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Supplement to the methodology for risk evaluation of biocides

Emission scenario document for biocides used in paper coating and finishing
(Product type 6, 7 & 9).

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1. INTRODUCTION.

The purpose of this document is to provide a realistic scenario for the release into the environment of biocides used in coating and finishing of the paper and board industry.

Biocides may be employed in different ways in the paper industry. Biocides used for the preservation of pulp and other aqueous fluids in the paper manufacture (such as slimicides) can remain in the end product. Slimicides are not included in this scenario. Many of the biocides used in coating additives are used as preservatives that can be divided in product types 6 "in-can preservatives" and 7 "film preservatives". In-can preservatives must not degrade quickly since they are often used to treat a coating, solutions or slurries of coating binders, speciality additives or the complete coatings that are stored in a tank for a period of time. They extend the shelf life as they retard microbial growth, including bacteria, fungi, and molds. Typically, preservatives would be needed to preserve the following types of preparations involved in paper coating: filler slurry, starch slurry, cooked starch, protein slurry, cooked protein, latex binders, coating thickeners, coating lubricants and pigmented coatings (Dykstra, 1999).

Film preservatives are added to ensure bactericidal treatment of the paper. They are used to protect surfaces against the adverse influence of micro-organisms, such as biodeterioration by bacteria and coverage by fungi (Bioexpo, 1998)

Furthermore the fibres in the paper itself may be preserved from attack by treating the paper with biocides of product type 9 "Fibre, leather, rubber and polymerised material preservatives".

Paper is made from wood fibres or recycled fibres which consist of cellulose, hemicellulose and lignin. Before papermaking, wood is broken up into fibres (wood cells), the process is called pulping. Paper is a felted sheet formed on a fine screen from a water suspension of fibres and non-fibrous additives. Paperboard is made in much the same way as paper. The main difference is that paperboard is often multi-layered and of thickness greater than 0.3 mm. Distinction between paper and paperboard can also be made on the basis of their grammage (i.e. the weight in grams of one square meter of paper): 25 – 300 g.m⁻² for papers, 170 – 600 g.m⁻² for paperboards.

The paper industry produces a wide variety of products. Different classifications of paper products exist according to their applications or end-uses. One of them divides products in (EU, 1996):

1. printing and writing paper
2. tissue paper
3. paper for newspaper printing (newsprint)
4. board, cartons and packaging and wrapping paper (packaging).

2. MAIN PROCESSES.

Manufacture of paper and paperboard can be divided into two steps: pulp making and paper / paperboard production which is the step of interest in this scenario.

Papermaking operations generally consist of the following processes (figure 1):

- pulp stock preparation,
- wet-end operations: formation of paper sheet from wet pulp,
- dry-end operations: drying of paper products, application of surface sizing,
- coating (optional),
- calendering,
- finishing (winding for storage).

2.1. Pulp stock preparation.

Pulp stock is processed to obtain desired qualities, such as surface, opacity, strength, and feel, in the finished paper and paperboard products. Stock preparation processes include pulp mixing and dispersion, beating and refining, and the addition of wet-end additives (resins, waxes, clays, silicas, talc, inorganic / organic dyes and certain inorganic chemicals) used to create paper products with special properties or to facilitate the papermaking process. Softwood and hardwood pulp are frequently combined to produce paper or paperboard of desired finished properties. Beating and refining make the finished product stronger, more uniform, more dense, more opaque, and less porous (US-EPA, 1999; US-EPA, 1995).

2.2. Wet-end operations.

The processed pulp is converted into a paper product via a paper production machine, the most common of which is the Fourdrinier paper machine. The first two operations performed by this machine, sheet formation and pressing, are referred to as "wet-end" operations. Fibres in the form of a fibre slurry are distributed evenly onto a thin moving wire mesh ("the wire") through which excess water drains. Suction from a series of hydrofoils, vacuum boxes, and vacuum rolls extracts water from the formed sheet. This water, containing entrained fibres is captured and recycled after a series of thickening and cleaning steps. The continuous sheet is then pressed between a series of rollers to remove more water and compress the fibres (US-EPA, 1999; US-EPA, 1995).

2.3. Dry-end operations.

The remaining operations – drying, application of surface sizing, reeling, winding and application of surface treatments – are referred to as "dry-end" operations. They are commonly divided in four steps:

- pre-drying,
- sizing,
- post-drying,
- reeling.

