoxybenzoicacid esters Quaternary ammonium compounds (concentration about 1%) 	+	

Product type	4 Food and feed area disinfectants	Assessment	Comments
		of existing	
		data	
Use			
Application techniques	 CIP (Clean In Place = disinfectant is added to the circulating water) for tools and machines Low and high pressure spraying Soaking and brushing Fogging 	-	
Quantities applied EG [g/m ²] [g/l], g/kg]	 used as liquid product used as powder product fog spray clean in place 	0	Data needs to be elaborated
Emissions at application	 used as solid/liquid product water fog air spray air clean in place water 	0	Data needs to be elaborated
Emissions during service life	Spray (gas) 100% into air	+	Data needs to be elaborated
Emissions at waste treatment		0	Data needs to be elaborated
Emissions at landfill and incineration		0	Data needs to be elaborated

Product type	5 Drinking Water	Assessment of existing data	
Areas of application	 5.0 Drinking water disinfection Competitive applications Cooling/process water (see 11) Disinfection of swimming pools (see 2) 	-	An ESD has to be executed for every application, because the expected emissions depend on the type of coating, the contact intensity with environmental mediums, the mechanical, chemical, and biological strain, etc.
Market data			
 Product quantities for areas of application -european-wide -sample country 	Drinking water [Mio. m^3/a] (1997):EU 15: 36.930A:450DK:350F:5.960D:5.450GR:950I:7.900IR:370P:360E:4.670UK:7.600FIN:420NL:1.100B:340Lux:40S1.000	0	No European market data available. No European-wide and country specific data for the quantities of single/individual areas of application available.
Product quantities by product categories		++	No European market data available. No European-wide and country specific data for the quantities of single/individual areas of application available.
Percentage of products, which are equipped with biocides	Nearly 100 %	+	No European market data available. No European-wide and country specific data for the quantities of single/individual areas of application available.
Biocide quantities in products	 chlorine compounds chlorine, gaseous hypochlorites chlor lime chlordioxide iodine compounds ozone Calciumhypochlorit Magnesiumhypochlorit 	+	Hydrogen cyanide is not allowed any more in the Netherlands.

Product type	5 Drinking Water	Assessment of existing data	Comments
	 Natriumhypochlorit 		
	Chlorine, hypochlorites are used in amounts up to 1,2 mg/l, chlordioxide up to 0,4 mg/l and ozone up to 10 mg/l		
	The following substances are used in special cases:		
	 Natriumdichlorisocyanurat-dihydrat and water free, Kaliumdichlorisocyanurat, Trichlorisocyanuracid 		
Use			
Application techniques	 Boiling (non-chemical) filtering (non-chemical) coagulation/flocculation techniques (non-chemical) oxidizing agents metal ions UV-radiation (non-chemical) Chlorination with salts of hypochlorous acid Chlorination with CIO₂, CIO₂ and CIO₃ Chloroisocyanate Ozone treatment Treatment with hydrogen peroxide Other desinfectants, used on smaller scale are: KMnO₄ (used for pre-disinfection, Bryant <i>et al.</i> 1992) Ag 	-	
Quantities applied EG [g/m ²] [g/l], g/kg]		0	Data needs to be elaborated
Emissions at application	 Soil Fresh surface water Sewage-water Air Marine surface water 	0	Data needs to be elaborated
Emissions during service life		0	Data needs to be elaborated
Emissions at waste treatment	Not relevant	-	
Emissions at landfill and incineration	Not relevant	-	

Product type	6 In-can Preservatives	Assessment of existing data	Comments
Areas of application	 6.1 Washing and cleaning fluids (professional use), human hygienic products and cosmetics (see product group 2) (professional and non-professional use) 6.2 Detergents (professional and non-professional use) 6.3 Paints and coatings (see 7 film preservatives), (professional and non-professional use) 6.4 Fluids used in paper-, textile and leather production (see 7 film preservatives and 9 fibre, leather, rubber and polymerised materials preservation), (professional use) 6.5 Lubricants (see 13 metal working fluid), (professional use) Competitive application Adhesive coating (see also 7) Paper coating (see also 21) 	-	An ESD has to be executed for every application, because the expected emissions depend on the type of coating, the contact intensity with environmental mediums, the mechanical, chemical, and biological strain, etc.
Market data			
 Product quantities for areas of application european-wide- -sample country 		0	No European market data available. No European-wide and country specific data for the quantities of single/individual areas of application available.
Product quantities by product categories	 Adhesives with water as a solvent (NL): 25 t/a Dispersion adhesives (NL): 60 t/a 	++	European wide data can be projected by the population
 Percentage of products, which are equipped with biocides 	60 % in all product categories (NL)	+++	The Dutch data can be used European-wide.
 Biocide quantities in products 	 Water borne coatings: 2 % (weight) Adhesives with water as a solvent: 0,3 % (weight) Dispersion adhesives: 0,3 % (weight) 	+++	The effect concentration for theses values is standardized at 100 %. A few examplesfor the in-can biocides 4,4-Dimethyloxazolidine (74,7 % ai) $0,05 - 0,3$ 1,2-Dibromo-2,4-dicyanobutane (25 % ai) $0,1 - 0,3$ 2[(Hydroxymethyl)-amino]ethanol (100 % ai) $0,1 - 0,3$ 1-(3-Chlorallyl)-3,5,7-triaza-1-azoniaadamantane chloride (69 % ai) $0,01 - 0,27$ 1,2-Benzisothiazolin-3-one (19 % ai) $0,04 - 0,125$

Product type	6 In-can Preservatives	Assessment of existing data	Comments
			$\begin{array}{cccc} & 5\text{-Chloro-2-methyl-4-isothiazolin-3-one1,15} & \% & ai) \\ & & 0,05-0,167 \\ & \text{Hexahydro-1,3,5-triethyl-s-triazine} & 0,01-0,1 \\ & 2\text{-Hydroxymethyl-2-nitro-1,3-propanediol} & (50 \ \% \ ai) \ 0,02-0,3 \\ \end{array}$
Use			
Application techniques	paint, spray, dunk	-	
Quantities applied EG [g/m ²] [g/l], g/kg]	 paint spray dunk	0	Data needs to be elaboratet (e.g. VOC-Emissions)
Emissions at application	 Paint air water soil Spray air water soil Dunk air water soil 	0	Data needs to be elaboratet (e.g. VOC-Emissions)
Emissions during service life		0	Data needs to be elaborated (e.g. abrasion)
Emissions at waste treatment			
Emissions at landfill and incineration	 Water borne coatings (NL): 25 % Adhesives with water as a solvent (NL): 15 % Dispersion adhesives (NL): 40 % 	++	The data has to be rated as diffuse emissions and cannot be associated with one compartiment The Dutch data can be used European-wide.

