Unclassified **ENV/JM/MONO(2006)6**

Organisation de Coopération et de Développement Economiques
Organisation for Economic Co-operation and Development

01-Feb-2006

English - Or. English

ENVIRONMENT DIRECTORATE
JOINT MEETING OF THE CHEMICALS COMMITTEE AND
THE WORKING PARTY ON CHEMICALS, PESTICIDES AND BIOTECHNOLOGY

OECD SERIES ON TESTING AND ASSESSMENT
Number 52

COMPARISON OF EMISSION ESTIMATION METHODS USED IN POLLUTANT RELEASE AND TRANSFER REGISTERS AND EMISSON SCENARIO DOCUMENTS: CASE STUDY OF PULP AND PAPER AND TEXTILE SECTORS

JT00200406

ENV/JM/MONO(2006)6
Unclassified

English - Or. English

OECD Environment Health and Safety Publications

Series on Testing and Assessment

No. 52

COMPARISON OF EMISSION ESTIMATION METHODS USED IN POLLUTANT RELEASE AND TRANSFER REGISTERS AND EMISSON SCENARIO DOCUMENTS: CASE STUDY OF PULP AND PAPER AND TEXTILE SECTORS

Environment Directorate
ORGANISATION FOR ECONOMIC CO-OPERATION AND DEVELOPMENT

Paris, 2006

Also published in the Series on Testing and Assessment:

No. 1, *Guidance Document for the Development of OECD Guidelines for Testing of Chemicals (1993; reformatted 1995)*

No. 2, *Detailed Review Paper on Biodegradability Testing (1995)*

No. 3, *Guidance Document for Aquatic Effects Assessment (1995)*

No. 4, *Report of the OECD Workshop on Environmental Hazard/Risk Assessment (1995)*

No. 5, *Report of the SETAC/OECD Workshop on Avian Toxicity Testing (1996)*

No. 6, *Report of the Final Ring-test of the Daphnia magna Reproduction Test (1997)*

No. 7, *Guidance Document on Direct Phototransformation of Chemicals in Water (1997)*

No. 8, *Report of the OECD Workshop on Sharing Information about New Industrial Chemicals Assessment (1997)*

No. 9, *Guidance Document for the Conduct of Studies of Occupational Exposure to Pesticides during Agricultural Application (1997)*

No. 10, *Report of the OECD Workshop on Statistical Analysis of Aquatic Toxicity Data (1998)*

No. 11, *Detailed Review Paper on Aquatic Testing Methods for Pesticides and industrial Chemicals (1998)*

No. 12, *Detailed Review Document on Classification Systems for Germ Cell Mutagenicity in OECD Member Countries (1998)*

No. 13, *Detailed Review Document on Classification Systems for Sensitising Substances in OECD Member Countries 1998)*

No. 14, *Detailed Review Document on Classification Systems for Eye Irritation/Corrosion in OECD Member Countries (1998)*

No. 15, *Detailed Review Document on Classification Systems for Reproductive Toxicity in OECD Member Countries (1998)*

No. 16, *Detailed Review Document on Classification Systems for Skin Irritation/Corrosion in OECD Member Countries (1998)*

No. 17, *Environmental Exposure Assessment Strategies for Existing Industrial Chemicals in OECD Member Countries (1999)*

No. 18, *Report of the OECD Workshop on Improving the Use of Monitoring Data in the Exposure Assessment of Industrial Chemicals (2000)*

No. 19, *Guidance Document on the Recognition, Assessment and Use of Clinical Signs as Humane Endpoints for Experimental Animals used in Safety Evaluation (1999)*

No. 20, *Revised Draft Guidance Document for Neurotoxicity Testing (2004)*

No. 21, *Detailed Review Paper: Appraisal of Test Methods for Sex Hormone Disrupting Chemicals (2000)*

No. 22, *Guidance Document for the Performance of Out-door Monolith Lysimeter Studies (2000)*

No. 23, *Guidance Document on Aquatic Toxicity Testing of Difficult Substances and Mixtures (2000)*

