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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

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16 Abstract

The BIOEXPO project is focussed on test data, required for the authorization of biocidal products. The draft EC Biocidal Products Directive distinguishes between a common core data set (Annex II) and an additional data set, with specific data requirements for biocidal product types (Annex III). The BIOEXPO study aims to provide an input to the European discussions on Annex III, by proposing data requirements for 23 biocidal product types.

In the project, criteria for setting data requirements were developed, and data requirements for the environmental compartments fresh surface water, marine surface water, soil, air and STP were proposed using these criteria. This is described in another report ("part 1: Framework and data requirements for environmental compartments").

This report describes the 23 biocidal product types that are distinguished in the directive. For each of the product types, a general description of the products, their use and their active ingredients is given. The application of the products and the use and disposal of the treated material is described. The environmental compartments which are exposed during the life cycle of the biocide are listed. With this information, and the information of Part 1, data requirements for each of the 23 product types (most of which are devided into subtypes) are proposed. Furthermore, some guidance on the relative importance of the proposed test data is given.

17 Keywords

Biocidal Products Directive, biocides, life cycle assessment, exposure assessment, emissions, data requirements

18. Price	19.	20.

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1. Introduction

This report (Part 2) is one of the two products of the BIOEXPO project. The aim of this project is to develop listings of test data, required for an environmental risk assessment of biocidal products, in the context of the Biocidal Products Directive (EC, 1997).

The starting points (framework) and methodology of the project are described in Part 1. The report proposes criteria for setting data requirements, and lists potential data requirements for the environmental compartments fresh surface water, marine surface water, soil, air and sewagewater treatment plant (STP).

This report comprises a description of 23 biocidal product types (conform the Biocidal Products Directive, Annex V), with the aim to identify the environmental compartments to which biocides are most likely emitted ('direct exposure compartments'). For this purpose, several stages in the life cycle of biocidal products have been analysed: The application of the biocide, the use of the treated material, and the disposal of the treated material. For each stage, environmental emissions have been indicated. The life cycle analysis and release inventory were based on an analysis of international literature, and communication with experts on the field of the various product types. The aim was to obtain a (qualitative) overview of the environmental compartments which are most likely exposed, not to estimate the emissions quantitatively.

Each chapter of this report describes a biocidal product type. In each chapter, a delineation of the product type is made, and the main biocides in use and applications are described (paragraph 1). The application, use and disposal are described, and environmental compartments to which emissions are directed are identified (paragraph 2). In the third paragraph, the "direct exposure compartments" are summarised. Furthermore, guidance is given on the relevance of the potential data requirements for direct exposure compartments, as proposed in Part 1. When exposure assessment models are available for the product type (available models are listed in Appendix B of this report), the data requirements are compared to the input data of the models. This is important in relation to the 'compatibility' criterion (see Part 1).

The presentation of the product types 14 to 19 (pest control products) is somewhat different. This is due the fact that it seemed most relevant to combine these product types, as application techniques and exposure pathways are largely identical.

The report concludes with a summary (chapter 20) of the direct exposure compartments and data requirements for all 23 product types.

2. Product type 1: Human hygiene biocidal products

2.1 Introduction

Biocidal products of product type 1 are used for disinfection in relation to human body hygiene. This product type comprises 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. Antiseptics reduce the concentration of transient micro-organisms on intact skin to a certain base-line level. These products contain an antimicrobial chemical substance, usually with a broad spectrum of activity, rapid action, and a certain degree of persistence. This product type includes, among others, skin antiseptics, antimicrobial soap, healthcare products, personal hand wash products. Preservatives used in cosmetics are not included in this product type.

In general, this product type is characterised by a large number of different products, and a large quantity of active ingredients. Another characteristic of this product type is a strong relation with other legislations, especially cosmetics and medicines legislation. Some examples of products which are likely to be covered by this product type are:

Antiperspirants and **deodorants** are available as roll-ons, sticks and aerosol sprays. The main active ingredients are aluminium salts, such as aluminium chlorohydrate, aluminium-zirconium tetrachlorohydroxy glycinate and aluminium-zirconium tetrachlorohydroxy glycinate. Another common active ingredient is triclosan.

Anti-dandruff shampoos contain many different active ingredients. Some of the most common are coal tar (concentration 0.5-5%), pyrithione zinc (1-2% when washed off immediately, 0.1-2% when left on the scalp), salicylic acid (1.8-3%), selenium sulphide (1%) or sulphur (2-5%).

Products to combat acne are available as soaps, masks, gels, bars, lotions, etc. Triclosan is an important active ingredient for hydrated soaps. Other active ingredients are salicylic acid (0.5-2%), sulphur, and resorcinol.

2.2 Release estimation

The environmental exposure of human hygiene biocidal products is very diffusive. Products are available as soap bars, liquid soaps, sprays, gels, pastes, shampoos, or baths, in small quantities (typical < 1 litre). The products are used in households. After application to the relevant parts of the human skin, the product will typically be rinsed or washed off, and the remaining product will be discharged to a sewage treatment plant (STP). The packaging material, with remnants of the product, will enter the municipal waste and be disposed on a waste dump (see Figure 1)

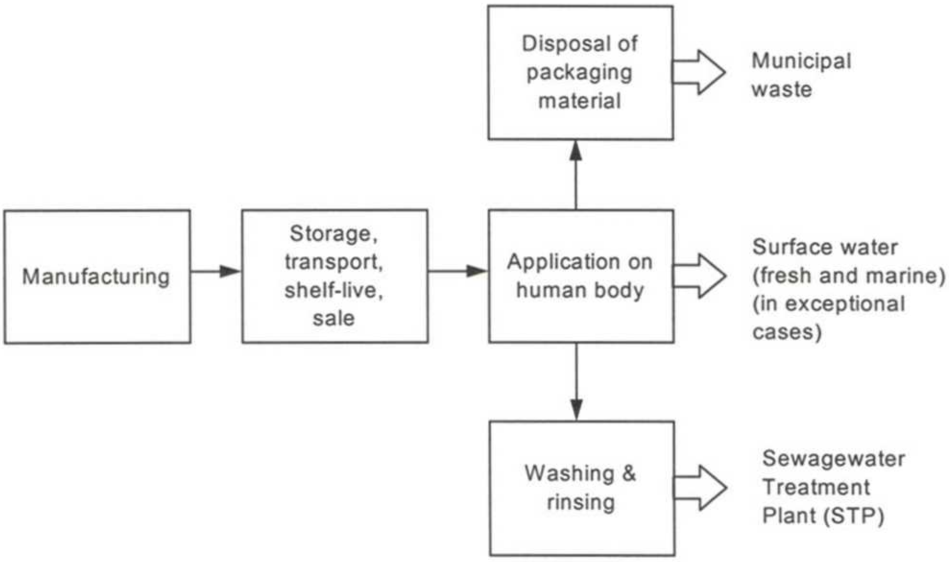

Figure 1 Environmental release of human hygiene biocidal products.

An exception are suntan products, which are likely to enter surface water (both fresh and marine) directly during bathing.

2.3 Data requirements for product type 1

The direct exposure compartments, which are introduced in the previous section, are summarised in Table 1.

Table 1 Direct exposure compartments for product type 1

Subtype	Products	Direct exposure compartments
1.1	Suntan products	Fresh surface water Marine surface water Sewagewater Treatment Plant
1.2	All other products	Sewagewater Treatment Plant

Guidance for demanding test data

Potential data requirements for products released to the environmental compartments fresh surface water, marine surface water and a sewagewater treatment plant are discussed in Part 1 (“Framework and data requirements for environmental compartments”), and are summarised in Appendix 1. These data requirements are a “long list” of data items which can be relevant, and some refinement can be made on basis of the formulation and application of the products in product type 1.

For the environmental compartment Sewagewater Treatment Plant, the data items IV.2 and IV.3 (continuous activated sludge test and inhibition of micro-organisms in a STP) are essential for a risk assessment. The data item IV.1 (inherent biodegradability test with pre-adapted inoculum) is relevant for product types which cause a continuous load for a STP (adaptation of micro-organisms in the STP). For products of this product type (except for suntan-products), with a wide-spread use in households, this test can be considered.

For the environmental compartments fresh surface water and marine surface water, emissions are only expected in the bathing-season and during day-time. 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. Therefore, additional toxicity tests (next to toxicity tests of Annex II of the Directive, and marine toxicity tests) are considered less important. Leaching tests (items I.4 and II.4) are not required.

For some test items, criteria are required, as the relevance of demanding test data depends on pre-stated conditions. The sediment-water partitioning coefficient (item I/II.1) is relevant only for non-organic substances. Additional bioconcentrations factors (item I/II.2) are relevant only for substances with a high bioaccumulation potential (based on P_{ow} or BCF from Annex II of the Directive). When bioaccumulation is likely, toxicity tests for fish-eating predators should be considered. Furthermore, criteria should be defined for demanding chronic toxicity data, based on characteristics of the product or substance. Chronic toxicity data should be demanded for substances which are not ready biodegradable, or which are hydrophobic (e.g., $\log P_{ow} > 3$), as these substances will adsorb to the solid phase. It has already been stated that biocides with a (semi-)continuous release pattern are likely to cause chronic exposure.

The items I/II.3 and I/II.4 (biomarkers and toxicity tests for degradation products) are relevant when (environmental) problems with specific toxic action or hazardous degradation products are reported.

No emission or exposure models are available for this product type (Appendix B).

3. Product type 2: Private area and public health area disinfectants and other biocidal products

3.1 Introduction

According to the Biocides Product Directive (Annex V), this product type includes:

"Products used for the 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)."

In short, this product type includes all disinfectants that are not included in another product type. The applications described in the Directive are in agreement with the definition of 'Public health area disinfectants' in a study by the Danish EPA (Frost & Hansen, 1994). The following applications are distinguished within the product type:

- swimming pool disinfectants
- waste water disinfectants
- infectious waste (incl. hospital waste)
- disinfection in accommodations for man (bathrooms, toilets, chemical closets, walls and floors in institutions)
- sterilisation of medical instruments in hospitals
- disinfection of rooms in hospitals
- disinfectants for air-conditioning systems
- disinfection of soil
- laundry disinfectants

For several items of the list, there is a potential overlap between the biocides and medicines legislation.

Swimming pool disinfectants
Biocides are used in swimming pools to (1) kill pathogens introduced in the pool by swimmers, and (2) control harmless organisms which create undesirable visible effects (Singer, 1990). Pathogens in swimming pools include bacteria (intestinal bacteria as *Streptococcus faecalis* and *Escherichia coli*, and organisms from the skin and ear, nose and throat passage), virusses, protozoa and fungi (e.g., *Trichophyton mentagrophytes* var. *granulosum*: Athlete's foot). Disinfection must extend beyond the pool water to the filters. In the filter plant, micro-organisms often find excellent conditions for rapid reproduction. Without adequate

disinfection, filter beds may harbour pathogenic organisms such as *Staphylococcus aureus* and *Pseudomonas aeruginosa*. Biocides used are mainly chlorine compounds (chlorine gas, sodium and calcium hypochlorites, chlorine dioxide in combination with chlorine gas, and chlorinated isocyanates). Many other disinfectants have become available in the past few years. These include elemental liquid bromine, sodium bromide plus hypochlorite, organic bromine releasing compounds based on bromochlorodimethylhydantoin, polymeric biguanides, and electrolytic generation of metal ions. Silver and/or copper ions have been used to disinfect small, usually domestic pools. In larger pools, metal ions alone are not recommended. More recently, combinations of metal ions and a chlorine or bromine based disinfectant have been used in larger pools.

Outdoors pools and some indoors pools exposed to sunlight may experience problems with algal growth, resulting in undesirable visual contamination. In these cases, algicides are applied. Most of the algicides applied in swimming pools are based on quarternary ammonium and polyoxyimino compounds, or are copper-based. Mercury-based algicides have been withdrawn from the market due to their unacceptable environmental effects.

Hydrogen peroxide is primarily used in combination with biguanid polymers for disinfection of swimming pools, to increase the biocidal potency of the polymers and to oxidise organic matter. Furthermore, hydrogen peroxide is used as oxidising agent in combination with quaternary ammonium compounds (VROM, 1994; Singer, 1990; Hurst, 1991; UBA, pers. comm.)

Waste water disinfectants

Waste water can be disinfected to reduce pathogen concentrations before discharge to the surface water. The disinfectants used are essentially the same as for drinking water disinfection (see product type 5: "Drinking water disinfection"). The most common biocides are chlorine, hypochlorous acid, chlorine dioxide and ozone (e.g., EPA, 1986; Aieta *et al.*, 1980; Legube *et al.*, 1987; Robson & Dice, 1990).

Infectious waste (incl. hospital waste)

Hospital waste includes sewage water (that can be hazardous, e.g., Gartiser *et al.*, 1996; Waltemade *et al.*, 1996) and solid waste, which partly consists of infectious waste. Infectious waste can include isolation wastes (from hospital patients), cultures and stocks of infectious agents, human blood and blood products, pathological wastes, contaminated wastes from surgery and autopsy, contaminated laboratory waste, contaminated sharps (needles, syringes), dialysis unit wastes, contaminated animal carcasses, body parts and bedding, discarded biologicals, contaminated food and other products, and contaminated equipment (Block, 1991).

Three main methods are available to treat infectious waste: (1) incineration; (2) autoclavation (hot steam) or dry air, and (3) shredding followed by chemical disinfection. In this study, only the third option is relevant.

Disinfection in accommodations for man (bathrooms, toilets, chemical closets, walls and floors in institutions)
This includes a very heterogeneous range of products: disinfection of houses, offices, working places, schools, hospitals and sport facilities. The main biocide used is chlorine. The delineation between disinfectants and household cleaning agents can be problematic.

A separate group within these products are biocides used in (mobile) chemical closets, used in locations that are not directly connected to a sewer (boats, busses, caravans). The main biocides used are aldehydes (formaldehyde, paraformaldehyde, glutaraldehyde), surfactants and quaternary ammonium compounds (Meijerink, 1995). Mobile chemical toilets should be emptied in a sewer system. When no collection points are present in a certain area, or when the capacity of the local sewer system is not sufficient, contamination of surface water can be expected.

Sterilisation of medical instruments
This subgroup comprises the sterilisation (and/or disinfection) of medical devises, equipment and other instruments which involve significant risks of transmitting infections to patients or hospital personnel. Several categories of instruments can be distinguished on the basis of their infection risk, from critical instruments (in contact with blood, or normally sterile areas) to non-critical instruments (only in contact with unbroken skin).

Heat-stable devises are usually autoclaved, but plastics or plastic-coated devises need 'cold' methods. A variety of biocides is available, with varying disinfection efficiency. The gas ethylene oxide is used for sterilisation of (cleaned and disinfected) instruments. Ethylene oxide and CFC mixtures are commonly used, although the volume decreases (VROM, 1994). Next to these, aqueous solutions of disinfectants are used. High-level disinfection can be obtained with glutaraldehyde, formaldehyde, chlorine dioxide, H_2O_2 and peracetic acid. Intermediate level disinfectants include alcohols (70-90% ethanol or isopropanol), chlorine compounds, certain phenolic and iodophor preparations. Low level disinfectants are quaternary ammonium compounds, certain iodophores, and phenolics (Favero & Bond, 1991).

Disinfection of hospital rooms
Disinfectants are used to reduce the level of micro-organisms in hospital rooms. An example of a disinfectant used for this purpose is formaldehyde. For the neutralisation of formaldehyde, ammonia is used.

Disinfectants for air-conditioning systems
In air-conditioning systems, biocides are applied incidentally to preserve water in moisturising systems. When the water is vaporised as steam, or when the systems are flushed, or when the water is removed on a regular basis, preservatives are not required. However, in larger systems (e.g., office buildings) a "hydrobiological fluid" can be added to the water reservoir. Another application of biocides is in car air-conditioning systems. There is no information available on the type of biocides (products) that are used.

Disinfection of soil
The non-agricultural use of soil disinfectants is to reduce the level of pathogens, e.g., on playing grounds for children.

Laundry disinfectants
In laundrettes, laundry from hospitals, hotel and catering business, nursing homes, and other services and industries is cleaned and disinfected. Disinfection takes place after an initial washing step, to remove the dirt. Disinfectants that are used have a combined function as bleaching agent and disinfectant. Common substances are chlorine, peroxide and peracetic acid.

3.2 Release estimation

Due to the large variability in applications within this product type, a single life cycle cannot be constructed. However, five simplified, characteristic life cycles are drawn up in Figure 2, based on emissions that occur. The main life cycle is that disinfectants are applied to a surface or to water, and that the spilled surfactant or the water containing the surfactant is emitted to the sewer (third life cycle in Figure 2). This is applicable for biocides used for disinfection of human accommodations, infectious waste, medical instruments (with a potentially high fraction emitted to the air, when gasses are used for disinfection), chemical closets, air conditioners, and laundry. A substantial emission to (outdoors) air is expected only for (some) swimming pool disinfectants. For disinfection of sewage water, the treated water is discharged to the surface water.

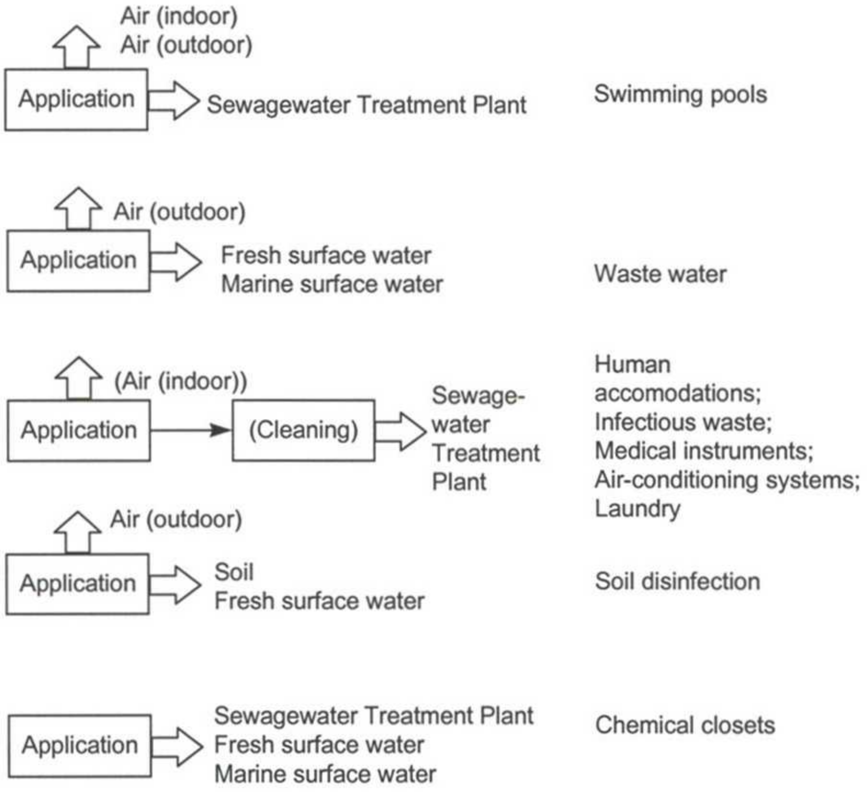

Figure 2 Environmental release of disinfectants of product type 2.

Swimming pool disinfectants

Basically, three types of swimming pools can be distinguished: the 'fill-and-draw' type (the pool is filled, and emptied at the end of the day); the flow-through type, and the recirculating flow types. The first two types are more difficult to disinfect than the latter. The type of pool will affect the amount of biocides required for disinfection. Most of the applied disinfectant will be quickly degraded, but remaining disinfectants will be discharged to the sewer system with the pool water. Emissions of disinfectant to the air can occur. By-products of the disinfection will be emitted both to the air (e.g. chloroform) and to the sewer.

Waste water disinfectants

The waste water disinfection process is similar to the drinking water disinfection process (see product type 5), with disinfection possible at various stages of the treatment process. The disinfectants that are not degraded in reactions with organic matter or emitted to the air will be transported to the receiving surface water.

Infectious waste (incl. hospital waste)

In a combined shredder / chemical disinfection system, as described above, the mixture of (shredded) waste and biocide-containing water is led to a sedimentation tank. The solid waste is separated and treated as 'normal' waste. The liquid fraction is discharged to the sewer system. It is assumed, that the main emission will be directed to the sewer system, with emissions to air (indoors or outdoors, depending on the location of the shredding-milling system.

Disinfection in accommodations for man (bathrooms, toilets, chemical closets, walls and floors in institutions)
Disinfectants are applied on a small scale, e.g. by (manually) brushing. It is assumed that disinfected surfaces and areas are rinsed with water after disinfection, which will cause remaining disinfectants to be emitted to the sewer system. Emissions to (indoors) air will occur.

In the EC Technical Guidance Document (1996), an emission scenario document is included to predict the release of products used for personal/domestic use (IC-5) and public domain (IC-6), including surface cleaning substances. In this document, an assumption of 100% release to water is used.

The contents of mobile chemical toilets will be collected at special sites, after which they are discharged to the sewer system. Direct (diffusive) discharges to the environment (e.g. from boats to surface water) may occur, but no quantitative information is available.

Sterilisation of medical instruments in hospitals
Sterilisation can take place with gasses, such as ethylene oxide, or with aqueous solutions (baths, sprays). This will determine whether the bulk of the emission is directed to air or to sewage water.

Disinfection of hospital rooms
Disinfectants are applied as sprays or aqueous solutions. When the room is cleaned with water afterwards, the remaining biocides will enter a sewagewater treatment plant.

Disinfectants for air conditioning systems
Emission will be directed to the indoors air, when the water (containing biocides) is vaporised. This will be especially relevant for human and occupational exposure, but less for environmental exposure. Part of the moisturiser water may be expected to be disposed to the sewer, during cleaning operations (STP exposure).

Disinfection of soil
Little is known regarding application techniques, but environmental emissions to (outdoors) air, soil and (to some extend) to surface water can be expected.

Laundry disinfectants
The washing (waste) water is discharged to the sewer system (STP).

3.3 Data requirements for product type 2

The direct exposure compartments, which were introduced in the previous sections, are summarised in Table 2.

Table 2 Direct exposure compartments for product type 2.

Subtype	Products	Direct exposure compartments
2.1	Waste water disinfection	Air (outdoors) Fresh surface water Marine surface water
2.2	Soil disinfection	Air (outdoors) Soil Fresh surface water
2.3	Disinfection of infectious waste, medical instruments, hospital rooms, human accommodations, air conditioners, laundry	(Air indoors) Sewagewater treatment plant
2.4	Chemical closets	Fresh surface water Marine surface water Sewagewater treatment plant
2.5	Swimming pools	Air (indoors, outdoors) Sewagewater treatment plant

Guidance for demanding test data
Potential data requirements for products released to the environmental compartments fresh surface water, marine surface water, soil, air and a sewagewater treatment plant are discussed in Part 1. However, from the formulation and application of the products, and specific problems occuring at this product type, some remarks for applying these generic data requirements can be stated.

A problem resulting from the use of strong oxidising agents such as NaOCl, O_3 and H_2O_2 is the formation of disinfection by-products (products of the reaction of the disinfectant with organic matter). This issue is described in detail in chapter 6 (Product type 5: drinking water disinfection). In swimming pools, the formation of chloramines can lead to irritation of eyes and mucous membranes and the characteristic "swimming pool smell". Chloroform has been detected above chlorinated swimming pools in concentrations of 0.05 - 0.8 $mg.m^{-3}$ (compared to a (Dutch) MAC value of 50 $mg.m^{-3}$). From waste water disinfection, identical problems as with drinking water disinfection are to be expected, i.e. formation of bromate (carcinogen) from bromide (after ozone treatment) and the formation of trihalomethanes (THM) after disinfection with chlorine.

The potential formation of disinfection by-products has its implications for the data requirements: Toxicity tests for hazardous degradation tests are important (item I/II.4), and specific toxic action tests (e.g., biomarkers for mutagenic action) can be considered.

Leaching tests (I.4 and II.4) are not relevant for this product type, as the chemicals are not inserted in a matrix.

As most active ingredients are reactive (oxidising) chemicals, chronic toxicity tests (I.5, II.7, III.7) and extended biodegradability testing (I.3, II.3, III.2) are of less importance.

A biodegradability test with pre-adapted inoculum is considered less important as STPs are not exposed continuously. However, for subtype 2.3 (which includes household cleaning and disinfection agents for human accomodations), it may be considered.

Two exposure scenarios are available for this product type (Appendix B). Next to the base set data, the fate of the substance in a STP is required. This is provided for in the proposed additional data.

4. Product type 3: Veterinary hygiene biocidal products

4.1 Introduction

Disinfectants in the veterinary range are used for various objectives (Lekkerkerk *et al.*, 1994):

- Animal health: to prevent the spreading of animal diseases;
- Human health: to prevent certain micro-organisms during the production of eggs, meat and milk
- Efficiency: to increase the production
- Quality: to improve the quality of products

Disinfectants are used in different application ranges:

- Cattle farms
- Pig farms
- Poultry farms
- Other veterinary purposes

In each of these application ranges, disinfectants are used for a number of applications (see below). At some of the stages described, the disinfection is proscribed by law.

Cattle farms

- Disinfection of vehicles after import of cattle, before export of cattle or for transportation of cattle to market places and slaughter houses
- Disinfection of materials/tools for milking, and milking machines
- Disinfection of paws (formaldehyde bath)
- Disinfection of storage places for dead bodies

Disinfection of stables is hardly performed in cattle breeding, except for disinfection of milking machines and disinfection of paws. Only in stables with calves, some disinfection is used.

Pig farms

- Disinfection of vehicles after transportation of pigs
- Disinfection of stables (spraying)
- Disinfection of footwear (bath), before entering the stables
- Disinfection of storage places for dead bodies

Poultry farms

- Disinfection of stables (spraying)
- Disinfection of footwear (bath)
- Disinfection of incubators and hatcheries (gas)
- Disinfection of transportation vehicles and crates (spraying)

- Disinfection of eggs
- Disinfection of storage places for dead bodies
- Disinfection of drinking water facilities

Other veterinary purposes

- e.g. sheep farming. Due to the great variety in applications, other veterinary use than use cattle, pig and poultry farms is not described in this report.

Aldehydes are the most important active ingredients from a quantitative point of view (~70%), followed by lyes (~24%) and chlorine compounds (~7%) (Table 3).

Table 3 Overview of active ingredients in different veterinary applications in the Netherlands (from: Lekkerkerk et al., *1994)*

	Pig breeding (kg.jr^{-1})	**Poultry farming (kg.jr^{-1})**	**Cattle breeding (kg.jr^{-1})**	**Total amount (kg.jr^{-1})**
Stables				
– Aldehydes	9 076	108 788		117 864
– Lyes	3 879	788		4 667
– Chlorine compounds	273	15		288
– quaternary ammonium salts	1144	255		1 399
Footwear				
– Aldehydes	82 355	7 059		89 414
– Lyes	57 330	4 194		61 524
– Chlorine compounds	1 820	156		1 976
– Quaternary ammonium salts	3 094	265		3 359
Transport vehicles				
– Lyes	18 900			18 900
– Chlorine compounds	120	3 180		3 300
Chicken hatching				
– Aldehydes		13 015		13 015
Paws(cattle)				
– Aldehydes			4 800 000	4 800 000
Milking machines				
– Lyes			1 627 444	1 627 444
– Chlorine compounds			489 557	489 557
Total	177 991	137 715	6 917 001	7 232 707

Typical substances used for veterinary applications are:

- Aldehydes (formaldehyde)
- Lyes (NaOH, KOH)
- Chlorine compounds (e.g. Sodiumhypochlorite, paratolueensulfon-chloramide-sodium, sodium dichloroisocyanurate)
- Quaternary ammonium compounds
- Phenols
- Iodophores

- Amphotensides (dodecine, dodecyl-amino-propylamino-acetic acid)
- Others, e.g. peroxides, isopropanol, enilconazol

For each application, more then one disinfectant can be chosen. Table 4 presents the suitability of various options for the disinfection of farm buildings, as an example (Quinn, 1991).

Table 4 Disinfectants suitable for use in farm buildings after routine cleaning.*

Part of building			Phenols	Coal tar derivatives	Cl_2	I_2	Aldehydes	Quaternary ammonium compounds
Floor:	Concrete	QACs and iodophors are expensive	+[a]	+	+	+	+	-
	Wood		+	+	±	±	±	-
	Earth		±	±	-	-	±	-
Walls and Roof			+	+	+	+	+	±
Water supply			-	-	+	±	-	-
Fittings		Fumigation possible only if building design suitable						
	Wood		+	+	±	+	-	-
	Metal		+	±	±	±	-	±
	Plastic		+	±	+	+	-	±
Air space[c]			±[b]	-	-	-	+	-
Footbaths			+	+	-	±	±[d]	-

[a] +, suitable; ±, of limited suitability; -, unsuitable

[b] Some aerosolised phenols suitable

[c] Application of an aerosolised acaricide and chemoattractant may be necessary for poultry houses with mite infections

[d] also suitable for use in footbaths for animals

* An outbreak of an known infectious disease in a group of housed animals may further limit the choice of disinfectant suitable for a building

Disinfectants for fish farming (aquaculture)
Disinfectants used for fish farming are also included in this product type. In fish farming, disinfectants are used for disinfection of shoes, hands, pipelines, containers, surfaces etceteras. For this purpose, halamite is the most common disinfectant, and other disinfectants include polyvinyl alcohols and formaline. Furthermore, biocides such as formol and malachite-green are added to the water to combat bacteria and fungi.

4.2 Release estimation

The overview in the previous section indicates, that veterinary hygiene products are used in a great variety of applications. Therefore, it is difficult to present one life cycle for all veterinary hygiene products. Relevant differences between products with regards to environmental emissions however are (1) indoors or outdoors use, and (2) the presence of manure reception facilities in the farm. Fish farming disinfectants are not included in these groups, as they differ from the other applications in the respect that they include marine systems, were sea water is used and possibly exposed. With this differentiation, the following life cycle can be constructed:

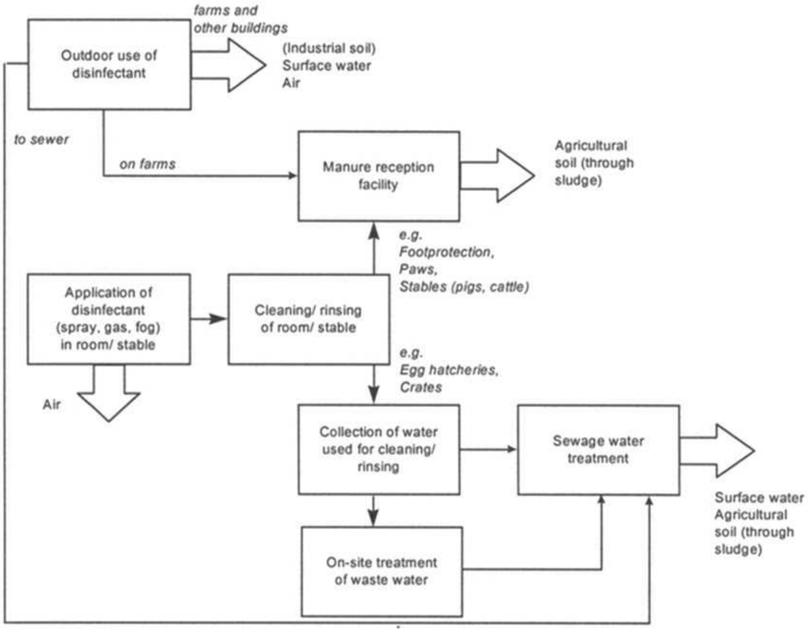

Figure 3 Environmental release of veterinary hygiene products.

Products used indoors farm buildings are partly emitted to the air (indoors the building), partly degraded (reaction with dirt and micro-organisms), and partly removed during the washing after disinfection. With the water, they will be transported to the manure reception facility (when present) or a collection point, from where they will be emitted to the sewer (STP), a local (farm) treatment installation, or to the surface water. The manure from the manure reception facility is spread on (agricultural) soil (e.g., Montfoort *et al.*, 1996; EMEA, 1996).

When disinfection is performed on the farmyard, the waste water will be directed to the local manure reception facility, to the sewer (STP), or will run off on the farm area, and be emitted to surface water or soil.