Pre-drying

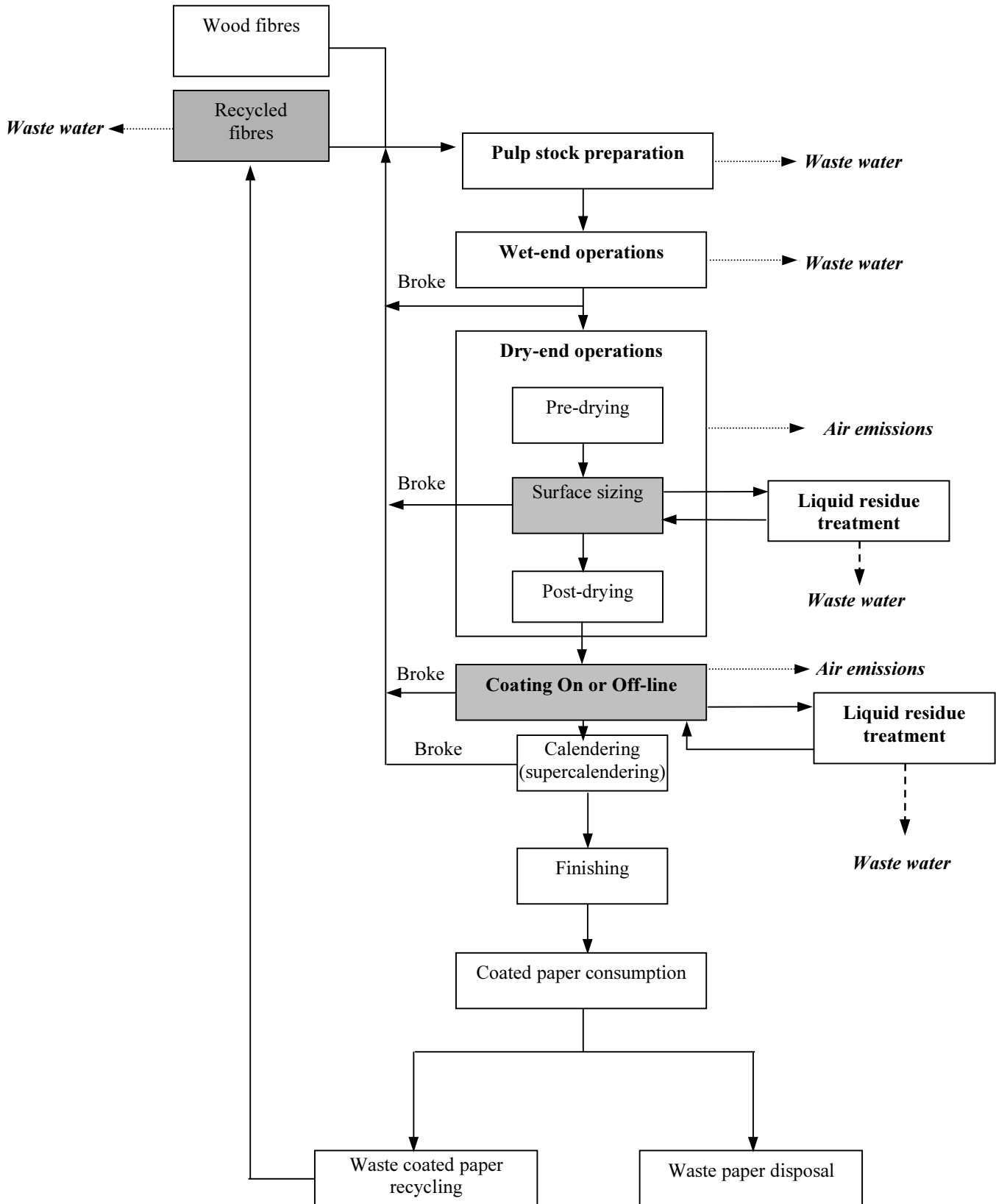
After pressing, the sheet still contains 50% of water. It enters a closed (which is the most common) or open drying section, where the paper fibres begin to bond together as steam heated rollers compress the sheets. The sheet is maintained against rollers by a heavy cotton felt or a drying fabric of cotton and synthetic fibres. The hot condensed water present in the drier cylinders is collected in order to send it back in form of steam in the process.

These rollers dry the paper from 40 - 50% to 5 - 10% wetness. The temperature during the process ranges from < 100°C up to 130 -140°C at a maximum (Personal communication Bayer, 2001).

Sizing and post-drying (optional)

This is the section of the machine where starches and other chemicals are applied to the surface of the paper by spraying, by dipping in the "size-press" or by transfer from a roll in the "metering size-press": a controlled amount of water based size mixture is added evenly to the paper sheet by first creating a uniform film thickness on the roll and then transferring the film onto the paper sheet in the nip of the "metering size-press". Surface sizing is mainly used for printing and writing papers and packaging grades made from recycled fibres.

Although surface sizing treatment is a form of paper coating to improve its surface properties, the term "coating" is usually reserved for the application of a pigmented slurry to the surface of the paper in order to improve its printability or for other specialist applications (IPPC, 2000).