No. 24, *Guidance Document on Acute Oral Toxicity Testing (2001)*

No. 25, *Detailed Review Document on Hazard Classification Systems for Specifics Target Organ Systemic Toxicity Repeated Exposure in OECD Member Countries (2001)*

No. 26, *Revised Analysis of Responses Received from Member Countries to the Questionnaire on Regulatory Acute Toxicity Data Needs (2001)*

No 27, *Guidance Document on the Use of the Harmonised System for the Classification of Chemicals Which are Hazardous for the Aquatic Environment (2001)*

No 28, *Guidance Document for the Conduct of Skin Absorption Studies (2004)*

No 29, *Guidance Document on Transformation/Dissolution of Metals and Metal Compounds in Aqueous Media (2001)*

No 30, *Detailed Review Document on Hazard Classification Systems for Mixtures (2001)*

No 31, *Detailed Review Paper on Non-Genotoxic Carcinogens Detection: The Performance of In-Vitro Cell Transformation Assays (draft)*

No. 32, *Guidance Notes for Analysis and Evaluation of Repeat-Dose Toxicity Studies (2000)*

No. 33, *Harmonised Integrated Classification System for Human Health and Environmental Hazards of Chemical Substances and Mixtures (2001)*

No. 34, *Guidance Document on the Development, Validation and Regulatory Acceptance of New and Updated Internationally Acceptable Test Methods in Hazard Assessment (in preparation)*

No. 35, *Guidance notes for analysis and evaluation of chronic toxicity and carcinogenicity studies (2002)*

No. 36, *Report of the OECD/UNEP Workshop on the use of Multimedia Models for estimating overall Environmental Persistence and long range Transport in the context of PBTS/POPS Assessment (2002)*

No. 37, *Detailed Review Document on Classification Systems for Substances Which Pose an Aspiration Hazard (2002)*

No. 38, *Detailed Background Review of the Uterotrophic Assay Summary of the Available Literature in Support of the Project of the OECD Task Force on Endocrine Disrupters Testing and Assessment (EDTA) to Standardise and Validate the Uterotrophic Assay (2003)*

No. 39, *Guidance Document on Acute Inhalation Toxicity Testing (in preparation)*

No. 40, *Detailed Review Document on Classification in OECD Member Countries of Substances and Mixtures Which Cause Respiratory Tract Irritation and Corrosion (2003)*

No. 41, *Detailed Review Document on Classification in OECD Member Countries of Substances and Mixtures which in Contact with Water Release Toxic Gases (2003)*

No. 42, *Guidance Document on Reporting Summary Information on Environmental, Occupational and Consumer Exposure (2003)*

No. 43, *Draft Guidance Document on Reproductive Toxicity Testing and Assessment (in preparation)*

No. 44, *Description of Selected Key Generic Terms Used in Chemical Hazard/Risk Assessment (2003)*

No. 45, *Guidance Document on the Use of Multimedia Models for Estimating Overall Environmental Persistence and Long-range Transport (2004)*

No. 46*,* *Detailed Review Paper on Amphibian Metamorphosis Assay for the Detection of Thyroid Active Substances (2004)*

No. 47, *Detailed Review Paper on Fish Screening Assays for the Detection of Endocrine Active Substances (2004)*

No. 48, *New Chemical Assessment Comparisons and Implications for Work Sharing (2004)*

No. 49, *Report from the Expert Group on (Quantitative) Structure-Activity Relationships [(Q)Sars] on the Principles for the Validation of (Q)Sars (2004)*

No. 50, *Report of the OECD/IPCS Workshop on Toxicogenomics (2005)*

No. 51, *Approaches to Exposure Assessment in OECD Member Countries: Report from the Policy Dialogue on Exposure Assessment in June 2005 (2006)*

About the OECD

The Organisation for Economic Co-operation and Development (OECD) is an intergovernmental organisation in which representatives of 30 industrialised countries in North America, Europe and the Asia and Pacific region, as well as the European Commission, meet to co-ordinate and harmonise policies, discuss issues of mutual concern, and work together to respond to international problems. Most of the OECD's work is carried out by more than 200 specialised committees and working groups composed of member country delegates. Observers from several countries with special status at the OECD, and from interested international organisations, attend many of the OECD's workshops and other meetings. Committees and working groups are served by the OECD Secretariat, located in Paris, France, which is organised into directorates and divisions.