The processes are regarded in more detail in the next sections.

Disinfection of transportation vehicles

Disinfectants are used as a spray to disinfect transportation vehicles. For the disinfection, 5 to 54 m^3 disinfectants (solved in water) per year per farm is used, containing 2.5 to 37.8 kilograms of disinfectant. The disinfection takes place in the open air. Emissions to the air occur. When collected, water is discharged to the sewer or to a manure reception facility (Lekkerkerk *et al.*, 1994).

Disinfection of dead bodies
Disinfection often takes place on the farm yard. No information about quantities or emissions is available.

Disinfection of footwear (for workers)
Disinfection takes place in a bath (volume: ~ 10 litres) at the entrance of the stables. Emissions to air (volatilisation) are to be expected for volatile biocides (e.g. aldehydes). When the contents of the bath is spoiled, the old disinfectants are typically discharged to a manure reception facility (pig farms) or is poured out on the farmyard (poultry farms). From the farmyard, emissions to soil and possibly surface water will occur. Montfoort *et al.* (1996) assume that 75% of the disinfectant is discharged to the manure storage facility, and that no emission to air occurs. 25% is assumed to be lost due to reaction and degradation.

Disinfection of stables
Stables are disinfected by spraying a disinfectant (pig farms) or gassing (poultry farms). The gassing will cause emissions to air. Remnants of disinfectants will be discharged to a manure reception facility (pig farms), or to a collection point (poultry farms). Disinfection of cattle stables is hardly ever performed, except for stables for calves. According to Montfoort *et al.* (1996), emissions occur to the air (10% in case of fogging; 25% during spraying) and to manure storage facilities (65% at fogging; 50% at spraying). Again, 25% is assumed to be lost due to inactivation. During gassing of poultry stables, a larger fraction may be expected to be emitted to the atmosphere.

Disinfection of crates
Disinfection of crates takes place indoors slaughterhouses. Disinfectants will be emitted to the sewer system.

Disinfection of paws
Paws are disinfected by means of a formaldehyde bath. Emissions of formaldehyde to the air occur. The spent formaldehyde is discharged to the manure reception facility. Assumptions by Montfoort *et al.* (1996) are a discharge of 50% to the air (volatilisation) and 25% to the manure storage facility. This type of disinfection only takes place at cattle farms (cows).

Disinfection of milking machines
Disinfectants used for the disinfection of milking machines will be discharged to the manure reception facility, to the sewer or to surface water. The discharge water (containing disinfectants) is about 6 to 25 litres per cow per day.

Disinfection of egg hatcheries
A hatchery is disinfected and cleaned daily with sprays or gasses. Disinfection comprises disinfection of eggs before brooding and during brooding, disinfection of chicks and eggshells, and rooms (daily). Gasses will be emitted mainly to the

air (by ventilation of the room). Sprayed biocides will be mainly emitted to waste water. Montfoort *et al.* (1996) assume that 25% of the biocides is emitted to the air, and 50% is emitted to waste water.

Disinfectants for fish farming (aquaculture)
Depending on the location of the farm, emissions will either be directed to a local sewer system, or to the surface water (fresh or marine). Furthermore, emissions to the air may occur for the more volatile products (e.g., formaline).

4.3 Data requirements for product type 3

The direct exposure compartments, which were introduced in the previous sections, are summarised in Table 5.

Table 5 Direct exposure compartments for product type 3.

Subtype	Products	Direct exposure compartments
3.1	farm buildings, indoors closed spaces	(air indoors) fresh surface water soil sewagewater treatment plant
3.2	farm-buildings, outdoors	air (outdoors) fresh surface water soil
3.3	other buildings, indoors closed spaces	(air indoors) sewagewater treatment plant
3.4	other buildings outdoors	air (outdoors) fresh surface water sewagewater treatment plant
3.5	fish farming (aquaculture) disinfectants	air (indoors and outdoors) fresh surface water marine surface water sewagewater treatment plant

Guidance for demanding test data
Potential data requirements for products released to the individual environmental compartments are discussed in Part 1. In general, the same guidance holds true as for the product types 1 and 2. However, the strong oxidising biocides, such as hypochlorous acid, are used to a much smaller extend in this product type, whereas aldehydes are the main biocides. This means that the focus in demanding test data should be less on hazardous degradation products, and more on degradation and toxicity testing. Leaching tests are not relevant for product type 3.

Several exposure scenarios are available for this product type (Appendix B). The base set data is sufficient to run these exposure scenarios.

5. Product type 4: Food and feed area disinfectants

5.1 Introduction

There is much attention for improving safety and hygiene in food and feed preparation and storage (Bryan, 1992). One of the instruments to reach this, is the use of biocides. The objective of using biocides during the production of food and feed is to reduce the level of potential food pathogens to minimise the risks of food-borne illnesses, and to reduce the total number of bacteria to prevent spoiling of the food and to extend the shelf-life. Hygiene during food and feed production includes cleaning and disinfection ('sanitizing', in American literature). Cleaning is performed to remove soil and food remnants, because they form a substratum for micro-organisms and attract pests such as insects and rodents. Cleaning precedes disinfection. It reduces the levels of micro-organisms somewhat, and can make the disinfection more effective. Surfaces to be disinfected include both environmental areas (e.g., floors, walls, conveyor lines, water treatment, air) and food contact surfaces (e.g., pipelines, fillers, mixing/storage tanks).

Another process in the food and feed industry where disinfectants are used is aseptic packaging (Von Bockelmann, 1991). The objective is to produce products that can be stored for months unrefrigerated. The aseptic packaging process is presented in Figure 4.

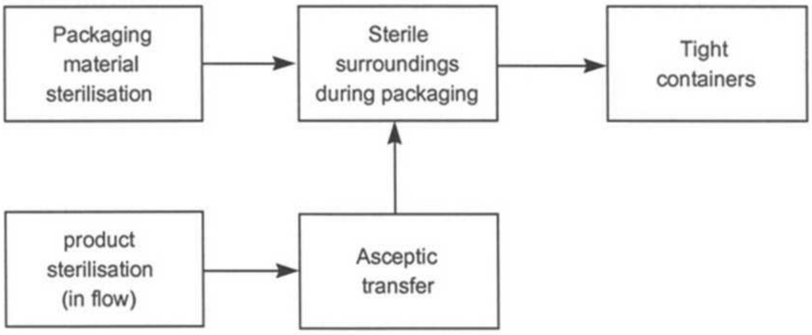

Figure 4 The aseptic packaging process (from: Von Bockelmann, 1991)

The food product is sterilised by UHT (Ultra High Temperature) treatment, no disinfectants are used. The filler and the transportation facilities are usually sterilised with hot air or hot steam, and no disinfectants are used. The sterilisation of the packaging material (step 4) however, depends on the type of packaging material. When possible, heat (hot air or steam) is used for disinfection, but if this is not possible, disinfectants are used.

With this product type, disinfectants for general use in food and feed processing industry and disinfectants for aseptic packaging are distinguished.

According to Walker & LeGrange (1991), the ideal sanitiser has the following characteristics: rapid destruction of micro-organisms, safe and non-irritable to employees, non-toxic for consumers and acceptable to regulatory agencies, rinsable, no adverse effects on food of feed (odour, flavour, appearance), economic, easily tested for concentration in used solutions, stable when concentrated and in solution, non-corrosive, compatible with other chemicals and readily soluble in water. As no compound with all those characteristics exists, and disinfectants therefore will be compromises between these characteristics, a wide variety of disinfectants is used in food and feed hygiene. Main disinfectants are (Walker & LeGrange, 1991; Banner, 1995):

- Chlorine compounds (hypochlorous acid, and organic chlorine-releasing species, as di-and trichloroisocyanuric acid), which have a broad kill spectrum;
- Iodine compounds (mainly iodophores: complexes of iodine, an organic carrier and a non-ionic surfactant in acid)
- QUACs (Quaternary ammonium compounds)
- Additionally, the following types of disinfectants are used:
- Acid anionic sanitisers
- Peracetic acid (used in equilibrium mixtures of acetic acid, hydrogen peroxide, peracetic acid and water)
- Amphoterics (surfactants)
- Polymeric biguanides (esp. polyhexamethylene biguanide)

The main disinfectant used for aseptic packaging is hydrogen peroxide (H_2O_2), heated to a temperature of 85 to 90°C, with an exposure time of 3 to 4 seconds (Von Bockelmann, 1991). Sometimes other disinfectants are used in combination with H_2O_2, e.g., formaldehyde.

5.2 Release estimation

The environmental release of biocides used for disinfection in food and feed processing industries is visualised in Figure 5. The disinfectant is applied to the surface to be disinfected, which is cleaned (rinsed with water) afterwards, to remove traces of disinfectant. The water after this cleaning is either directed to a sewagewater treatment plant, or directly to the surface water. During the application, emissions to the air can occur (depending on the way of application).

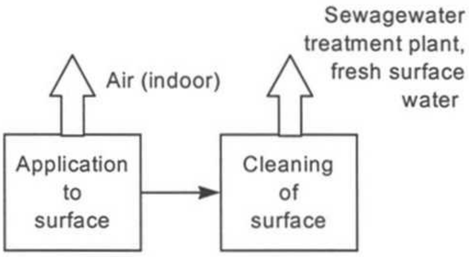

Figure 5 *Environmental release of disinfectants for food contact surfaces and environmental areas during food or feed processing.*

The environmental release of disinfectants (mainly H_2O_2) used for aseptic packaging is presented in Figure 6. The disinfectant is removed (immediately after the required contact time) by hot air treatment, which will cause the major part of the remaining disinfectant to be emitted to air.

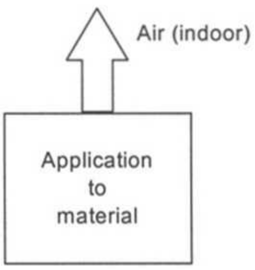

Figure 6 *Environmental release of disinfectants for aseptic packaging*

Disinfection of floors, surfaces and equipment within plants

The disinfection of food or feed contact surfaces and environmental areas can be performed in many different ways. Spraying (low pressure and high pressure) of disinfectants is common practise; concentrations used are 100-200 ppm available chlorine from hypochlorous acid (contact time 1-2 minutes). Other ways of application include soaking and manually brushing. Fogging can take place, to disinfect hard-to-reach areas. When performed with chlorine, the ventilation system is turned off, chlorine is fogged in concentrations of 200 - 600ppm, and when all surfaces are thoroughly wetted the ventilation system is turned on again. Personnel is vacated during this procedure. Tool and machines can be disinfected with a CIP (Clean In Place) system, to which disinfectants are added to the circulating water.

Disinfectants will react rapidly (e.g. with organic matter) when applied, and remaining disinfectant will be washed to the sewage water treatment plant. Although it is not likely due to their high reactivity, disinfectants can be discharged to (fresh) surface water via the STP. Furthermore, direct emission to surface water (without passing through a STP) can occur. The discharge of (potentially harmful) reaction products to STP and subsequently fresh surface water is possible. During fogging, a significant fraction is released to the air.

However, as the plant is a closed system and disinfectants are highly reactive, significant emissions to outdoors air are not expected.

In-plant chlorination
The sanitation with chlorine often takes place as 'in-plant chlorination': chlorine is added to the water supply of the entire plant. The chlorine is in the form of hypochlorous acid (HOCl, see Product type 5). The hypochlorous acid can be added in several ways: by adding a powder (calcium hypochlorite of lithium hypochlorite) or liquid (aqueous solution of sodium hypochlorite) or by on-site production (electrolysis of sodium chlorite). Concentrations used for in-plant chlorination range from 5-7 ppm, maximum 15-20 ppm during cleanup operations. The fraction of the disinfectant that is not degraded is expected to end up in the sewer system.

Disinfection of package material
The disinfection is usually performed by immersing the package material (e.g., glass bottle, plastic bottle, laminates) in a bath of 30% (15 to 35%) H_2O_2 at temperatures of 50 to 60 °C or more, followed by drying with hot, sterile air. This causes the main emission to be emitted to the air within the plant. As described earlier, emissions from the plant to the outdoors air are not expected.

5.3 Data requirements for product type 4.

The direct exposure compartments, which were introduced in the previous sections, are summarised in Table 6

Table 6 Direct exposure compartments for product type 4.

Subtype	Products	Direct exposure compartments
4.1	food contact surfaces, environmental areas in food and feed processing	air (indoors); sewagewater treatment plant fresh surface water
4.2	aseptic packaging	air (indoors)

Guidance for demanding test data
Potential data requirements for products released to the environmental compartments air and a sewagewater treatment plant (STP) are discussed in Part 1.

Environmental and health problems related to disinfection in food and feed processing mainly involve the exposure of workers to aggressive chemicals (irritation of eyes and skin, due to (e.g.) chlorine, H_2O_2 and peracetic acid). Examples are halamite-eczema at bakeries (using it as a cleaning agent) and exposure of vegetable-washers to ozone in washing water. The use of chlorine can lead to disinfection by-products, such as trihalomethanes and chloramines. The presence of remnants of disinfection agents in food is strongly guarded, as any amount of disinfectant is considered unacceptable. Only in cases of accidents, the public health is at risk.

For the compartment sewagewater treatment plant, especially the data items IV.2 and IV.3 are useful. The relevance of the test with a pre-adapted inoculum is less clear: A STP may be expected to be loaded on a regular basis with biocides from a food or feed processing plant, but the exposure is not continuous.

No emission or exposure scenarios are available for this product type (Appendix B).

6. Product type 5: Drinking water disinfectants

6.1 Introduction

This section concerns biocides used for the disinfection of drinking water (Product type 5). It does not concerns the disinfection of cooling water or process water (Product type 11), disinfection of waste water (Product type 2) or disinfection of swimming pools (Product type 2).

Drinking water is disinfected to destroy infectious micro-organisms, so that the water cannot transmit disease-producing biological agents. Therefore, disinfection should always be the final step of drinking water treatment.

According to EU legislation, no harmful micro-organisms are allowed in water for human consumption. Indicators organisms are micro-organisms of the coliform group (total and thermo-tolerant: *Escherichia coli*), faecal streptococci and sulphite-reducing *Clostridia*.

Three types of disinfection can be distinguished:

- Primary disinfection at the water treatment plant. The main purpose is to kill micro-organisms, in order to prevent them to disturb other processes at the treatment plant (e.g., clogging of filter systems)
- "stand by disinfection" . Disinfectants used at relatively high concentrations, to disinfect the distribution system when a microbial contamination has been observed, or when a new system is taken into use
- residual disinfection, as last stage in the water treatment process, in order to maintain an antimicrobial potential in the distribution system.

The most important chemical disinfection methods (biocides) include:

- chlorination with salts of hypochlorous acid
- chlorination with ClO_2, ClO_2^- and ClO_3^-
- chloroisocyanate
- ozone treatment
- treatment with hydrogen peroxide
- Other disinfectants, used on smaller scale, are:
- $KMnO_4$ (used for pre-disinfection, Bryant *et al.* 1992)
- Ag

Other (non-chemical) disinfection methods include:

- UV-disinfection
- filtration techniques
- coagulation / flocculation techniques

These non-chemical techniques, although important in drinking water disinfection, are not elaborated in this study because no biocides are used.

The biocidal properties of most of these disinfectants are based on their strong oxidising capacity. For an environmental risk assessment, and therefore for the dataset to be included in Annex II and III of the Directive, it is important to consider not only the biocides, but also their degradation products and products formed during reactions with compounds present in the drinking water. In the following, the main biocides currently in use are described, together with their reaction products.

Chlorine compounds

The addition of chlorine gas to pure water results in the formation of a mixture of hypochlorous acid and hydrochloric acid:

$Cl_2 + H_2O \Leftrightarrow HOCl + H^+ + Cl^-$

The main biocide is hypochlorous acid (HOCl). The hypochlorous acid dissociates in water, depending on the pH, according to:

$HOCl \Leftrightarrow H^+ + OCl^-$

The degree of dissociation depends on pH and (to a minor extend) on temperature. At pH < 6, dissociation is poor. At pH > 8,5, there is nearly complete dissociation, causing a decrease of biocidal activity. Hypochlorous acid and the hypochlorite ion (OCl^-) are defined as 'free available chlorine'.

When ammonia or nitrogen-containing compounds are present in the water, hypochlorous acid reacts with the nitrogen to form chloramines (e.g. monochloramine, dichloramine, trichloramine). The formation of chloramines decreases the biocidal activity, although chloramines have only slight biocidal properties. The N-chloro compounds are known as 'combined available chlorine'.

Hypochlorous acid is very reactive, and is therefore only present for a limited time. Different principles can be used to obtain a biocidal residual in the system. Ammoniation (addition of ammonia) is used to maintain a residual biocidal potential of chloramines in the system. (Dychdala, 1991). Another technique is breakpoint chlorination: addition of a sufficient amount of hypochlorous acid to ensure a free available chlorine residual.

Chlorine dioxide (ClO_2) is another chlorine-based disinfectant, although its main functions in water treatment are odour and taste control. Chlorine dioxide is produced on-site from chlorine and sodium chlorite ($NaClO_2$) or sodium chlorate ($NaClO_3$). Its role as an oxidising chemical is based on the reactions:

$ClO_2 + 1e^- \Leftrightarrow ClO_2^-$

$ClO_2^- + 2H_2O \Leftrightarrow Cl^- + 4\ OH^-$

The first step is the most important for disinfection purposes (Bryant *et al.*, 1992).

Iodine compounds

Iodine is not used on a large scale as a drinking water disinfectant, but has been applied on smaller scales (e.g. Florida correctional institutes at a concentration of 1 mg.l^{-1}, Hurst 1991). Furthermore, it is used as emergency disinfectant and disinfectant for small individual (e.g. military) supplies. Iodine is an effective disinfectant, less influenced by pH, organic substances or nitrogen-containing substances as much as chlorine.

Elemental iodine (I_2) reacts with water according to:

$I_2 + H_2O \Leftrightarrow HOI + H^+ + I^-$

The equilibrium is strongly pH dependent, with 99% present as iodine at pH 5 and 88% present as hypoiodous acid at pH 8.

Molecular iodine (I_2), hypoiodous acid (HOI) and the iodine cation (H_2OI^+, present at very low concentrations compared to HOI) possess biocidal properties. According to Gottardi (1991) drinking water disinfected with iodine contains 0.25 - 2.5 ppm iodine, mainly present as I_2 (aq) and HOI.

Ozone

Ozone (O_3) is a very effective disinfectant, due to its strong oxidising potential. Addition of ozone to water causes free radicals and reactive compounds to be formed, e.g. $OH^{\cdot}$, O_3^{-}, O_2^{-}, HO_2^{-} and H_2O_2. These compounds cause organic matter (including micro organisms) to be degraded. It is used for drinking water disinfection in water treatment plants, in Europe and especially in France.

Ozone is believed to be a stronger disinfectant than chlorine, and is less influenced by pH and temperature. The problems with ozone treatment are the instability of the O_3 molecule, the low solubility, and the difficulty to produce high partial pressures of ozone. Because of the instability, it is produced on-site, by the corona discharge of high-voltage electricity in dry air. Ozone is a promising alternative for chlorine, but does not provide any residual biocidal working. This problem can be solved by combining disinfection techniques, for example a pre-disinfection with chlorine, a main disinfection with ozone followed by a residual disinfection with ammonia and hypochlorous acid.

6.2 Release estimation

Emissions of drinking water treatment biocides occur in two stages: during the disinfection process, and during consumption of the water (see Figure 7). The emissions during the disinfection process can occur for all biocides, and depend on the disinfection process. The emissions can lead to operator exposure and exposure of surface water or soil. Emissions in the consumption-phase are relevant in two cases:

1. For biocides that remain present as a residual (e.g., chloramines), or
2. For compounds formed during disinfection (e.g., TriHaloMethanes).

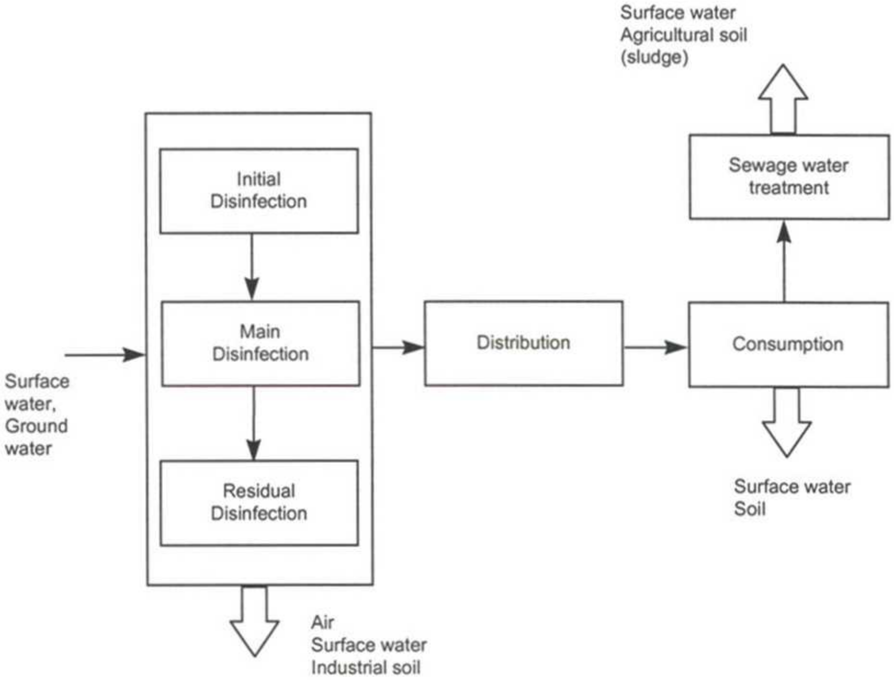

Figure 7 *General life cycle of drinking water disinfectants, and emissions to the environment (broad arrows).*

The emissions depend on whether the disinfectant is used as initial disinfectant, or for the main disinfection, or to obtain a biocidal residual, or for 'stand-by' purposes (in case of contamination), which will affect the exposure time (continuous or incidental) and exposure concentration (for stand-by disinfection, higher concentrations are used).

Application of disinfectant

The application technique depends on the disinfectant that is used. The following steps can be distinguished:

- Production of disinfectant: Ozone is produced on-site by an electric corona discharge in oxygen gas or air.
- Storage of disinfectant: Chlorine is stored in tanks, containing mainly liquid chlorine but also gaseous chlorine
- Contact between disinfectant and water: With gaseous disinfectants as ozone, Cl_2 and ClO_2 the gas is dispersed through a partial water flow. The water flow containing the disinfectant is then added to the main water flow. The contact time has to be long enough to enable effective disinfection. The contact with gasses is performed in closed spaces. Ozone contact tanks are supplied with destructors to remove ozone from the air before it is emitted.

The place of disinfection can vary, depending on the configuration of the drinking water treatment plant. As stated before, a disinfectant can be added:

- as initial disinfectant, after removal of organic matter to kill micro-organisms, or to remove (oxidise) both organic matter and micro-organisms
- main disinfection
- residual disinfection, to obtain a biocidal residual in the distribution system
- furthermore, stand-by disinfectants are used to disinfect the distribution system in case of contamination.

Quantitative information about emissions (mainly to air, and possibly to soil) from a water treatment plant due to the application of disinfectants to drinking water is not known.

Consumption of disinfected water
As drinking water is consumed by humans and animals, all biocidal residual, biocide degradation products or disinfection by-products still present in the water the moment it leaves the distribution network will result in direct exposure. The Association of Rhine and Meuse Water Supply Companies have performed measurements in surface water and drinking water on a large number of substances (Van Genderen *et al.*, 1994). For some substances, the results indicate that they are introduced during the water treatment process (e.g. chloroform, bromodichloromethane, dibromochloromethane, N,N-diethylacetamine).

6.3 Data requirements for product type 5

The direct exposure compartments, which were introduced in the previous sections, are summarised in the table below.

Table 7 Direct exposure compartments for product type 5.

Subtype	Products	Direct exposure compartments
5	All products	Air (outdoors) Fresh surface water Marine surface water Soil Sewagewater treatment plant

Guidance for demanding test data
Potential data requirements for products released to individual environmental compartments are discussed in Part 1. However, some remarks for applying these generic data requirements can be stated.

A main problem associated with drinking water disinfectants (strong oxidising compounds) is the formation of "disinfection by-products" (DBP): Products of the reaction of the oxidiser with organic matter (e.g. algae, micro-organisms, suspended matter, humic substances). These compounds are typically short-chained organic substances, that can be halogenated (Cl, I, Br). Some of these compounds are toxic or carcinogenic. In the text box (see below), some background information is presented about the by-products formed during disinfection.

Disinfection by-products

Chlorination of surface water can lead to the formation of chloroform and trihalomethane compounds (THM compounds). THM compounds are formed during a reaction with humic or fulvic acids, and are toxic and possibly carcinogenic. Chloroform is a known carcinogen for test animals. In Dutch drinking water, chloroform concentrations of 0 - 25 µg.l^{-1} are found (Tukker *et al.* 1995).

The reactivity of chlorine dioxide with humic and fulvic acids is lower then of hypochlorous acid, causing less THM to be formed. According to Van Hoof (1986), quinones, hydroquinones and mono- and dicarboxylacids can be formed during ClO_2 disinfection.

Ozone treatment causes the formation of low-molecular weight organic compounds (AOC: Adsorbable Organic Carbons), e.g. aldehydes and carboxyl acid (Van Hoof, 1986). The identification of by-products is difficult, because of the lack of adequate analytic techniques. An acknowledged problem is the formation of bromate (BrO_3^-, carcinogen) from bromide during ozonisation. The formation of bromate depends on the bromide concentration, the ozone dosage, the DOC concentration, ammonium concentration and pH, temperature and alkalinity. The EU standard for bromate is 10 µg.l^{-1}. Versteegh *et al.* (1995) sampled bromate in drinking water in the Netherlands, from plants using ozone disinfection. They found a maximum average bromate concentration of 3.6 µg.l^{-1}, corresponding with a risk for death by cancer of 7.10^{-6}. Other possible formation products include bromoform, a trihalomethane (Bryant *et al.*, 1992).

The hazard posed by disinfection by-products causes test item I/II.4 (Toxicity test for hazardous degradation products) to be of special importance.

With respect to extensive biodegradability testing in relation to the reactive nature of the products, the same holds true as stated for product type 2.

A special feature of drinking water disinfectants is that they are used and emitted continuously. The consequence is that a biodegradability test with a pre-adapted inoculum can be considered as relevant (item IV.1). Furthermore, chronic exposure toxicity tests are important (I.5, II.7, III.7).

No leaching rate is required for this product type.

No emission or exposure scenarios are available for this product type (Appendix B).

7. Product type 6: In-can preservatives

7.1 Introduction

Biocides for in-can preservation are used to prevent microbial deterioration of industrial fluids stored in cans, tanks or other closed containers. Examples of applications for in-can preservatives are:

- Paints and coatings
- Washing and cleaning fluids
- Fluids used in paper-, textile and leather production
- Lubricants
- Machine oils

There is a potential overlap with product type 7 (film preservatives), for products stored in can and applied in films, such as paints, coatings and glues. Another area of overlap can be the slimicides (product type 12).

General

Aqueous fluids often provide an excellent medium for the proliferation of micro-organisms, such as bacteria, yeast and fungi. Biocides are added to combat microbial development in cans and tanks.

Biodeterioration of aqueous fluids is expressed by:

- Reduction of pH
- Loss of viscosity (or sometimes increase)
- Evolution of gas
- Coagulation
- Foul smell
- Colour changes
- Breaking of emulsion
- Colonies on surface

The result is that the fluid is unfit for its intended use. The deterioration process is irreversible.

In-can preservation is applied for many different industrial fluids. Examples are (Paulus, 1993):

- Air washer
- Bitumen emulsions
- ceramic glazes
- enzyme solutions
- Electrodeposition paints
- Fountain solutions (printing)
- Humidifiers

- Inks
- Mineral slurries
- natural latex rubber
- Pigment slurries
- Photographic process fluids
- Polishes
- Textile processing fluids
- Water bed fillings
- Wax emulsions

Criteria for biocides used for in-can preservation are:
- Type of aqueous fluid
- pH of the fluid
- Final use of the fluid
- Heat resistance (depending on the processes to which the fluid will be subjected)
- Low P_{ow} (must be active in the water phase)

Polymer emulsions
Polymer emulsions are fine dispersions or suspensions of synthetic polymers in aqueous media, and are intermediates in the production of emulsion paints, adhesives, paper and textile coatings, non-woven fabrics and carpet-backing compounds (Gillat, 1990). Over 70% is used for paints and coatings, adhesives, paper and carpet backings (Paulus, 1993). Examples of latex, acrylics, polyvinylalcohol, polyvinylacetate and vinyl-acrylics. They are manufactured from monomers (e.g., acrylic acid, ethylene, styrene, vinyl acetates), initiators (to initiate polymerisation), stabilisers and a number of additives to improve their properties, including biocides.

Polymer emulsions are highly susceptible to microbial deterioration. Often, the polymer itself is not degraded, but micro-organisms may break down other constituents of the formulation. A specific problem is the excretion of cellulases by bacteria and fungi, an enzyme which can hydrolyse cellulose at concentrations as low as $1e^{-5}$ units per ml. As cellulases are not inhibited by biocides, the application of biocides will not stop the deterioration. Application in an earlier stage (prevention) is the solution to this problem. Biocides used for in-can preservation of polymer emulsions include (Gillat, 1990; Paulus, 1993):
- aldehydes, e.g., formaldehyde
- formaldehyde releasing compounds, e.g., triazines
- heavy metals, e.g., mercury-based
- dimethoxane
- amides
- heterocyclic N,S compounds
- 1,2 dibromo-2,4-dicyanobutane
- 1,2 benzisothiazolin-3-one

Mercury based biocides have the advantage that mercury ca inhibit cellulase activity, but due to increased environmental concern, mercury-based biocides have almost disappeared. Formaldehyde donors and 1,2 benzisothiazolin-3-one are also used less. A new development is a mixture of 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one.

Preservation of fuels
Fuel (gasoline, kerosine) is stored in containers. When water enters these containers, either through seepage or through condensation, favourable conditions for micro-organisms are present. The micro-organisms can proliferate in the water phase, whilst feeding on hydrocarbons in the fuel. These micro-organisms include aerobic bacteria, which can produce sludge and slimy mats, clogging filters and pipelines, and anaerobic bacteria, which can produce corrosive acids. As the entry of water cannot be prevented, biocides are used to prevent biodeterioration (Paulus, 1993; Hill, 1995).

Biocides for the in-can preservation of fuel have to fulfil the following criteria:
- Active in low dosages (no dilution of the fuel);
- No interference with the combustion process
- Broad spectrum of effectiveness
- Soluble in water as well as in fuel; low Pow
- Non-corrosive

Examples of biocides used are formaldehyde donors, pyridine-derivatives, and heterocyclic N,S compounds (Paulus, 1993).

7.2 Release estimation

In-can preservatives are used in the storage of many different aqueous fluids, which are used in many different processes. In Figure 8, a generalised life cycle is presented. When biocides are added to the fluid which is to be preserved, small losses (few percent) can occur. During the in-can storage, no environmental emissions take place. When the aqueous fluid is used after storage, the remaining (not-degraded) biocide can be released. The amount released depends on the type of fluid, the type of biocide, and the process. When the fluid is used in private or public households, or is used in industrial processes, the biocides are likely to end up in a Sewagewater Treatment Plant (STP). When the fluid is used in agricultural application, part of the fluid is likely to end up in a manure storage tank, and emissions to soil or surface water may occur when the manure is distributed oon farmlands.