■ Biocide application

⋯▶ Biocide release

Figure 1: Biocides application and releases during paper coating and finishing.

2.4. Coating.

For further finishing, surface treatments may be applied, to improve printing properties, gloss, colour, and opacity. Coating consists of applying a "sauce" made up of water, pigments (calcium carbonate, clay, talc...), binders and co-binders, and additives (insolubilizers, lubricants, foam control agents, colorants, optical brighteners, preservatives) on the surface of the sheet with roller, air knife, blade or bar. Biocides may be part of the "sauce" (Valette and de Choudens, 1992).

The application of coatings may be achieved on-line (lighter coatings) or off-line (heavy coatings) machine. The high-quality printing papers are coated several times. In such a case, there is a precoating performed on machine (sizing) and one coating, or more, performed off-line (after the paper machine). For boards, usually just one side is coated (COPACEL, 2000; Valette and de Choudens, 1992).

Off-line coating machines consist of an unwinder, one or more coating stations (coating application units), a drying section and a reel. The coated sheet is dried by a short steam-heated cylinder section, by infrared radiation, by hot air or combination of those. Dryers may be topped by a hood blowing hot air (IPPC, 2000; Valette and de Choudens, 1992).

The coating slurry is generally re-circulated through the system with constant filtering to remove fibres and other contamination in order to maintain the slurry quality.

Added chemicals may be applied to the surface by spraying or dipping (i.e. directly in the "sauce"). This is more controlled and involves only water for washing and cleaning, yet, this is possible only for a few applications. Liquid residues from coating can be treated separately in a precipitation step or by use of ultra-filtration (IPPC, 2000).

Most of the writing and printing papers are coated nowadays. Depending on grades of coated paper and boards, different amounts of coatings are applied, as shown in table 1. Biocides represent usually less than 1% of the sizing solution.

Table 1: Amount of coatings applied according to the different types of paper (values from IPPC, 2000).

Types of paper	Amount of coatings applied (g.m ⁻² per side)	Remarks
Art paper	> 20	3 or more coats per side
Machine-coated papers	18	Often double coat
Lightweight Coated (LWC) papers	5-12	
Folding boxboard and chromoboard	12-33	Precoat + topcoat

2.5 Calendering.

After drying, the paper sheet is passed through a series of polished, close-stacked metal rollers known as a "calender". The sheet is then pressed between heavy rolls in the calender that reduce the thickness of the paper and create a smooth surface. This is often the last operation carried out on a machine. Papers, to improve glossiness and smoothness can pass through supercalenders which have traditionally been off-line equipment but are now being installed also into the drying section of the paper machine itself, to save production costs.

2.6 Finishing (winding).

Finally the sheet is rolled onto a long reel, called a log and removed from the paper machine for intermediate storage. Reels of paper are then cut out and packed in reams of 500 sheets, or cut out in smaller reels adapted to further uses (COPACEL, 2000).

3. BIOCIDES.

Biocides used for paper preservation are: ascorbic acid, sodium-, potassium-, calcium- and magnesium ascorbates, benzoic acid, sodiumbenzoate, formic acid, hydrobenzoic acid ethylester (adduct of 70% benzylalcohol and 30% formaldéhyde), glutardialdehyde, 2-bromo-2-nitropropanediol (BNPD), thione, isothiazolinones, Bromohydroxy-acetophenone, dodecylguanidine hydrochloride (Bioexpo, 1998; Dykstra, 1999).

There is a lack of information about the quantity used.

Realistic values of biocides application are 0.1 to 4% in the paper mass (dry weight) (Baumann et al, 2000). For biocides applied for protection of the fibres (Pt 7: film preservation & Pt 9: fibre protection), a high fixation rate can be assumed for the substance to achieve a high efficacy. A realistic worst case estimation for the fixation rate on paper seems to be 80%. For in-can preservatives (Pt 6), the substance is not designed for fixation onto fibres and it can be assumed that no specific fixation occurs.

4. RELEASE ESTIMATION.

4.1. Production estimation.

There are 142 industrial sites of different size and 226 paper machines, in France, as shown in Table 2. The production for 1999 was 9.57×10^6 tonnes of paper (COPACEL, 2000). The production volumes per site, as determined in a survey in Germany (Böhm et al., 1997) is shown in table 3. Table 4 shows the annual production for each category of papers and boards in France and Europe.