Product type	7 Film Preservatives	Assessment of existing data	Comments
Areas of application	 7.1 Paints and coatings (see 6 in can preservatives), (professional and non-professional use) 7.2 Plastics (see 9 fibre, leather, rubber and polymerised materials preservation), (professional use) 7.3 Glues and adhesives (professional and non-professional use) 7.4 Fluids used in paper-, textile and leather production (see 6 in can preservatives and 9 fibre, leather, rubber and polymerised materials preservation), (professional use) Competitive application Ship coating (see also 21) In-can preservatives (see also 6) 	-	An ESD has to be executed for every application, because the expected emissions depend on the type of coating, the contact intensity with environmental mediums, the mechanical, chemical, and biological strain, etc.
Market data Product quantities for areas of application European-wide- -sample country 		0	No European market data available. No European-wide and country specific data for the quantities of single/individual areas of application available.
Product quantities by product categories	 Water borne coatings (NL): 310 t/a Adhesives with water as a solvent (NL): 25 t/a Dispersion adhesives (NL): 60 t/a 	++	European wide data can be projected by the population
 Percentage of products, which are equipped with biocides 	60 % in all product categories (NL)	+++	The Dutch data can be used European-wide.
Biocide quantities in products	 Water borne coatings: 2 % (weight) Adhesives with water as a solvent: 0,3 % (weight) Dispersion adhesives: 0,3 % (weight) zinc pyrithione in a latex paint: 0.1% to 0.5 % of active material on wet paint weight. 3-lodo-2-propynyl butyl carbamat (100 % ai) 0,1-0,5% 2-n-Octyl-4-isothiazolin-3-one (45 % ai) 0,1 - 0,3% Diiodomethyl-p-tolylsulphone (95 % ai) 0,2 - 0,7% 	+++	The effect concentration for theses values is standardized at 100 %. A few examples for the in-can biocides (see 6) 4,4-Dimethyloxazolidine (74,7 % ai) $0,05 - 0,3$ 1,2-Dibromo-2,4-dicyanobutane (25 % ai) $0,1 - 0,3$ 2[(Hydroxymethyl)-amino]ethanol (100 % ai) $0,1 - 0,3$ 1-(3-Chlorallyl)-3,5,7-triaza-1-azoniaadamantane chloride (69 % ai) $0,01 - 0,27$ 1,2-Benzisothiazolin-3-one (19 % ai) $0,04 - 0,125$ 5-Chloro-2-methyl-4-isothiazolin-3-one1,15 % ai) Hexahydro-1,3,5-triethyl-s-triazine $0,01 - 0,1$ 2-Hydroxymethyl-2-nitro-1,3-propanediol (50 % ai) $0,02 - 0,027$

Product type	 Film Preservatives N-(Trimethylthio) phthalimide (88 % ai) 	Assessment of existing data	Comments 0,3
Use	1 – 3%		
Application techniques	paint, spray, dunk	-	
Quantities applied EG [g/m ²]	 paint spray dunk 	0	Data needs to be elaborated (e.g. VOC-Emissions)
Emissions at application	 Paint air water soil Spray air water soil Dunk air water soil 	0	Data has to be elaborated (e.g. VOC-Emissions)

	9.1 Fibre (Textile and fabrics (w (professional use) 9.2 Leather and Hides (professional us	ood, cotton),	_	
•	 9.3 Rubber, Plastics and polymeri (professional use) 9.4 Paper and cardboard (professional Competitive application: Film preservatives (see 7) In-can preservatives (see 6) 	sed material	-	An ESD has to executed for every application, because the expected emissions depend on the type of coating, the contact intensity with environmental mediums, the mechanical, chemical, and biological strain, etc.
Market data				
application -european-wide- • -sample country	Leather and hidesCountryNo of tanneriesProdu- [1.00]Austria750Belgium722Denmark213Finland918France113123Germany37108Greece15046Ireland442Italy2.400194Netherlands1436Norway311Portugal110106Spain255471Sweden422Switzerland455United55135Kingdom55135	0m ³] 11 26 30 41 300 300 50 50 50 17 40 380 165 00 28	++	

Product type	9 Fibre, leather, rubber and polymerized materials preservation	Assessment of existing data	Comments
 Product quantities by product categories Percentage of products, which are equipped with biocides Biocide quantities in products 	CountryProduction [Mio. t] (1996)Austria3,6Belgium1,2Denmark0,3Finland10,1France8,2Germany13,3Greece0,4Ireland-Italy6,6Netherlands3,1Norway2,1Portugal1,1Spain3,5Sweden8,8United Kingdom5,8	++	
Use	Application in masses, dunk, point, aprov		
Application techniques Quantities applied EG [g/m ²]	Application in masses, dunk, paint, spray	0	Data needs to be elaborated
Emissions at application	Fibre: 20 – 30 % (70 – 80 % are adsorbed by the fabric) Paper and cardboard: 20 % (release of 80 % in the paper) Leather: 5 % (95 % fixation)	++	

Product type	9 Fibre, leather, rubber and	Assessment	Comments
	polymerized materials preservation	of existing	
		data	
Emissions during service life		0	Data needs to be elaborated
Emissions at waste treatment		0	Data needs to be elaborated
Emissions at landfill and incineration		0	Data needs to be elaborated