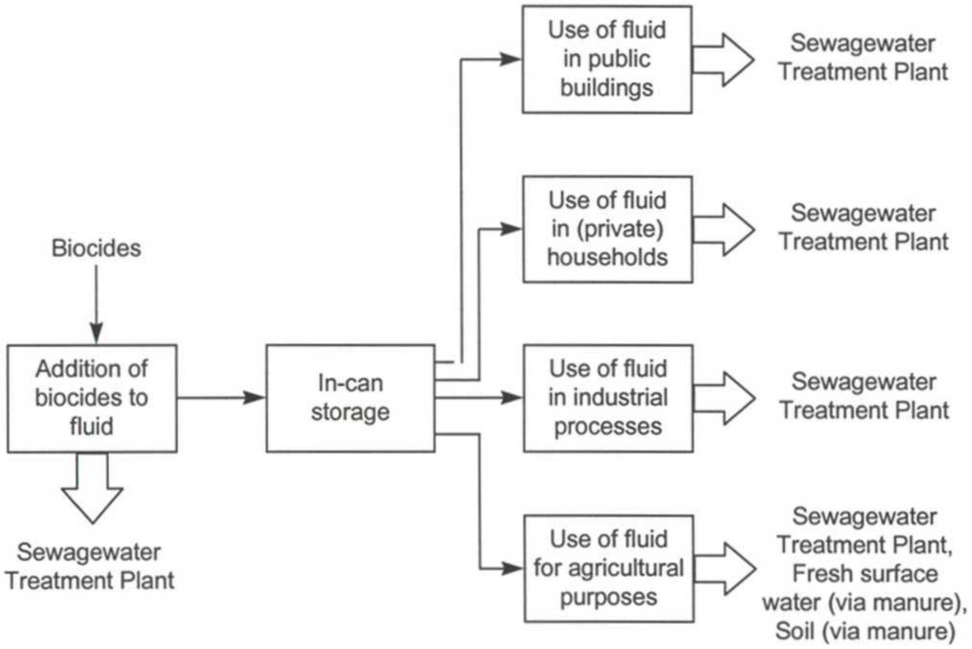

Figure 8 Environmental release of in-can preservatives

For biocides in polymer emulsions, an emission pattern according to Figure 8 will occur. For biocides for the in-can storage of fuels, an emission to a STP will not occur. The biocide may be expected to be degraded during combustion.

In general, in-can preservatives are used in low dosages in a wide variety of applications, resulting in a diffusive emission.

7.3 Data requirements for product type 6

The direct exposure compartments, which were introduced in the previous sections, are summarised in Table 8.

Table 8 Direct exposure compartments for product type 6.

Subtype	Products	Direct exposure compartments
6.1	Canned fluid used in public buildings	STP
6.2	Canned fluids used in households	STP
6.3	Canned fluids used in industrial processes	STP
6.4	Canned fluids used for agricultural purposes	STP, Soil, Fresh surface water

Guidance for demanding test data

Potential data requirements for products released to the environmental compartments fresh surface water, marine surface water and a sewagewater treatment plant are discussed in Part 1. However, from the formulation and application some remarks for applying these generic data requirements can be stated:

Regarding the environmental compartments fresh surface water and soil, a leaching test is not required, as the biocide is not inserted in a matrix. As emissions are diffusive, and in-can preservatives are likely to be persistent in the environment, and therefore chronic test data and extended biodegradation testing is considered relevant.

No emission or exposure scenarios are available for this product type (Appendix B).

8. Product type 7: Film preservatives

8.1 Introduction

Film preservatives are biocides used to protect surfaces against the adverse influence of micro-organisms, such as biodeterioration by bacteria and coverage by fungi. Examples of products to be preserved are:

- Paints and coatings
- Plastics
- Glues and adhesives
- Paper

This product type can overlap with product type 6, because many of these products are used as films are stored in-can before application. Examples are paints and coatings. Furthermore, an overlap occurs with products for the preservation of polymerised materials (product type 9).

Antifouling biocides are not included in this product type; they form a separate category in product type 21.

Paints and coatings
In damp rooms (kitchens, bathrooms, cellars, breweries), painted surfaces can be covered by algae and fungi. As this is both unattractive and unhygienic (e.g., in the foods industry), fungicidal or algicidal treatment of the coating is required.

Microbial growth on the coating under damp conditions, in which nutrients from the polymer, plasticizer or other auxiliary is used, is called primary infestation. Secondary infestation is the growth of microbes on dirt, which is gathered on the painted surface. To prevent secondary infestation, it is important to keep the surface clean. To prevent primary infestation, biocides are included in the coating.

The biocides used to preserve paint films have to fit a large number of criteria:

- Low toxicity
- Good light stability
- Good compatibility with other constituents of the coating
- Non-volatile
- Colour fast
- Colour less
- Insoluble in water (non-leaching)
- Economical

Biocides fit for the preservation of films are (Paulus, 1993):

- amides
- carbamates
- pyridine derivatives
- azoles
- heterocyclic N,S compounds
- N-haloalkyl thiocompounds

Glues and adhesives

Glue and adhesive film can be contaminated by fungi under humid conditions, with loss of function as a result. Therefore, biocides are incorporated to prevent mould growth. In the choice of biocide, it should be considered whether the adhesive will come into direct contact with foodstuffs. This requires low toxicity preservatives which are odourless and tasteless.

Appropriate biocides for the fungicidal treatment of glues and adhesives are (Paulus, 1993):

- Dichlorophen
- Carbamates
- Pyridine derivatives
- Heterocyclic N,S compounds
- N-Haloalkylthio compounds

Plastic and paper

Preservatives for the preservation of plastic and paper are described in Chapter 10 (Product type 9: Fibre, leather, rubber and polymerised materials preservatives).

8.2 Release estimation

Paints

A typical life cycle for biocides used in exterior paints is presented in Figure 9. Biocides can be added in various stages of the paint formulation. The formulated paint is stored (were in-can preservation is required, see Product type 6), and applied after some time. Application of paints is often performed within a spray-booth. A water curtain prevents emissions to air to spread, and emissions will be directed primarily to a STP.

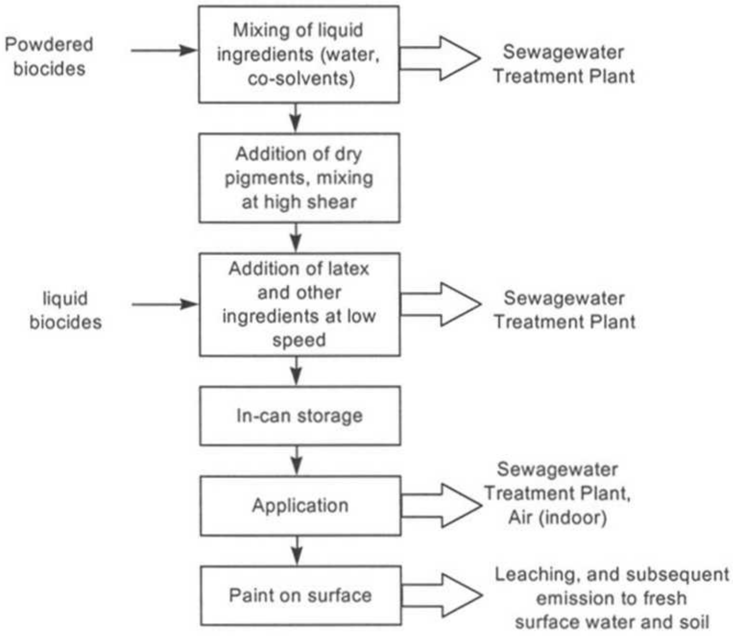

Figure 9 Environmental release of biocides in a typical water-based exterior paint (after: Downey, 1995).

The emissions after application are strongly dependent on the area were the paint is used. Contact with water (e.g., rainwater) may result in leaching of the biocide, causing environmental emissions to soil or surface water. In farm buildings, leaching may occur during cleaning of the walls, and emissions to soil and (fresh) surface water can occur (through manure). Emissions from the paint layer to the air are not to be expected, as biocides with a very low volatility are used.

Glues and adhesives

Little is known about the environmental emissions of preservatives in glues and adhesives. It can be expected that emissions occur in a similar way as for paints, i.e. after leaching in wet conditions.

8.3 Data requirements for product type 7

The direct exposure compartments, which are introduced in the previous section, are summarised in Table 9.

Table 9 Direct exposure compartments for product type 7

Products	Direct exposure compartments
All products	STP Air (indoors) Soil Fresh surface water

Guidance for demanding test data

Potential data requirements for products released to the environmental compartments fresh surface water, soil and a sewagewater treatment plant are discussed in Part 1. However, from the formulation and application some remarks for applying these generic data requirements can be stated.

An important aspect of this product type is that the biocides are inserted in a matrix, and that the substances must be released from the matrix before environmental exposure takes place. As biocides in this product type are selected to be non-volatile, leaching to (rain or cleaning) water is the most important release process. A leaching rate is required for environmental risk assessment.

Specific leaching tests for film preservatives are not available. The efficacy of the product is tested by either:

- Laboratory simulation tests: A sample of material (e.g., wood, metal, concrete) is treated with the preserved paint, and placed in a humid atmosphere at controlled temperature. After 4-6 weeks, the microbial growth on preserved films is compared to untreated blanks. Examples of test guidelines are ASTM D3273, and BS 3900, part G6.
- Field trials: Biocide-treated paints are applied to panels, which are exposed to a variety of climatic conditions. The extend of microbial growth is assessed and compared to blanks. This is a true performance test, but lengthy. An example of a protocol is ASTM D3456.

Although these tests give some information about leaching of the preservative, leaching rates cannot be determined. A test for leaching to soil is relevant, provided that the film is in direct contact with soil, which is usually not the case. Substances used for film preservation can be expected to be persistent (at least, in the film matrix). Therefore, biodegradability tests are considered as important.

The relevance of chronic toxicity test is questionable (based on the emission pattern): The release to a STP (during application) is a single event, and the release during leaching will especially occur during rain or cleaning events (contact with water). However, the (possible) persistence of substances may be an other reason to demand chronic toxicity tests (criteria required: see product type 1).

The two available exposure scenarios for this product type (Appendix B) do not need additional test data next to the base set data.

9. Product type 8: Wood preservatives

9.1 Introduction

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. An overview of the applications for preserved wood is presented in Table 10.

Table 10 Applications for preserved wood

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

The application of biocides is executed on various scales and with various techniques. An overview is given in Table 11. 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 conserved 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 12, 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 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 13 and Table 14, the production volume of biocide products in Germany is summarised.

Table 11 Overview of the preservation and curation of wood with biocides.

Type	Scale	Conservation process
Preventive	Industrial	Vacuum pressure Immersion
	Sawmills, Joinery manufacturers	Immersion Brushing Spraying Pills
	Do-it-yourself	Brushing Spraying Pills
	Professional	Injection in soil
Curative	Professional	Fumigation
	Do-it-yourself	Brushing Spraying Pills Injection

Table 12 Biocides used for wood conservation, categorised on solvent type (Boonstra et al., 1991; Beentjes & Visée, 1994)

Type	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, zincnaphtalate, coppernaphtalate, permethrin, deltamethrin
Coal-tar derivates	creosote oils, carbolineum
Emulsions	azaconazole, ethylhexanoate, isothiazoline, copperquinolinolate, thiocyanate, quats
Gasses	Methylbromide

Table 13 *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 14 *Use of wood conservation biocides in Germany, differentiated to purpose (Brückner & Willeitner, 1992).*

	Salts	Coal tar	Other
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 15). 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 15 *Biocides 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
immersion/ soaking	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.

9.2 Release estimation

The data that is required for authorisation of biocide products should depend on the environmental compartments to which biocide products are emitted, and on the way humans and the environment are exposed. Therefore, it is necessary to know the life cycle of the biocide product, and the emissions (receiving environmental compartment and an indication of the magnitude of the emissions) that occur during this life cycle.

The life cycle of wood preservation biocides is outlined in Figure 10 (for wood preservation biocides) and Figure 11 (wood curation biocides). Several stages can be distinguished:

- production of biocide product (including production of the biocidal and other components and subsequent formulation).
- application to the wood that has to be preserved or cured
- disposal of remnants of the biocidal product and packaging materials
- use of the treated wood
- disposal of the treated wood

In this study, the processes from the application of the biocide product until the disposal of the treated wood are considered.

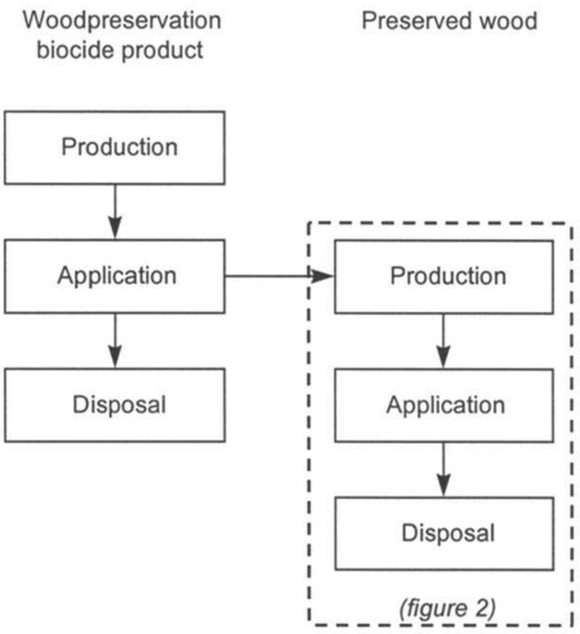

Figure 10 *Life cycle of wood preservation biocides and the preserved wood (from: Bringezu, 1992).*

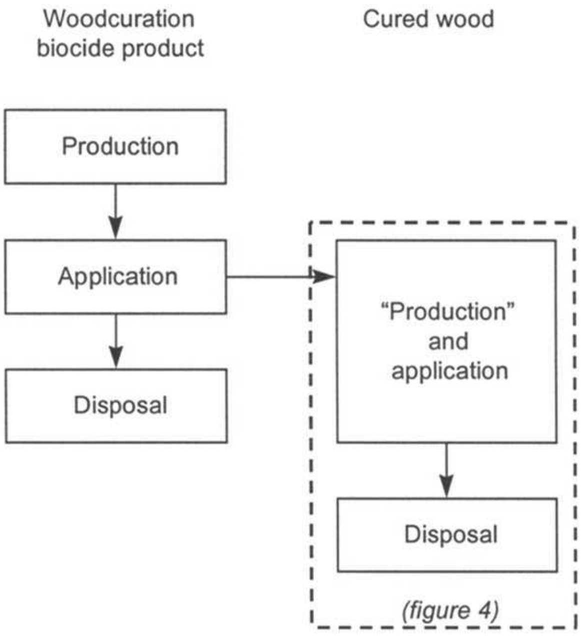

Figure 11 *Life cycle of wood curation biocides and the "cured" wood.*

Many different processes for application and disposal are in use. To be able to asses which emissions and subsequent exposures occur a more detailed life cycle description is required. This is performed in Figure 12 to Figure 14 (wood preservation) and Figure 15 (wood curation). Figure 12 and Figure 15 include emissions (arrows). The receiving (primary) environmental compartment is indicated in the figures.

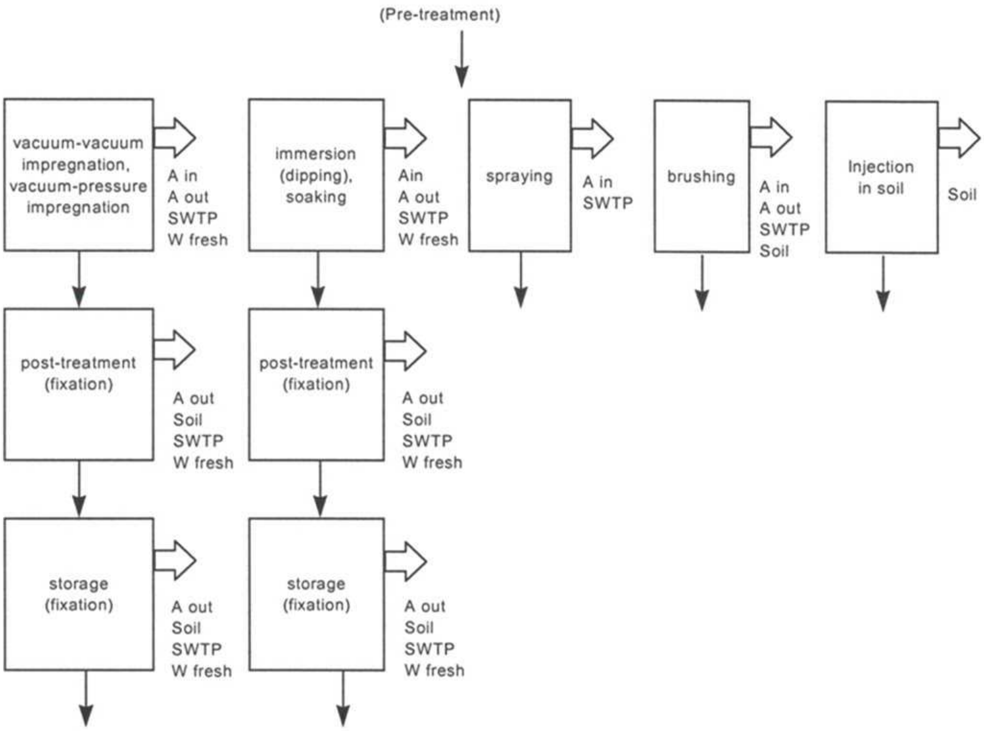

Figure 12 Processes and emission points during the life cycle of wood preservation biocides: application of wood preservatives. The broad arrows indicate emissions points. The abbreviations indicate the receiving environmental compartments: A in = Air, Indoors; A out = Air, Outdoors; W fresh = Fresh surface water; W sea = Sea water; STP = Sewagewater Treatment Plant; Soil = soil. Wood preservation by pills is not included in the scheme; environmental emissions during application are not expected.

In the application of wood preservatives (production of preserved wood) several processes can be distinguished (see Figure 12): impregnation, immersion or soaking, spraying, brushing, and the use of pills. Sometimes (in the case of preservation on a large, professional scale) a pre-treatment of stored, not-yet preserved wood is performed to preserve the wood until preservation takes place. Impregnation and immersion / soaking can be followed by a fixation phase, passive (storage) or active (post-treatment).

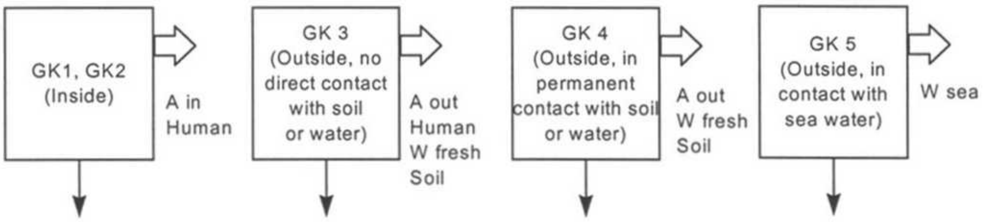

Figure 13 *Processes and emission points during the life cycle of wood preservation biocides: application of preserved wood (explanation: see Figure 12)*

For the application of preserved wood a distinction between different application types is made, based on European classification in classes (implemented in German law as Gefährdungsklassen, GK) (see Figure 13).

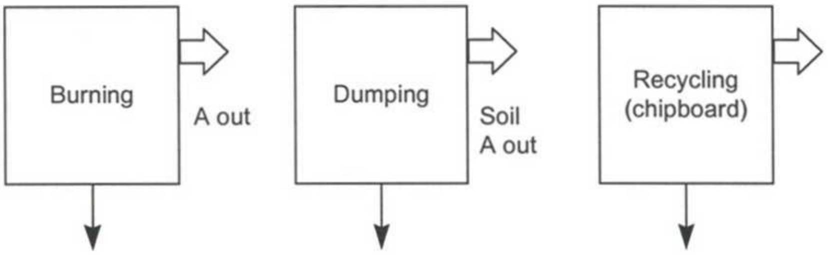

Figure 14 *Processes and emission points during the life cycle of wood preservation biocides: disposal (explanation: see figure Figure 12)*

The disposal of preserved wood (see Figure 14) can be burning, dumping or recycling (to chipboard).

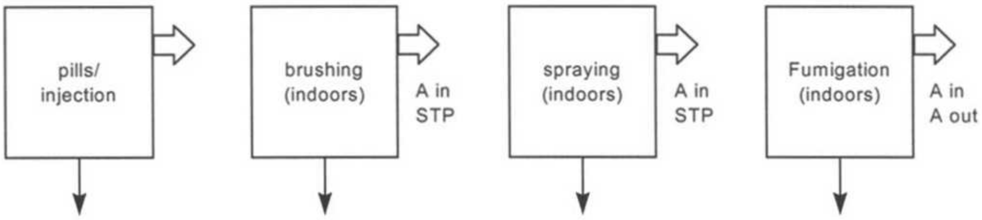

Figure 15 *Processes and emission points during the life cycle of wood curation biocides. The figure describes the application of wood curatives combined with the application of the cured wood (see Figure 11). The disposal of cured wood (not in this figure) is identical to Figure 14 (explanation: see Figure 12).*

The curation of wood (see Figure 15) mainly takes place indoors. Biocides are applied by pills or injection, by brushing, by spraying or by fumigation.

Pre treatment of wood to be preserved

Pre-treatment of wood is performed for short-term protection from wood moulds. Wood is impregnated by immersion (dipping), to prevent deterioration of the wood while it is stored for later impregnation. No research is performed on emissions during this phase. However, the consequent immersion and storage of the wood can cause considerable leaching losses of biocide product.

Application of wood preservatives ("production" of preserved wood) with vacuum-vacuum and vacuum-pressure methods

The wood is inserted in an impregnation tank. Under vacuum, air is removed from the pores and cavities in the wood. The impregnation fluid enters the tank while maintaining the vacuum. The pressure is increased to atmospheric pressure (vacuum-vacuum method) or high pressure (vacuum-pressure method) to force the impregnation fluid into the wood. The remaining impregnation fluid is pumped out of the tank, and surplus impregnation fluid is removed with a second vacuum. This preservation method is mainly executed at (specialised) plants.

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 16).

Table 16 Indication of the water contamination from a "standard" wood impregnation plant (from: CUWVO, 1986).

Conservation with creosote		Conservation with CCA salt	
Production (wood)	8000 $m^3.yr^{-1}$	Production (wood)	3000 $m^3.yr^{-1}$
Condensation water	200 $m^3.yr^{-1}$	Condensation water	2 $m^3.yr^{-1}$
Phenols	200 $kg.yr^{-1}$	Copper	~1 $kg.yr^{-1}$
PAH (19)	40 $kg.yr^{-1}$	Chromium	~1 $kg.yr^{-1}$
PAH (6)	0.8 $kg.yr^{-1}$	Arsenic	~1 $kg.yr^{-1}$
COD	1000 $kg.yr^{-1}$		
BOD	600 $kg.yr^{-1}$		

A second source of contamination -next to contaminated water vapour- is leakage of impregnation fluid. After impregnation, the impregnation tank is opened and lorries 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 waste water. 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 STP or to surface water. Exposure of workers in the plant may be expected. 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 STP or fresh surface water (when the area is paved).

Application of wood preservatives ("production" of preserved wood) by immersion (dipping) or soaking
Immersion (dipping) is the immersion of wood into a preservative. Typical immersion times are 10 minutes to several hours. The biocide enters the wood by diffusion. After the immersion, remaining impregnation fluid is removed (drips off). It is performed in immersion tanks. The soaking method is equal to the immersion method, but the immersion time is much longer (>12 hours). It is suited for wood species that are difficult to impregnate (Beentjes & Visée, 1994a). For immersion or soaking on a professional scale, the same emission pathways as for impregnation can be expected.

Application of wood preservatives ("production" of preserved wood) with spray or brush
In the brushing method, the biocide product is applied with a brush (protective or curative). It is suited for local preservation. In the spraying method, the biocide product is applied by spraying in a spray cabin. It is applied on a more professional scale than brushing. Emissions from spraying will be directed to a STP (spilled biocide) and the (indoors)air. Emissions from brushing will be more divers and diffusive, because of the smaller scale of use.

Application of wood preservatives ("production" of preserved wood: Fixation
After impregnation, the preservative has to be bound firmly to the wood. Metal salts are bound to the wood structure by a chemical reaction. The speed of the reaction is increased by increasing temperature and increasing humidity. 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 17. 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 17 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.).

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 Woodtechnology 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 18 (metals) and Table 19 (PAH).

Table 18 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-typeC)	0.41	2.0	0.025

Table 19 *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 on the storage area of a "standard" impregnation plant (Table 20). The advanced impregnation assumes improved processing techniques and impregnation fluids (modified creosote) and treatment of the impregnated wood (fixation).

Table 20 *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 yr^{-1})	20000	3000
Storage area (m^2)	4000	350
Discharge rainwater ($m^3.yr^{-1}$)	1200-2000	105-175
Calculated leaching loss (kg.yr^{-1})		
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 21. 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.

Table 21 *Emission factors during impregnation with the vacuum-pressure method (conservation, fixation, storage) (Quarles van Ufford, 1994).*

Substance	**Average 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			
Naphtalene	8	3	?		300
Fenanthrene	8	0.8	?	3-1000	150
Fluoranthene	4	0.125	50	3-1000	150
Benzo(a)pyrene	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.	

Application of preserved or cured wood
In the use phase, it is relevant to distinguish between different application types. The following have been distinguished:

- No chemical preservation required (GK 0)
- Under a roof, insecticides required (GK 1)
- Under a roof, indoors or outdoors, insecticides and fungicides required (GK 2)
- In the open, no direct contact with soil or water: insecticides and fungicides required (GK 3)
- In the open, in permanent contact with soil or water: additional fungicides required (GK 4)
- In the open, in permanent contact sea water (GK 5)

The results of leaching experiments simulating the use of impregnated wood under water is presented in Table 22 (Berbee, 1989). The cumulative leaching varies with flow conditions, post-treatment (steam fixation), wood species and biocide substance.

Table 22 *Results of leaching experiments with CCA impregnated wood (expressed as % of the initial amount of substance present).*

Experiment	**Cumulative leaching starting day 1, percentage**					
	day 1-50	**day 1-365**	**day 1-50**	**day 1-365**	**day 1-50**	**day 1-365**
Spruce/running	4.1	4.6	1.9	2.3	7.2	18.5
Spruce/running/ follow-up treatment	5.8	7.5	1.0	1.3	4.5	10.5
Spruce/stagnant	9.6	11.4	2.3	2.7	5.3	14.8
Scotch pine/running	1.7	2.6	0.6	0.7	6.2	12.8
Scotch pine/ running/follow-up treatment	2.1	5.7	0.3	0.4	4.7	12.7
Scotch pine/stagnant	2.0	2.9	0.3	0.3	2.7	9.5

Berbee (1989) presents percentages of biocide (PAH) that are released (cumulative) after 26 years of use. The results are presented in Table 23.

Table 23 *PAH leached out of creosoted wood after 26 years of use (%).*

Wood type	**fluoranthene**	**phenanthrene**	**pyrene**	**anthracene**
Spruce	6	4	6	34
Scotch pine	6	7	7	25

Esser & Suitela (1993) report results of remaining PAH in poles used 45 years as bank revetment. On average, 43 % of the original creosote retention was still present. The loss of 57% includes emissions to the surface water and sediment, but also emissions during the conservation process. It is estimated that max. 23% of the creosote retention was emitted to surface water and sediment.

Application of wood curatives by pills or injection

Local treatment can be achieved by inserting pills with biocide into the wood. Principles are:

- Pills with a biocide product (bifluorides, boric acid) are fit with a coating of hydrophilic compound. The biocide will be set free when the wood becomes moist.
- Glass pills containing a biocide product are broken when they are on the right place in the wood, causing the biocide to be set free.

Injection is the insertion with force of a biocide, usually, for curative purposes. When applied properly, no emissions are to be expected.

9.3 Data requirements for product type 8

In the previous section, several types of wood preservatives have been introduced, together with many different application processes. The direct exposure compartments were also mentioned. However, to define data requirements, it is necessary to aggregate the different wood preservatives and curatives into a limited number of groups. This is summarised in Table 24.

Table 24 Direct exposure compartments for product type 8.

Subtype	Products	Direct exposure compartments
8.1	Preservation, GK 1 and 2	fresh surface water, sewage water treatment plant, soil, air (indoors and outdoors)
8.2	Preservation, GK 3 and 4	fresh surface water, sewage water treatment plant, soil, air (indoors and outdoors)
8.3	Preservation, GK5	marine surface water, sewage water treatment plant, soil, air (indoors and outdoors)
8.4	Curative, pills and injection	sewagewater treatment plant, air (indoors)
8.5	Curative, brushing and spraying	sewagewater treatment plant, air (indoors)
8.6	Curative, fumigation	sewagewater treatment plant, air (indoors, outdoors)

Guidance for demanding test data

Potential data requirements for products released to individual environmental compartments are discussed in Part 1. However, from the formulation and application some remarks for applying these generic data requirements can be stated.

As the biocides are inserted in the wood, environmental exposure can only take place when the biocides are released from the matrix. This release can be volatilisation, or leaching to water (fresh, marine) or soil. A leaching rate is therefore an important parameter for products in direct or indirect contact with soil or water (subtype 8.2, 8.3). Several leaching tests are available for wood, and are listed in the text box (see below).

NEN-EN 84 Wood preservatives - Accelerated ageing of treated wood prior to biological testing. Leaching procedure.
This test method is developed to accelerate ageing of small preservative treated wood samples, prior to durability testing (e.g. NEN-EN 113). The duration of the test is 14 days in which the leachates will be collected and changed 9 times. In the past this test method was occasionally used as a leaching test. However, because the samples were impregnated with water (vacuum method), the results do not reflect a practice situation.

European standard, produced by CEN-TC-38, under a provisional mandate for the Construction Products Directive (CPD). This leaching method was designed to test the permeability of active ingredients of wood preservatives in treated wood and the effect. The effect of leaching is measured by performing a biological test (against specific fungi, marine borers, or a mix of soil-fungi) on the leached wood blocks. Wood preservatives will have to comply with these tests, as indicated in EN 599 (listing performance requirements for wood preservatives). Most preservatives are currently nationally registered using this leaching method.

ENV 1250-2 Wood preservatives - Methods for measuring losses of active ingredients from treated timber - Part 2: Laboratory method for obtaining samples for analysis to measure losses by leaching into water or synthetic sea water.
This test method is recently derived from the EN84 to measure losses by leaching in water or synthetic sea water of active ingredients and other preservative ingredients from preservative treated wood samples (Scots pine sapwood, 50 x 25 x 15 mm). The wood samples will be leached during 6 periods, with an increasing leaching period (1 to 48 hrs). During the leaching period the water will be stirred with a magnetic stirrer.

Is accepted as an experimental standard. Is not included in the performance requirement system of EN 599. CEN-TC 38 has no mandate to develop standards related to environmental aspects. This method is not used yet for registration.

NEN 7345 Leaching characteristics of building and solid waste materials - Leaching tests - Determination of the leaching behaviour of inorganic components from building materials, monolithic waste and stabilised waste materials.
Tank test method, originally developed the determine the leaching characteristics of granular materials, but also applied to determine the leaching characteristics of preservative treated wood (CCA and creosote treated wood). The duration of the test is 64 days in which the leachates will be collected and changed 8 times.

This is a Dutch standard, officially applicable to non-organic building materials, and related to the Dutch Building Substances Decree. It has no official status for wood, but is currently used in the Netherlands and Belgium for measuring medium-term leaching, since a protocol of this type is lacking for preservative treated wood.

Shower test - A leaching test for assessing preservative losses from treated timber under simulated open storage conditions (IRG/WP 93-50001, pp. 77-90)
This test method aims to determine the leaching characteristics of preservative treated timber under simulated open storage conditions. The test enables the leaching of preservatives components from treated wood during storage to be quantified for extreme climatic conditions. The wood samples (total volume 0.5 m3) will be tested for five days. Every day the wood samples will be showered for one hour using 20 litre demineralised water.

This is a Dutch protocol for leaching of industrially treated wood. The protocol is accepted by the Dutch Ministry VROM. It is now used for control of Dutch Preservative treatment plants, that have to comply with leaching limits expressed in a Ministerial guideline. It is also used for Certification of preservative treated wood in the Netherlands (KOMO-keur). The shower test is now often linked to a very simple quick boring-test for companies, shaking wood-borings in water for a few minutes. It is currently studied, whether acceptable correlation's exist between the shower-test and this shake-test. The certification-guideline (BRL) is being revised at this moment.