The Environment, Health and Safety Division publishes free-of-charge documents in nine different series: **Testing and Assessment**; **Good Laboratory Practice and Compliance Monitoring**; **Pesticides and Biocides**; **Risk Management**; **Harmonisation of Regulatory Oversight in Biotechnology**; **Safety of Novel Foods and Feeds; Chemical Accidents; Pollutant Release and Transfer Registers; and Emission Scenario Documents.** More information about the Environment, Health and Safety Programme and EHS publications is available on the OECD's World Wide Web site (http://www.oecd.org/ehs/).

This publication was produced within the framework of the Inter-Organisation Programme for the Sound Management of Chemicals (IOMC).

The Inter-Organisation Programme for the Sound Management of Chemicals (IOMC) was established in 1995 following recommendations made by the 1992 UN Conference on Environment and Development to strengthen co-operation and increase international co-ordination in the field of chemical safety. The participating organisations are FAO, ILO, OECD, UNEP, UNIDO, UNITAR and WHO. The World Bank and UNDP are observers. The purpose of the IOMC is to promote co-ordination of the policies and activities pursued by the Participating Organisations, jointly or separately, to achieve the sound management of chemicals in relation to human health and the environment.

This publication is available electronically, at no charge.

**For this and many other Environment,
Health and Safety publications, consult the OECD's
World Wide Web site (www.oecd.org/ehs/)**

or contact:

**OECD Environment Directorate,
Environment, Health and Safety Division**

**2 rue André-Pascal
75775 Paris Cedex 16
France**

Fax: (33-1) 44 30 61 80

E-mail: ehscont@oecd.org

FOREWORD

Emission estimation plays a key role in the risk assessments of chemical pollutants. Emission estimation methods are used to calculate emissions by both regulatory agencies and emitting facilities in OECD member countries. The purpose of regulatory agencies is to evaluate the risk of chemical pollutants to human health and the environment based on emission estimates: the evaluation is commonly facilitated with the use of Emission Scenario Documents (ESD's). On the other hand, emitting facilities are required to estimate and report their emissions to Pollutant Release and Transfer Registers (PRTR's). Although both ESD's and PRTR's are intended to deal with emissions from the same sources, different methods of analysis may be used.

The purpose of this document is to identify the similarities and differences between the emission estimation methods used in PRTR's and ESD's. The applicability of PRTR methods to the risk assessments is also evaluated. The study is focused on two sectors: pulp and paper manufacture, and textile wet processing.

It is anticipated that further examples allowing direct comparison of PRTR and ESD methods will become available over time. With the aim of improving our understanding of how PRTR approaches may be most suitably applied in development of ESD's, readers are encouraged to submit discussions of such cases to the OECD Environment, Health and Safety Division (env.riskassessment@oecd.org).

This document was produced by Environment Canada and overseen by the OECD Task Force on Environmental Exposure Assessment and the OECD Task Force on PRTRs.

This document is published on the responsibility of the Joint Meeting of the Chemicals Group and Management Committee of the Special Programme on the Control of Chemicals of the OECD.

TABLE OF CONTENTS

EXECUTIVE SUMMARY

Emission estimation methods are used to calculate emissions by both regulatory agencies and emitting facilities. The purpose of regulatory agencies is to evaluate the risk of chemical pollutants to human health and the environment based on emission estimates: the evaluation is commonly facilitated with the use of Emission Scenario Documents (ESD's). On the other hand, emitting facilities are required to estimate and report their emissions to Pollutant Release and Transfer Registers (PRTR's). Although both ESD's and PRTR's are intended to deal with emissions from the same sources, different methods of analysis may be used.