The Technical Guidance Document (TGD) suggests a default value between 40 and 200 t.d⁻¹ for the production of tissue and between 100 and 1 000 t.d⁻¹ for newsprint, packaging and board and writing and printing paper if no other information is available (EU, 1996). The industrial activity can be up to 350 days per year, 24 hours per day (COPACEL, 2000). According to these values and Tables 2 and 3 an estimated "realistic worst case" value would be 500 t.d⁻¹ per site. It seems that half of the writing and printing production was coated (12.8×10^6 t/year for Europe) and half of the board production (COPACEL, 2000; IPPC, 2000).

Table 2: Representative distribution of production sites in France in 1994 (adapted from CTP/Ademe, 1996).

Size of facilities (CTP)	Production of paper (t/y)	Distribution of number of sites (%)
Small	< 5 000	18
Medium	5 000-15 000	9
	15 000-50 000	36
	50 000-100 000	15
Large	> 100 000	22

Table 3: Daily production volumes in Germany (Böhm et al., 1997)

Type of paper	Number of sites	Average production volume [t.d ⁻¹]
Newsprint	33	449
Printing and writing paper	14	66
Paper and cardboard for packaging	48	237
Paper for sanitary and domestic use (tissue paper)	16	222
Special and industrial paper	43	102
Overall paper and cardboard	117	329

Table 4: Paper and cardboard annual production (COPACEL, 2000).

	Annual production (10 ³ tonnes) in France (1999)	Annual production (10 ³ tonnes) in EU (1996)
Paper for graphic uses	4 339	34 843
Newsprint (paper for newspaper printing)	1 090	7 969
Printing and writing paper	3 249	26 874
Paper and cardboard for packaging and conditioning	4 388.4	27 243
Corrugated board	3 205.7	
Packaging paper and cardboard	423	
Flat cardboard	759.7	
Paper for sanitary and domestic use (tissue paper)	540	7 158
Special and industrial paper	302.6	
Total paper and cardboard	9 570	69 244

4.2. Water consumption.

The amount of water released in paper production depends on the grade of the paper produced and the nature of raw material (table 5).

Water consumption for coated paper is typically between 10 and 15 m³.t⁻¹ of paper.

About 1 – 1.5 m³.t⁻¹ of paper (10%) is usually evaporated in the dryer section of a machine and lost from the process.

Table 5: Water release per ton of paper produced for different types of paper (IPPC, 2000).

Type of paper	Water release (m ³ .t ⁻¹)
Printing/writing, uncoated	5-40
Printing/writing, coated	5-50
Paper board	0-20
Speciality paper	10-300
Tissue	10-50

In a survey performed in Germany (Böhm et al., 1997), covering 89% of the paper production in Germany, the above figures were confirmed. The overall mean for water release was 23.9 m³.t⁻¹.

By linking the water releases presented in table 5 with the daily paper production quantities presented in table 3, it can be estimated that the average water releases per production site are:

- approx. 2 500 - 25 000 m³.d⁻¹ for printing and writing paper,
- approx. 0 - 10 000 m³.d⁻¹ for paper board,
- approx. 2 000 - 10 000 m³.d⁻¹ for tissue paper,
- approx. 1 000 - 30 000 m³.d⁻¹ for speciality paper.

For a default risk assessment according to EU (1996), it is usually assumed that the waste water from industrial sites is released to a municipal sewage treatment plant (STP) and that the total effluent flow in the STP is 2 000 m³.d⁻¹. Given the figures above, it is evident that a higher flow of the waste water treated in the STP should be assumed. A provisional figure of 5 000 m³.d⁻¹ can be proposed.

It is recognised though that the trend is towards lowering the amounts of waste water released. The degree of closure of production processes is indeed rising (cf. section 4.3.3). The default value of 5 000 m³.d⁻¹ should therefore be revised periodically.

4.3. Releases.

4.3.1. Release distribution.

The input of biocides to the system together with other wet-end chemicals (e.g. starch, polyacryl amide), fillers (slurry of calcium carbonate) or reused fibres (recycled papers) has to be taken into account for the assessment of the mass flow of biocides. Papermaking generates also a number of solid waste residuals, such as coating residue and broke from finishing operations; broke may be re-pulped and returned to the stock preparation area (IPPC, 2000). Broke may be defined as any formed paper, from the beginning of the papermaking process to the finished product, that has been discarded anywhere in the process of manufacture (IPPC, 2000). Coating residues are generated when the coating slurry is cleaned before recirculation and when spent coating liquid is treated.

In general, the potential releases of chemical additives such as biocides are:

- to waste water at pulp stock preparation and wet-end operations (from coated broke) ; after wastewater treatment the biocides – as far as not biodegraded – can be released to surface water and end up in the sewage sludge ;
- to waste water in the case that spent coating slurry is discharged directly into the sewerage or biocides remain in the water at treatment of the spent liquid ;
- to exhaust air from the drying section of the paper machine and the coating machine respectively.