A promising new development could be the combination of leaching and toxicity tests, in order to obtain an indication of toxicity under realistic exposure conditions. An example is a combination of EN84 with DIN 38412 part 30/31/33. In this combined test, which is being developed by the German UBA at this moment, the toxicity of (diluted) first leachate is tested on algae, fish and Daphnids (Lucks, pers. comm.; Wegen & Lucks, in press).

Due to the heterogeneous application techniques, exposure pathways, and type of products, no general statements can be made regarding the persistence of the biocides, or the exposure pattern (continuous or batch-wise). This means, that no potentially relevant test data can be excluded.

A number of exposure scenarios are available for this product type. In general, the base set test data together with a leaching rate is sufficient to run these scenarios. The leaching rate is included in the additional data that is proposed in this report.

10. Product type 9: Fibre, leather, rubber and polymerised materials preservatives

10.1 Introduction

This product type concerns products for the preservation of polymers: compounds with a high molecular weight with a structure composed of multiple interacted simpler chemical entities. Polymers can be highly elastic, such as elastomers or rubbers, highly crystalline, such as fibres, or none of these two, such as plastics.

Examples of products in this product type are products to preserve:
- Fabrics (wool, cotton)
- Paper and cardboard
- Hides and leather
- Rubber and gummy
- Plastics

Biocides are used to prevent deterioration by insects, fungi, algae, and micro-organisms. Therefore, there is a potential overlap with the product types insecticides (product type 18), repellents (product type 19) and slimicides (product type 12).

Textile and fabrics
Fabrics are made of three types of fibres. Synthetic fibres are hardly ever subject to deterioration by micro-organisms or insects. Keratin fibres (e.g., wool), are susceptible for attack by micro-organisms (bacteria, fungi) and insects. Cellulose fibres (e.g., cotton) are susceptible to attack by micro-organisms, but not by insects (Luiken, TNO, pers. comm.).

Keratin fibres include wool (used for clothing, furnished fabrics, decoration materials, technical textiles, carpets), hair (carpets), fur (clothing), down and feathers (filler materials). Keratin fibres are vulnerable for attack by insects, such as cloth moths, seed moths, carpet beetles and fur beetles. In the past, dieldrin was used in large quantities against insects. At the moment, products such as Eulan (on sulfonamide basis) and Mitin are used, and organophosphorus compounds. A relatively new development is the use of pyrethroids. Microbiocides used for the protection of keratin fibres are pentachlorophenyl laurate, dichlorophen, ortho-phenyl phenol, pentachlorophenol, and TBTO (Peter & Rouette, s.a.;Graf & Lanz, 1984; Mayfield, s.a.).

Cellulose fibres include, next to cotton, viscose, jute and linen. Microbial deterioration occurs especially in a humid, warm environment. Fabrics exposed to outdoors conditions are the most prone to attack by micro-organisms, such as tents, sails, carpets, fishing nets and fire hoses. Microbiocides used include metallic compounds of copper, zinc, tin and mercury; phenolic and halogenated phenolic compounds, other halogenated compounds and N- and S-containing species (Peter & Rouette, s.a.; Graf & Segmüller, 1977).

Biocides are often applied in the finishing process of the fabrics, were the biocides are added together with antistatics, flame retardants, watter repellents, dyes, etceteras. They are applied in watery solutions of 0.25 - 1% in baths, through which the fabric is transported. Excess fluid is removed.

Next to this, biocides can be applied (e.g., sprayed) to finished fabric to combat microbial deterioration, for example on tents or other camping gear. Substances such as coppernaphtenate, copperchinolate, cadmium selenide, pentachlorophenol fatty acid esters, salicylanilide, PCP, trialkyltin compounds, and organomercury compounds (Peter & Rouette, s.a.).

In The Netherlands, ca. 100.000 m^3 wastewater is produced each year during the finishing of fabrics. Concentrations of preservatives in (untreated) wastewater flows range from < 2mg/l to up to 50 g/l (CUWVO, 1993). The total amount of biocides purchased for preservation of fabrics (finishing) amounted ca. 20 tons/year (organochlorines) (Heuvelman & Matthijsen, 1993).

Synthetic plastics

Plastics consist of one or more polymers and a large number of additives. The polymers do not support microbial growth. The explanation is that the chain ends are unavailable for initial oxidation, or that the conditions for microbial enzymes are not favourable due to the hydrophobicity of the polymers.

The most important additives used in plastics include (Klausmeier & Andrews, 1981):

- plasticizers (increase flexibility)
- antioxidant
- antistatic agents
- colorants
- fillers (to add strength)
- flame retardants
- heat stabilisers (assist in processing)
- biocides
- UV-radiation stabilisers

The greatest bulk of the additives is formed by the plasticizer, which can take up to 40% of the total weight of the plastic (flexible vinyl films). Phthalate-esters are the most used plasticizers.

The biodeterioration of plastics can take place in different forms:

- deterioration of the plasticizer or other additives, which causes the plastic to loose its functioning
- surface growth on organic debris (contamination) on the surface of the plastic. This leads to aesthetic deterioration, and can cause the plastic to loose specific properties, such as isolation.
- many fungi capable of growing on plastics secrete coloured metabolites, which can dissolve in the plasticizer, and thus can cause aesthetic problems

Biodeterioration of plastics can be prevented by choosing the proper polymer and additives (e.g., choice that affords almost no nutrients) or by incorporation of biocides.

To prevent biodeterioration, biocides have to be present in sufficient amounts on the surface of the plastic. Therefore, the biocide has to be able to diffuse to the surface, but must not leach out (e.g., during rainfall) or 'bloom' (concentrate on the surface in excessive quantities). Sometimes (e.g., in vinyl systems), the biocide is incorporated in the plasticizer.

Some representative commercial biocides used in plastic formulations include (Klausmeier & Andrews, 1981):

Chemical group	Active substances
mercury-containing compounds	phenyl mercury salicylate phenyl mercury phthalate phenyl mercury saccharin
other metal-containing compounds	copper-8-quinolinolate tributyl tin oxide arsine-epoxy-soy complex diphenyl antimony ethylhexoate
sulphur-containing compounds	zinc dimethyldithiocarbamate tetramethylthiuram disulphide dithiopyridine dioxide
quaternary ammonium compounds	dodecyl dimethylbenzyl ammonium naphthenate
halogenated compounds	dibromosalicylanilide

Rubber

Rubber is produced from Latex, which is harvested from the tree *Hevea brasiliensis*. The latex is processed locally to natural rubber sheets, which are transported to plants, were the rubber is improved and processed to the end product. The rubber processing industry is described in Huizinga *et al.*, 1992.

The polymer of natural rubber consists of repeating isoprene units. Although this polymer is subject to microbial biodegradation, it is often the additives that provide the nutrients for micro-organisms to thrive on rubber (Allsop & Seal, 1986), as is the case with plastics.

Leather, hides and skins

In the leather industry, preservatives are used at many different stages. The leather-making process consists of several steps (i.o., curing, soaking, unhairing, bating, pickling, tanning, oiling, finishing; see Figure 16). Biocides are used during the first step (curing) and the last step (finishing). Next to this, slimicides (bactericides and fungicides, product type 12) are used in any of these steps.

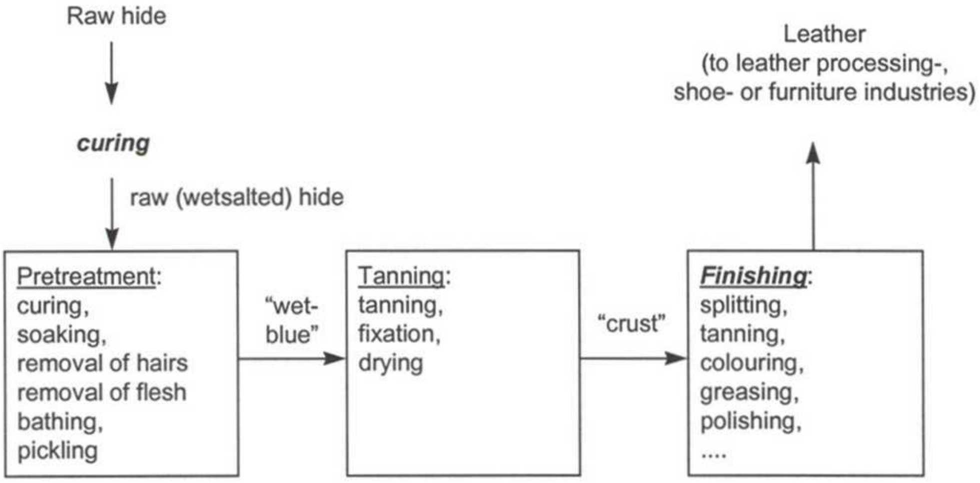

Figure 16 The leather tanning process.

In the first step, biocides of product type 9 are used incidentally. Curing is the preservation of the fresh skin to protect it during storage and transport. Usually, the skin is preserved by salting. The skin is impregnated with sodium chloride with dry salt or a brine. Although salt is an excellent preservative, halophilic or halotolerant bacteria may grow on the cured hides, causing 'red or purple heat' (chromogenic pink, red or violet coloured bacteria). Chemicals are added to the salt to prevent red heat, such as sodium metabisulphite, boric acid and naphthalene (at 1-2% of the salt weight). Furthermore, biocides are tested as alternative for salt. The skin can be immersed in a biocide, or the biocide can be sprayed on the flesh surface of the hide. Preservation with biocides is more costly than preservation with salt, unless hides are stored in air-tight containers (which makes the biocides in-can preservatives) (Haines, 1981).

Having been tanned, the finished leather is relatively safe from destruction by micro-organisms. However, as oils and greases are added to the leather in the finishing steps, it is susceptible to moulds. Mildew is undesired from an aesthetic point of view, and can cause stiffness and cracking of the leather due to removal of oils and greases from the leather. Biocides are introduced in the leather by dissolving them in the greases used in the finishing operations. Biocides used for this application are (Block, 1967):

- p-nitrophenol (at 0.3% of the weight of the leather), especially for military purposes;
- 2-chloro-4-nitrophenol;
- tetrachlorohydroquinone
- bis(4-nitrophenyl)carbonate
- bis(2-chloro-4-nitrophenyl)carbonate
- 5,6-dichloro-2-benzoxazolinone

Furthermore, insecticides are used to protect finished leather against beetles.

Paper and cardboard
For some types of paper, a specific insecticidal, fungicidal or bactericidal working is required. This is the case for paper used for wrappings, cupboard paper, hygienic and toilet papers, and papers for wrapping food such as bread and cheese.

Two categories of biocides can be distinguished in the paper industry. Slimicides used for the preservation of pulp and other aqueous fluids in the paper manufacturing can remain in the end-product (paper). This is only a fraction of the slimicides used in the processing (see: product type 12), and the (maximum) amount of slimicides in paper is regulated by law, for example for paper used in applications with foodcontact.

The second category of biocides in the paper industry is preservatives, added to ensure bactericidal working of the paper. Biocides used for this purpose include (Baumann & Herberg-Liedtke, 1993):
- ascorbic acid
- sodium, potassium, calcium and magnesium ascorbates
- benzoic acid
- sodiumbenzoate
- formic acid
- hydrobenzoic acid ethylester, adduct of 70% benzylalcohol and 30% formaldehyde

In museums, libraries and other storage places for books and papers, biocides are used to combat insects and fungi (e.g. Uspenskaya & Kobiakova, 1997; Hanus *et al.*, 1997).

10.2 Release estimation

In Figure 17, a generalised life cycle for biocides used in polymerised materials is presented. The biocides can be added to the material to preserved in two ways: By adding it together with other auxiliaries to the polymer, so that it is included in the material (e.g., plastics), or by adding it in the finishing stage (e.g., some types of paper). During the processing, emission to a STP can occur. Emissions during the use of the finished product can occur due to leaching (or washing, in case of textiles). No quantitative information is available regarding the amount of leaching.

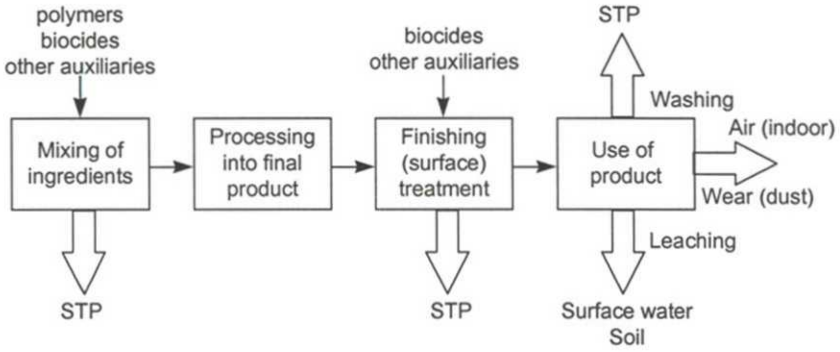

Figure 17 Environmental release of biocides in polymerised materials

10.3 Data requirements for product type 9

The direct exposure compartments, which were introduced in the previous section, are summarised in Table 25.

Table 25 Direct exposure compartments for product type 9.

Subtype	Products	Direct exposure compartments
9	All products	Sewagewater Treatment Plant Air (indoors) Soil Fresh surface water

Guidance for demanding test data

Potential data requirements for products released to individual environmental compartments are discussed in Part 1. Due to the heterogeneity in applications within this product type, it is difficult to give general guidance on the relevance of specific data items.

Information on leaching of substances during contact with (rain) water or during washing and cleaning (textiles) is important for this product type, to assess environmental release.

Specific standard leaching tests to determine a leaching rate suitable for risk assessment are not available. Information from efficiency tests can be used to gain information about leaching (reduction of biocidal activity). Test methods for biocidal efficacy testing are usually based on one of the following test methods:

- mixed inoculum agar plate tests. Strength loss in compounds to reference or visual assessment of micro-organisms is used as endpoint
- controlled atmosphere test, for materials (e.g. textiles) that are exposed to fungi mainly through the air.
- soil burial test, which is the most severe efficacy test.

Some standard efficacy test for textile preservatives based on these principles are reviewed by McCanthy (1987) and Wales *et al.* (1987).

The available exposure scenarios (for biocides in leather processing and textile finishing, see appendix B) require a "degree of fixation" in addition to base set data. In the emission scenarios, a default is used for this parameter. However, it could be considered to request this item as a test result, as it is an important parameter for the risk assessment.

11. Product type 10: Masonry preservatives

11.1 Introduction

This product type (10) includes all products used to protect or cure building materials. Wood, however, is excluded as it is covered by product type 8. Examples of products covered by this product type are product for the preservation of:
- Mortar (between brickwork)
- Concrete (against anaerobic bacteria)
- Concrete additives
- Other building materials

Preservatives for building materials are used only in exceptional cases, and in small quantities. Indoors buildings, mould growth is the main problem, while outdoors, algae and mosses are the major causes of biodeterioration.

Stone

Biodeterioration of stone starts with surface detritus on the stone surface (dust and dirt). On this surface detritus, lichens, algae, fungi, bacteria and plants can settle (Allsopp & Seal, 1986):
- Lichens (associations of a fungus and an algae) are important deteriogenic organisms. The expansion of hyphae embedded in the stone, the successive expansion on wetting and drying, and the trapping of water in the stone (and subsequent frost) can cause physical damage to the stone. Furthermore, organic acids can be excreted, dissolving minerals from the stone. The "dirty" appearance of some buildings can be caused by very small dark lichens.
- Algae can grow were light and water are available in sufficient quantities. They can cause mechanical damage (in much the same way as lichens) and excrete organic acids. However, probably the most important damage by algae is "aesthetic biodeterioration" (soiling).
- Fungi can produce a variety of acids, and therefore can play an important role in the deterioration of stone
- Bacteria can also produce acids, which cause deterioration of the stone
- Plants do not only cause "aesthetic biodeterioration", but can also cause physical damage to stone (roots).

The removal of algae and other growths from stonework is initially performed mechanically, for example with a high velocity water jet. When the growths are removed, an aqueous algicide can be sprayed to kill of organisms. However, this is only effective for a short period of time.

Indoors buildings, hydrofobing is used to combat moist, and therefore fungi. The hydrofobing fluid which is used to impregnate walls (few cm) can combat biocides, to give further protection against moulds.

Sometimes invertebrates can play a role in the deterioration of masonry. Masonry bees, such as Davies's Colletes (*Colletes daviesanus*) can colonise soft mortar between brickworks, and thus cause problems in the UK. Insecticides are used against these organisms.

Tiano (1987) gives an indicative overview of biocides used on monuments:

Table 26 Biocidal products used on monuments (according to Tiano, 1987)

Name of product	Active substance	Application mode
Hydrogen peroxide	Hydrogen peroxide	Spray
Formol	HCHO	Spray
ETO	H_2COCH_2	Spray
Santobrite	pentachlorophenolate	Spray, brush
Hyamine 1622	Di-isobutyl phenoxy-ethoxyethyl dimethyl benzyl ammonium chloride	Spray, brush
Lito 3	Fluorometuron	Spray, pack
Velpar L	Hexazinone	Spray, injection

Table 27 Efficacy of biocidal products used on monuments to several fouling organisms (according to Tiano, 1987)

Biocide	Algae	Lichens	Mosses	Weeds
Hydrogen peroxide	+++	++	+	+/-
Formol	+++	+++	++	+
ETO	++++	++++	++++	++++
Santobrite	++	++	-	-
Hyamine 1622	+++	++	+	+/-
Lito 3	+++	+	++	++
Velpar L	++	+	+++	+++

Concrete

Concrete is a mixture of course-grained aggregate, hydraulic binding agents (e.g., cement, gypsum, lime, asphalt) and water. Concrete can be colonised as soon as the initial high pH (>10) falls after a period of weathering. Deterioration is caused by bacteria (sulphate-reducing bacteria, nitrifying bacteria, heterotrophic bacteria).

Concrete additives

Concrete additives are substances that control the viscosity and hardening of concrete. Most concrete additives are based on lignosulphonates (by-product of wood pulping). As they are highly susceptible to microbial degradation, preservatives are required to ensure the functioning of these additives. Examples of biocides used for the preservation of concrete additives are aldehydes, formaldehyde-releasing compounds, phenolics, sodium N-dimethyldithiocarbamate, sodium pyrithione, heterocyclic N,S compounds and 1,2-dibromo-2,4-dicyanobutane (Paulus, 1993).

Geotextiles
Geotextile fabrics are used as an alternative to natural construction materials. Applications include wetland mats, shorelines, revetment walls and containment linings. Depending on the application, a high persistence or a high biodegradability can be required. Geotextiles are often used in direct contact with soil (and/or surface water).

11.2 Release estimation

For a life cycle description, a distinction can be made between products used in building materials, to prevent biodeterioration, and products used on building materials, for curative purposes (e.g., on monuments).

Products used in building materials (Figure 18), are added during the formulation phase. The main environmental emissions are due to leaching of the product from the construction material, when the construction material is in contact with (rain-) water or soil. Leached out biocides may be expected to end up in soil, or in surface water.

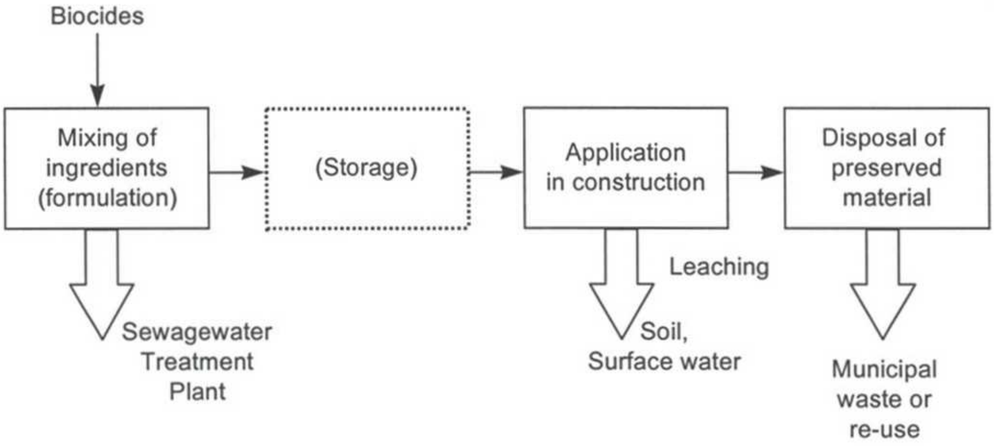

Figure 18 Environmental release of biocides used as preservatives in building materials

For products used on building materials, such as products use to protect monuments, emission can occur during the application of the product (with a spray or brush technique), or after the application (leaching of biocides from the stone).

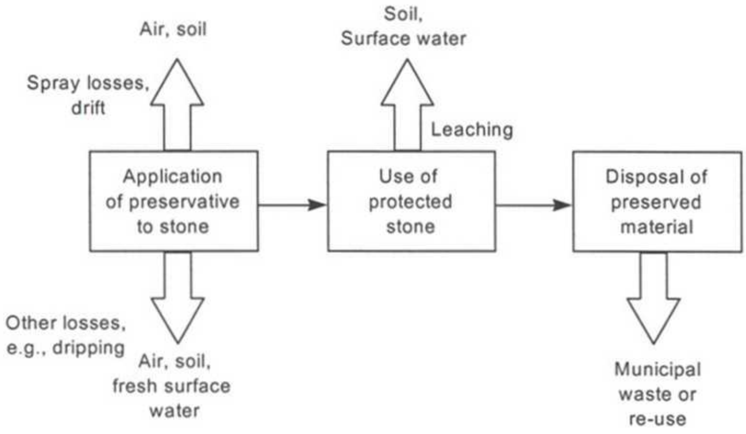

Figure 19 Environmental release of biocides used as curatives on building materials

11.3 Data requirements for product type 10

The direct exposure compartments, which were introduced in the previous section, are summarised in Table 28.

Table 28 Direct exposure compartments for product type 10.

Subtype	Products	Direct exposure compartments
10.1	Building materials preservatives (preventive)	Soil Fresh surface water
10.2	Building materials preservatives (curative)	Soil Fresh surface water Air (outdoors)

Guidance for demanding test data

Potential data requirements for products released to the environmental compartments fresh surface water, soil and air are discussed in Part 1. However, from the formulation and application some remarks for applying these generic data requirements can be stated.

For the use of biocides in building materials (subtype 10.1), it is expected that especially persistent substances are used. Therefore, chronic toxicity data and biodegradability data is important.

Leaching test data is required to estimate the environmental emissions. Standardised leaching tests, developed to establish a leaching rate (suitable for risk assessment), are available, such as the Dutch NEN7340 test guideline (compare to section 9.3), which yields a cumulative leaching rate. Furthermore, efficacy tests, developed especially for biocides, are available (e.g. Grant & Bravery, 1987), with different substrates (natural or artificial), weathering (natural or artificial) and test organisms (algae, moulds). These tests, however, yield a (reduction of) biocidal action, and not a leaching rate (although they yield some information about the disappearance of the active ingredient).

In the treatment of statues and monuments (curative), less persistent substances are used, decreasing the importance of chronic data. The need for a leaching test for curatives can be disputed. The biocides are not inserted in the matrix, but the biocide may be absorbed in the top layer of the material, and leach out later. The necessity of a leaching test result will depend on the method of application, and on the persistence of the biocide, and should be decided on a case-to-case basis.

No emission or exposure models are available for this product type (Appendix B).

12. Product type 11: Preservatives for liquid-cooling and processing systems

12.1 Introduction

This product type concerns biocides used in cooling and process water for industrial purposes. It includes closed cooling systems, open cooling systems and flow-through cooling systems. Biocides used for drinking water treatment are not included in this product type (but are part of product type 5).

Biocides for cooling water are used to prevent the growth of (micro-)organisms in cooling water systems. Bacteria, fungi, algae and invertebrates such as mussels can affect the functioning of the cooling water system. (Micro-)biological problems in cooling systems can be divided into four categories (Lutey, 1995):

Development of biological slime (biofilm).
Slime consists almost entirely of microbial biomass. The main component is formed by heavily encapsulated fast-growing micro-organisms, such as *Aerobacter*, *Arthrobacter*, *Proteus*, *Bacillus*, *Pseudomonas*. Biological slime can develop in very short time scales (hours). Especially on heat transfer systems, often in high flow velocity environments

Plugging and fouling.
Fouling is the development of a mixed microflora of filamentous bacteria, fungi, and algae. In contrast to slime, the primary component is non-microbiological organic mass (organic substances, dirt, silt, scale fragments, corrosion by-products, other debris). Filamentous micro-organisms act as 'binding agent' for the deposits. The development of a fouling community takes several days to weeks. Fouling and plugging is the most commonly encountered problem in cooling towers, heat transfer systems, screens/filters, etceteras. In marine environments, extensive macrofouling with (a.o.) barnacles and mussels can occur (e.g. Whitehouse *et al.*, s.a.).

Deterioration of wood.
Many wooden components can be present in cooling systems, especially cooling towers. Two kinds of deterioration are distinguished: 'Internal' or 'dry rot' and 'soft' or 'surface rot'. The combatment of the micro-organisms responsible for this deterioration falls under this product type insofar it concerns biocides used in the cooling water. Wood preservatives (used in or on the wood) fall under product type 8.

MIC: Microbiologically Induced Corrosion.
Micro-organisms can induced or accelerated corrosion in cooling water systems, which poses an important problem. Micro-organisms can bind suspended solids

and cause scaling. A differential oxygen diffusion gradient in this layer causes corrosion. Specific micro-organisms, important in the context of MIC, are sulphate-reducing bacteria (*Desulphovibrio*, *Desulphotomaculum*), iron-oxidising bacteria (*Gallionella*, *Sphaerorotilus*, *Arthrobacter*) and slime-forming micro-organisms. MIC in cooling systems is a relatively new problem, due to changes in process water management.

Biocides are applied either to control, or to kill micro-organisms:

- Control of micro-organisms: biocides are maintained at a sufficient concentration to inhibit microbial growth, i.e. keep the population in the lag-phase at a sufficiently low population density (biostats);
- Cleaning of a fouled (dirty) system: First, old algal and fungal residues, and slime and other deposits should are removed by mechanical or chemical cleaning. As a second step, it is treated with a sufficiently high dosage of biocide (rule of thumb: 3 to 5 times the maintenance dose) (shock treatment).

In the past, chromate was used as main preservative in cooling water systems. It is an efficient corrosion-inhibitor, and can be used at low pH, thus preventing scaling. Due to its toxicity, microbial growth and sliming is inhibited. However, due to increased environmental concern, the use of chromates is limited, and alternatives are used (Savelkoul, 1993).

Microbiocides used in cooling water systems include (McCoy, 1980):

- Oxidising agents. For industrial applications especially chlorine (bromine and iodine to expensive for large-scale applications). These biocides have a non-specific mode of action: components of the cell or cell wall are oxidised. Due to the rapid toxic action, they are the main biocides for once-through systems.
- Non-oxidising agents: Enzyme poisons can react with the terminal thiol group of cysteine, an amino acid essential to the biological activity of many enzymes, or chemicals that can block the electron transfer through iron atoms in cytochromes. Examples are methylene bisthiocyanate, chloroethylene bisthiocyanate, acrolein, heavy metals. Toxicants that disrupt the cell wall and cytoplasm orient at the surface of the cytoplasmic membrane and produce cytolytic damage. Examples are dodecylguanidine hydrochloride, chlorophenols, quaternary ammonium salts.

In Europe, ca. 20 active ingredients are used as preservatives for process and cooling water. Quantities of biocides used are ca. 520 tons/a for Germany, and ca. 1800 tons/a for Europe (UBA, 1996a). Table 29 gives an overview of the cooling process water biocides registered in the Netherlands in July 1995 (Source: CTB, cited from Baltus & Berbee, 1996). Sodium hypochlorite is the most used biocide. Isothiazolines are the major non-oxidising biocides (based on the Dutch situation).

Table 29 *Biocides registered for cooling water systems in the Netherlands, July 1995, and concentration range of active substance in the cooling water (Baltus & Berbee, 1996).*

Type	Active substance	Concentration in cooling water (mg/l)
Oxidising	sodium hypochlorite	0.1-0.2 (active chlorine)
	chlorine dioxide	?
	1-bromo-3-chloro-5,5-dimethylhydantoine	2-7
	sodium bromide	?
	ozone	0.015-0.2
	hydrogen peroxide	?
Isothiazolins	2-methyl-4-isothiazolin-3-on	1-5 (isothiazolins)
	5-chloro-2-methyl-4-isothiazolin-3-on	“”
Quats	alkyldimethylbenzylammoniumchloride	3-50 (quats)
	alkyldimethylethylbenzylammoniumchloride	“”
	didecyldimethylammoniumchloride	“”
	poly(oxyethylene-(dimethyliminio)-ethylene-(dimethyliminio)-ethylenedichloride)	“”
Others	β-bromo-β-nitrostyrene	1-5
	2-bromo-2-nitro-(1,3)-propanediol (bronopol)	1-25
	2,2-dibromo-3-nitriloproprionamide	4-10
	glutaraldehyde	25-50
	methylenebisthiocyanate	2-6
	2,2-dithiobisbenzamide	?
	1,2-benzoisothiazolin-3-on	?

12.2 Release estimation

A general life cycle for biocides used in cooling and processing water systems is depicted in Figure 20.

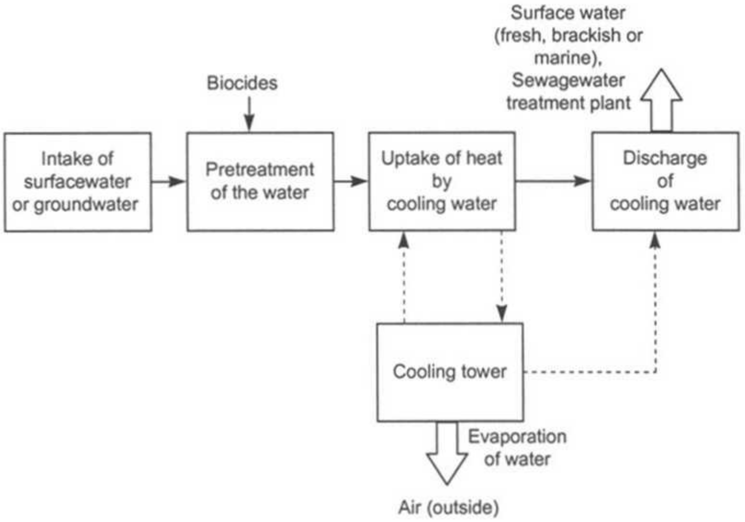

Figure 20 *Environmental release of preservatives used in cooling water*

Water (surface water, ground water, or water from river banks) is taken in, and (if necessary) pre-treated. The water is used for heat exchange in the cooling process. Depending on the type of cooling system, the water is discharged immediately to the surface water, or cooled first in a cooling tower and subsequently discharged, or recirculated after cooling in a cooling tower. Biocides are added in the pretreatment step. Emissions occur during discharge of the cooling water, or in the cooling tower (evaporation).

The processes and emissions are described in more detail in the next section.

Once-through cooling systems
There are many different cooling water systems in practise, but (generalising) some basic designs can be distinguished (Held & Schnell, 1994). The most simple design is a once-through cooling system (Figure 21). Water is extracted from a river, canal or lake and transported through a heat-exchange system. The water absorbs heat, and the heated water is discharged (downstream) to the surface water. Instead of surface water, ground water or spring water may be used.

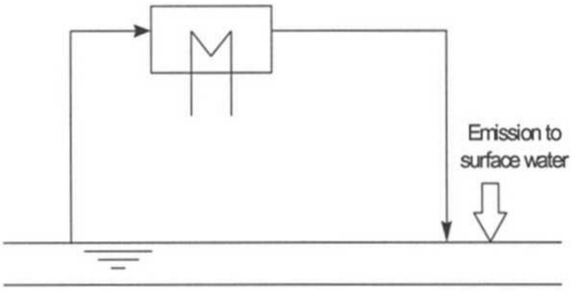

Figure 21 Once-through cooling system (after: Held & Schnell, 1994)

As the increase of the temperature of the cooling water is regulated in most countries, cooling towers are used in once-through systems to reduce the heat content of the cooling water before discharge (Figure 22). In a cooling tower, the water is sprayed over a complex structure with a large surface area, thus ensuring intensive contact between water and air. Thus, heat exchange takes place. After this exchange, the water is discharged to the surface water. In the cooling tower, evaporation of water takes place, and water droplets are emitted from the cooling tower. A distinction can be made between very small droplets (~ 10 µm), which are transported over large distances and can be observed as a haze above the cooling tower. The microdroplets hardly contain any salts (Held & Schnell, 1994), and therefore it is expected that they do not contain dissolved biocides. However, larger droplets are emitted from cooling towers, despite structures to remove water from the air. These droplets reach the earth within a distance of several hundreds of meters from the cooling tower, and (measured in salt) have about the same composition of the cooling water. In modern cooling towers, a water discharge of ca. 0.1% of the total water volume to the air is expected.