Product type	10 Protective Agents for Masonry	Assessment of existing data	Comments
Areas of application	 10.1 Coating systems (professional use) 10.2 Injection agents (professional use) 10.3 Plasters (professional use) 10.4 Screed (professional use) 10.5 Concrete additives (professional use) Competitive applications In-can preservatives (see 6) Film preservatives (see 7) Insecticides, acaricides and products to control other arthropods (see 18) 	-	An ESD must be calculated for each application, since the emissions depend on the type of application, the intensity of contact with the environment, the mechanical, chemical and biological wear and other factors.
Market data			
 Product quantities for areas of application European-wide sample country 		0	No European-wide market data available. No European- wide or country specific data available about the amounts of individual areas of application
 Product quantities by product categories 	Coating systems of plaster bound with artificial resins Elastic, crack covering coats Base coat Silicon colour systems	0	No European-wide market data available. No European- wide or country specific data available about the amounts of individual areas of application
	 Building proofing and -restoration Special plasters Glue/resins 		
	Concrete restoration Overground workings Bridges/Surface protection		
	Ground coats Screed additives, mortar, filler Impregnation/sealing Injection resins Protective coats for oil rooms Glueing/jointing		
	Front protection and -restoration Joint restoration systems Hydrophobic impregnation Cleaning Restoration Stabilizing		

Product type	10 Protective Agents for Masonry	Assessment	Comments
		of existing	
		data	
	 Mineral plaster systems Front plaster systems for frame houses Front plaster systems according to DIN 18550-2,5 		
	 Scratch coat pre-treatment Sanitating plaster systems Special mortar Heat insulation plaster systems DIN 18550-3 Additives and abherents Concrete abherents Mortar-, plaster- and concrete additives 		
Percentage of products which are equipped with biocides		0	No information available
Biocide quantities in products	 Preservatives for concrete Formaldehyde producers: about 0,1 weight% Phenolic compounds: 0,2 to 0,5 weight% Isothialozinic formulations (for example chlormethylisothiazolinon/methylisothiazolinon): 0,02 to 0,2 weight%. Inhibitors to delay the hardening of concrete 0,2 - 2 weight % (cement) Accelerators to accelerat the hardening of concrete 3 and 5 weight% (cement). Air-entraining agents 2-20 weight% (active substance) with dosages of 0,05 to 1 weight% (cement) 	++	For the calculation of the final quantity of the biocides (active substances) in concrete, resulting from biocides in concrete additives, it is necessary to know the additive dosage.
	Concrete liquefiers and solvents Liquefiers: 0,2 to 0,5 weight% (concrete), active substances in the liquefiers: 10–40 weight% (liquefier) Solvents: 0,8 to 2 weight% (concrete), active substances in the solvent: 10–40 weight% (solvent) (Example: dosage of 2 weight% in a 40 weight% solution results in a 0,1 weight % biocide in		

	10 Protective Agents for Masonry	Assessment of existing data	Comments
	concrete)		
	Preservatives (Biocides) for other concrete additives 0,5 weight% in relation to the additive weight Recycling agents		
	10 – 20 weight% (active substance)		
Use	Mixing injecting coating (painting)		
Application techniques	Mixing, injecting, coating (painting)	-	Data paada ta ba alabaratad
Quantities applied EG [g/m ²] [g/l], g/kg] etc.	for an assessment 0,5 weight% relative to the finished product	+	Data needs to be elaborated
Emissions at application	Solvents and liquefiers into water: 10 weight% within 7 days after application	+	
Emissions during service life	 Preservatives for concrete Into air: formaldehyde: 0,01 ppm – 0,03 ppm (1 m³ chamber) Ammonia: 0,02 ppm (1 m³ chamber) Solvents and liquefiers into water: 10 weight% within 7 days after application For an assessment for emissions to the aquatic system: 10 % of the effective substance (0,05 % of the 	+++	Max. recommended indoor air-formaldehyde concentration for wood working materials: < 0.1 ppm
Emissions at waste treatment Emissions at landfill and incineration	finished product or 0,5 kg/t finished product)	0	Data needs to be elaborated Data needs to be elaborated

Product type	11 Preservatives for liquid-cooling	Assessment	Comments
		of existing	
		data	
Areas of application	 11.1Flow-through cooling (professional use) 11.2Open recirculating cooling systems (professional use) 11.3Closed recirculating cooling systems (see 7 film preservatives), (professional use) Competitive applications Film preservatives (see 7) 	-	An ESD has to executed for every application, because the expected emissions depend on the type of coating, the contact intensity with environmental mediums, the mechanical, chemical, and biological strain, etc.
Market data			
 Product quantities for areas of application -european-wide- -sample country 		0	Data needs to be elaboratet
 Product quantities by product categories 		0	Data needs to be elaboratet
 Percentage of products, which are equipped with biocides 		0	Data needs to be elaboratet
 Biocide quantities in products 	 flow-through cooling Oxidizing open recirculating cooling systems oxidizing non-oxidizing closed recirculating cooling systems organic compounds 	+	
Use			
Application techniques			
Quantities applied EG [g/m ²] [g/l], g/kg]	Oxidizing active ingredient: 0,1-7 mg/L Isothiazolins: 1–5 mg/L Quaternary ammonium compounds: 3–50 mg/L	+	Data needs to be elaboratet
Emissions at application		0	Data needs to be elaboratet
Emissions during service life		0	Data needs to be elaboratet
Emissions at waste treatment		0	Data needs to be elaborated
Emissions at landfill and incineration		0	Data needs to be elaborated