Soil may be affected via waste disposal (composting, use of paper sludge in agriculture, landfilling).

4.3.2. Release from on-line (size-pressing) and off-line coating.

Waste water: In both on-line and off-line coating, the potential release to waste water from size application is negligible. Such a release could occur in case of accidents in the paper chain. During normal operations one may assume that the release to waste water from coating is negligible.

Release from treatment of spent coating liquid or from cleaning of the coating equipment is possible.

Coating discharges can be divided into two main types of waste water (IPPC, 2000):

- Undiluted surplus coating (about 50 - 70% dry solids) from coating kitchen and coater station. In case of product changes and during breaks the system has to be washed (disperger, chests, pumps, piping, and coater station). Furthermore, sometimes not all of the coating can be completely used and the rest is washed as well. The concentrated discharge can be collected in tanks or mobile containers for solid waste disposal.
- Diluted coating components from washing water from tanks etc.
The dry solids content of dilute effluent is typically 2 - 4%. If they are discharged to the treatment plant sudden high organic loads have to be handled in the treatment (COD values > 10 000 mg/l up to 100 000 mg/l). The diluted spills are collected in tanks and pre-treated before discharge to the external waste water treatment plant.

No release scenario can yet be proposed.

Air emissions: air emissions consist mainly of water with little or no particulate matter emitted by the dryers after the coating steps. 1 to 1.5 m³ of water per tonne of paper is usually evaporated in the dryer section of a machine and lost from the process (IPPC, 2000).

4.3.3. Releases from "broke".

The amount of broke produced during papermaking is usually 5 to 20% of the machine capacity and can reach amounts of 50% of normal production (IPPC, 2000). Broke is reintroduced in the stock preparation.

The expected discharge of additives to waste water is directly related to the retention of the chemicals to the paper product (rate of fixation) and the degree of closure of the water circuit shown in table 6.

Table 6: Degree of closure of water system according to the type of paper (EU, 1996).

Type of paper	Degree of closure (%)
Printing and writing	40 – 70
Tissue	40 – 70
Newsprint	65 – 85
Packaging and board	> 95

In a survey performed in Germany (Böhm et al., 1997) and covering 70 sites, 4.2% reported degrees of closure of 1 – 49%, 17.1% reported degrees of closure of 50 – 80%, 15.7% reported degrees of 80 – 90% and 60% reported degrees of closure > 90%.

As indicated in EU (1996), the degree of closure will not affect the concentration of a substance in the waste water, it will determine the volume of water and therefore the total amount of substance emitted.

Note: this will not be true for slimicides, as higher concentrations in the system will be needed to retain efficacy for higher degrees of closure.

For assessment purposes, unless contrary information is available, it is suggested to use the average values of the ranges reported in table 6 in the risk assessment.

4.3.4. Release from paper recycling.

The recovery rate is the amount of paper and board recovered compared to the total consumption of paper and board. In the EU, this recovery rate is not homogeneous: indeed, according to COPACEL (2000), this rate was 40.7% and 70.2% in France and Germany respectively in 1997. The paper recycling rate, i.e. the fraction of recycled fibres used for paper production, is more homogeneous within EU.

Almost half (49.1% in France) of the fibres used for papermaking came from recycled paper and boards. The average recycling rate in the EU is approx. 50% (COPACEL, 2000).

Table 7 and table 8 present average percentages of recycled fibres used in the production of different types of paper in Germany and in France respectively.

Table 7: Fraction of recycled paper used in Germany in 1998 (VDP, 2000).

Types of paper	Use of recycled fibres (%)
All types	61
Printing and writing paper	37
Newsprint (paper for newspaper printing)	117
Board/Packaging	96
Paper for sanitary and domestic use (tissue paper)	69
Special and industrial paper	48

Table 8: Fraction of recycled paper used in France in 1998 (COPACEL, 2000)

Types of paper	Use of recycled fibres (%)
All types	53.8
Corrugated board	91.6
Flat cardboard	89.5
Newsprint (paper for newspaper printing)	58.3
Paper for sanitary and domestic use (tissue paper)	46.4
Special and industrial paper	33.8
Packaging paper and cardboard	32.9
Printing and writing paper	10.9

Some of the recycled paper and board is coated. During the re-pulping step, part of the solubilised coating, including biocides, may then be released. There are two main processes for recycling fibres: processes with exclusively cleaning and processes with cleaning and deinking. Most of the coated papers pass through cleaning (washing which releases substances to waste water) and deinking (flotation which produces a sludge which is dewatered and disposed of as a solid). The fraction of the recycled paper which will go to the deinking process is about 25 % in Germany (Böhm et al., 1997) and about 30% in France (Personal communication CTP, 2001). Up to 50% ink froth and rejects are dewatered separately in a centrifuge or wire press type equipment (IPPC, 2000; EU, 1996).