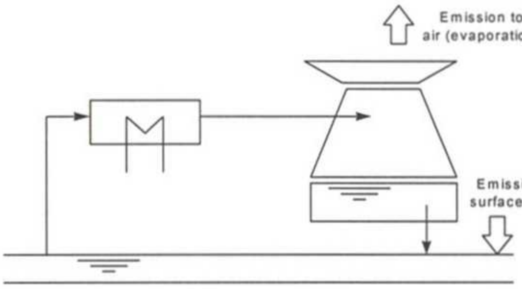

Figure 22 Once-through cooling system with cooling tower

Chlorine is the most-used biocide in open once-through cooling systems (especially sodium hypochlorite. For economic reasons, a discontinuous treatment is used in these systems, e.g., 10 ppm active chlorine, or a combination of a dispersant and 1-3 ppm active chlorine (Solvay, s.a.). Assink (1991) reports 0.2 mg/l active chlorine for 10-60 minutes, one or more times a day. Longer treatments (up to days) are required when large mussels have to be removed from brackish or marine water cooling systems.

Open recirculation cooling systems
In recirculation cooling systems, the cooling water is cooled down in a cooling tower, and used again for cooling (Figure 23). A limited amount of surface water is required to replenish water that is lost by evaporation (suppletion water). This amounts ca 1-3% of the water flow of a once-through system with the same cooling capacity (Van Donk & Jenner, 1996). When air temperatures are high, part of the cooling water may be discharged to surface water.

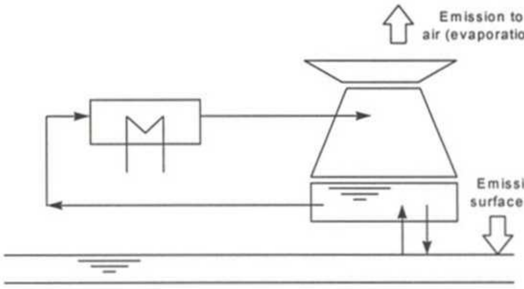

Figure 23 Recirculation cooling system

Both oxidising and non-oxidising biocides are used. Most biocide formulations are water based. Biocides are applied as liquids or sometimes pellets, manually or (in larger systems) with an automatic dosage system. Concentrations of non-oxidising active substances range from 1-50 mg/l (Table 29); concentrations of oxidising substances are 0.1-0.2 mg/l active chlorine (breakpoint chlorination, see Product type 5).

Biocides are emitted through wind and spray losses (<0.2% of the recirculating water volume, in modern cooling towers < 0.01%) and discharged water (ca. 5% of the recirculating water volume) (Assink, 1991) (see Figure 24). The cooling water can be discharged either directly to the surface water, or to a sewagewater treatment plant. In the Netherlands, ca. 37% of the cooling water containing oxidative biocides is treated, and ca. 35% of the cooling water containing non-oxidative biocides. Ca. 23% of the cooling water containing isothiazolines is treated. For the European situation, this implicates that most cooling water discharged from open recirculating systems is not treated.

Baltus & Berbee performed model calculations to estimate the amount of biocide released from an open recirculating cooling water system (released to surface water or a STP). Depending on pH and temperature, this amounted 8% for β-bromo-β-nitrostyrene, 24 % for methylenebisthiocyanate, 80-95% for isothiazolins, and 93-99.8% for bronopol.

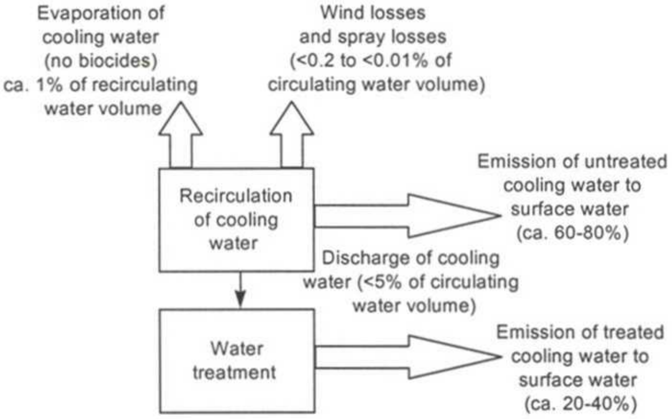

Figure 24 Mass balance of water (and dissolved biocides) in open recirculating cooling water systems (After: Assink, 1991).

Closed recirculation cooling systems
When only a limited amount of water is available, dry cooling may be applied in cooling towers instead of the 'wet' cooling described above. The water is not sprayed into the cooling tower, but brought into contact with air by a fine-maze system of tubes. The air is circulated by means of ventilators. These dry recirculation systems have a minimal water loss, and therefore very low amounts of biocides can be used. Evaporation and wind or spray losses do not occur. The amount of cooling water discharged is <2% of the recirculating water volume (Assink, 1991).

The most important biocides in closed recirculation cooling systems are the organic biocides (e.g., Table 29). As the losses are very limited, high concentrations are used (0.5 - 4 g/l) (Solvay, s.a.).

The cooling water of the recirculating cooling water systems (both open and closed) is removed ca. once a year, to clean the system. This is performed by professional companies, who treat the (concentrated) cooling water.

Combined systems
Many combinations of the systems described above are used. For example, a closed system can be used in combination with a wet cooling system in a cooling tower, to combine the advantages of both systems, or ventilators may be used in wet cooling towers.

12.3 Data requirements for product type 11

The direct exposure compartments, which are introduced in the previous section, are summarised in Table 30.

Table 30 Direct exposure compartments for product type 11.

Subtype	Products	Direct exposure compartments
11.1	Once through cooling systems	Fresh surface water Marine surface water
11.2	Open recirculating cooling system	Fresh surface water Marine surface water Sewagewater Treatment Plant Soil (due to wind and spray losses) Air (outdoors)
11.3	Closed recirculating cooling system	Sewagewater Treatment Plant Fresh surface water Marine surface water

Guidance for demanding test data
Potential data requirements for products released to individual environmental compartments are discussed in Part 1. However, from the formulation and application some remarks for applying these generic data requirements can be stated.

For the once-through cooling systems (subtype 11.1), biocides with a rapid toxic action are used, due to the short contact-time. This implies that especially the acute toxicity is important, and chronic toxicity and extensive biodegradability testing will be less relevant.

For the subtypes 11.2 and 11.3, more persistent chemicals are used, requiring chronic toxicity data and further biodegradability testing. Leaching tests are not relevant for this product type, as the biocides are not used within a matrix.

No emission or exposure models are available for this product type (Appendix B).

13. Product type 12: Slimicides

13.1 Introduction

Slimicides are biocides used to control slime-producing micro-organisms in industrial processes (Eriksson & Johnson, 1996). Examples of processes were slimicides are used in large quantities are:

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

Considering the target organisms, there is a potential overlap with cooling water biocides (slime production in cooling systems). Furthermore, an overlap with in-can preservatives can occur.

General

Slimicides are used in industrial process fluids, in cases were slime formation may cause hampering of the process-operation, or deterioration of intermediate or end products. Two main fields of application of slimicides are in the pulp- and paper industry, and for secondary oil recovery. These two applications are considered in this technical note.

Pulp and paper industry

The materials used in the pulping process and paper manufacture offer a favourable environment for the growth of micro-organisms. The presence of micro-organisms is unavoidable: The pulp is a rich source of both organic and inorganic nutrients, and there are many sources of contamination. Troublesome micro-organisms in the paper manufacturing process are species of bacteria, fungi and yeasts; algae and protozoa are rarely a problem.

Micro-organisms can be harmful by producing slime, which can interfere with the processing. Some organisms may cause corrosion by the anaerobic reduction of sulphur compounds to sulphite, or by the (aerobic) oxidation of sulphur compounds to sulphuric acid. Pink slimes are formed by the bacteria *Alcaligenes*, *Bacillus* and *Flavobacterium*, as well as species of the yeast *Monilia*. Bacteria that can form ferric hydroxide (*Cenothrix*, *Gallionella*, *Lephothrix*) form red or brown slimes. Fungi can cause blue stain (Eagon, 1995).

Biocide treatment of slime forming micro-organisms in the paper industry is difficult, as each pulp has its own specific environment, and therefore a variety of biocides is required. Biocides aim to suppress microbial growth, and not sterility of the pulp. This can be achieved by a continuous supply of a biostatic, by a single or repeated shock treatment with elevated doses. Alternatives are treatment with non-biocidal agents to prevent the forming of slime, and good housekeeping.

Slimicides used in the paper industry include aldehydes, phenol derivatives, heterocyclic N, S compounds, thiocarbamates and thiocyanates. The amount of slimicide products used is 20 - 200 grams per ton produced paper. The fraction of active substance in the products is ca. 25% (Baumann & Herberg-Liedtke, 1993).

Oil industry

Biocides are applied by specialised service companies, who provide a complete package of chemicals for oil and gas operations (biocides, corrosion inhibitors, oxygen and H_2S scavengers, etceteras). In oil and gas production, biocides are used for many different applications, such as preservation of the drilling muds, preservation of completion/workover fluids, fracturing fluids, packer fluids, preservation of hydraulic fluids and preservation of injection water. From a quantitative point of view, biocides used in drilling muds and injection water are the most important.

Drilling

Biocides are used for the preservation of drilling muds (synonym: drilling fluids). Drilling muds (oil based or water based) are substances injected in the well during drilling operations, to cool and lubricate the drill bit, and to remove drill cuttings from the well. In the drilling muds, thickeners such as sugar, starch and modified cellulose are used, which are easily biodegraded. Biocides are used to prevent this biodegradation (Paulus, 1993).

The most important biocides for use in drilling muds used to be chlorinated phenols, but they have been abandoned for environmental reasons. At this moment, paraformaldehydes (especially in the US) and isothiazolines (at 200-500 $mg.l^{-1}$) are used. Furthermore, quaternary ammonium salts, amines, thiocarbamates, and triazines are used in lesser quantities.

Production

When it is no longer possible to drive crude oil out of a reservoir by the reservoir natural energy, sea water is pumped into the well to drive out the oil (secondary recovery). The mixture of injected 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 micro-organisms can lead to a number of problems, such as corrosion or the formation of H_2S gas. Additionally, slime and biofilm forming bacteria can produce slime, clogging filters, rock formations and sand beds. The clogging can close porous sand strata, and thus hamper the oil recovery. Biocides are used to prevent this slime forming (Paulus, 1993). The most widely used is glutaraldehyde.

The main biocides used in oilfield operations are (Herbert, 1995):

- aldehydes (acrolein, glutaraldehyde, formaldehyde)
- biguanides (esp. cationic polymeric biguanides)
- isothiazolines
- detergents, such as quaternary ammonium compounds, diamines and amine acetate salts)

13.2 Release estimation

In Figure 25, a process scheme of a paper processing plant is presented. Biocides (additives in the scheme) are added at the mixing tank, were the various pulps and additives are mixed. Much of the process water is recycled, after mechanical water treatment. Most paper plants have a biological water treatment facility, the effluent of which is discharged to the (fresh) surface water.

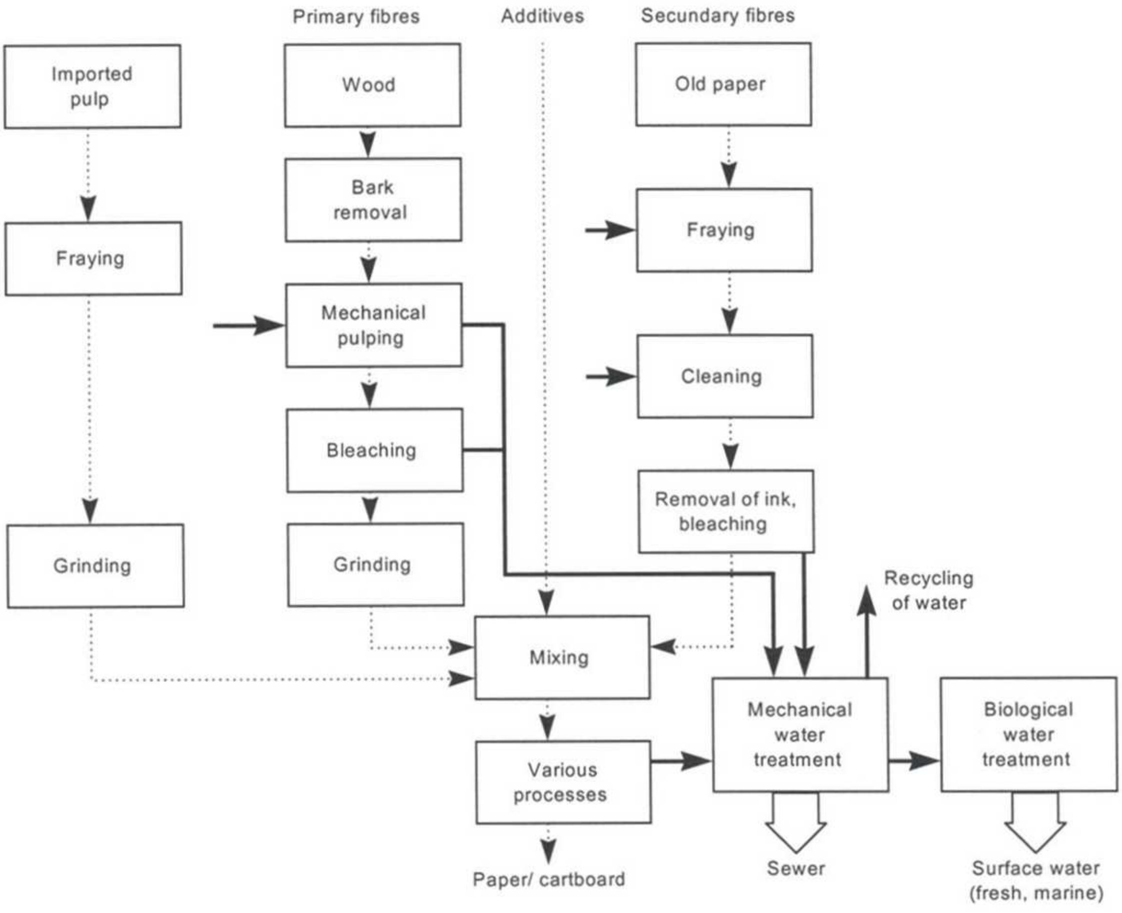

Figure 25 Process scheme of a paper processing plant (from: Huizinga et al., 1992). Dotted lines indicate mass flows, solid lines indicate water flows.

In the secondary oil recovery process, sea water is pumped into the oil reservoir (after pre-treatment, during which slimicides are added). Part of the water (including biocides) may remain in the formation, but the rest is transported to the platform as an oil/water mixture. On the platform, it is separated, and the water is either re-used or discharged as produced water.

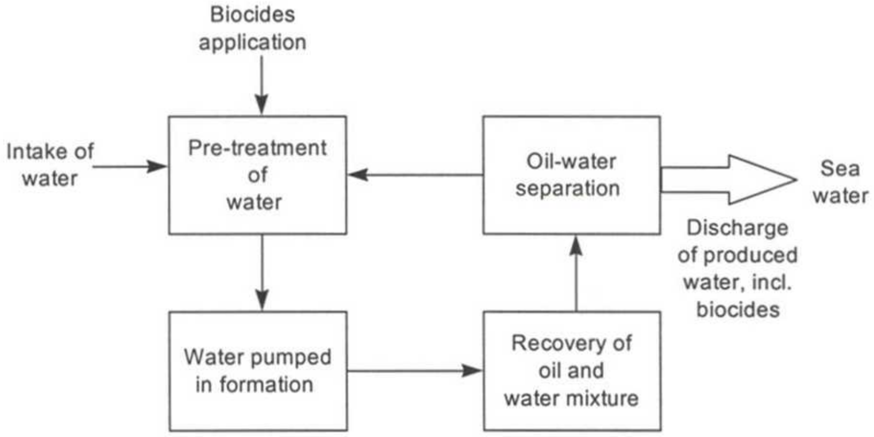

Figure 26 *Schematic overview of the use of biocides in secondary oil recovery processes*

In the paper industry, slimicides are added to the process water in the pulping process. As much water is recycled in the plant, the emission of slimicides will be limited. Slimicides will be either degraded during processing, or remain in the and end-product (paper, cardboard), but the major part will be discharged to a sewage treatment plant, either a municipal plant after pre-treatment (e.g., mechanical) at the paper mill, or to a biological water treatment facility belonging to the plant itself. The main direct exposure compartment (see: framework document) will be a STP, and the main indirect exposure compartments (fresh) surface water and sediments.

Slimicides used for secondary oil recovery can remain in the subsea rock formation, but the major part of slimicides will be emitted to the sea, with produced water from the platform. The main direct exposure compartment (see: framework document) is sea water.

13.3 Data requirements for product type 12

The direct exposure compartments, which were introduced in the previous section, are summarised in Table 31.

Table 31 Direct exposure compartments for product type 12.

Subtype	Products	Direct exposure compartments
12.1	Paper industry	Sewagewater Treatment Plant Fresh surface water Marine surface water
12.2	Secondary oil recovery	Marine surface water
12.3	Other products	Sewagewater Treatment Plant

Guidance for demanding test data
Potential data requirements for products released to the environmental compartments fresh surface water, marine surface water and a sewagewater treatment plant are discussed in Part 1.

As slimicides are used on many different locations for many different purposes, general guidance is difficult to give. The exposure pattern is diffuse, and chronic test data is therefore probably more important than acute data. Slimicides contain persistent active ingredients (at least, in the fluid that they should preserve), and biodegradation data is therefore important. Leaching tests are not relevant for this product type.

The available exposure scenarios for slimicides require no data additional to the base set.

14. Product type 13: Metalworking-fluid preservatives

14.1 Introduction

In the metal industry a great variety of processes are employed. The metal industry can be divided in 6 main work areas :

1. blast furnaces plants, were steel is being produced.
2. iron foundry, were steel is moulded into half- or end-products.
3. rolling mills, were the steel is being rolled in halfproducts to be used by the steel production industry.
4. metal forming in which metal products are being forced in the shape of the end product.
5. metal cutting, whereby products are created by cutting away chips of the product.
6. galvanic industry, whereby protective metalcoatings are applied to metal products.

In **blast furnaces plants**, **iron foundry** and **rolling mills** (1, 2, 3) the main activities are carried out at higher temperatures. Because of these high temperatures, there is no need for the use of biocides in the working process. Some biocides are employed in the cleaning of air filters used in these surroundings.

In the **metalforming industry** (4) non-water-miscible metalworking fluids (so called cutting oils) are used in small quantities. These non-water-miscible fluids consist generally of mineral oils with or without additives. The additives are used to improve the lubricating properties, protection against wear, protection against corrosion and resistance against ageing. No additives are used for microbial attack.

In the **metalcutting industry** (5) large amounts of metalworking fluids are used. These metalworking fluids are mainly used for cooling and lubricating the products made by this industry. There are many types of metalworking fluids available on the market, however, the following divisions appear appropriate in consideration of the practical importance to the users (Figure 27):

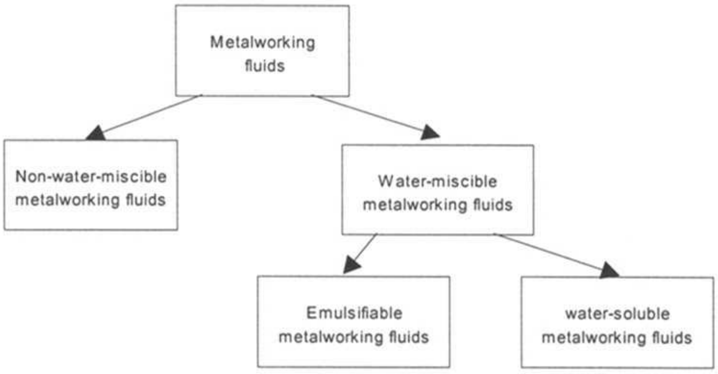

Figure 27 Metal working fluids used in cutting processes (Leiseder, 1991).

In the non-water-miscible metalworking fluids no biocides are employed. The water-miscible metalworking fluids all contain, in low concentrations, biocides.

In the modern **galvanic industry** (6) a wide variety of treatments are applied. In most of these treatments no biocides are used. There is though one technique which makes use of biocides, that of metal degreasing .
The main objectives of metalworking fluids are reduction of friction (lubrication), removal of heat and flushing away chips.

Metalworking fluids are put on the market as concentrates, which are diluted before use. The quantity of (concentrated) water miscible metalworking fluids amounts 52.000 tons per year in Germany (1992) (Baumann & Herberg-Liedtke, 1996). For the Netherlands, this quantity amounts 3.000 tons per year (Bremmer, 1988). The percentage concentrate in metal working fluids averages 4 to 5%. Assuming a biocide concentration of ~ 0.1% (see next section), the amount of biocides used water miscible metalworking fluids amounts 52 tons in Germany and 3 tons in the Netherlands.

The exact composition of the water-miscible metal working fluids is not available. Producers are, from a competitive point of view , rather secretive about their compositions. The water-miscible metal working fluids always consists of the basic oil (mineral oil or synthetic hydrocarbons) and particular additives, the most important being (Leiseder, 1991; Klingenberg, 1990):

- emulsifiers
- corrosion inhibitors
- extreme pressure (EP) additives
- anti-foaming agents
- biocides
- mineral oil
- others (including stabilisers and solubilisers, complexing agents)

The biocides are often describes as preservative but also as bactericide or microbiocides. The most important biocides are formaldehyde-donors. Phenols are also important, but the use decreases. Important biocides used in water-miscible metalworking fluids are (CUWVO, 1981 and pers. comm. producer metalworking fluids):

- 1-bromo-1-nitroethane
- p-nitrophenol
- ortho-phenyl-phenol
- 2-nitro-1-phenyl-1-propanol-acetate
- cyclohexanon
- 2-nitro-1-butanol
- 1,3-dibromo-5,5-dimethyl-hydratoin
- methyl-5-nitro-2-furfuryl-ether
- tris-hydroxymethyl-nitromethane
- 2,4,5-trichlorophenol
- 5,5-dichloro-2,2-dihydroxy-diphenylmethane
- 1,3,5-tris-hydroxyethyl-hexahydrotriazine
- triazine derivates
- oxazolidine derivates
- sodiumpyridinethiol-N-oxid

An overview of biocides used in water miscible metalworking fluids is presented by Baumann & Herberg-Liedtke (1996).

14.2 Release estimation

To decide which data is necessary for the authorisation of a biocide, information is required about environmental compartments to which emissions take place. The life-cycle for biocides in water miscible metal working fluids is presented in Figure 28. Metal working fluid concentrates are diluted, and used to cool and lubricate in a circulation system during metal working processes. The chips are removed from the fluid. The chips, including metalworking fluid adsorbed to it, are stored on the premises, which can cause local emissions to soil. The used fluid is examined and reused. Depending on the condition of the fluid, the fluid can be regenerated first or the fluid can be in such a condition that it is collected and treated. The oil and water phase can be separated, and the oilphase is treated as chemical waste. The water phase is emitted to the sewer or the water treatment plant of the factory.

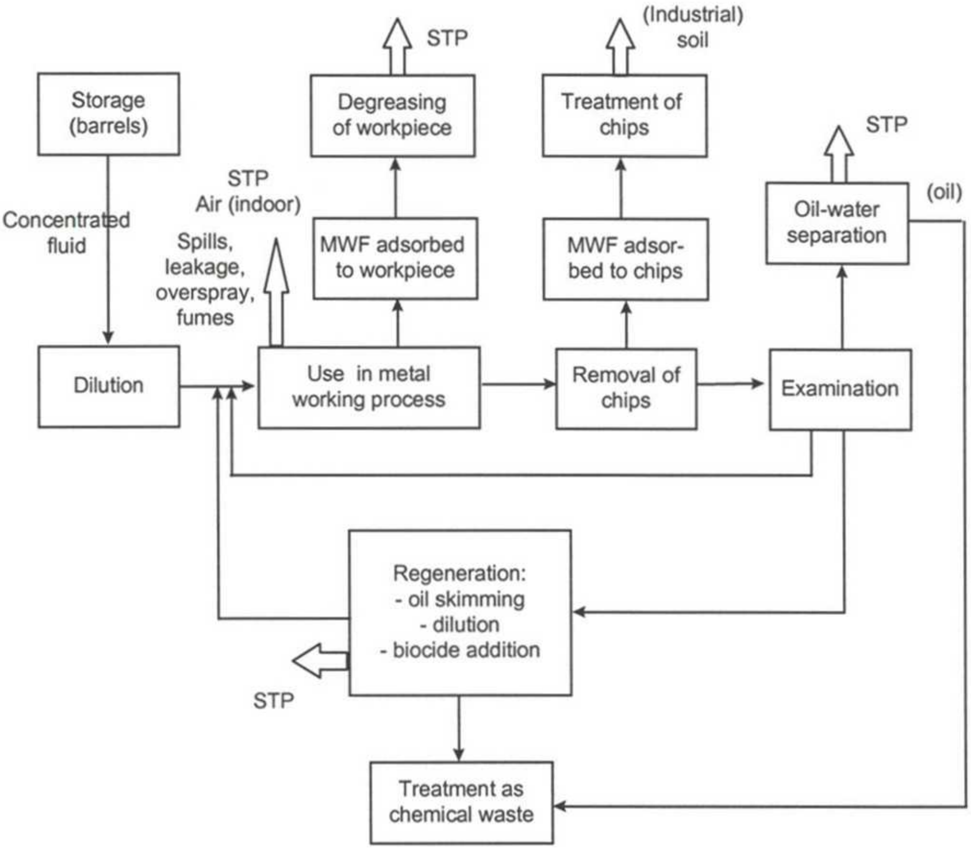

Figure 28 Environmental release during the use of water miscible metal working fluids.

Preparation of the fluid

The water-miscible metal working fluids are supplied in concentrated form in plastic or metallic containers, ranging from 60 to 1000 litres and stored in special leak free rooms. At the factories the metal working fluids are diluted and the dilution depends on the use of the fluids (metalworking process) (range 1-20%, with an average of 4 to 5%), either by means of automatic dilution mixer or by weighing the amounts.

Use and reuse of the fluid

Formerly all the chip-cutting machines had their own reservoir for metal-working fluids and those fluids were pumped to the work piece and the cutting area and constantly recirculated. The fluids were filtered over a coarse filter to remove the chips. The condition of the working fluid was examined by the machine operator. After certain periods depending on the use the whole amount of fluid was replaced.

In very big industries, for instance in the car manufactories, central reservoirs with water-miscible working fluids are employed from which the fluids are pumped to the different cutting machines.

At present one is more aware of the economical and environmental consequences of renewing the water-miscible fluids. The water-miscible fluids are nowadays regularly examined, by the operator or by the supplier, and when the condition of the water-miscible fluids is decreasing adequate measurements are employed. This can be skimming when the oil when the oil content gets to high (run off oil of the machine), but can also be by diluting the fluid because of evaporation. In small factories these examination will not be very extensive but in the big factories they are. One of the analyses that are also been carried out is the determination of the number of bacteria. When the bacteria count is too high (> ca. 1×10^5 per ml) concentrated biocides are added to make up a concentration of 0.01 to 0.2 % of total metal working fluid. Others are measuring the concentration of metalworking fluid, measuring the pH, the corrosion protection capacity or the stability (Leiseder, 1991).

Emissions occur at various points during the use of cutting fluids. The results of a mass balance study, in which the emissions are estimated, are presented in Figure 29.

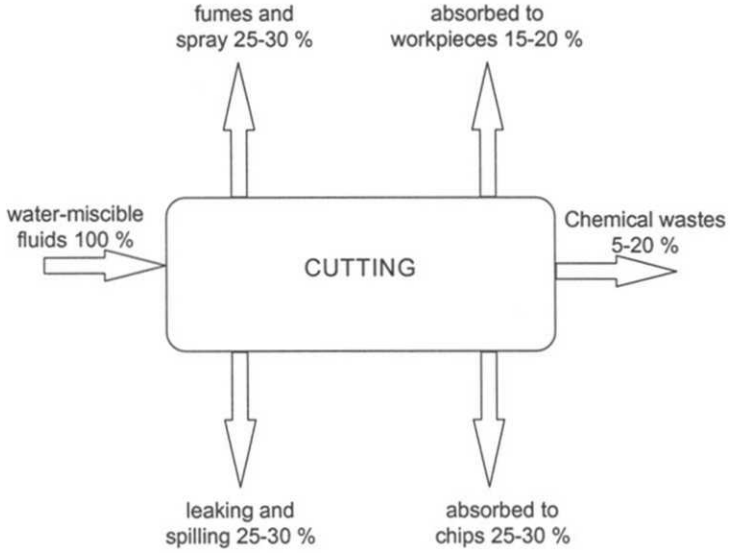

Figure 29 *Percentages of losses of water miscible metal working fluids in metal cutting operations. (according to prevention factsheet STIMULAR, 1993)*

Reinders (1983) gives emission factors for the emission to air and water of different metalworking fluids. The emission factors are listed in Table 32.

Table 32 Emission factors from cutting fluids to air and water (in g.kg^{-1})

Type of MWF	Emission to air	Emission to water
Drilling & cutting oil	?	70
Oil emulsions	350	350
"semi-synthetic" fluids	400	400
"synthetic" fluids	400	600

Loos (1992) lists the emissions that occur during metalworking (based upon a TNO study), *as a percentage of the total emission* (which is one of the causes that the values are higher than the values in Table 32). The percentages are listed in Table 33. The total loss of metal working fluid is 60-70% of the total fluid applied.

Table 33 Loss of metalworking fluid (as percentage of the total loss) (Loos, 1992)

	Loss (%)
Evaporation, spray	25-60
Leakage, spills	20-35
Adsorbed to work pieces	15-20
Adsorbed to chips	5-20

Bremmer (1988) concludes on a literature survey that the loss of metal working fluids (as percentage of the total emissions) is 30% fumes and spray, 15% adsorbed to work pieces, 20% adsorbed to chips and 35% leakage and spilling. This agrees with the ranges presented earlier.

In 1994 en 1995 an study was carried out by TNO-Metal Institute on behalf of the SCOM (Stichting Collectief Onderzoek Metaal). The spending of metalworking fluids was studied in 9 factories in the Netherlands. The results are summarised in Table 34.

Table 34 Losses of water-miscible metal working fluids in 9 metal cutting factories in the Netherlands 1994-1995 (pers. comm. John Keus TNO-MI)

Factory	1	2	3	4	5	6	7	8	9
conc. Fluids (l)	1400	1450	1025	1500	440	4200	360	520	1000
prep. Fluids (l)	40000	70000	20000	37500	17000	95260	17300	17300	28570
losses (l)	34000	45000	16400	28500	12000	59090	11800	8900	18570
waste (l)	6000	25000	3600	9000	5100	36170	5500	8400	10000
% to environment	85	64	82	76	70	62	68	51	65

In 1992 the total Dutch industry used 36 x 10^6 l prepared water-miscible metal working fluids (CBS, 1992). Considering the losses to be in the order of 70 % with a biocides concentration of 0.01 to 0.05 % the total amount of biocides spent is 2520 tot 12600 kg per year in the metal cutting industry.