Product type	12 Slimicides	Assessment of existing data	Comments
Areas of application	12.1 Pulp and Paper industry (professional use) 12.2 Oil industry (professional use) 12.2 Sugar industry (professional use) Competitive applications	-	An ESD has to executed for every application, because the expected emissions depend on the type of coating, the contact intensity with environmental mediums, the mechanical, chemical, and biological strain, etc.
Market data			
 Product quantities for areas of application -european-wide -sample country 		0	Data needs to be elaboratet
 Product quantities by product categories 		0	Data needs to be elaboratet
Percentage of products, which are equipped with biocides		0	Data needs to be elaboratet
Biocide quantities in products	 Pulp and Paper 50-1000 g/to dry fibre 0,25-50 ppm in process water 	+	A few examples for the biocides used in slimicides 2-brom-2-nitropropane-1,3-diol 2-Hydroxymethyl-2-nitropropane-1,3-diol 2,2,-Dibromo-2-cyanoacetamide 3,4-Dichloro-5-oxo-1,2-dithiol Glutardialdehyde 5-Chloro-2-methyl-4-isothiazolin-3-one
	 Oil Industry 100 mg/l CTAB(cetyltrimethyl-ammonium bromide, glutaraldehyd) (Board et al. 1987) 30-100 mg/l against planktonic SRB 50-800 mg/l sessile SRB 	+	
	Other	0	Data needs to be elaborated
Use			
Application techniques	 continuos supply of biostatic products single or repeat shock treatment 		
Quantities applied EG [g/m ²] [g/l], g/kg]	 BHAP 0,9 mg/l (S) Bronopol 2 mg/l (GB) TCMTB 2-9 μg/l 	0	Data needs to be elaboratet
Emissions at application		0	Data needs to be elaboratet

Product type	12 Slimicides	Assessment of existing data	Comments
Emissions during service life		0	Data needs to be elaboratet
Emissions at waste treatment Emissions at landfill and incineration		0	Data needs to be elaborated

Product type	13 Metalworking fluids	Assessment of existing	Comments
		data	
Areas of application	13.1 Metal forming/cutting	-	An ESD has to executed for every application, because the expected emissions depend on the type of coating, the contact intensity with environmental mediums, the mechanical, chemical, and biological strain, etc.
Market data			
 Product quantities for areas of application european-wide- sample country 	 Cooling lubricant emulsion 7700 t/y (GB) Aqueos cooling lubricant solutions 8500 t/y (GB) 	+	Data needs to be elaboratet
 Product quantities by product categories 		0	Data needs to be elaboratet
 Percentage of products, which are equipped with biocides 		0	Data needs to be elaboratet
 Biocide quantities in products 	1-5 % of biocide in concentrated oil	+	
Use			
Application techniques			
Quantities applied EG [g/m ²] [g/l], g/kg]	0,15 % in working solution	+	Data needs to be elaboratet
Emissions at application		0	Data needs to be elaboratet
Emissions during service life		0	Data needs to be elaboratet
Emissions at waste treatment			
Emissions at landfill and incineration		0	Data needs to be elaborated

Product type	14 Rodenticides	Assessment of existing	Comments
		data	
Areas of application	 14.1Fumigation products used outdoors (professional use) 14.2Fumigation products used with fumigation installation (professional use) 14.3Fumigation products for indoor-use, products used on skin (indoors), (professional use) 14.4Pest control products for powder application, powders, dust, powder concentrates and tracking powders (contact powders) used in closed spaces (professional and non- professional use) 14.5Baits used in outdoors (professional and non- professional use) 14.6Baits used in sewer systems (professional and non-professional use) 14.7Baits used in closed spaces and animal housings (professional and non- professional use) Competitive application 	-	An ESD has to be executed for every application, because the expected emissions depend on the type of coating, the contact intensity with environmental mediums, the mechanical, chemical, and biological strain, etc.
Market data			
 Product quantities for areas of application -european-wide -sample country 		0	No European market data available. No European-wide and country specific data for the quantities of single/individual areas of application available.
Product quantities by product categories		0	No European market data available. No European-wide and country specific data for the quantities of single/individual areas of application available.
Percentage of products, which are equipped with biocides		0	No European market data available. No European-wide and country specific data for the quantities of single/individual areas of application available.
Biocide quantities in products	 Alpha-naphthyl-thiourea Arsenic Barium carbonate Brodifacoum: (0,25 % liquid feed poison for preparation of pourable baits with 2 % a.i.; R) (0,005 % a.i. pourable baits; R) 	++	Hydrogen cyanide is not allowed any more in the netherlands. R – Anwendungsbereich in Räumen F – Anwendungsbereich im Freiland

Product type	14 Rodenticides	Assessment	Comments
		of existing	
		data	
	(0,005 % a.i. ready use wax block bait; R)	dulu	
	Bromadiolon:		
	(0,23 % liquid Feed poison for preparation of		
	pourable baits with 2 % a.i.; F, R)		
	(0,005% a.i. pourable baits; F, R)		
	 Chlorphacinon: 50 – 250 mg/kg bait 		
	Coumachlor		
	Coumafuryl		
	Coumatetralyl:		
	(0,04 % a.i. pourable baits; F, R)		
	(0,755 % liquid Feed poison for preparation of		
	pourable baits with 5 % a.i.; F, R)		
	• Difenacoum:		
	(0,005 % a.i. pourable baits; R)		
	(0,25 % liquid Feed poison for preparation of pourable baits with 2 % a.i.; R)		
	(0,005 % a.i. ready use formbaits (Rat baits); R)		
	 Difethialon: 		
	(0,0025 % a.i. pourable baits; F, R)		
	(0,0025 % a.i. paste as ready use Baits; R)		
	Diphenadione		
	Flocoumafen:		
	(0,005 % a.i. pourable Formbaits); R)		
	Fumasol		
	 Hydrogen cyanide: (49 %for gassing; R) 		
	Methylbromide		
	Phosphine		
	Phosphorus		
	• Pindone		
	Prolin		
	Sodium flouroacetamide		
	Sodium flouroacetate		
	Strychnine The lives		
	ThalliumValone		
	 Warfarin: (0,04 % (granule); 0,055 % (Ready use baits); 		
	0,079 % (Ready usebaits); 0,08 % (Ready use baits);		