The purpose of this study is to identify the similarities and differences between the emission estimation methods used in PRTR's and ESD's. The applicability of PRTR methods to the risk assessments is also evaluated. The study is focused on two sectors: pulp and paper manufacture, and textile wet processing.

Direct monitoring or measurement, mass balance, emission factors, and engineering calculations are four emission estimation methods found in the PRTR programs of Canada, the US, Australia, and the UK. Engineering judgment is recommended for use in PRTR's by the Organization for Economic Cooperation and Development (OECD). It is, however, not included in the PRTR programs of Canada, Australia, and the UK, but may be considered under the category of engineering calculations in the US PRTR program. Engineering calculations consist of several types such as fuel analysis, indirect monitoring, and computer models.

One primary approach included in ESD's for estimating water emissions is similar to emission factors described in PRTR's. It is based on the use of fixation rate and has been adopted for several sectors such as textile, pulp and paper, and leather, though not for every sector. The approach is referred to as the fixation-based method in this study in order to distinguish it from the methods described in PRTR's.

Emission factors and mass balance are judged to be applicable to the risk assessments. Several calculation examples showed that the PRTR mass balance and emission factor methods yielded more conservative estimates than the ESD fixation-based method by up to 80%. The PRTR mass balance method was found to present a thorough analysis on parameters such as multiple substance sources and recycles which could impact emissions to wastewater. These parameters were apparently not accounted for in the ESD method, which might be the cause for higher emission estimates from the PRTR method.

It has been found that emission factors for water releases are scarce. Published emission factors are primarily focused on air emissions. Although a wide range of data is available to the ESD fixation-based method, it has not been possible to compare it with the PRTR emission factor method in many cases due to the absence of aqueous emission factors. Conversely, there were no examples to compare air emissions, due in part to the fact that most ESD's are lacking in air emission information.

It is anticipated that further examples allowing direct comparison of PRTR and ESD methods will become available over time. With the aim of improving our understanding of how PRTR approaches may be most suitably applied in development of ESD's, readers are encouraged to submit discussions of such cases to the OECD Environment, Health and Safety Division (env.riskassessment@oecd.org).

1 – INTRODUCTION

1. Emission estimation plays a key role in the risk assessments of chemical pollutants. These assessments have been facilitated with the use of Emission Scenario Documents (ESD's) developed by member countries of the Organization for Economic Cooperation and Development (OECD). An ESD provides a description of activities related to emissions and methods used to estimate these emissions. The estimates are then used to calculate the pollutant exposure level in the environment in order to determine the risk to human health and the environment.

2. For the purpose of the risk assessments carried out by OECD member countries, environmental exposure levels are determined from emission estimates and classified into four types: 1) bounding or worst-case estimates; 2) reasonable worst-case estimates; 3) typical exposure values; and 4) actual exposure values (OECD, 2000). The majority of existing ESD's have been aimed at providing reasonable worst-case estimates.

3. Emission estimation is also performed by emitting facilities under Pollutant Release and Transfer Register (PRTR) programs in many countries. A PRTR is an environmental database of potentially harmful chemicals released to air, water and soil (on-site releases) and transported to treatment and disposal sites (off-site transfers). Emitting facilities are required to report to their respective PRTR's on a regular, normally annual, basis. A PRTR allows for reporting facilities, industry associations, governments, and the public to track environmental performance, identify priority issues and develop appropriate pollution reduction strategies.

4. The purpose of this study is to identify the similarities and differences between the emission estimation methods used in PRTR's and ESD's. The study will then determine the applicability of the methods provided in PRTR's to the risk assessments intended by ESD's. Pulp and paper manufacture and textile wet processing are the two industry sectors focused on in this study.

2 – REVIEW OF PRTR EMISSION ESTIMATION METHODS

2.1 – Pollutant Release and Transfer Register

5. A Pollutant Release and Transfer Register (PRTR) is an environmental database or inventory of potentially harmful releases to air, water and soil (on-site releases) as well as waste transported off-site for treatment and disposal (off-site transfers) (OECD, 2001, p.12; OECD, 1999, p.1). Under a PRTR program, facilities are required to report on the amounts of substances released and/or transferred and the data is then made available to the public. A PRTR allows for reporting facilities, industry associations, governments, and the public to keep track of environmental performance, to identify priority issues and to develop appropriate pollution reduction strategies.