Disposal of spilled fluids and other waste

Several wastes are formed in relation to metal working fluids. Spilled metal working fluid is treated as chemical waste. During the regeneration of metal working fluids, oil that is skimmed off is collected, which has to be treated. The sewer system of metal working plants is often equipped with an oil/water separator, in which (contaminated) oil is formed. The spilled and contaminated oil has to be collected. In Germany, the fate of this oil after collection (chemical waste or transformation into fuel) and the costs for the collection of the oil depend on the degree of contamination. Furthermore, metal chips which are filtered out of the metal working fluid during recycling are collected and stored in bins, usually on the yard of the factory. These chips contain metal working fluids, which can leak out of the bins and cause soil contamination. Cutting oils can be separated from the chips by centrifugation, but water miscible metal working fluids are difficult to separate from the chips. According to Klingenberg (1990), 56 000 tons of contaminated metal are formed every year in the Netherlands. He also states that 70% of the metalworking fluids will enter the environment in an "uncontrolled way".

14.3 Data requirements for product type 13

The direct exposure compartments, which were introduced in the previous section, are summarised in Table 35.

Table 35 Direct exposure compartments for product type 13.

Subtype	Products	Direct exposure compartments
13	All products	Sewagewater Treatment Plant

Guidance for demanding test data

Potential data requirements for products released to a sewagewater treatment plant are discussed in Part 1.

As stated before, the biodegradation test with pre-adapted inoculum (IV.1) is relevant only in case the STP is continuously exposed to the biocides. For metalworking fluids, this is not the case. Therefore, test item IV.1 is considered less important for this product type.

Two exposure scenarios are available for this product type (Appendix B). Next to the base set data, the fate of the substance in a STP is required. This is provided for in the proposed additional data.

15. Product types 14 to 19: Pest control products

15.1 Introduction

In this chapter, the product types Rodenticides (product type14), Avicides (15), Molluscicides (16), Piscicides (17), Insecticides and acaricides (18) and Repellents and attractants (19) are described. As many products in these product types are formulated in similar ways, and are applied with similar techniques, it was decided to describe them together in one chapter. Although some biocides of the above mentioned groups have agricultural use too, only the non-agricultural use is discussed here.

Rodenticides (product type 14) are biocidal products used to control rodents such as different types of mice and rats. Their non-agricultural use is in and around homes, commercial and industrial sites, lawns, golf courses, highway medians, etceteras.

Avicides (product type 15) are biocides for control of nuisance birds. Their non-agricultural use is predominantly against pigeons and sparrows around 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.

Molluscicides (product type 16) are biocidal products that control molluscs such as snails and slugs. Their non-agricultural use is, among others, to prevent contamination of (international) cargo with foreign pests. Molluscicides used to combat aquatic (marine or freshwater) bivalves are not included in this product type. They are described under either product type 11 (Preservatives for liquid-cooling and processing systems) or product type 21 (antifouling products).

Piscicides (product type 17) are biocidal products that are used to control fish. They are used as part of water body management. There are a variety of reasons to reduce or control a fish population in a water body. It may have become contaminated with undesirable fish, there may be a disrupted predator-prey balance or some species may become overabundant and stunted (MSU Extension, 1993). Piscicides are excepted from mutual recognition by the member states.

Insecticides (product type 18) are biocides for controlling insects in non-agricultural settings. **Acaricides** are biocides toxic to 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.

Repellents and attractants (product type 19) are biocides that are not intended to control organisms, but to control harmful organisms by repelling or attracting them (sometimes in combination with an insecticide).

The non-agricultural pesticide product types each include a number of different application techniques (e.g., bait, fumigation) and active ingredients, depending on the actual purpose. In this section, a brief overview of each of the product types (14 to 19) will be presented.

Much of the information comes from the Extension Toxicology Network (EXTOXNET, 1993), which is a pesticide information project of Cooperative Extension Offices of Cornell University, Michigan State University, Oregon State University and University of California at Davis. Furthermore, the following literature was consulted: Woods (1974); Allsopp and Seal (1986); Nijs (1990); Dent (1991); Bakker (1993); Brown (1994); Buckle (1994); Council of Europe (1994b); Meyer (1994); Scholl (1996)

Rodenticides

The most important target rodents in north-western Europe are the Norway rat (*Rattus norvegicus*), the Black rat (*Rattus rattus*) and the House mouse (*Mus musculus*).

Rodenticides are applied indoors many different buildings and other objects. The application range includes public buildings, industrial areas, transport facilities, animal housings and living areas (houses). Rodenticides to combat rodents in closed spaces are applied by professionals and are also used for do-it-yourself purposes. The 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. Furthermore, rodenticides are applied in public and private grounds, on water banks, in and around sewer systems, and around waste disposal sites and waste dumps. The main formulation for outdoors use is baits, for example wax blocks. Fumigation can be used outdoors to combat rats in their burrows.

The most important active ingredients among the rodenticides are the anticoagulants (WHO, 1995). They are chronic poisons, which interfere with the action of vitamin K, and reduce the coagulating (clotting) powers of the blood. They are usually applied in bait. Several feeds are required to accumulate lethal amounts, which reduces the risks for non-target animals. Next to anticoagulants, acute working poisons are used, such as hydrogen cyanide and phosphine (fumigation).

Some important rodenticides are:

- *Warfarin*, also known as coumafene or zoocoumarin, is an anti-clotting pesticide that causes internal bleeding after ingestion. It is used for controlling rats and house mice in and around homes, animal and agricultural premises, and commercial and industrial sites. Warfarin comes in ready-to-use bait, concentrate, powder, liquid concentrate, nylon pouch, coated talc and dust formulations. Recently, problems of resistance against warfarin have occurred. For this reason it is not allowed any more on the Dutch market since 1994.
- *Diphacinone* is an anti-coagulent rodenticide bait used for control of rats, mice, voles and other rodents, It is available in meal, pellet, wax block and liquid bait formulations, as well as in tracking powder and concentrate formulations.
- *Zinc phosphide* is an inorganic biocide that is used to control rats, mice, voles, ground squirrels, muskrats and other rodents. Its non-agricultural use includes the use on lawns, golf courses, highway medians and as tracking powder for the control of house mice. It may be formulated as grain based baits, as scrap bait or as a paste.

In Germany, 9 substances are used as rodenticides in ca. 50 products (UBA, pers. comm.):

Active substance:	Target organisms:
Hydrogen cyanide	Rats, mice
Brodifacoum	Rats, mice
Bromadiolon	Rats, mice
Chlorphacinon	Rats, mice
Difenacoum	Rats, mice
Difethialon	Rats, mice
Flocoumafen	Rats, mice
Warfarin	Rats
Zincphosphide	Mice

Avicides

Avicides are used against nuisance birds such as sparrows and pigeons in and around buildings and animal housings. Other bird pests include weaver finch (especially in Africa), or wood pigeons. The main formulation for avicides bait, both ready-to-use bait (pellets) and liquid concentrates to prepare baits. In some situations, gassing (fogging or fumigation; in closed spaces) or contact paste (in roosting areas) are used. Avicides are mainly used by professionals.

Two main biocides are:

- *4-Aminopyridine* (4-AP or better known by its trade name "Avitrol") is probably the most prominent of the avicides. Avitrol repels birds by poisoning a few individual members of a flock of birds, causing them to become hyperactive and to utter distress calls which signal other birds to leave the site. Avitrol is available as grain baits and powder concentrate.

- Based on its high toxicity to birds, the insecticide *Fenthion* is used in various parts of the world for weaver finch control. It has also been used to control pigeons around public buildings. For bird control use is made of fenthion's contact action. It is then applied as a paste to roosting areas.

Molluscicides

Snails and slugs are considered pests because they can cause damage to stored food, and because they can act as vectors for diseases (for example bilharzia, with *Schistosoma* spp. as vector). Molluscicides are used in buildings (houses, industrial and public buildings, food- and feed preparation and storage, veterinary purposes) and outdoors (gardens, roads, open spaces). The formulations used are baits (stomach poison in the form of pellets, granules and powders) but also other forms are used (contact poison in the form of (wettable) powders and aqueous solutions/dispersions/suspensions)

Some important molluscicides are:

- *Metaldehyde* produces its toxic effects primarily in the stomach after ingestion. Metaldehyde is available in the form of granules, sprays and (pelleted) bait.
- Although mainly used as fungicide, *copper sulfate* is also used as molluscicide. It is available as dust, wettable powder and fluid concentrates.
- *Propoxur* is a non-systemic insecticide that is also used as a molluscicide. It belongs to the group of carbamates that has cholinesterase-inhibiting properties. It is available in many formulations including, ready-to-use liquids and aerosols, emulsifiable concentrates, wettable powders, granular baits and dusts.
- Azinphos-methyl is a non-systemic broad spectrum insecticide that is also used as a molluscicide. It belongs to the group of organophosphates. It is used primarily as a foliar application and it works both as a contact and a stomach poison. It is available in emulsifiable liquid, liquid flowable, ULV (Ultra Low Volume) liquid and wettable powder formulations.
- *Carbaryl* is wide-spectrum carbamate insecticide that is also used as a molluscicide. It is both a contact and a stomach poison. It is available in many types of formulation including baits, dusts, wettable powder, granules, aqueous dispersions and suspensions.

Piscicides

The application of piscicides is limited to fish culture. The main application technique is the use of bait (e.g., pellets). An example is:

- *Rotenone* is a botanical, selective, non-specific insecticide which is also used for fish elimination as part of water body management.

Insecticides and acaricides

Insecticides are used in many different applications. They are used indoors buildings, outdoors, in sewer systems and for veterinary purposes in animal housings. The use indoors 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 divers. They formulations include products for spraying (e.g., aerosols, solutions, suspensions, emulsions), for pouring, for brushing, dusts, granules, 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): ca. 32%
2. Do-it-yourself products used in relation to pets: ca. 8%
3. Products used on farms for pest control: ca. 20%
4. Products used for professional pest control: ca. 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). 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).

Repellents and attractants

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. They are used indoors buildings (private houses, public and industrial buildings, such as museums, 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 repellents are:

- Smoke
- Plant extracts, for example oil of citronella (geraniol, citronellol, terpenes). These compounds are used to repel flying mosquito's
- Dimethylphthalate is used in skin preparations and for impregnation of clothes
- N,N-diethyl-m-toluamide

- In mothballs, naphthalene and paradichlorobenzene are used. It is not clear whether their action is based on insecticidal or repelling properties

Environmental and health problems are reported for several of the biocides described in the previous paragraph. They include toxic effects on non-target organisms, occupational poisoning and poisoning of household residents as a result of indoors spraying and injudicious use. Specific problems depend on the specific biocide and will not be discussed here. A special case is formed by the disinfection of structures and commodities with methyl bromide. Although the effects on the local ecosystem are probably low, the use of methyl bromide and the associated emissions to the air lead to destruction of the ozone layer.

15.2 Release estimation

The environmental compartments exposed to a non-agricultural pesticide depend not only on the type of biocidal product (e.g., rodenticide, avicide, insecticide) but much more on the application technique (e.g., fumigation, bait pellets) and the location were the product is applied (e.g., in closed rooms, in surface water). The consequence is, that the data required for the authorisation of a certain product is also related to its application technique and application field.

Regarding the location were non-agricultural pesticides are applied, four categories are distinguished by the German UBA (UBA, personal communication). This distinction in four application sites is maintained in this study, is relevant with regards to demanding test data:

1. Outdoors: In surface waters, waste dumps, public sites. The environmental compartments potentially at risk include soil (both soil through direct exposure or through drift), surface water (direct exposure, via drift, or runoff from soil), groundwater (leaching from the soil), and air.
2. Closed spaces: In (private) houses, public buildings, industrial buildings, food- and feed production and storage and the transport sector. The primary compartment to which emissions are directed will be air. During cleaning operations, pesticides can be emitted to the sewer, and subsequently to Sewage water Treatment Plants (STP) or to surface water.
3. Animal housing: Differs from closed spaces in the fact that pesticides can become bound to manure, and subsequently be distributed on the land. When this is the case, soil and surface water can also be at risk, and air and groundwater. Furthermore, the pesticides can be discharged to the sewer, as in the case of closed spaces.
4. Sewers: Non-agricultural pesticides (e.g., rodenticides) can be used in sewer systems and water treatment plants. Emission of the pesticide to the sewage water and subsequently to surface water or soil (through sewage sludge) can occur.

The derivation of data requirements for non-agricultural pesticides is complex, as the data required is dependent on (1) location were the product is used (e.g., in closed spaces, or outdoors); (2) the application technique (e.g., fumigation, bait) and (3) the target organisms (e.g., rodents, birds). In this chapter, the following approach is followed to establish data requirements for the non-agricultural pesticide product types:

1. First, for each product type, the application techniques are inventoried. Furthermore, it is indicated where the products are used (outdoors, closed spaces, etc.). This leads to one or more combinations of application technique and site of application (location) for each product type.
2. Second, the emissions and exposed environmental compartments for each of the combinations of an application technique and location (e.g. baits - outdoors) are described.
3. As a final step, the exposed environmental compartments per product type are derived using the relevant combinations of application technique and site of application (location). This will be performed in section II-3.

Within each product type, biocides are applied in many different ways, and on different locations (in closed spaces, outdoors, etc.). In the previous section, a brief overview is given of the application techniques per product type. In Table 36, the information of this section is summarised. From the table, it can be derived which combinations of application technique and location (site of application) are relevant for each product type.

Table 36 Application techniques for the different biocidal product types

Application techniques	Rodenticides	Avicides	Molluscicides	Piscicides	Insecticides/ acaricides	Repellents/ attractants
Fumigation/Gassing (Gas)	Outdoors, Closed spaces	Closed spaces	-	-	Closed spaces	Outdoors
Wet surface application (Spray, aerosol, liquid forms, foam)	-	-	Outdoors	-	Closed spaces, Animal housings, outdoors	Outdoors, Closed spaces, animal housings
Baits (Pellets, nylon pouch, wax blocks, liquid baits, liquid concentrates, granules)	Outdoors, Closed spaces, Animal housings, Sewer systems	Outdoors, Closed spaces, Animal housings	Outdoors, Closed spaces	Outdoors	Outdoors, Closed spaces, Animal housings, Sewer systems	Outdoors, Closed spaces, animal housings
Skin application (Collars, shampoo, powder, ear-marks)	-	-	-	-	Outdoors, closed spaces, animal housings	Outdoors, closed spaces, animal housings
Powder application (Powder, dust, powder concentrate, tracking powder)	Closed spaces	-	Outdoors, closed spaces	-	Closed spaces, Animal housings	-
Others (Spot-on, contact paste, gel)	-	Outdoors	-	-	Closed spaces, Animal housings	Outdoors, Closed spaces, Animal housings, Sewer systems

From section 15.1 it becomes clear, that many different application techniques are relevant for non-agricultural pesticides. The variety in application techniques is due to the variety in:

- Target organisms (e.g. rodents, birds, molluscs)
- Location of applications (e.g. outdoors, in closed space)
- Exposure routes of the pesticides (e.g. oral, dermal, inhalation)
- Users (professional, do-it-yourself)

In Table 37, a number of application techniques have been clustered. For each cluster, it has been indicated in which locations the biocides are used (outdoors, closed spaces, animals housings and sewer systems) and which environmental compartments are exposed to the biocide. From Table 37, the exposed environmental compartments for each combination of application techniques and site of application (location) can be derived. The table summarises the next sections, were the application techniques and exposed compartments are described in more detail.

Table 37 Application techniques and relevant environmental compartments

Application techniques	Outdoors	Closed spaces	Animal housing	Sewer systems
Fumigation/Gassing Gas	air outdoors soil	air indoors air outdoors	-	-
Wet surface application Spray, aerosol, liquid forms, foam	air outdoors surface water soil	air indoors STP	air indoors STP soil (via manure) fresh surface water	-
Baits Pellets, nylon pouch, wax blocks, liquid baits, liquid concentrates, granules	surface water soil	-	-	STP
Skin application Collars, shampoo, powder, ear-marks, sprays, rollers	air outdoors soil fresh surface water	air indoors STP	air indoors STP soil (via manure) fresh surface water	-
Powder application Powder, dust, powder concentrate	air outdoors surface water soil	air indoors STP	air indoors STP soil (via manure)	-
Others Spot-on, contact paste and gel	air outdoors surface water soil	air indoors STP	air indoors STP soil (via manure) fresh surface water	STP

In the next sections, an overview of application techniques for non-agricultural pesticides is presented. The application techniques are clustered into groups (conform Table 36 and Table 37), so that the environmental exposure routes are more or less the same for the application techniques in one cluster. The review is not exhaustive, but aims to illustrate the application techniques covered by a cluster, and to identify the environmental exposure routes. The overview is based on Nijs (1990); Dent (1991); Bakker (1993) and Buckle (1994).

Fumigation

Several types of non-agricultural fumigation can be distinguished:
- Fumigation of structures (e.g., buildings, warehouses, elevators);
- Fumigation of mobile objects (e.g., trucks, containers, aircraft, ships
- Fumigation/gassing of burrows in soil to control or repel rodents

Fumigants have a relatively high vapour pressure. The toxicity is a function of the concentration and exposure time. Several substances can be used for fumigation, e.g., methylbromide, hydrogen phosphide and ethylene dibromide.

At fumigation of structures, the object (building) is made gastight as good as possible first. Then a certain dosage of biocide (e.g., methylbromide) is brought into the space of the object, and the object is left closed for a certain time period. After this period, the object is ventilated to remove the remainder of biocide. The initial concentration of biocide has to be much higher than the threshold concentration, due to adsorption, but mainly due to leakage through all kinds of (small) openings. Adsorbed biocide can desorb during ventilation. For substances that do not degrade rapidly (such as methylbromide), 100% emission to the (outdoors) air is expected eventually.

Mobile objects such as clamps and trucks can be fumigated by covering the object with gastight plastic, and introducing biocide under this cover. Objects such as aircraft, containers and ships can be regarded as "closed boxes" in which a biocide can be introduced. For small, vulnerable objects, fumigation installations can be used. They consist of a gastight installation with a controlled ventilation (air extraction) system. The installation is filled with the object(-s), and the biocide is introduced. Afterwards, the air is filtered over an active-carbon filter, to remove the biocide. Emissions to the environment (air) can occur by desorption of adsorbed biocide during subsequent transport.

Emission factors for several non-agricultural fumigation processes (methylbromide used as fumigant) are presented in Table 38.

Table 38 Emission factors for various fumigation processes, with methylbromide as fumigant. From: Bakker (1993).

Object type	**Object**	**Total emission factor (%)**	**Loss due to leakage during the first 24 h after fumigation (%)**
Structures	Building	100 after ventilation	50 - 99
	(Grain) elevator	100 after ventilation	10 - 20
Mobile objects	Sealed ship's hold or container	100 after ventilation	20 - 40
	Container or pallet under a cover	100 after ventilation	75 - 85
	Flowers and other objects in special fumigation installations	<50 during subsequent transport	none

In Figure 30, the emissions are summarised.

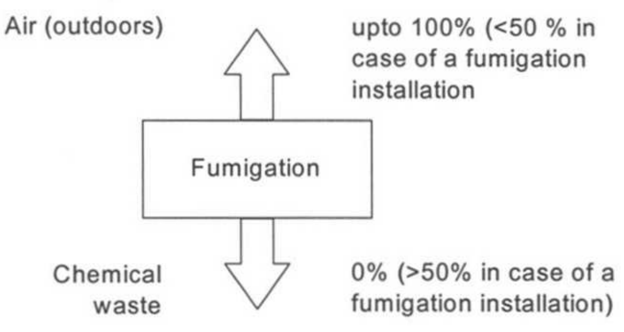

Figure 30 Schematic presentation of the emissions during fumigation

Products for wet surface application
This cluster includes the application techniques in which a liquid product (commercially available, or made from a commercially available product by dilution of addition of a solvent and/or water) is used for spraying or fogging, usually to combat pests on surfaces. Many formulations are available for this purpose.

In the past, high solutions of organic solvents were used to prepare **solutions** of biocide. At this moment, only water soluble substances are used in solutions, or organic solvents are used in Ultra Low Volume applications. **Emulsion concentrates** are substances dissolved in an organic solvent, which is emulsified in water using an emulsifying agent. **Water dispersable powders** are biocides that are insoluble in water, but can be dispersed. The product can be a solid (finely ground, with surfactants added to increase the dispersion), a liquid or a liquid adsorbed to a finely ground solid. Agitation is required to maintain the dispersion in the application tank. Water dispersable powders are usually applied in high volumes, with low biocide concentrations. **Suspension concentrates** are formulated as finely ground solids held in suspension in a (non-solvent) liquid. For application, the suspension is diluted with the same liquid (usually water). Several **additives** can be added before application: dispersants for wettable powders, emulsifiers to stabilise emulsions, or additives to improve activity in the field (surfactants, spreaders, penetrants, stickers, humectants).

The liquid formulations described above can be applied to a surface with a **spray**, with a pumping mechanisms or with a propellant. An other application technique is a **fogger** (or **total release aerosol**). A fogger disperses its content through a closed space (e.g., ‘bug bombs’). An additional technique has to be used to cover places which cannot be reached by the fog, e.g., under furniture.

When applied in a closed space (indoors public or private buildings, or animal housings), the main emissions will be to the air, initially the indoors air and subsequently the outdoors air, and adsorption to the treated surface or space. After cleaning or decontamination, a large part of the (remaining) active ingredient is expected to end up in the sewer system (STP). In animal housings (stables), active ingredients adsorbed to manure may be transported to soil. However, this is not expected to be a major route. When used outdoors, emissions to soil, surface water and the air may occur. The emission pathways are summarised in Figure 31.

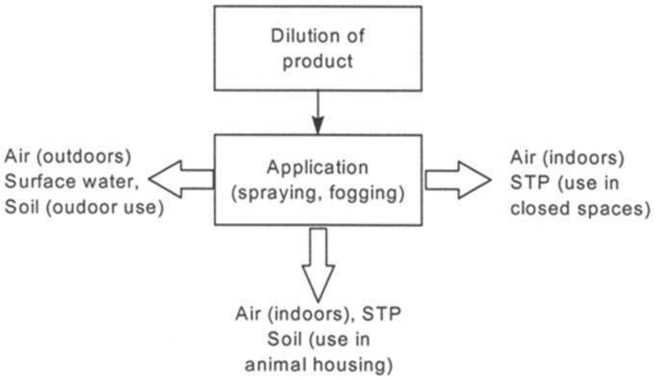

Figure 31 *Emissions and direct exposure are compartments for (wet) products applied on surfaces.*

Baits

Bait formulations combine (a) biocidal substance(-s) with an attractant. The attractant is usually a potential food source, but can also be sex pheromone.

Baits come in many different formulations. **Grain baits** consist of cereal grains, either whole or broken or ground, with the biocide (dust) attached with a 'sticker', for example oil. This means, that the biocidal substance is only present on the outdoors of the grains. This can cause problems with palatability, and problems with weathering (separation of biocide and grain matrix). Furthermore, problems can arise because the grain is recognisable as a human food source (exposure of humans after eating). **Pellets** are finely milled cereal grains, mixed with an active ingredient, and forced through a die under pressure. Pellets have the advantage that the active ingredient is uniformly mixed with the pellet matrix, and are very palatable. Pellets are recommended for indoors applications, and use in bait boxes. They are less suited for outdoors applications, or use in stables, as they are attractive to granivorous birds. As grain baits, they are weatherable. **Wax blocks** are compose of cereal, mixed with active ingredient, to which a substantial quantity (15-40%) of paraffin wax is added. They can be processed in many different shapes. They are less palatable then pellets, but are more resistant to weathering and less attractive for non-target species. They are used in outdoors applications (usually in bait boxes), and for application in damp places such as sewers. **Pastes** and **gels** are based on fat or liquids held into shape by a hydrating agent. Their 'softness' makes them attractive for some target species, and enables application in less-accessible places (caulking gun). **Liquid baits** are effective in situations were water is scarce and dry food is available, such as grain stores.

Baits can also be prepared by pest-control practitioners from appropriate food stuff in combination with a **concentrate**. In the past, powders and dusts were used for concentrates, but due to the risk of inhaling dust particles, liquid concentrates are now used predominantly.

When baits are applied in closed spaces (including animal housings), no significant environmental exposure is expected. Non-used bait can usually be recovered. When used outdoors, some leaching of biocides from the bait to soil (weathering) or release to fresh water may occur. However, major emissions to soil or surface water can be expected when the bait is moved by (target) animals. A specific problem of baits is consumption by non-target organisms, e.g., non-target rodents, or granivorous birds.

An overview of the emissions is included as Figure 32.

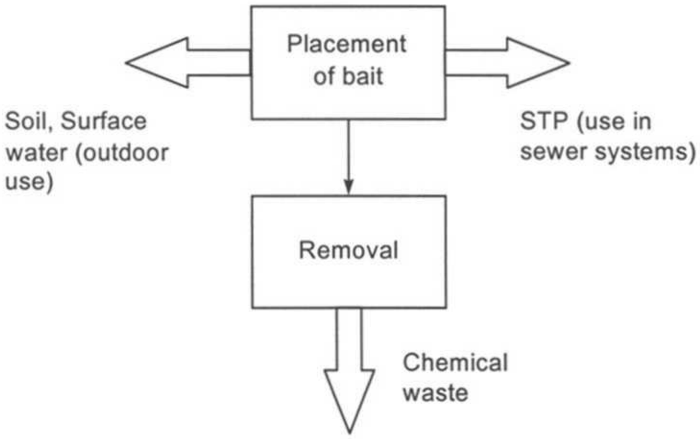

Figure 32 Emissions and direct exposure compartments for baits.

Products for skin application
In several application techniques, the active ingredient is brought on (or close to) the skin (of pet animals, or humans). Examples are the combatment of pests (fleas, mites) on the skin of pet animals, or insect repellents used on human skin.

Shampoos containing biocide are used to wash animals (such as dogs and cats) with, in order to combat fleas. In many cases, it is not clear whether the effects are due to toxic effects of the biocide, or mechanic effects of the washing. Also for the combat of fleas are **powders** intended to be used on animal skins. **Flea collars** and **ear-marks** are intended to be worn on the animal body. The biocide is included in a PVC matrix. There are flea collars based on vaporisation, liquids, or particles. A disadvantage is that the collars still contain high concentrations of biocide, after their effective life has ended. Repellent **sprays** or **rollers** are used to bring a liquid containing the active ingredient on the skin.

Emissions (Figure 33) are mainly directed to the air (evaporation) and sewage water, after washing of the skin. Active ingredients that have an action *through* the skin (systemic use) are not considered here, as they probably do not fall under the Biocidal Products Directive. Most likely, all systemic biocides fall under the veterinary medicines regulations.

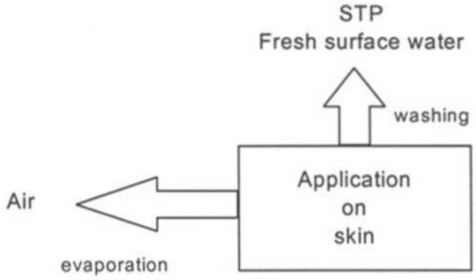

Figure 33 Emissions and direct exposure compartments for products used on the skin.

Products for powder application

Powders or dusts are biocidal products mixed with an inert carrier, which is then ground to a fine powder. It can be applied as foliage application with a dust blower machine. **Contact dusts** or **tracking dusts** are used as rodenticides. They become attached to the feet and fur of rodents, and are ingested during grooming. Disadvantages are the high concentrations of active ingredients, and the high risk of the dust becoming airborne with subsequent transport or human exposure.

The emissions associated with the use of dusts are summarised in Figure 34.

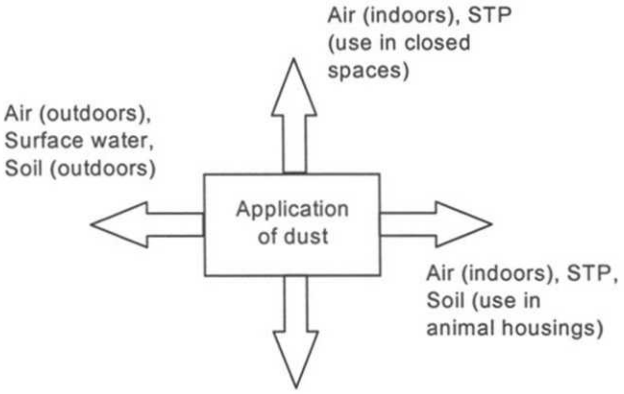

Figure 34 Emissions and direct exposure compartments for dust formulations.

Other application techniques
Apart from the formulations mentioned in the previous sections, other formulations are available. They include for example contact pastes, gels and spot-on products.

15.3 Data requirements for product types 14 to 19

Data requirements for environmental exposure and effects assessment
In this chapter, data requirements for Annex III of the Biocidal Products Directive will be proposed. The data is based on the application techniques and sites of application described in section 15.2. From this section, it can be derived (1) which application techniques (e.g., baits) and site of application (e.g., outdoors) are relevant for the non-agricultural pesticides, and (2) which environmental compartments are exposed for a combination of application techniques and site of application.

In this chapter, data requirements for the 6 non-agricultural pesticide product types are formulated. Three steps will be followed:

1. First, for each product type, the relevant combinations of application techniques and site of application are summarised (using the information of section 15.2).
2. Second, the exposed environmental compartments for each of the relevant combinations of an application techniques and site of application (e.g. baits - outdoors) are summarised.
3. Step one and two lead to the environmental compartments which are exposed to a certain product techniques, used in a specific site with a specific application techniques. Using the generic data requirements for environmental compartments of Part 1, data requirements can be produced.

Other data requirements
The method described above is only valid for the derivation of data requirements for environmental exposure and effects assessment. For some specific application techniques, test results may be required to estimate the emission of active ingredients to environmental compartments (e.g., weathering rate of baits applied outdoors, to estimate emissions to soil). In other cases, additional test results may be required to assess the exposure of specific non-target organisms (e.g., palatability to grainivorous birds). This type of test results (data requirements) will be covered on a case-to-case basis in this section.

Rodenticides
From Table 36, it can be deduced that the following combinations of application technique and site of application are relevant for rodenticides:

- Fumigants used outdoors and in closed spaces

- Baits used outdoors, in closed spaces, in animal housings, and in sewer systems
- Powders used in closed spaces

Using these combinations, and using Table 37, the following environmental compartments are relevant:

Table 39 Relevant exposed environmental compartments for rodenticides, as a function of application techniques and location. Shaded cells indicate that the combination is not relevant. 1=air (indoors, outdoors); 2=surface water (fresh); 3=soil; 4=STP.

Application techniques	Outdoors	Closed spaces	Animal housings	Sewer systems
Fumigants	1, 3	1		
Baits	2, 3	none	none	4
Powders		1, 4		

For baits, the following additional items should be covered by data requirements:
- Weathering of baits (leaching of active ingredients)
- Palatability to birds and non-target mammals

Avicides

From Table 36, it can be deduced that the following combinations of application techniques and site of application are relevant for avicides:
- Fumigants used in closed spaces
- Baits used outdoors, in closed spaces and in animal housings
- Other application techniques (contact pastes) used outdoors

Using these combinations, and using Table 37, the following environmental compartments avicides:

Table 40 Relevant exposed environmental compartments for avicides, as a function of application techniques and location. Shaded cells indicate that the combination is not relevant. 1=air (indoors, outdoors); 2=surface water (fresh); 3=soil; 4=STP.

Application techniques	Outdoors	Closed spaces	Animal housings	Sewer systems
Fumigants		1		
Baits	2, 3	none	none	
Other	3			

For baits, the following same additional items as mentioned for rodenticides should be covered by data requirements:
- Weathering of baits (leaching of active ingredients)
- Palatability to birds and non-target mammals

Molluscicides

From Table 36, it can be deduced that the following combinations of application technique and site of application are relevant for molluscicides:

- Wet surface application products used outdoors
- Baits used outdoors and in closed spaces
- Powders used outdoors and in closed spaces

Using these combinations, and using Table 37, the following environmental compartments are relevant for the molluscicides:

Table 41 Relevant exposed environmental compartments for molluscicides, as a function of application techniques and location. Shaded cells indicate that the combination is not relevant. 1=air (indoors, outdoors); 2=surface water (fresh); 3=soil; 4=STP.

Application techniques	Outdoors	Closed spaces	Animal housings	Sewer systems
Wet surface application	1, 2, 3			
Baits	2, 3	none		
Powders	1, 2, 3	1, 4		

For baits, the following same additional items as mentioned for rodenticides should be covered by data requirements:

- Weathering of baits (leaching of active ingredients)
- Palatability to birds and non-target mammals

Piscicides

From Table 36, it can be deduced that the following combinations of application techniques and site of application are relevant for piscicides:

- Baits used outdoors

As the baits are only used in water systems, the only exposed environmental compartment is surface water. Piscicides can be used in fresh water as well as in sea water.