Contaminants and clusters are removed continuously during the operation by a dirt trap (e.g. screen plate) and are sent to a reject conveyor, in order to avoid the contaminants breaking

into small pieces or accumulating in the pulper. Normally the water for disintegration is totally re-circulated process water that comes as white water from the paper machine.

Waste water from a recovered fibre paper mill is mainly generated during cleaning steps. It consists of water from reject separation by screens and centrifugal cleaners, filtrates from washers, thickeners and sludge handling, and excess white water depending on the rate of recycling (IPPC, 2000).

The pH of the deinking water is generally alkaline, it ranges between 9.5 and 10.5 (Personal communication CTP, 2001). Moreover, the temperature during the deinking process is about 45°C. The hydraulic retention time (HRT) is high because the process works in a closed circuit. Finally, solid retention time (SRT) ranges between 1.5 and 8 hours. Based on hydrolysis studies with the substance, the fraction decomposed during deinking can be estimated.

No specific figures are available regarding release to waste water of biocides during the washing and/or deinking stage. However, the fixation rate is not the same for fibre preservatives and for coating preservatives (cf. section 3). For coating preservatives which are easily soluble substances, a default value for release during the washing and/or deinking stage of 100% can be assumed.

During primary on-site wastewater treatment, it can be assumed that 80 – 100% of easily soluble substances remain in waste water while 50 – 90% of poorly soluble substances are removed (IPPC, 2000 ; EU, 1996). If the fixation rate onto paper fibres during application is known, this value can be used as a default here as well.

EU (1996) suggests that the number of sites where recycling takes place is 10, i.e. each site processes 10% of the annual tonnage. Taken for the whole of the EU, the number of recycling sites seems to be grossly underestimated. For Germany alone, according to Böhm et al. (1997), 78 paper producers use recycled paper and there are 18 deinking installations. In France, there are 11 factories which have deinking installations.

It is therefore proposed for substances which are produced at a high tonnage and which are used throughout the EU to apply the so-called 10% rule. Calculations are performed for a densely populated area of 200 × 200 km with 20 millions inhabitants. It is assumed that 10% of the European production and use takes place within this region, i.e. 10% of the estimated emission is used as input for the region. Within the region, it can then be assumed that the size of the main local source of emissions into the local environment represents 10% of the total emissions within the region (fraction of main source $f = 0.1$). This would then be coherent with the results from Böhm et al. (1997).

For new substances or existing substances produced at low volumes and which are not used homogeneously through out the EU, it can be assumed in a first approach that the whole EU production volume is used within the region.

EU (1996) suggests that the number of working days is 250 d.y⁻¹. For Germany, according to Böhm et al. (1997) factories work in average 317 days per year. In France, according to CTP (Personal communication, 2001), the number of working days is about 350 d.y⁻¹. A figure of 320 d.y⁻¹ is proposed as a default value.

In principle, some biocides present in finished paper products may return via paper recycling, where the same biocide is applied again, thus accumulating on the long run, depending on removal rates at repulping as well as the fixation rate on fibres. This aspect is not yet taken into account in this document.

4.3.5. Releases due to other life-cycle stages.

Releases may occur during other life-cycle stages, e.g. the final use of paper or cardboard articles and the elimination of paper or cardboard articles.

A large part of the biocides remaining in the finished articles can be released to the environment during the service life of the paper or cardboard articles. For volatile substances, a total release to the atmosphere can be assumed. All of these releases will be diffuse and relevant only for a regional exposure assessment. No precise quantitative release estimations can be proposed for the time being.

Regarding waste elimination, a generic model for releases from landfills is under development and might be used once the model is available.

4.4. Waste water treatment.

Usual treatments of waste water from paper and board industries are:

- Primary treatment (physical and chemical)
- Secondary treatment (biological treatment)
- Anaerobic biological treatment
- Combined anaerobic-aerobic treatments (Valette and de Choudens, 1992)

Usually waste waters from paper and board industry require a separate pre-treatment in a physico-chemical plant. If waste waters are not treated before biological treatment, they may cause disturbances in the performance of the biological waste water treatment plant (suspended solids).

In recent years the membrane filtration technology has produced good results in coating colour recycling (IPPC, 2000).

4.5. Emission scenarios.

Release estimation is performed on a local scale. A release estimation model is presented below.

4.5.1. Release from drying sections after size-pressing and coating.

Releases in waste water from the coating steps are negligible, only the release to air is taken into account here.