6. Many countries have established publicly accessible PRTR's. At its 1992 Earth Summit, the United Nations (UN) called for the establishment of and public access to PRTR's. In response to the UN's call, the Organization for Economic Co-operation and Development (OECD) began to work on PRTR's in 1993 and published a Guidance Manual in 1996 (OECD, 2002a, p.5). The OECD then recommended that publicly available PRTR's be implemented among member countries. Today countries with publicly available PRTR's include Australia, Canada, Denmark, France, Ireland, Japan, Korea, the Netherlands, Norway, the Slovak Republic, Switzerland, the U.K. and the U.S.

7. A PRTR is intended to accomplish a number of objectives. Firstly, it provides a means for collecting and collating data on releases and transfers, by source, of potentially harmful chemicals to air, water and land, and of waste transferred off-site (OECD, 2001, p.12-20). Secondly, a PRTR makes the reported data available to the public. Thirdly, a PRTR enables the integration into one place of the data critical to governments for pollution prevention and chemical management programs. Finally, a PRTR assists the public in tracking changes in environmental performance over time and assessing the impact of other regulatory programs.

8. A PRTR is not an emission inventory per se. Rather, it is a system that brings together data on releases to all environmental media and transfers of chemicals off-site (OECD, 2001, p.12-20). The primary advantage of a PRTR over an emission inventory is the consistency in and timeliness of facility-specific release and transfer data. This unique advantage helps track the generation, release, management and fate of a chemical over time. It further enables governments to set priorities for reducing or eliminating the most potentially damaging releases and transfers.

9. All existing PRTR programs are established based on the principles found in the OECD PRTR Council Act (OECD, 2001, p.9-10). It should be emphasized that each PRTR program is designed differently due to different national environmental needs, priorities and circumstances. Nevertheless, all the PRTR programs each consist of a set of common key components as listed below:

- definition of terms, in particular, release and transfer;
- chemicals covered by a PRTR;
- who is required to report;
- reporting thresholds;
- inclusion of diffuse sources;
- mandatory or voluntary reporting;
- dissemination of data
- estimation techniques used to quantify releases and transfers;
- temporal variations in the release of PRTR data to the public;
- confidentiality provisions;
- source classification; and
- general PRTR management.

2.2 – Approach to Emission Estimation

10. The OECD has adopted a two-step approach to emission estimation for the purpose of PRTR's (OECD, 2002a, p.16; OECD, 1999, p.3). The first step is to characterize releases and/or transfers, while the second step is to estimate the amounts of pollutants released and/or transferred using appropriate emission

estimation methods. It is important to have a clear understanding of the characteristics of the releases/transfers concerned and the overall objective of the estimation effort. Without such an understanding, there is a risk of selecting an estimation technique that is inappropriate for the intended purpose or yields inaccurate results.

11. The releases and/or transfers concerned can be characterized by the following attributes (OECD, 2002a, p.16; OECD, 1999, p.3):

1. Pollutant type
2. Release medium
3. Source type
4. Spatial scale
5. Temporal scale

12. A pollutant type can be discrete or aggregate (OECD, 2002a, p.16; OECD, 1999, p.3). A discrete pollutant represents an individual chemical compound. For example, toluene is a discrete pollutant. An aggregate type, on the other hand, describes a group of pollutants which have common chemical properties or environmental effects. For example, polycyclic aromatic hydrocarbons (PAH's) or heavy metals are of an aggregate type defined by chemical structure, while ozone depleting substances are of another aggregate type defined by a specific environmental effect. A pollutant type can also be defined by the effect of emissions, rather than emissions per se and chemical oxygen demand (COD) is an example of such type.