Product type	14 Rodenticides	Assessment of existing data	Comments
	 baits) a.i. pourable baits; F, R) (0,055 % (Ratring); 0,075 % (Ratdiscs) a.i. ready use Formbaits; F, R) (0,48 % liquid Feed poison for preparation of pourable baits with 10 % a.i.; F, R) (0,75 % liquid Feed poison for preparation of pourable baits with 6 % a.i.; F, R) (0,79 % liquid Feed poison for preparation of pourable baits with 10 % a.i.; F, R) (0,79 % liquid Feed poison for preparation of pourable baits with 10 % a.i.; F, R) (0,79 % liquid Feed poison for preparation of pourable baits with 10 % a.i.; F, R) (0,79 % liquid Feed poison for preparation of pourable baits with 6 % a.i.; F, R) Warficide Zinc phosphide: 		
Use			
Application techniques	 Ready-to-use-baits like coated talc, granules, pellets, powders, nylon pouch, dust, meal, wax block,grain (spread as solid product) Liquids to prepare baits (spread as solid product) Liquid concentrations (spread as liquid) Gas (spray) Contact paste also as liquid pastes (used as layer on surfaces) 	-	
Quantities applied EG [g/m ²] [g/l], g/kg]	 spread as liquid product spread as solid product bait preparation and spread as solid product spray paint on 	0	Data needs to be elaborated
Emissions at application	 Ready-to-use-baits (spread as solid/liquid product) water soil Bait preparation water soil Spray (gas) air used as layer on surfaces (contact paste) 	0	Data needs to be elaborated Loss to the environment: baits should be recovered but it is estimated that the loss during rodent control is 20% (Balk).

Product type	14 Rodenticides	Assessment of existing data	Comments
	- water - soil		
Emissions during service life	Spray (gas) 100% into air	+	Data needs to be elaborated
Emissions at waste treatment	Not relevant	-	
Emissions at landfill and incineration	Not relevant	-	

Product type	15 Avicide	Assessment of existing data	Comments
Areas of application	 15.1Fumigation products for indoor-use (professional use) 15.2Baits used in outdoors (professional use) 15.3Baits used in animal housings and closed spaces (professional use) 15.4Contact pastes used outdoors (professional use) Competitive application repellents (see also 19) 	-	
Market data			
 Product quantities for areas of application -european-wide -sample country 		0	No european market data available. No european-wide and country specific data for the quantities of single/individual areas of application available.
Product quantities by product categories		0	No european market data available. No european-wide and country specific data for the quantities of single/individual areas of application available.
Percentage of products, which are equipped with biocides		0	No european market data available. No european-wide and country specific data for the quantities of single/individual areas of application available.
Biocide quantities in products	 Antraquinone: 800 g ai/kg (seed treatment) Chloralose: 15 g ai/kg grain Methiocarp: 200 g ai per ha (seed treatment) 	++	The data refers mainly to seed treatment and is therefore more relevant for the agricultural sector.

Product type	15 Avicides	Assessment of existing data	Comments
Use			
Application techniques	 Ready-to-use-baits (spread as solid product) Liquids to prepare baits (spread as solid product) Gas (spray) Contact paste (lay on) 	-	
Quantities applied EG [g/m ²]	 spread as solid product bait preparation and spread as solid product spray lay on 	0	Data needs to be elaborated
Emissions at application	 Ready-to-use-baits (spread as solid product) water soil Bait preparation water soil Spray (gas) air Lay on (contact paste) water soil 	0	Data needs to be elaborated
Emissions during service life	Spray (gas) 100% into air	+	
Emissions at waste treatment	Not relevant	-	
Emissions at landfill and incineration	Not relevant	-	

Product type	16 Molluscicides	Assessment of existing	Comments
Areas of application	 16.1 Pest control products for wet surface application, powders, and other products used outdoors (professional and non-professional use) [Products for wet surface application includes the application techniques in which a liquid product or an available product by dilution of addition of a solvent and/or water.] 16.2Baits used in outdoors (professional and non-professional use) 16.3Baits used in closed spaces and animal housings (professional and non-professional use) 16.4Powders used outdoors (professional and non-professional use) 16.5Powders used in closed spaces (professional and non-professional use) 16.5Powders used in closed spaces (professional and non-professional use) Competitive application Preservative for liquid-cooling and processing systems (see also 11) Antifouling products (see also 21) 	-	An ESD has to be executed for every application, because the expected emissions depend on the type of coating, the contact intensity with environmental mediums, the mechanical, chemical, and biological strain, etc.
Market data Product quantities for areas of application -european-wide -sample country 		0	No European market data available. No European-wide and country specific data for the quantities of single/individual areas of application available.
Product quantities by product categories		0	No European market data available. No European-wide and country specific data for the quantities of single/individual areas of application available.
Percentage of products, which are equipped with biocides		0	No European market data available. No European-wide and country specific data for the quantities of single/individual areas of application available.
Biocide quantities in products	 3,4-dichloro BNT (0,13 mg/l for toxicity tests) 3,5-dichloro BNT (0,15 mg/l for toxicity tests) Azinphosmethyl Aluminium sulfat Carbamate 	++	Some mixtures were testet in toxicity tests like the following: Metaldehyde (2 %) + Carbaryl (5 %) Metaldehyde (2 %) + Methiocarb (1 %)

Product type	16 Molluscicides	Assessment of existing data	Comments
	 Carbaryl (Sevin) Complexone (6-12 % by weight) Cooper chloride Cooper sulfat Dimethylaminoaniline Deltamethrin (Decis) Methiocarb: 10-40 g/kg bait Methiocarb: 200 g a.i. per ha pellets Methiocarb: 2-6 % by weight Metaldehyd: 50-60 g/kg pellet Metaldehyd: 2-7,5 % by weight MGK-264 N-tritylmorpholine Niclosamide (0,1-1 mg/l for toxicity tests) Organophosphorus Pesticides ROGOR (0,10- 0,35 ml/l for toxicity tests) Piperonyl butoxide Propoxur Pyrethroid Sulfoxid 		
Use			
Application techniques	 Ready-to-use-baits like coated granules, granules, pellets, powders (spread as solid product) Liquids to prepare baits (spread as solid product) Gas (spray) Contact paste also as liquid pastes (used as layer on surfaces) 	-	Molluscicides are not used by professionals in the EU, but non-professional use is in gardens. In the EU they are not used in the aquatic environment (Balk).
Quantities applied EG [g/m ²] [g/l], g/kg]	 spread as solid product bait preparation and spread as solid product spray paint on 	0	Data needs to be elaborated
Emissions at application	 Ready-to-use-baits (spread as solid product) water soil Bait preparation 	0	Data needs to be elaborated