Table 42 *Relevant exposed environmental compartments for piscicides, as a function of application techniques and location. Shaded cells indicate that the combination is not relevant. 1=air (indoors, outdoors); 2=surface water (fresh); 3=soil; 4=STP, 5=sea water.*

Application techniques	Outdoors	Closed spaces	Animal housings	Sewer systems
Baits (fresh water)	2			
Baits (sea water)	5			

Insecticides and acaricides

From Table 36, it can be deduced that the following combinations of application techniques and site of application are relevant for insecticides and acaricides:

- Fumigants used in closed spaces
- Wet surface application products in closed spaces and animal housings
- Baits used outdoors, in closed spaces, in animal housings, and in sewer systems
- Powders used in closed spaces and animal housings
- Other application techniques used in closed spaces and in animal housings

Using these combinations, and using Table 37, the following environmental compartments are relevant for insecticides and acaricides:

Table 43 *Relevant exposed environmental compartments for insecticides and acaricides, as a function of application techniques and location. Shaded cells indicate that the combination is not relevant. 1=air (indoors, outdoors); 2=surface water (fresh); 3=soil; 4=STP.*

Application techniques	Outdoors	Closed spaces	Animal housings	Sewer systems
Fumigants		1		
Wet surface application	1, 2, 3	1, 4	1, 3, 4	
Baits	2, 3	none	none	4
Powders		1, 4	1, 3, 4	
Other		1, 4	1, 3, 4	

For baits, the following same additional items as mentioned for rodenticides should be covered by data requirements:

- Weathering of baits (leaching of active ingredients)
- Palatability to birds and non-target mammals

Repellents and attractants

From Table 36, it can be deduced that the following combinations of application technique and site of application are relevant for repellents and attractants:

- Baits used in animal housings, outdoors and in closed spaces
- Wet surface application products used in animal housings, outdoors and in closed spaces
- Skin application products used in animal housings, outdoors and in closed spaces
- Other application techniques used outdoors, in closed spaces, in animal housings and in sewer systems

Using these combinations, and using Table 37, the following environmental compartments are relevant for repellents and attractants:

Table 44 Relevant exposed environmental compartments for repellents and attractants, as a function of application techniques and location. Shaded cells indicate that the combination is not relevant. 1=air (indoors, outdoors); 2=surface water (fresh); 3=soil; 4=STP.

Application type	Outdoors	Closed spaces	Animal housings	Sewer systems
Wet surface application	1, 2, 3	1, 4	1, 4, (3)	▨
Baits	2, 3	none	1, 4, (3)	▨
Skin application	1, 2, 3	1, 4	1, 4, (3)	▨
Other	1, 2, 3	1, 4	1, 3, 4	4

For baits, the following same additional items as mentioned for rodenticides should be covered by data requirements:

- Weathering of baits (leaching of active ingredients)
- Palatability to birds and non-target mammals

Summary and guidance for demanding data

The product types 14 to 19 were treated together, because the application techniques, and therefore the environmental exposure, shows a large overlap between the product types. Therefore, the application techniques in combination with the location of use are chosen as relevant distinction in the summarising table (Table 45).

Table 45 Direct exposure compartments for product type 14-19.

Subtype	Products	Direct exposure compartments
14-19.1	Fumigation products used outdoors	Air (outdoors), soil
14-19.2	Fumigation products for indoors-use, products used on skin (indoors)	Air (indoors and outdoors)
14-19.3	Products for wet surface application, powders and other products used *outdoors*	Air (outdoors) Surface water Soil
14-19.4	Products for wet surface application, powders and other products used in *closed spaces*	Air (indoors) Sewagewater Treatment Plant
14-19.5	Products for wet surface application, powders and other products used in *animal housings*	Air (indoors) Sewagewater Treatment Plant Soil
14-19.6	Baits used outdoors	Fresh surface water Soil
14-19.7	Baits used in sewer systems	Sewagewater Treatment Plant
14-19.8	Baits used in closed spaces and animal housings	No direct exposure compartments
14-19.9	Products used on skin (outdoors)	Air (outdoors)

Potential data requirements for products released to a specific environmental compartment are discussed in Part 1.

Leaching tests are not relevant for this product type. However, in case products are formulated as baits, a weathering (leaching) test should be performed, to determine the environmental release of the biocide.

Furthermore, when baits are used as formulation, a palatability test is required, to test the palatability for mammals and birds. This is indicated with the asterix (*) at data items I/II.5 and III.10.

16. Product type 20: Preservatives for food or feedstocks

There is some discussion regarding the delineation of this product type. According to the directive, product type 20 comprises:

"Products used for the preservation of food or feedstocks by the control of harmful organisms"

However, preservatives in food to prevent microbial deterioration do not fall under the Biocidal Products Directive. Biocides applied during the preparation of food or feed are covered by product type 4 (Food and feed area disinfectants). Products used to combat harmful organisms during the storage of food or feed are (partly) covered by non-agricultural pesticides (product type 14: rodenticides; product type 18: insecticides).

Therefore, this product type is interpreted as biocides used (for disinfection) in rooms were prepared food or feedstock is stored, such as grocery store, supermarkets, silo's etceteras. This can cause overlap to occur with product type 2 (private area and public health area disinfectants and other biocidal products), for example with regards to disinfectants used in private and public buildings.

The exact scope of the product type, biocides in use, and application techniques are erroneous to describe, due to the strong interaction with other product types. It is advised to refer to data requirements for other product types as much as possible, the relevant product type being defined by the target organism (micro-organisms, insects, rodents).

17. Product type 21: Antifouling products

17.1 Introduction

Fouling is the successive development of a characteristic community on surfaces exposed to natural (sea)water. When a clean surface is placed in sea water, macromolecules, dissolved in the water, will form a layer on the surface. This layer facilitates anchoring of bacteria, a process which can take place within a few hours. The bacteria layer enables the settling of micro-organisms such as protozoa and algae (especially diatoms). The biofilm formed by the microbial community attracts spores and larvae of macroalgae, mussels, barnacles and other macro-organisms. The result is a typical fouling community. Fouling communities are described by Peters *et al*. (1994) (marine environment) and Watermann *et al*. (1990) (fresh water).

Fouling occurs on all objects below the water surface, from ships' hulls to marine organisms. Objects likely to develop a fouling community include:

- ships' hulls
- offshore constructions
- buoys and other small, static objects
- mariculture equipment
- sluice doors
- harbour constructions
- inlet pipes of cooling water systems
- marine sensors

This chapter is focused on antifouling products for ships' hulls, as it is the major application (from quantitative point of view). Fouling occurs in both salt and fresh water, but the fouling process is more rapidly and intense in salt water than in fresh water.

Fouling is a process with negative economic consequences. Fouling of a ships' hull causes the water resistance of a ship to increase strongly, causing an almost exponential increase in fuel demand with increasing thickness of the fouling layer. Therefore, biocides are applied to prevent fouling.

Antifouling biocides (see Table 46) are applied as paint, which forms a protective top layer on the ship hull. From the paint, biocides are released. Almost all application of antifouling paint concerns ship hulls; the protection of other objects can be ignored from a quantitative point of view.

Table 46 Main biocides (substances) used for antifouling purposes. (Schablowski, pers. comm.)

Type	Biocides
Organotin compounds	TBTO, TBTF, TPTF
Copper compounds	Copper(I)oxide, copper, copperthiocyanate, copperresinate, coppersulphate, coppernaphthenate
Others	zincnaphthenate, zinc-pyrithion, zinc, zineb (thiram, maneb diuron, irgarol, sea-nine 211, densil, chlorthalonil, 2-thiocynomethylthio-benzothiazol, dichlofluanid, folpet, methylene-bis-thiocyanate

The main biocides (substances) in use are organotin compounds (TBTO, TBTM, TPTF) and copper compounds (copperoxide, copperthiocyanate).

Antifouling biocide products (paint systems) often contain more then one biocide substance. Tin and copper compounds can be combined, to give good protection during mooring as well as during sailing. Next to copper, organic biocides are also often added to improve antifouling effects.

It is important to distinguish between different antifouling systems, because the life cycle and the leaching process varies between antifouling systems. This may result in different data requirements for different antifouling systems.

Antifouling systems can be divided into the following categories:
1. Soluble matrix type
2. Insoluble matrix type
3. Ablative or polishing tin free paints
4. Self-polishing organotin paints
5. Self-polishing tin free paints
6. Non-stick coatings (synonyms silicon coatings, foul release coatings, low-surface energy coatings)
7. Cole tar
8. Other techniques

In the soluble and insoluble matrix types (1 and 2), the main factor controlling the biocide release is the diffusion rate. The biocide substances, which are not bound to the matrix, diffuse through the paint layer to the surface, and are released to the water. This implies an exponentially decreasing release rate of the biocide substances. The initial release rate will be very high, but after some time the release rate will be too slow to prevent fouling. This is an environmental and economical disadvantage. The binding compound of soluble matrix antifoulings dissolves slowly in the water. Insoluble matrix antifoulings do not dissolve in water. The time after which the paint layer has to be renewed depends on the biocide used: 0.5 years for copper based paints to 1.5 years for organotin based paints. According to Willemsen (pers. comm.), the protection time is 1 to 2 years for soluble matrix types, and approximately 2 years for insoluble matrix types.

In ablative paints (or polishing paints, type 3), the biocide is not bound to the matrix, similar to the first two types (same leaching characteristics), but the paint erodes like the selfpolishing types. This increases emission due to diffusion, because of the shorter diffusion path.

In selfpolishing antifoulings, the biocide is bound to a matrix. At this moment, only tinbased selfpolishing coatings are commercially available (type 4). Tin is present as tributyltinmethacrylate co-polymere. When exposed to water, the matrix hydrolyses and the biocide is released. This causes a constant release rate when the ship is moving. To guarantee a prevention of fouling when the ship is not moving (and the hydrolysis of the matrix is inhibited), (free moving) copper is usually added to the paint. The selfpolishing antifouling with other biocides than tin (type 5) is still under development and not operational.

The most promising coating without biocides is the non-stick (type 6) coating. The top layer of this coating is formed by a layer with very low surface tension, which gives fouling organisms no opportunities to attach firmly. This type of coating (most are on a silica basis) is commercially available at the moment, and is promising for the future. Another promising antifouling system is coatings that hydrolyse layer by layer like the SPC, but do not contain (the same amount of) biocides. The dissolving top layer should prevent fouling organisms to attach.

Cole tar is used to protect the ship hull, and has an anticorrosive effect. The antifouling effect is small. Cole tar is only used on fresh water ships, where fouling is not so strong as in salt water. The main active substances are polycyclic aromatic hydrocarbons (PAH). Cole tar can be used ‘pure’ and as mixtures.

Other techniques to prevent fouling include ultrasound, surface vibrations, heat, electricity, pH changes, etceteras. In this study, only biocide containing paint systems are considered. Cole tar is not specifically used for antifouling purposes, and therefore falls beside the scope of this study.

In fresh waters, the main types of antifouling system in use are matrix- and ablative types, with copper as the most important active substance. Selfpolishing types are too expensive to use in fresh waters, and there is no necessity for them because of the slow fouling conditions. As they are based on organotin, they are forbidden on ships < 25 meters. In some countries, cole tar is used extensively on ships (as anticorrosive with antifouling properties) or other anticorrosives without biocides are used (on ships >= 25 meters length).

The main type of antifouling on seagoing ships is the selfpolishing organotin paint (80% of the ships). Other types in use for seagoing ships are ablative and matrix types. The selfpolishing type is more effective than matrix and ablative types, but is more expensive. The use of organotin biocides on vessels smaller than 25 meters is prohibited.

17.2 Release estimation

There is no general life cycle for antifouling systems; the application and removal of the paint vary, and with respect to emissions a distinction between coating types in the use phase is relevant (due to different leaching characteristics). Based on typical combinations of paint type, application method and removal method, several 'characteristic' life cycles have been constructed:

- The use of matrix and ablative antifoulings on recreational ships in fresh water;
- The use of matrix and ablative antifoulings on seagoing ships;
- The use of selfpolishing antifouling paints on seagoing ships.

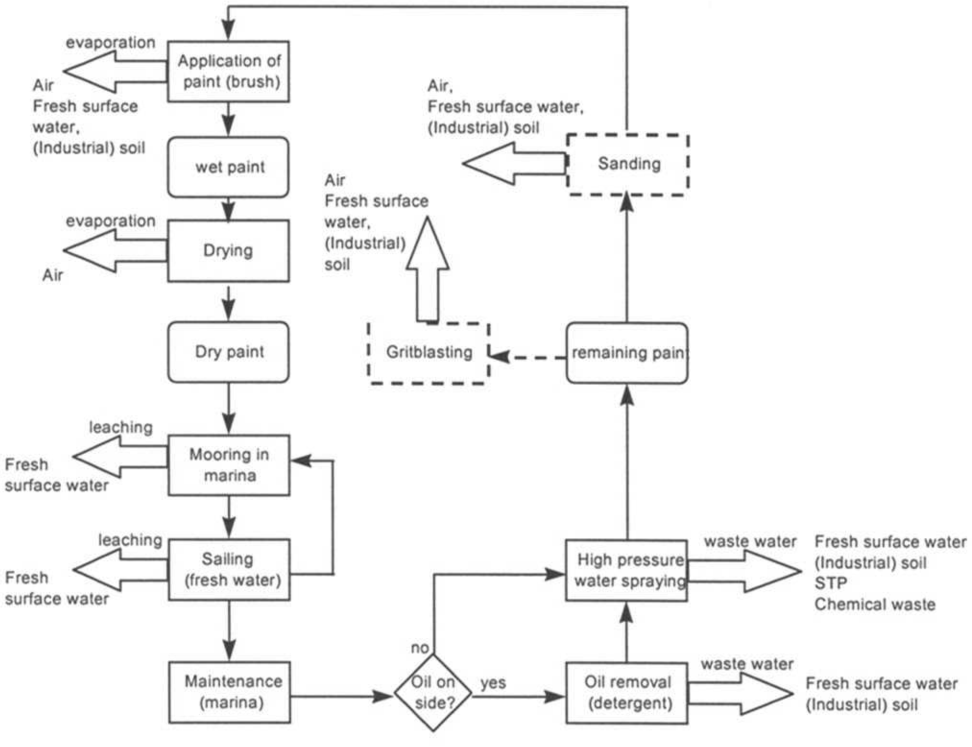

Figure 35 Environmental release of biocides from matrix type and ablative antifoulings (fresh water)

Scenario 1 Matrix and Ablative Paints on freshwater ships
The use of matrix type antifoulings and ablative antifoulings on recreational ships in fresh water is described in Figure 35. Paint is usually applied with a brush (small scale). In the spring or autumn, the ship is taken out of the water (in a marina, dock or parking lot, depending on the size of the ship and the available facilities) and the hull is cleaned (e.g., Nickels, 1997). Usually, only high pressure water blasting will be used to remove the fouling community. In some cases, gritblasting may be applied (always within a dock). New paint is applied on top of the old layer, or after removal of the old layer by sanding or gritblasting.

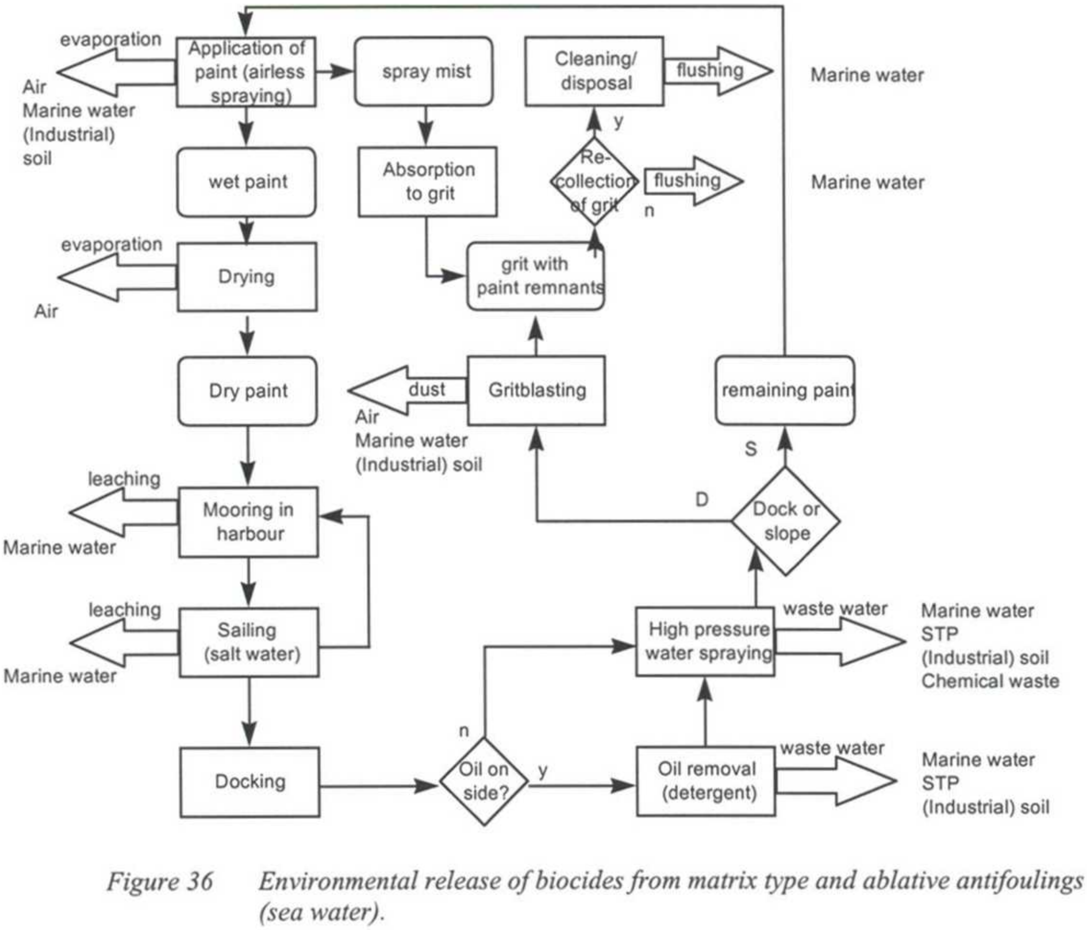

Figure 36 Environmental release of biocides from matrix type and ablative antifoulings (sea water).

Scenario 2 Matrix and Ablative Paints on seagoing ships
This emission scenario is described in Figure 36. Paint is applied by airless spraying, which causes emissions due to spray mist (overspray) and evaporation of paint (compounds). Old paint is removed by gritblasting within a dock.

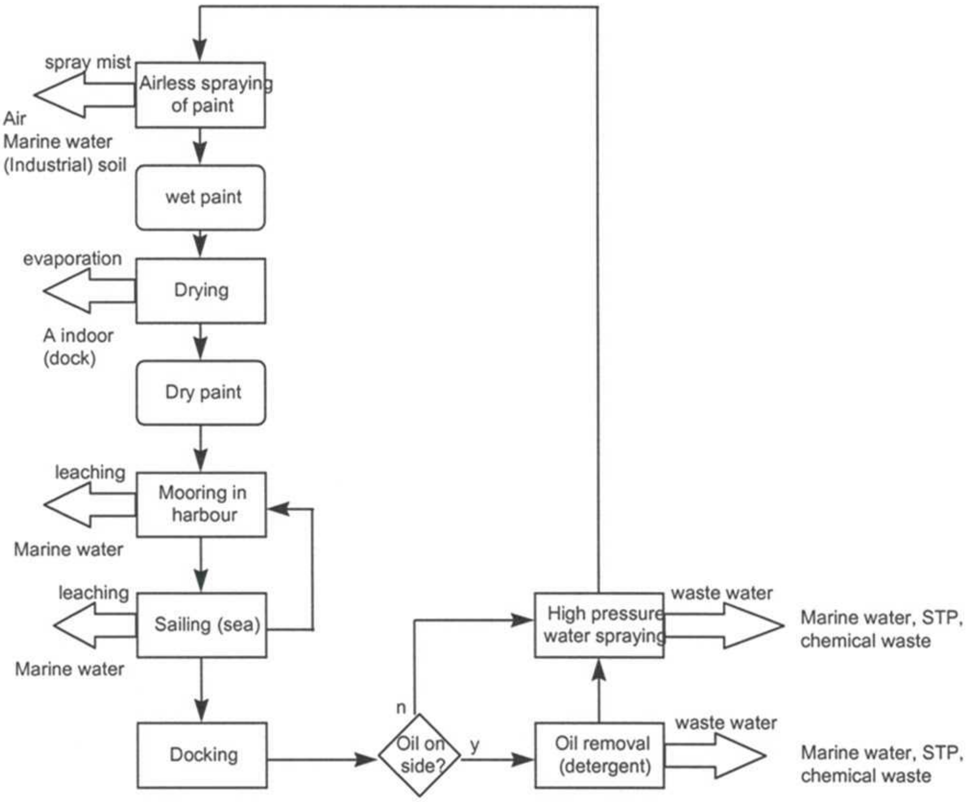

Figure 37 *Environmental release of biocides from self-polishing antifoulings (sea water)*

Scenario 3 Selfpolishing Paints on seagoing ships

For this emission scenario (Figure 37) it is assumed that the matrix and ablative types are cleaned (removal of old paint layers) by gritblasting, and that selfpolishing coatings are polished thus, that high pressure water blasting is enough to prepare the ship for the application of a new coating. In practise however, gritblasting of selfpolishing paints can occur.

Application of antifouling paint

Application with a brush or a roller is common practise for smaller ships (cargoships for inland waters, pleasure boats), while airless spraying is applied at larger (seagoing) ships (CUWVO, 1991b). Emissions during this spraying can be rather large, as a result of overspray. Paint losses can be up to 45% (see Table 47). According to CUWVO (1991a), 20% of the paint is lost due to overspray and blowing, and 25% is directly emitted to the surface water. These numbers apply to airless spraying.

Table 47 Paint losses during the application of paint (from: CUWVO, 1991b)

Application technique	Percentage loss
Brush or roller, indoors halls	0-5
Brush or roller, outdoors	2-5
Pneumatic spraying	50-60
Airless spraying	5-45

Leaching during the use of antifouling paints

A difference has to be made between leaching during mooring (in the harbour), and leaching during sailing (see Table 48). The leaching rates differ between the two situations, depending on the type of antifouling system that is used.

Table 48 Leaching rates of TBT from antifouling paints (from: Willemsen & Ferrari, 1992)

Coating type	Sailing (µg Sn.cm^{-2}.d^{-1})	Mooring (µg Sn.cm^{-2}.d^{-1})
SPC	4-5	3
Matrix/ablative	5	2-3

Emissions of copper from antifouling systems are estimated to be 10 µg.cm^{-2}.d^{-1} (Isensee *et al.*, 1994).

The erosion rate of a selfpolishing paint is about 0,1 µm.day^{-1} (speed of 16-18 knots, 25°C). If the number of sailing days per year is taken into account (120-160 days per year), the erosion rate is about 12-16 µm per year. The thickness of an antifouling coating ranges from 50 to 150 µm. Due to variation in thickness of the paint layer and variations in erosion rate, the paint is renewed after max. 5 years.

Removal of antifouling paints

High pressure water blasting is performed with pressures of 50-250 bar (max. up to 700). Fouling, rust and paint not so firmly attached can are removed. Emissions consist of fouling organisms (accumulation of biocides) and pieces of coating, and sometimes oil and dispergent. It is performed at wharves with slopes or small docks for fishery and recreational ships, at yachting wharves, at winter storage areas for yachts and at marina's. The washing water should be treated as chemical waste (Nickels, 1997).

Factors determining the amount of paint still present at the moment of docking are

- thickness of paint layer after application
- location on the hull
- age of the coating
- sailing conditions (route, scheme, speed, season, salinity,....)

Emissions during waterblasting are estimated at 90-2800 (1000) mg Cu; 10-1500 (400) mg tin and 24-237 (90) g SS per (recreation) ship. Emissions from an average water blasting facility (fresh water, situation in the Netherlands, capacity ca. 250 ships) are 200 grams copper, 80 grams organotin and 18.9 kg suspended solids per year (CUWVO, 1991a).

Another removal process is gritblasting. Hard pieces of grid are blown to the paint surface, and remove the paint layer. The technique can be applied to roughen or to remove the entire paint layer. At the pneumatic grit blasting technique, the grit is used one time. At the warp grit blasting technique, grit is reused. Emissions consist of grid and paint remnants (emitted as dust). The environmental impact of the grid is low (CUWVO, 1991b), so the hazard of the emissions is determined by the composition of the paint dust. Used grit should be treated as chemical waste, because of high concentrations of metals (CUWVO, 1991a; 1991b). Gritblasting is performed at larger wharves (with docks/slopes for seagoing ships), at wharves with slopes/smaller docks for fishery and recreational ships, and at specialised companies (conservation plants).

Average emissions from a seagoing ship (waterblasting, cooling and ballast water, cleaning of the dock) are about 1000 g oil and 20 kg suspended solids (containing 270 grams of copper and 40 grams of organotin) (see Table 49). For an average maintenance wharf (seagoing ships), with 150 dockings per year, the emissions are 4 tons of suspended solids, 40 kg copper, 7 kg organotin and 150 kg oil per year (CUWVO, 1991b).

Table 49 Average emissions per ship during maintenance activities (from: CUWVO, 1991b)

	Unit	Water blasting	Grit blasting	(Total)	Paint
Suspended Solids	kg	10	13	23	9
Copper	g	130	140	270	410
Organotin	g	10	30	40	60
Oil	g	150	890	1040	360

17.3 Data requirements for product type 21

The direct exposure compartments, which are introduced in the previous section, are summarised in Table 50

Table 50 Direct exposure compartments for product type 21.

Subtype	Products	Direct exposure compartments
21.1	Matrix and ablative coatings for fresh water	Fresh surface water, air (outdoors), soil, sewagewater treatment plant
21.2	Matrix and ablative coatings for marine waters	Marine surface water, air (outdoors), soil, sewagewater treatment plant
21.3	Selfpolishing coatings for marine waters	Marine surface water, air (outdoors), soil, sewagewater treatment plant

Guidance for demanding test data

Potential data requirements for products released to the individual environmental compartments are discussed in Part 1. However, from the formulation and application some remarks for applying these generic data requirements can be stated.

Antifouling biocides have caused a specific environmental problem. The antifouling paints containing tributyltin (TBT) were introduced in the mid-1960s, and had become widespread in use in the 1980s (Gibbs & Bryan, 1994). As a consequence, leaching of TBT resulted in relatively high concentrations, in particularly near marinas. In the 1970s, it appeared that the females of certain gastropod (snail) species exhibited masculine morphological features, which were later recognised to be due to even very low levels of TBT. The term 'imposex' has been applied for these symptoms, which include masculinisation in the form of penis development, and vas deferens and oviducal convolution. Since 1990, imposex has been studied in many species world wide and are found to appear in neogastropod species. It is already induced at very low levels of approximately 1 $ng.l^{-1}$, and the degree of development is dose-controlled. As a result of imposex, females are no longer able to reproduce, and populations were recorded to have disappeared from near marina areas. In less seriously contaminated environment, elevations of the incidence of imposex are found, or the morphological changes are less pronounced. For demanding data requirements, it means that the specific toxic action tests (biomarkers) are especially important.

Anti-fouling biocides are known to be persistent in the environment (Bruchmann, 1995), and therefore chronic toxicity test data are relevant, as well as extensive biodegradation and fate testing.

To assess the environmental release, a leaching rate (leaching from paint matrix to surface water) has to be established (Council of Europe, 1994a). Because of the differences in leaching processes, different leaching tests are required for matrix-and ablative coatings (diffusive process) and selfpolishing coatings (hydrolysis of matrix). Leaching tests are described in Table 51.

Table 51 *Potential data requirements (additional to the core data set) for the estimation of emissions of biocides from matrix and ablative type coatings in fresh water*

Coating type	Potential data requirements, additional to annex III	Benefits/ rationale	Compatibility	Feasibility
Matrix, ablative	Maximum leaching (emission) rate (e.g. maximum emission during 1day) as function of pH, S, T, size of ship	Enables 'worst case' risk evaluation	- Current risk evaluation models use average leaching rate	- Operational definition of 'maximum' required: a.o. standardised test available
	Average leaching rate over relevant time span (e.g. 1 year) as function of pH	Required for risk evaluation	+ Current risk evaluation models use average leaching rate	+ Test guidelines available from Cu and TBT
Selfpolishing	Erosion rate of coating as function of pH, S, T, size of ship	Required for emission assessment for selfpolishing coatings	+ Basis for calculation of average emission rate, compatible with current risk evaluation models	+/- Erosion rates can be calculated. Standardised test guidelines avaulable
	Concentration of matrix-bound biocide in coating	Required for emission assessment for selfpolishing coatings	+ Basis for calculation of average emission rate, compatible with current risk evaluation models	+

Leaching rates can be determined by inserting a painted small panel into a small volume of water, and measuring the concentration of biocides in the water. The panels may be rotated (more relevant for polishing coatings). As an alternative for chemical analysis of the water, bioassays may be used to accellerate leaching (Furtado & Fletcher, 1987).

An ISO Draft guideline for determining the leaching rate of antifouling biocides, based on a painted rotating cylinder exposed in artificial seawater, is available (ISO 15181, part 1). Specific parts for analysis of copper (part2) and tin-based biocides (part3) are published. Additionally, an ASTM test guideline for determining the leaching of organotin compounds to seawater is available (rotor-apparatus) (ASTM D5108-90). For other active ingredients than organo-tin or copper no standardised leaching tests are available. At this moment, a proposal for modification of the ASTM test for copper compounds has been proposed to IMO. Furthermore, mass-balance based calculation methods for average leaching rates are being developed (Schablowski, pers. comm.). The leaching rate is strongly dependant on environmental factors such as pH, salinity (S) and temperature (T). Furthermore, it depends on the sailing speed and the size of the ship.

It has to be kept in mind that self-polishing coatings can contain additional biocides (next to the matrix bound TBT), for which a specific leaching rate can be required.

The available exposure assessment models (see Appendix B) need a leaching rate next to the base set data. The leaching rate is included in the additional data that is proposed in this report.

18. Product type 22: Embalming and taxidermist fluids

18.1 Introduction

Embalming is the (temporary) preservation of a human corpse. It is performed for three main reasons:
- Public health concern: Human remains offer an ideal environment for microbial growth (disinfection);
- Retard decomposition (preserve the body), to allow the body to be burried at other places than the place of death (preservation);
- Restore the body to an acceptable physical appearance (restoration).

During embalming, the body is washed and disinfected thoroughly (disinfecting soap). Then, the embalming chemicals are injected into the body through one or more accessible arteries, while body fluids are drained through corresponding veins. The chemicals kill bacteria, and change the physical structure of the body proteins (cross-linkages), to ensure preservation. Surface embalming is performed on areas that cannot be reached by arterial injection. Furthermore, cavity fluids are used for cavity embalming (e.g., thorax).

The main biocide and fixative is formaline (37% formaldehyde). Other embalming chemicals with biocidal properties are isopropylalcohol, liquefied phenol, castor oil (phorbyol), DL-camphor ('spirit of camphor') and glyoxal (oxaldehyde) (based on information of Mortech Manufacturing Co.; National Funeral Directors Association; University of California; Frigid Fluid Company).

Thanatopraxis is the temporary preservation of a human corpse. The objective is to obtain short-term preservation, for transport or presentation objectives. As with embalming, a fluid is injected in the body, while blood is removed. The fluid is similar to embalming fluids, but the concentration of formalin is much lower.

Taxidermy includes all methods of reproducing a life-like three dimensional representation of an animal for permanent display. In some cases, the actual skin is preserved and mounted over an artificial armature. Biocides and other chemicals are used to preserve the skin and make it appear life-like (Based on information of WASCO Manufacturing Inc.).