No specific air estimation technique for paper coating has been developed yet. In the absence of the specific paper coating estimation, it is proposed to use the estimations derived for plastic coatings (BRE, 1998). For preservatives, the following release rates depending of the vapour pressure of the substance have been proposed for open processes:

Table 9: Estimated release fractions due to drying of the paper (adapted from BRE, 1998)

Fraction of release	Volatility
0.0025	High: 133 Pa at 100°C
0.0005	Medium: 13.3 Pa at 100°C
0.0001	Low: 1.3 Pa at 100°C

The division between the classes of high, medium and low volatility is arbitrary and each substance should if possible be assessed individually. The approximate ratio between high, medium and low volatility losses is 5:1:0.2 taking medium volatility as a standard (BRE, 1998).

An indicative method for estimating vapour pressures at 100°C is presented below.

A commonly used approach for the estimation of vapour pressure is by means of the Clausius Clapeyron equation. Provided that the latent heat of vaporisation is known, then the vapour pressure (P_T) at a given temperature T can be estimated from the known vapour pressure at a different temperature (e.g. 200°C) according to the expression:

$$\ln P_T = \ln P_{200} + \frac{L}{R} \left(\frac{1}{473} - \frac{1}{T} \right)$$

If R (the universal gas constant) is 8.31 J/(mol K) and L (latent heat) is taken as a nominal 100 kJ/mol, then the expression for vapour pressure P (measured in atmospheres) at 373 K (100°C) becomes simply:

$$\ln P_{100} = \ln P_{200} - 3.0$$

For more information, see the Handbook of Property Estimation Methods for Chemicals: Environmental and Health Sciences (Boethling & Mackay, 2000).

If information is available about stability of the substance at 100°C, it can be taken into account in the emission estimation.

Air emissions from drying sections may then be calculated using the following model.

Table 10: Emission scenario for calculating the releases from drying sections after size-pressing and coating

Variable/parameter (unit)	Symbol	Unit	Default	S/D/O/P
Input:				
Quantity of coated paper produced per day (cf. section 4.1, table 3)	Q_{paper}	t.d^{-1}		P
Quantity of active substance applied per ton of paper for each application step	Q_{active}	kg.t^{-1}		S
Evaporation rate (cf. table 9)	F_{evap}	-		S/P
Decomposition rate during drying	F_{decomp}	-	0	S
Output:				
Local emission of active substance to air for one treatment step	$E_{\text{local}_{\text{air}}}$	kg.d^{-1}		O

Model calculation:

$$E_{\text{local}_{\text{air}}} = Q_{\text{paper}} \times Q_{\text{active}} \times F_{\text{evap}} \times (1 - F_{\text{decomp}})$$

4.5.2. Release from "broke".

Broke is released from the paper machine in the stock preparation. The release depends then on the rate of fixation of the active substance and the degree of closure of the water system and may be calculated using the model below.

Table 11: Emission scenario for calculating the releases from "broke"

Variable/parameter (unit)	Symbol	Unit	Default	S/D/O/P
Input:				
Quantity of coated paper produced per day (cf. section 4.1)	Q_{paper}	t.d^{-1}		P
Quantity of active substance applied per ton of paper	Q_{active}	kg.t^{-1}		S
Degree of closure of the water system (cf. table 6)	F_{closure}	-		S/P
Fraction of coated broke produced compared to overall production	F_{broke}	-	0.2	S/D
Fixation rate (cf. section 3)	F_{fix}	-	0	S/D
Output:				
Local emission of active substance to waste water	$E_{\text{local}_{\text{water}}}$	kg.d^{-1}		O

Model calculation:

$$E_{\text{local water}} = Q_{\text{paper}} \times Q_{\text{active}} \times F_{\text{broke}} \times (1 - F_{\text{fix}}) \times (1 - F_{\text{closure}})$$

4.5.3. Release from paper recycling.

The emission in waste water for recycling coated paper may be estimated using the model below.

Table 12: Emission scenario for calculating the releases from paper recycling

Variable/parameter (unit)	Symbol	Unit	Default	S/D/O/P
Input:				
Relevant tonnage in EU for this application	TONNAGE	t.y ⁻¹		S
Relevant tonnage in the region for this application	TONNAGEREG	t.y ⁻¹		O
Fraction of the region	F _{reg}	-	0.1	D
Fraction of main source	f	-	0.1	D
Paper recycling rate (table 8)	F _{recycling}	-	0.5	D/P
Deinking yield (cf. section 4.3.4)	F _{deinking}	-	1	S/D
Fraction decomposed during deinking	F _{decomp}	-	0	S
Fraction removed from waste water during preliminary on-site treatment (cf. section 4.3.4)	F _{preliminary}	-		S
Number of working days	N _d	d.y ⁻¹	320	D
Output:				
Local emission of active substance to waste water	E _{local water}	kg.d ⁻¹		O