Product type	16 Molluscicides	Assessment of existing data	Comments
	 water soil Spray (gas) air used as layer on surfaces (contact paste) water soil 		
Emissions during service life	Spray (gas) 100% into air	0	Data needs to be elaborated
Emissions at waste treatment	Not relevant	-	
Emissions at landfill and incineration	Not relevant	-	

Product type	17 Piscicide	Assessment	Comments
		of existing	
		data	
Areas of application	17.1Baits used in outdoors (professional and non-professional use)17.2Liquids used in outdoors (professional and	-	This Product type should be covered the agricultural sector, because piscicides are mainly used in the fish industry.
	non-professional use) Competitive applications		
Market data			
 Product quantities for areas of application european-wide- sample country 		0	No european market data available. No european-wide and country specific data for the quantities of single/individual areas of application available.
Product quantities by product categories		0	No european market data available. No european-wide and country specific data for the quantities of single/individual areas of application available.
 Percentage of products, which are equipped with biocides 	100%	+++	
Biocide quantities in products	 Trician: 250-500 mg/l (depending on the kind of fish in the fish tank) TFM: 36 % active ingredient (for toxicity tests) Antimycin: 99 % active ingredient (for toxicity tests) Rotenone: 2,5 % active ingredient (for toxicity tests) 	+	These values belong to the results of the toxicity test series.
Use			
Application techniques	Baits-(spread as solid product), (admitted as liquid product)	-	
Quantities applied EG [g/m ²]	 Baits spread as solid product admitted as liquid product) 	0	Data needs to be elaborated
Emissions at application	 Baits spread as solid product Water admitted as liquid product) Water 	0	Data needs to be elaborated
Emissions during service life	100 % into surface water	+++	
Emissions at waste treatment	Not relevant	-	
Emissions at landfill and incineration	Not relevant	-	

Product type	18 Insecticides, Acaricides	Assessment of existing data	Comments
Areas of application	 18.1 Aerosol/Fumigation products used outdoors (professional and non-professional use) 18.2 Aerosol/Fumigation products used with fumigation installation (professional and non-professional use) 18.3 Aerosol/Fumigation products for indoor-use, products used on skin (indoors), (professional and non-professional use) 18.4 Pest control products for wet surface application and other products used outdoors (professional and non-professional use) [Products for wet surface application for wet surface application includes the application techniques in which a liquid product or an available product by dilution of addition of a solvent and/or water.] 18.5 Pest control products for wet surface application, powders, and other products used in closed spaces (professional and non-professional use) 18.6 Pest control products for wet surface application, powders, and other products used in animal housings (professional and non-professional use) 18.7 Baits used outdoors (professional and non-professional use) 18.8 Baits used in closed spaces and animal housings (professional and non-professional use) 18.9 Baits used in closed spaces and animal housings (professional and non-professional use) 18.10 Pest control products used on skin (outdoors) (professional and non-professional use) 18.10 Pest control products used on skin (outdoors) (professional and non-professional use) 18.10 Pest control products used on skin (outdoors) (professional and non-professional use) 18.10 Pest control products used on skin (outdoors) (professional and non-professional use) 18.10 Pest control products used on skin (outdoors) (professional and non-professional and non-professional		An ESD has to be executed for every application, because the expected emissions depend on the type of coating, the contact intensity with environmental mediums, the mechanical, chemical, and biological strain, etc.

Product type	18 Insecticides, Acaricides	Assessment of existing data	Comments
Market data			
 Product quantities for areas of application european-wide sample country 		0	No European market data available. No European-wide and country specific data for the quantities of single/individual areas of application available.
Product quantities by product categories		0	No European market data available. No European-wide and country specific data for the quantities of single/individual areas of application available.
Percentage of products, which are equipped with biocides		0	No European market data available. No European-wide and country specific data for the quantities of single/individual areas of application available.
Biocide quantities in products	See table in product type 18	+	
Use Application techniques	Ready-to-use-baits like coated talc, granules,		
	 pellets, powders, dust, meal, wax block,grain, impregnated materials e.g., strips, balls, nets (spread as solid product) Liquids to prepare baits (spread as solid product) Liquid concentrations (spread as liquid e.g. pouring, brushing, etc.) Spraying (e.g., aerosols, solutions, suspensions, emulsions), Gas (fumigants, fogs, mists, smoke) Contact paste as pastes, gels, foam (used as layer on surfaces) 		
Quantities applied EG [g/m ²] [g/l], g/kg]	 spread as liquid product spread as solid product bait preparation and spread as solid product spray paint on pouring brushing gasing 	0	Data needs to be elaborated
Emissions at application	Ready-to-use-baits (spread as solid/liquid product)	0	Data needs to be elaborated

Product type	18 Insecticides, Acaricides	Assessment of existing data	Comments
	product) - water - soil Bait preparation - water - soil Spray (gas) - air used as layer on surfaces (contact paste) - water - soil		
Emissions during service life	Spray (gas) 100% into air	+	Data needs to be elaborated
Emissions at waste treatment	Not relevant	-	
Emissions at landfill and incineration	Not relevant	-	

Product type	19 Repellents	Assessment	Comments
		0	
Areas of application	 19. Repenents 19.1 Aerosol/Fumigation products used outdoors (professional and non-professional use) 19.2 Pest control products for wet surface application, powders, and other products used outdoors (professional and non- professional use) [Products for wet surface application includes the application techniques in which a liquid product or an available product by dilution of addition of a solvent and/or water.] 19.3 Pest control products for wet surface application, powders, and other products used in closed spaces (professional and non-professional use) 19.4 Pest control products for wet surface application, powders, and other products used in animal housings (professional and non-professional use) 19.5 Baits used outdoors (professional and non- professional use) 19.6 Baits used in closed spaces and animal housings (professional and non- professional use) 19.7 Skin application used in outdoors (professional and non-professional use) 19.8 Skin application used in closed spaces (professional and non-professional use) 19.9 Skin application used in closed spaces (professional and non-professional use) 19.9 Skin application used in animal housings 	of existing data	An ESD has to be executed for every application, because the expected emissions depend on the type of coating, the contact intensity with environmental mediums, the mechanical, chemical, and biological strain, etc.
	(professional and non-professional use) Competitive applications		
	 Textile- and leather industry (see 9) 		
	 Insecticides, Acaricides (see 18) 		
.	Feed and food store (see 20)		
Market data			
 Product quantities for areas of application -european-wide 		0	No European market data available. No European-wide and country specific data for the quantities of single/individual areas of application available.