18.2 Release estimation

Embalming is performed in mortuaries, crematoria, hospitals, universities and research institutions. For mortuaries and crematoria, small scale embalming units are available; for hospitals embalming laboratories are available. During embalming (see Figure 38), embalming fluids which contain biocides will be emitted to the sewer system (sewage water treatment plant). During the process, emissions to the indoors air will occur, as volatile organic chemicals (such as formaldehyde) are used. When the embalmed body is cremated, emissions to the (outdoors) air can occur. However, as most embalming biocides are organic, non-halogenated chemicals, no significant emissions are expected. In the case chlorinated chemicals are used, hazardous degradation products may occur. When embalmed bodies are buried, release of chemicals to the soil, and subsequently ground water, can be expected.

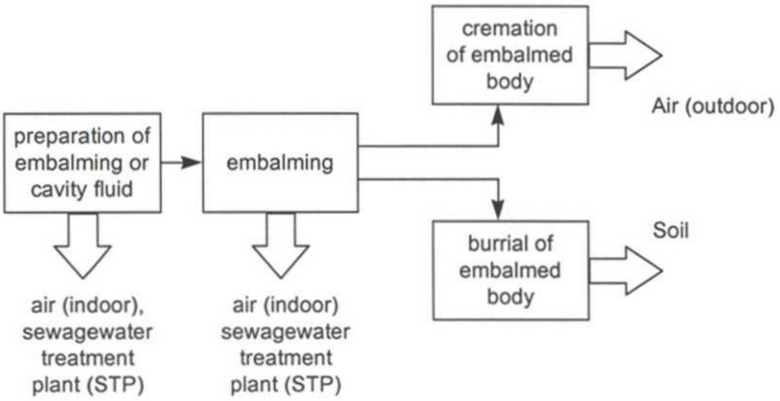

Figure 38 Environmental release of biocides used for embalming.

Taxidermy is mostly performed by individuals (hobby). This causes the discharge of chemicals to be very diffusive, and emitted to the sewer. Emissions to the (indoors) air may be expected. However, very little is known regarding the uses of chemicals and subsequent environmental emissions with respect to taxidermy. Preserved specimens are displayed in private houses, restaurants, museums, etc. They can be expected to end up as municipal waste.

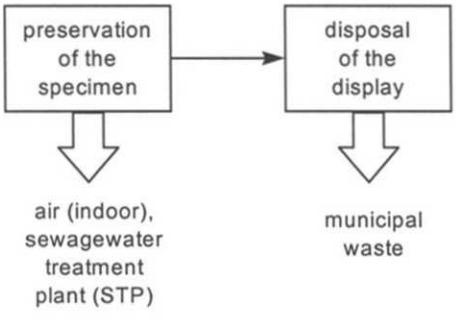

Figure 39 Environmental release of biocides used in taxidermy

18.3 Data requirements for product type 22

The direct exposure compartments, which were introduced in the previous section, are summarised in Table 52.

Table 52 Direct exposure compartments for product type 22.

Subtype	Products	Direct exposure compartments
22.1	Embalming chemicals	Air (outdoors, indoors) Soil Sewagewater treatment plant
22.2	Taxidermy chemicals	Air (indoors) Sewagewater treatment plant

Guidance for demanding test data

Potential data requirements for products released to the environmental compartments air, soil and a sewagewater treatment plant are discussed in Part 1.

From the generic data requirements, especially the leaching test to ground water (III.2) seems relevant for this product type.

No emission or exposure scenarios are available for this product type (Appendix B).

19. Product type 23: Control of other vertebrates

19.1 Introduction

This product type includes, according to the directive, "Products used for the control of vermin". Product type 23 is excepted from mutual recognition by the member states.

This product type shows a large similarity with rodenticides (product type 14), 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 vole, whereas this product type is aimed at all other groups of vertebrate pests. The most important non-rodent pests are probably rabbits and hares (order: *Lagomorpha*).

The data requirements for this product type are derived from the data requirements for rodenticides.

19.2 Release estimation

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 (Table 53). The table is based on chapter 15 (non-agricultural pesticides).

Table 53 *Direct exposure compartments for vertebrate control products, as function of the application technique and application site (location).*

Application technique	Outdoors	Animal housings
Fumigation/ gassing	air (outdoors) soil	-
Wet surface application	-	-
Baits	soil fresh surface water	no direct exposure compartments
Skin application	-	-
Powders application	-	-
Others	-	-

19.3 Data requirements for product type 23

The direct exposure compartments, which are introduced in the previous section, are summarised in Table 54.

Table 54 Direct exposure compartments for product type 23.

Subtype	Products	Direct exposure compartments
23.1	Fumigants, used outdoors	Air (outdoors), soil
23.2	Baits, used outdoors	Soil, fresh surface water
23.3	Baits, used in animal housings	No direct exposure compartments

Guidance for demanding test data
Potential data requirements for products released to the individual environmental compartments are discussed in Part 1.

For bait formulations, the same holds true as stated earlier for non-agricultural pesticides. A weathering test for baits (that are used outdoors) is important, as well as a palatability test for mammals and birds. This is indicated with the asterix (*) at data items I/II.5 and III.10.

No emission or exposure scenarios are available for this product type (Appendix B).

20. Summary: Data requirements for biocidal product types

In the previous chapters, the direct exposure compartments were discussed. They are summarised in Table 55 to Table 58.

Table 55 Direct exposure compartments for Maingroup 1: Disinfectants. '+' = relevant; '-' = not relevant.

Product type	**Products**	**Fresh surface water**	**Marine surface water**	**Soil**	**Air (outdoor)**	**STP**
1.1	Suntan products	+	+	-	-	+
1.2	All other biocidal human hygiene products	-	-	-	-	+
2.1	Sewage water disinfection	+	+	-	+	-
2.2	Soil disinfection	+	-	+	+	-
2.3	Disinfection of infectious waste, medical instruments, hospital rooms, human accommodations, air conditioners, laundry	-	-	-	-	+
2.4	Disinfection of chemical closets	+	+	-	-	+
2.5	Swimming pool disinfection	-	-	-	+	+
3.1	Disinfection of farm buildings, closed spaces	+	-	+	-	+
3.2	Disinfection of farm-buildings, outdoors	+	-	+	+	-
3.3	Disinfection for veterinary hygiene on non-farm buildings, in closed spaces	-	-	-	-	+
3.4	Disinfection for veterinary hygiene on non-farm buildings, outdoors	+	-	-	+	+
3.5	Fish farming (aquaculture) disinfection	+	+	-	+	+
4.1	Disinfection of surfaces in food and feed industry	+	-	-	-	+
4.2	Aseptic packaging in food and feed industry	-	-	-	-	-
5	Drinking water disinfection	+	+	+	+	+

Table 56 Direct exposure compartments for Maingroup 2: Preservatives. '+' = relevant; '-' = not relevant.

Product type	Products	Fresh surface water	Marine surface water	Soil	Air (outdoor)	STP
6.1	Preservation of canned fluid used in public buildings	-	-	-	-	+
6.2	Preservation of canned fluid used in households	-	-	-	-	+
6.3	Preservation of canned fluid used in industrial processes	-	-	-	-	+
6.4	Preservation of canned fluid used for agricultural purposes	+	-	+	-	+
7	Film preservation	+	-	+	-	+
8.1	Wood preservation, GK 1 and 2	+	-	+	+	+
8.2	Wood preservation, GK 3 and 4	+	-	+	+	+
8.3	Wood preservation, GK5	-	+	+	+	+
8.4	Wood curation, pills and injection	-	-	-	-	+
8.5	Wood curation, brushing and spraying	-	-	-	-	+
8.6	Wood curation, fumigation	-	-	-	+	+
9	Fibre, leather, rubber, and polymerised materials preservatives	+	-	+	-	+
10.1	Building materials preservation (preventive)	+	-	+	-	-
10.2	Building materials preservation (curation)	+	-	+	+	-
11.1	Biocides in once-through cooling systems	+	+	-	-	-
11.2	Biocides in open recirculating cooling systems	+	+	+	+	+
11.3	Biocides in closed recirculating cooling systems	+	+	-	-	+
12.1	Slimicides in paper industry	+	+	-	-	+
12.2	Slimicides for secondary oil recovery	-	+	-	-	-
12.3	Other slimicides	-	-	-	-	+
13	Metalworking-fluid preservation	-	-	-	-	+

Table 57 Direct exposure compartments for Maingroup 3: Pest control. '+' = relevant; '-' = not relevant.

Product type	Products	Fresh surface water	Marine surface water	Soil	Air (outdoor)	STP
14-19.1	Fumigation products used outdoors	-	-	+	+	-
14-19.2	Fumigation products for indoors-use, products used on skin (indoors)	-	-	-	+	-
14-19.3	Pest control products for wet surface application, powders, and other products used *outdoors*	+	-	+	+	-
14-19.4	Pest control products for wet surface application, powders and other products used in *closed spaces*	-	-	-	-	+
14-19.5	Pest control products for wet surface application, powders and other products used in *animal housings*	-	-	+	-	+
14-19.6	Baits used outdoors	+	-	+	-	-
14-19.7	Baits used in sewer systems	-	-	-	-	+
14-19.8	Baits used in closed spaces and animal housings	-	-	-	-	-
14-19.9	Pest control products used on skin (outdoors)	-	-	-	+	-

Table 58 Direct exposure compartments for Maingroup 4: Other biocidal products. '+' = relevant; '-' = not relevant.

Product type	Products	Fresh surface water	Marine surface water	Soil	Air (outdoor)	STP
20	See product types 2,4, 14, 18					
21.1	Antifoulings in matrix and ablative coatings for fresh water	+	-	+	+	+
21.2	Antifoulings in matrix and ablative coatings for marine waters	-	+	+	+	+
21.3	Antifoulings in selfpolishing coatings for marine waters	-	+	+	+	+
22.1	Embalming chemicals	-	-	+	+	+
22.2	Taxidermy chemicals	-	-	-	-	+
23.1	Fumigants for control of other vertebrates, used outdoors	-	-	+	+	-
23.2	Baits for control of other vertebrates, used outdoors	+	-	+	-	-
23.3	Baits for control of other vertebrates, used in animal housings	-	-	-	-	-

The data which can be required to improve a risk assessment for each of the compartments fresh surface water, marine surface water, soil, air and a sewagewater treatment plant (in comparison to a risk assessment based upon data from the common core data set) is listed in Part 1, and summarised in Appendix I of this report. However, these lists include all data which could be demanded. Before actually demanding the data by including it into Annex III of the directive, a discussion between competent authorities and industry should take place, based on the argument listed in Part 1 and the life cycles described in this report.

However, as input for this discussion, some guidance on interpreting the "long lists" can be given on the basis of the life cycle. Notes of guidance were introduced in each chapter of this report, and they are summarised in Table 59 to Table 62

Table 59 Guidance for demanding data requirements; product types 1-5.

Test data	Product (sub-) type														
	1.1	1.2	2.1	2.2	2.3	2.4	2.5	3.1	3.2	3.3	3.4	3.5	4.1	4.2	5
I.1	+	.	+	+	.	+	.	+	+	.	+	+	.	.	+
I.2	+	.	+	+	.	+	.	+	+	.	+	+	.	.	+
I.3	(+)	.	(+)	(+)	.	(+)	.	+	+	.	+	(+)	.	.	(+)
I.4	-	.	-	-	.	-	.	-	-	.	-	-	.	.	-
I.5	+	.	(+)	(+)	.	(+)	.	+	+	.	+	(+)	.	.	+!
I.6	(+)	.	+	+	.	+	.	+	+	.	+	+	.	.	+
I.7	+	.	+	+	.	+	.	+	+	.	+	+	.	.	+
I/II.1	+*	.	+*	+*	.	+*	.	+*	+*	.	+*	+*	.	.	+*
I/II.2	+*	.	+*	+*	.	+*	.	+*	+*	.	+*	+*	.	.	+*
I/II.3	(+)	.	+*	+*	.	+*	.	+*	+*	.	+*	+*	.	.	+*
I/II.4	(+)	.	+!	+!	.	+!	.	+*	+*	.	+*	+!	.	.	+!
I/II.5	+*	.	+*	+*	.	+*	.	+*	+*	.	+*	+*	.	.	+*
II.1	+	.	+	.	.	+	.	.	.	.	.	+	.	.	+
II.2	+	.	+	.	.	+	.	.	.	.	.	+	.	.	+
II.3	(+)	.	(+)	.	.	(+)	.	.	.	.	.	(+)	.	.	(+)
II.4	-	.	-	.	.	-	.	.	.	.	.	-	.	.	+
II.5	+	.	+	.	.	+	.	.	.	.	.	+	.	.	+
II.6	+	.	+	.	.	+	.	.	.	.	.	+	.	.	+
II.7	+	.	(+)	.	.	(+)	.	.	.	.	.	(+)	.	.	+!
II.8	(+)	.	+	.	.	+	.	.	.	.	.	+	.	.	+
III.1	.	.	.	+	.	.	.	+	+	.	.	.	.	.	+
III.2	.	.	.	+	.	.	.	+	+	.	.	.	.	.	+
III.3	.	.	.	(+)	.	.	.	+	+	.	.	.	.	.	(+)
III.4	.	.	.	-	.	.	.	-	-	.	.	.	.	.	-
III.5	.	.	.	+	.	.	.	+	+	.	.	.	.	.	+
III.6	.	.	.	(+)	.	.	.	+	+	.	.	.	.	.	+
III.7	.	.	.	+	.	.	.	+	+	.	.	.	.	.	+
III.8	.	.	.	+	.	.	.	+	+	.	.	.	.	.	+
III.9	.	.	.	+	.	.	.	+	+	.	.	.	.	.	+
III.10	.	.	.	+	.	.	.	+	+	.	.	.	.	.	+
IV.1	+!	+!	.	.	+!	+!	+!	+!	.	+	+	+!	+!	.	+!
IV.2	+!	+!	.	.	+!	+!	+!	+!	.	+	+	+!	+!	.	+!
V.1	.	.	+	+	.	.	+	.	+	.	+	+˙	.	.	+
V.2	.	.	+	+	.	.	+	.	+	.	+	+˙	.	.	+
V.3	.	.	+	+	.	.	+	.	+	.	+	+˙	.	.	+

-	not relevant
(+)	could be demanded, but considered less relevant
+	could be demanded
+!	could be demanded, and is considered relevant
+*	could be demanded under specific conditions (development of criteria required)

Table 60 Guidance for demanding data requirements; product types 6-10.

Test	**Product (sub-) type**													
data	**6.1**	**6.2**	**6.3**	**6.4**	**7**	**8.1**	**8.2**	**8.3**	**8.4**	**8.5**	**8.6**	**9**	**10.1**	**10.2**
I.1	.	.	.	+	+	+	+	.	.	.	.	+	+	+
I.2	.	.	.	+	+	+	+	.	.	.	.	+	+	+
I.3	.	.	.	+	+	+	+	.	.	.	.	+	+	+
I.4	.	.	.	+	+!	(+)	+!	.	.	.	.	+	+!	-
I.5	.	.	.	+	+*	+	+	.	.	.	.	+	+	+
I.6	.	.	.	+	+	+	+	.	.	.	.	+	+	+
I.7	.	.	.	+	+	+	+	.	.	.	.	+	+	+
I/II.1	.	.	.	+	+*	+*	+*	+*	.	.	.	+*	+*	+*
I/II.2	.	.	.	+	+*	+*	+*	+*	.	.	.	+*	+*	+*
I/II.3	.	.	.	+	+*	+*	+*	+*	.	.	.	+*	+*	+*
I/II.4	.	.	.	+	+*	+*	+*	+*	.	.	.	+*	+*	+*
I/II.5	.	.	.	+	+*	+*	+*	+*	.	.	.	+*	+*	+*
II.1	.	.	.	.	.	.	.	+	.	.	.	.	.	.
II.2	.	.	.	.	.	.	.	+	.	.	.	.	.	.
II.3	.	.	.	.	.	.	.	+	.	.	.	.	.	.
II.4	.	.	.	.	.	.	.	+!	.	.	.	.	.	.
II.5	.	.	.	.	.	.	.	+	.	.	.	.	.	.
II.6	.	.	.	.	.	.	.	+	.	.	.	.	.	.
II.7	.	.	.	.	.	.	.	+	.	.	.	.	.	.
II.8	.	.	.	.	.	.	.	+	.	.	.	.	.	.
III.1	.	.	.	+	+	+	+	+	.	.	.	+	+	+
III.2	.	.	.	+	+	+	+	+	.	.	.	+	+	+
III.3	.	.	.	+	+	+	+	+	.	.	.	+	+	+
III.4	.	.	.	+	+*	+	+	+	.	.	.	+	+!	-
III.5	.	.	.	+	+	+	+	+	.	.	.	+	+	+
III.6	.	.	.	+	+*	+	+	+	.	.	.	+	+	+
III.7	.	.	.	+	+	+	+	+	.	.	.	+	+	+
III.8	.	.	.	+	+	+	+	+	.	.	.	+	+	+
III.9	.	.	.	+	+	+	+	+	.	.	.	+	+	+
III.10	.	.	.	+	+	+	+	+	.	.	.	+	+	+
IV.1	+	+	+	+	+!	+!	+!	+!	+!	+!	+!	+!	.	.
IV.2	+	+	+	+	+!	+!	+!	+!	+!	+!	+!	+!	.	.
V.1	.	.	.	.	.	+	+	+	.	.	+	.	.	+
V.2	.	.	.	.	.	+	+	+	.	.	+	.	.	+
V.3	.	.	.	.	.	+	+	+	.	.	+	.	.	+

-	not relevant
(+)	could be demanded, but considered less relevant
+	could be demanded
+!	could be demanded, and is considered relevant
+*	could be demanded under specific conditions (development of criteria required)

Table 61 Guidance for demanding data requirements; product types 11-19.

Test	**Product (sub-) type**															
data	**11.1**	**11.2**	**11.3**	**12.1**	**12.2**	**12.3**	**13**	**14-19.1**	**14-19.2**	**14-19.3**	**14-19.4**	**14-19.5**	**14-19.6**	**14-19.7**	**14-19.8**	**14-19.9**
I.1	+	+	+	+	.	.	.	.	.	+	.	.	+	.	.	.
I.2	+	+	+	+	.	.	.	.	.	+	.	.	+	.	.	.
I.3	(+)	+	+	+	.	.	.	.	.	+	.	.	+	.	.	.
I.4	-	-	-	-	.	.	.	.	.	-*	.	.	-*	.	.	.
I.5	(+)	+	+	+	.	.	.	.	.	+	.	.	+	.	.	.
I.6	+	+	+	+	.	.	.	.	.	+	.	.	+	.	.	.
I.7	+	+	+	+	.	.	.	.	.	+	.	.	+	.	.	.
I/II.1	+*	+*	+*	+*	+*	.	.	.	.	+*	.	.	+*	.	.	.
I/II.2	+*	+*	+*	+*	+*	.	.	.	.	+*	.	.	+*	.	.	.
I/II.3	+*	+*	+*	+*	+*	.	.	.	.	+*	.	.	+*	.	.	.
I/II.4	+*	+*	+*	+*	+*	.	.	.	.	+*	.	.	+*	.	.	.
I/II.5	+*	+*	+*	+*	+*	.	.	.	.	+*	.	.	+*	.	.	.
II.1	+	+	+	+	+	.	.	.	.	.	.	.	.	.	.	.
II.2	+	+	+	+	+	.	.	.	.	.	.	.	.	.	.	.
II.3	(+)	+	+	+	+	.	.	.	.	.	.	.	.	.	.	.
II.4	-	-	-	-	-	.	.	.	.	.	.	.	.	.	.	.
II.5	+	+	+	+	+	.	.	.	.	.	.	.	.	.	.	.
II.6	+	+	+	+	+	.	.	.	.	.	.	.	.	.	.	.
II.7	(+)	+	+	+	+	.	.	.	.	.	.	.	.	.	.	.
II.8	+	+	+	+	+	.	.	.	.	.	.	.	.	.	.	.
III.1	.	+	.	.	.	.	.	.	+	+	.	+	+	.	.	.
III.2	.	+	.	.	.	.	.	.	+	+	.	+	+	.	.	.
III.3	.	+	.	.	.	.	.	.	+	+	.	+	+	.	.	.
III.4	.	-	.	.	.	.	.	.	-*	-*	.	-*	-*	.	.	.
III.5	.	+	.	.	.	.	.	.	+	+	.	+	+	.	.	.
III.6	.	+	.	.	.	.	.	.	+	+	.	+	+	.	.	.
III.7	.	+	.	.	.	.	.	.	+	+	.	+	+	.	.	.
III.8	.	+	.	.	.	.	.	.	+	+	.	+	+	.	.	.
III.9	.	+	.	.	.	.	.	.	+	+	.	+	+	.	.	.
III.10	.	+	.	.	.	.	.	.	+	+	.	+	+*	.	.	.
IV.1	.	(+)	(+)	(+)	.	(+)	(+)	.	.	.	+	+	.	+	.	.
IV.2	.	+!	+!	+!	.	+!	+!	.	.	.	+	+	.	+	.	.
IV.3	.	+!	+!	+!	.	+!	+!	.	.	.	+	+	.	+	.	.
V.1	.	+	.	.	.	.	.	+	.	+	.	.	.	.	.	+
V.2	.	+	.	.	.	.	.	+	.	+	.	.	.	.	.	+
V.3	.	+	.	.	.	.	.	+	.	+	.	.	.	.	.	+

-	not relevant
(+)	could be demanded, but considered less relevant
+	could be demanded
+!	could be demanded, and is considered relevant
+*	could be demanded under specific conditions (development of criteria required)

Table 62 Guidance for demanding data requirements; product types 20-23.

Test data	Product (sub-) type								
	20	21.1	21.2	21.3	22.1	22.2	23.1	23.2	23.3
I.1		+	.	.	.	.	.	+	.
I.2		+	.	.	.	.	.	+	.
I.3		+	.	.	.	.	.	+	.
I.4		+!	.	.	.	.	.	+*	.
I.5		+	.	.	.	.	.	+	.
I.6		+	.	.	.	.	.	+	.
I.7		+	.	.	.	.	.	+	.
I/II.1		+*	+*	+*	.	.	.	+	.
I/II.2		+*	+*	+*	.	.	.	+	.
I/II.3		+!	+!	+!	.	.	.	+	.
I/II.4		+*	+*	+*	.	.	.	+	.
I/II.5		+*	+*	+*	.	.	.	+*	.
II.1		.	+	+	.	.	.	.	.
II.2		.	+	+	.	.	.	.	.
II.3		.	+	+	.	.	.	.	.
II.4		.	+!	+!	.	.	.	.	.
II.5		.	+!	+!	.	.	.	.	.
II.6		.	+	+	.	.	.	.	.
II.7		.	+	+	.	.	.	.	.
II.8		.	+	+	.	.	.	.	.
III.1		+	+	+	+	.	+	+	.
III.2		+	+	+	+!	.	+	+	.
III.3		+	+	+	+	.	+	+	.
III.4		-	-	-	-	.	-	+*	.
III.5		+	+	+	+	.	+	+	.
III.6		+	+	+	+	.	+	+	.
III.7		+	+	+	+	.	+	+	.
III.8		+	+	+	+	.	+	+	.
III.9		+	+	+	+	.	+	+	.
III.10		+	+	+	+	.	+	+	.
IV.1		+!	+!	+!	+!	+!	.	.	.
IV.2		+!	+!	+!	+!	+!	.	.	.
V.1		+	+	+	+	.	+	.	.
V.2		+	+	+	+	.	+	.	.
V.3		+	+	+	+	.	+	.	.

-	not relevant
(+)	could be demanded, but considered less relevant
+	could be demanded
+!	could be demanded, and is considered relevant
+*	could be demanded under specific conditions (development of criteria required)

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Appendix A: Generic data requirements for biocidal products

Tabel A.1 Potential test data for Annex III of the Directive (from: BIOEXPO, Part 1)

Compartment	Nr.	Potential tests for Annex III
Fresh surface water (incl. sediments)	I.1	Die-away biodegradation test with specific chemical analyses or using a radiolabel at environmentally realistic biocide concentrations (fresh water)
	I.2	Aerobic/anaerobic biodegradation in freshwater sediment/water systems, with specific chemical analyses or using a ^{14}C radiolabel.
	I.3	Biodegradation in fresh water microcosms or mesocosms, i.e. field simulation tests.
	I.4	Leaching rate (from treated material to fresh surface water)
	I.5	Chronic fresh water toxicity tests
	I.6	Fresh water mesocosm (semi-field scale) toxicity tests
	I.7	Toxicity test (fresh water) sediment-dwelling species
Fresh or marine surface water	I/II.1	Sediment-water partitioning coefficient (fresh or marine)
	I/II.2	Bioconcentration factor for other aquatic organisms than fish (fresh or marine)
	I/II.3	Specific toxic action tests (biomarkers) (fresh or marine)
	I/II.4	Toxicity test for hazardous degradation products (fresh or marine)
	I/II.5	Toxicity test for fish-eating predators (fresh or marine)
Marine water (incl. sediments)	II.1	Seawater die-away biodegradation test with specific chemical analyses or using a radiolabel at environmentally realistic biocide concentrations.
	II.2	Aerobic/anaerobic biodegradation in marine sediment/water systems, with specific chemical analyses or using a ^{14}C radiolabel.
	II.3	Biodegradation in marine microcosms, i.e. field simulation tests.
	II.4	Leaching rate (from treated material to marine surface water)
	II.5	Toxicity test for marine fish, algae, crustacean
	II.6	Toxicity test sediment-dwelling species (marine)
	II.7	Chronic marine toxicity tests
	II.8	Marine mesocosm (semi-field scale) toxicity tests
Soil (incl. groundwater)	III.1	Aerobic biodegradation in soil, using specific chemical analysis or a ^{14}C label
	III.2	Leaching rate (to ground water) in disturbed or undisturbed soil columns.
	III.3	Biodegradation and leaching rate (to ground water) in lysimeter studies
	III.4	Leaching rate (from treated material to soil)
	III.5	Acute toxicity tests for soil-dwelling species
	III.6	Chronic toxicity test for soil dwelling species
	III.7	Soil micro-organism community test
	III.8	Toxicity test for terrestrial plants
	III.9	Bioconcentration test in soil-dwelling animals and terrestrial plants
	III.10	Toxicity test for worm-eating predators
STP	IV.1	Continuous activated sludge test
	IV.2	Inhibition of activity of micro-organisms in STP
Air	V.1	Photodegradation rate and degradation rate by OH radicals in air
	V.2	Evaporation rate (from treated material to air)
	V.3	Acute and chronic toxicity for exposure by air

Appendix B: Emission and exposure scenarios for biocidal products

In this appendix, existing emission scenarios and exposure scenarios (and models) are listed, and the data required as input for the scenario or model is listed. The data that is included in the base set (Annex II of the Directive), is not listed seperately.

Product type	Description model	Required test data	Ref.
2 (disinfection of accomodations)	Local exposure scenario for inclusion in Dutch USES model. Estimates concentration in receiving water from production/ use characteristics and product characteristics	base set + percentage removal in a STP	3
2 (disinfectants in swimming pools)	Local exposure scenario for inclusion in Dutch USES model. Estimates concentration in receiving surface water, from production/ use characteristics and product characteristics	base set	5
2 (chemicals used in hospitals)	(draft) 'MATHCAD' scenario from German UBA. Calculates concentration in surface water from use and product characteristics	base set	9
3 (disinfection of animal housing facilities)	Exposure scenario for inclusion in Dutch USES model. Estimates concentration in sewage sludge and emission to air from production/ use characteristics (defaults) and product characteristics	base set	6
3 (disinfection of footware or animals' feet)	same as previous	base set	6
3 (disinfection of milk extraction systems)	same as previous	base set	6
3 (disinfection of means of transport)	same as previous	base set	6
3 (disinfection of hatcheries)	same as previous	base set	6
7 (film preservatives)	EC emission scenario document; losses during several life stages can be taken from tables	base set	4
7 (film preservatives)	'MATHCAD' scenario from German UBA. Spreadsheet version of EC emission scenario document (see above)	base set	9

Product type	Description model	Required test data	Ref.
12 (slimicides used in pulp, paper and board industry)	'MATHCAD' scenario from German UBA. Spreadsheet version of EC emission scenario document (see above)	base set	9
12 (slimicides used in paper and cardboard industry)	Local exposure scenario for inclusion in Dutch USES model. Estimates concentration in receiving water from production characteristics	base set	3
13 (metalworking fluids)	EC emission scenario document; estimates emission from the amount of biocide, production characteristics and product characteristics	base set + percentage removal in a STP	4
13 (metalworking fluids)	'MATHCAD' scenario from German UBA. Spreadsheet version of EC emission scenario document (see above)	base set + percentage removal in a STP	9
13 (preservatives in metal industry)	Local exposure scenario for inclusion in Dutch USES model. Estimates concentration in receiving water from production and product characteristics.	base set + percentage removal in a STP	3
14-19 (household products used for fogging)	Calculates emission to air for fogging of closed spaces from the amount used and product information	base set, fraction retention in goods, fraction disintegration	5
21 (antifoulings in Northsea)	Annual load of TBT, triazine and Cu calculated from leaching rate and number of ships; homogeneous distribution over North Sea assumed	base set + leaching rate	1
21 (antifoulings in port environment)	Concentration in port calculated from volume port and total leaching from ships (based on leaching rate); environmental processes degradation, refreshment and interaction with sediments taken into account	base set + leaching rate	2
21 (antifoulings in yacht-basin)	Comparable to previous model. Proposed for incorporation in Dutch USES model	base set + mean leaching rate of compounds	3

References used in the table:
(1) Isensee *et al.*, 1994; (2) Johnson & Luttik, 1995; (3) Luttik *et al.*, 1993; (4) EC, 1996; (5) Luttik *et al.*, 1995; (6) Montfoort *et al.*, 1996; (7) Hooftman *et al.*, 1995; (8) Bringezu, 1992; (9) UBA, 1996

Product type	Description model	Required test data	Ref.
8 (creosote impregnation, salt impregnation, drenching and dipping, remedial timber treatment)	Local exposure scenarios for inclusion in Dutch USES model. Estimate concentration in receiving water, concentration in air and loading of soil from production/ use characteristics and product characteristics	base set, fraction removal in STP, quantity preservative per unit of wood	3
8 (leaching from impregnated wood to surface water)	Local exposure scenario for inclusion in Dutch USES model. Calculates concentration at end of receiving waterway with box-model, from use characteristics and product characteristics	base set, mean leaching rate of compounds	3
8 (leaching from impregnated wood to soil and ground water)	Local exposure scenario for inclusion in Dutch USES model. Calculates concentration in soil and ground water, from use characteristics and product characteristics	base set, mean leaching rate over 1 year	5
8 (exposure of water to wood preservatives from bank revetment)	Box model to calculate concentrations in a model ditch and canal due to leaching of preservatives from bank revetment. Interaction with atmosphere, sediment, suspended solids and biota included.	base set, maximum and "average" leaching rate	7
8 (exposure of soil to wood preservatives)	Box model to calculate concentrations in soil due to direct contact with preserved wood (e.g., poles). Chemical and biological processes included.	base set, maximum leaching rate	7
8 (wood preservatives)	Considerations and example calculations for exposure of soil, water and ground water to wood preservatives applied in GK3 and 4	base set, leaching rate	8
9 (chemicals used in leather processing)	EC emission scenario document; estimates emisson from the amount of biocide and production characteristics	base set, degree of fixation	4
9 (chemicals used in leather processing)	'MATHCAD' scenario from German UBA. Spreadsheet version of EC emission scenario document (see above)	base set, degree of fixation	9
9 (chemicals used in textile finishing)	EC emission scenario document; estimates emisson from the amount of biocide and production characteristics	base set, degree of fixation (inluding chemical conversion)	4
9 (chemicals used in textile finishing)	'MATHCAD' scenario from German UBA. Spreadsheet version of EC emission scenario document (see above)	base set, degree of fixation (inluding chemical conversion)	9
9 (chemicals in textile industry)	Local exposure scenario for inclusion in Dutch USES model. Estimates concentration in receiving water from production and product characteristics	base set + degree of fixation + percentage removal in a STP	3
12 (slimicides used in pulp, paper and board industry)	EC emission scenario document; estimates emisson from the amount of biocide and production characteristics	base set	4