Model calculation:

$$\text{TONNAGEREG} = F_{\text{reg}} * \text{TONNAGE}$$

For new substances or existing substances produced at low volumes and which are not used homogeneously through out the EU, it can be assumed in a first approach that F_{reg} = 1.

$$E_{\text{local water}} = \text{TONNAGEREG} \times F_{\text{recycling}} \times f \times F_{\text{deinking}} \times (1 - F_{\text{preliminary}}) \times (1 - F_{\text{decomp}}) \times 1\,000 / N_d$$

4.6. Example calculation.

4.6.1. Release from drying sections.

$$Q_{\text{paper}} = 500 \text{ t.d}^{-1}$$

$$Q_{x_active} = 0.2 \text{ kg.t}^{-1}$$

$$F_{\text{evap}} = 0.0005$$

$$E_{\text{local}_{\text{air}}} = 500 \times 0.2 \times 0.0005 = 0.05 \text{ kg. d}^{-1}$$

4.6.2. Release from "broke".

$$Q_{\text{paper}} = 500 \text{ t.d}^{-1}$$

$$Q_{\text{active}} = 0.2 \text{ kg.d}^{-1}$$

$$F_{\text{broke}} = 0.2$$

$$F_{\text{fix}} = 0.8$$

$$F_{\text{closure}} = 0.8$$

$$E = 500 \times 0.2 \times 0.2 \times (1 - 0.8) \times (1 - 0.8) = 0.8 \text{ kg.d}^{-1}$$

4.6.3. Release from recycling paper.

$$\text{TONNAGEREG} = 25\,000 \text{ kg.y}^{-1}$$

$$f = 0.1$$

$$F_{\text{recycling}} = 0.5$$

$$F_{\text{deinking}} = 1$$

$$F_{\text{decomp}} = 0$$

$$F_{\text{preliminary}} = 0.8 \text{ (poorly soluble substance)}$$

$$N_d = 320$$

$$E_{\text{local}_{\text{water}}} = [25\,000 \times 0.5 \times 0.1 \times 1 \times (1 - 0.8) \times (1 - 0)] / 320 = 0.78 \text{ kg.d}^{-1}$$

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GLOSSARY

Board: papers of 220 gsm (gram per square meter) and over are generally called boards. They have often more than one ply.

Broke: any formed paper, from the beginning of the papermaking process to the finished product, that has been discarded anywhere in the process of manufacture and is usually repulped.

They are two kinds – wet broke, which is accumulated at any stage on the dry end of the machine, trimmings from the reeling, slitting and cutting operations, as well as paper or board rejected during sorting.

Calender: a machine intended to smooth or otherwise finish the paper and consisting essentially of a certain number of superimposed rolls of which only one is power driven.

Coated papers: paper to which a coating has been applied on one or both sides, using a mix of clay or carbonates and latex to create a high quality printing surface.

Corrugated (paper or paperboard): paper which has undergone a treatment in order to give it a regular and permanently undulated aspect.

Deinking: the process of removing ink from printed waste papers, but also involving general removal of other undesirable materials.

Dry-end: part of the papermaking process after formation of the paper web.

Fillers (or loadings): papermaking additives in the form of powder or slurry, usually mineral clays or calcium carbonates, used to improve smoothness, opacity, brightness and dimensional stability of paper and board.

Grammage: mass of the paper / board, usually expressed as g/m².

Paper: sheet of fibres with a number of added chemicals. According to the basic weight it can be distinguished: paper < 150 g/m² < paperboard (or board) < 250 g/m² < cardboard.

Paper grades: paper is classified into different grades according to the end use, the pulp used and the treatment of the paper.

Ream: a term denoting a number of sheets of paper ranging from 480 to 516, most commonly 500.

Recycled fibre pulp: fibrous material that has already passed through paper and/or board production.

Save-all: an apparatus used for reclaiming fibres and fillers from white water. It usually operates on a filtration, sedimentation, flocculation, or flotation principle.

Size: non-fibrous materials used in papermaking to control the absorbency of paper. Rosin, Alum, starch and gelatine are the most commonly used.

Stock: terms used to describe the papermaking material in all stages, but usually referring to the wet pulp before it is fed onto the paper machine.

Supercalender: machine for giving paper a very smooth surface by passing it through a series of alternate metal and composition rolls, revolving with high speed and pressure.

Tissue paper: absorbent paper used for a variety of hygienic purposes.

Wet-end: part of the papermaking process prior to formation of the paper web.

White water: a general term for all waters of a paper mill that have been separated from the stock or pulp suspension, either on the paper machine or accessory equipment, such as thickeners, washers, save-alls, and from pulp grinders. It carries a certain amount of fibre and may contain varying amounts of fillers and dyestuffs.