Product type	19 Repellents	Assessment of existing data	Comments
 -sample country 			
Product quantities by product categories		0	No European market data available. No European-wide and country specific data for the quantities of single/individual areas of application available.
Percentage of products, which are equipped with biocides		0	No European market data available. No European-wide and country specific data for the quantities of single/individual areas of application available.
Biocide quantities in products	 2-amino-4',5'-methoxyacetophenone anise oil bay leaf oil capsicum oleoresin caraway oil cardamon oil clove oil coriander oil cumin oil dimethylphthalate: repellent for personal protection from biting insects, alone or in creams, concentration (Worthing and Hance, 1991) fennel oil garlic oil jasmine oil lavender oil meta- and para-methoxyacetophenone methyl-anthranilate N,N-diethyl-m-toluamide: 5-95% formulated in ethylalcohol Naphthalene nutmeg oil oil of citronella (geraniol, citronellol, terpenes) Ortho-, meta- and para-aminoacetophenone paradichlorobenzene peppermint oil Renardine rosemary oil 	+	

Product type	19 Repellents	Assessment of existing data	Comments
	 sage oil Smoke thyme oil vanilla oleoresin veratyl amine white pepper oil Ziram 	uuu	
Use			
Application techniques	 impregnated materials e.g., strips, balls, nets (spread as solid product) Liquids to prepare baits (spread as solid product) Liquid concentrations (spread as liquid e.g. pouring, brushing, etc.) Spraying (e.g., aerosols, solutions, suspensions, emulsions), Pump sprays Lotion,crème, milk 	-	
Quantities applied EG [g/m ²] [g/l], g/kg]	 spread as liquid product spread as solid product bait preparation and spread as solid product spray Gasing 	0	Data needs to be elaborated
Emissions at application	 Ready-to-use-baits (spread as solid/liquid product) water soil Bait preparation water soil Spray (gas) air used as layer on surfaces (contact paste) water soil 	0	Data needs to be elaborated

Product type	19 Repellents	Assessment of existing data	Comments
Emissions during service life	Spray (gas) 100% into air	+	Data needs to be elaborated
Emissions at waste treatment	Not relevant	-	
Emissions at landfill and incineration	Not relevant	-	

Product type	20 Preservatives for food or feedstock	Assessment of existing data	Comments
Areas of application	 20.1 Products added to the food or feedstock (professional and non-professional use) 20.2Products used for the treatment of food surface coatings (professional and non- professional use) Competitive applications 	-	
Market data			
 Product quantities for areas of application European-wide- -sample country 		0	
Product quantities by product categories		0	
 Percentage of products, which are equipped with biocides 		-	
Biocide quantities in products	 Surface coatings: up to 70 mg/kg legal Ingredients: depending on food and preservative up to 2 g/kg are legal 	+++	 The effect concentration for theses values is standardized at 100 %. A few examples for the food or feedstock biocides Preservation in vegetable products: 250 mg/kg benzoic acid or derivates 50 – 100 mg/kg SO₂ or related 550 – 2.500 mg/kg SO₂ on dehydrated products Feedstocks (preservation of crops, e.g. hay, silage, high moisture grain): 2 – 6 % by weight (dry matter) urea Prepacking (on farm): Acetic acid-solution: 5 – 7 % (2 minutes dipping) Organic acids and esters: 100 –5.000 mg/kg food (medium: 1.000 mg/kg) Preservation of cheese: 2,5 mg/kg nisin (antibiotic) Preservation of meat: 1 – 50 mg/kg nisin (antibiotic) Preservation of drinks: 2,5 – 25 mg/l nisin (antibiotic), 5 – 18 % ethanol, 0,01 – 1 % anti-oxidantia (Russe and Gould, 1991)

Product type	20 Preservatives for food or feedstock	Assessment of existing data	Comments
Use			
Application techniques	Dunk, ingredient, gasses, rubbed on	-	
Quantities applied EG [g/m ²] [g/l], g/kg]		0	
Emissions at application	 gassing air water soil ingredient air water soil Dunk air water soil Rubbed on air water soil 	0	
Emissions during service life		0	Data needs to be elaboratet (e.g. VOC-Abrasion)
Emissions at waste treatment		0	
Emissions at landfill and incineration		0	

Product type	21 Antifouling Porducts	Assessment of existing data	Comments
Areas of application	 21.01 Professional use on inland craft >25 m 21.02 Non-professional use on inland craft < 25 m 21.03 Professional use on commercial craft 21.04 Professional use on seagoing craft 21.05 Aquaculture equipment and other immersed structure Competitive applications 	-	An ESD has to be executed for every application, because the expected emissions depend on the type of coating, the contact intensity with environmental mediums, the mechanical, chemical, and biological strain, etc.
Market data			
 Product quantities for areas of application European-wide- -sample country 		0	No European market data available. No European-wide and country specific data for the quantities of single/individual areas of application available.
Product quantities by product categories		0	No European market data available. No European-wide and country specific data for the quantities of single/individual areas of application available.
 Percentage of products, which are equipped with biocides 		0	No European market data available. No European-wide and country specific data for the quantities of single/individual areas of application available.
Biocide quantities in products	 Traditional paints: up to 80 % copper (I)oxide (Haskoning, 1995) Modern paints: around 25 % copper (I)oxide) (Balk, 1999) Insoluble antifouling coatings: 10 – 12 % anorganotin (Balk, 1999) Self-polishing antifoulings: 10 – 30 % tributyltinoxide (Balk (1999) 	+	
Use			
Application techniques	brush or roll, airless or pneumatic spraying	-	
Quantities applied EG [g/m ²]	 brush roll airless spraying pneumatic spraying 	0	Data needs to be elaborated (e.g. VOC-Emissions)
Emissions at application	brush - air	+	Brush or roller, indoor halls: $0-5\%$ Brush or roller, outdoor $2-5\%$

Product type	21 Antifouling Porducts	Assessment of existing	Comments
		data	
	 water soil roll air water soil airless spraying air water soil pneumatic spraying air water soil soil 		Airless spraying 5 – 45 % Pneumatic spraying 50 – 60 %
Emissions during service life	During use, 65 % by weight is lost to the aquatic environment, 30 % by weight remains as film on the ship (Balk, 1999)	+	Leaching rates of TBT from antifouling paints: Sailing: 2.3 (μ g/cm2/day) (Rexrode, M.; Spatz, D. (1997) Sailing (self polishing coatings): 4 – 5 (μ g/cm2/day) (Willemsen et al., 1992) Mooring (self polishing coatings): 3 (μ g/cm2/day) (Willemsen et al., 1992) Sailing (matrix/ablative coatings): 5 (μ g/cm2/day) (Willemsen et al., 1992) Mooring (matrix/ablative coatings): 2-3 (μ g/cm2/day) (Willemsen et al., 1992) Erosion rates: self polishing coatings: 0,1 μ m/day (16 – 18 knots, 25°C) 120 – 160 sailing days and a thickness of the coating is between 50 to 150 μ m à the paint is to be renewed every 5 years.
Emissions at waste treatment		0	
Emissions at landfill and incineration	5 % by weight is removed during remedial treatments and disposed off as chemical waste	0	(Balk, 1999)

Product type	22 Embalming and taxidermist fluids	Assessment of existing data	Comments
Areas of application	22.1Embalming chemicals (professional use) 22.2Taxidermist chemicals (professional use) Competitive applications	-	
Market data			
 Product quantities for areas of application european-wide- -sample country 		0	Data needs to be elaborated
 Product quantities by product categories 		0	Data needs to be elaborated
 Percentage of products, which are equipped with biocides 	100 %	+++	
Biocide quantities in products		0	Data needs to be elaborated
Use			
Application techniques	Surface disinfection, fluids for arterial injection, cavity fluids		
Quantities applied EG [g/m ²]	Embalming for a long-term-conservation: 3.6 to 15 % formaline (37 % formaldehyde), 2 to 6 litre per human corpse For delay funeral: 0,2 % formaline	++	
Emissions at application		0	Data needs to be elaborated
Emissions during service life		0	Data needs to be elaborated
Emissions at waste treatment		-	
Emissions at landfill and incineration	Not relevant	-	

Product type	23 Other Vertebrates	Assessment of existing data	Comments
Areas of application	 23.1 Fumigants for control of other vertebrates, used outdoors (professional and non-professional use) 23.2 Baits for control of other vertebrates, used outdoors (professional and non-professional use) 23.3 Baits for control of other vertebrates, used in animal housings) (professional and non-professional use) Competitive application 	-	An ESD has to be executed for every application, because the expected emissions depend on the type of coating, the contact intensity with environmental mediums, the mechanical, chemical, and biological strain, etc.
Market data			
 Product quantities for areas of application -european-wide -sample country 		0	No European market data available. No European-wide and country specific data for the quantities of single/individual areas of application available.
 Product quantities by product categories 		0	No European market data available. No European-wide and country specific data for the quantities of single/individual areas of application available.
 Percentage of products, which are equipped with biocides 		0	No European market data available. No European-wide and country specific data for the quantities of single/individual areas of application available.
Biocide quantities in products	 Multidose substance: doses 0,005 - 0,01 % (Haskoning 1995) Bromadialon: bait (50 mg/kg), single dose, formulation for preparation of bait: 0,25g/l of dry powder Chlorofacinon (old fashion) 50 - 250 mg/kg bait Chloralose ≤ 40 g/kg bait against mice, trained personnel (Tomlin 1997) Hydrogen cyanide: fumigating enclosed spaces (stored grain in warehouses, glasshouses, rabbit burrows, rat runs (trained personnel) Formulations packed in metal containers; also absorbed on porous material, formulation 400 g a.i./kg (water soluble powder) (Tomlin 1997) 	++	
Use			
Application techniques	 Ready-to-use-baits like coated talc, granules, 	-	

Product type	23 Other Vertebrates	Assessment	Comments
		of existing	
		data	
	tablets, pellets, bags, powders, nylon pouch,		
	dust, meal, wax block,grain (spread as solid		
	product)		
	• Liquids to prepare baits (spread as solid product)		
	Liquid concentrations (spread as liquid) Case (answit)		
	Gas (spray)Contact paste also as liquid pastes (used as		
	layer on surfaces)		
	Ignitable cartridges		
	 Flakes 		
	Tacky gel		
Quantities applied EG [g/m ²] [g/l], g/kg]	 spread as liquid product 	0	Data needs to be elaborated
	spread as solid product		
	bait preparation and spread as solid product		
	• spray		
Emissions at application	 paint on Ready-to-use-baits (spread as solid/liquid 	0	Data needs to be elaborated
	product)	0	Data fields to be elaborated
	- water		Loss to the environment: baits should be recovered but it is
	- soil		estimated that the loss during rodent control is 20% (Balk).
	Bait preparation		
	- water		
	- soil		
	• Spray (gas) - air		
	 used as layer on surfaces (contact paste) 		
	- water		
	- soil		
Emissions during service life	Spray (gas) 100% into air	+	Data needs to be elaborated
Emissions at waste treatment	Not relevant	-	
Emissions at landfill and incineration	Not relevant	-	