13. A release medium corresponds to an environmental compartment entered by emissions. Common release media include air, surface water, underground or ground water, and land (OECD, 2002a, p.17; OECD, 1999, p.3). Releases can be either on-site releases and/or off-site transfers for disposal. On-site releases include air emissions, effluent discharges and landfill disposal.

14. Emissions are generally divided between point, diffuse and mobile sources (OECD, 2002a, p.17; OECD, 1999, p.5). Point sources vary widely in size and, as a result, small and large point sources may be treated differently for emission estimation. Some PRTR's, however, use the same emission estimation methods for both small and large point sources, while others treat a collection of small point sources as a diffuse source. Mobile sources generate diffuse patterns of pollutant releases and are generally dealt with via modeling.

15. The spatial scale defines the spatial scope for the emission data reported. It can range from a local to provincial, national and global scale (OECD, 2002a, p.17; OECD, 1999, p.5). When small point sources and diffuse sources are treated as an aggregate, it is necessary to define the spatial scale of the aggregation. Emission estimation methods that are applicable at a global or national scale may not be useful or accurate, if the intent is to collect data on a provincial or local scale.

16. The temporal scale defines the time span for the emission data reported. As in the case for spatial data aggregation, the desired averaging time can affect applicable emission estimation methods (OECD, 2002a, p.17; OECD, 1999, p.5). Methods suited for yielding estimates of annual averages may introduce significant uncertainty when they are applied over shorter intervals.

17. As the characteristics of releases and/or transfers are defined, appropriate emission estimation methods are selected to determine the quantities of pollutants released and/or transferred. These methods are discussed in details in the following section.

18. Lastly, emission information needs to be made available for public scrutiny within a reasonable period of time in order to insure timeliness and accuracy of data. It is generally agreed that a period of one year or less for reporting this information is the acceptable time frame.

2.3 – Emission Estimation Methods

19. Emission estimation methods are a key aspect of a PRTR program. They are used to generate data on facility-specific releases and transfers (OECD, 2002a, p.7-10). In 2000, a task force was established by the OECD to work on the identification and improvement of emission estimation methods. The *Resource Compendium of PRTR Release Estimation Techniques* was prepared in 2002 to help accomplish this goal. The intent of the compendium is to provide OECD member countries with basic information on emission estimation methods typically used in a PRTR program to quantify releases and transfers.

20. The *Resource Compendium of PRTR Release Estimation Techniques* consists of three separate documents (OECD, 2002a, p.10). These documents deal with the three main source categories: point sources, diffuse sources, and transfers. The first document provides a summary of emission estimation methods used for estimating point source releases. The second document describes methods and techniques used for diffuse sources. The third document outlines methods used to estimate the concentration of chemicals in transfers.

21. This project focuses on PRTR emission estimation methods for industrial point sources for the purpose of evaluating their applicability to risk assessments. These methods range from simple intuitive evaluation to sophisticated empirical models. They are classified in the *Resource Compendium of PRTR Release Estimation Techniques* into the following five categories (OECD, 2002a, p.10):

1. Direct monitoring
2. Mass balance
3. Emission factors
4. Engineering calculations
5. Engineering judgement

22. The above five categories are intended to cover all possible methods applicable to emission estimation. Each OECD member country may, however, not include all of them in implementing a PRTR program. In the US PRTR program, engineering judgement is considered under the category of engineering calculations. Provided below is a general description of these methods and their applications.

2.3.1 – Direct Monitoring

23. Direct monitoring provides emission estimates through measurements of a broad range of pollutants (OECD, 2002a, p.19). Direct monitoring can be either continuous or periodic. Continuous monitoring is intended for specific pollutants and is generally expensive. In contrast, periodic monitoring is conducted less frequently than continuous monitoring. The frequency may range from daily to once or twice a year. In some cases, periodic monitoring of certain pollutants can be used to represent other pollutants by applying average ratios.

24. Direct monitoring is considered as the most preferred method in many OECD member countries. The guidance manuals provided from these countries suggest that monitoring of releases at source tends to result in the most accurate estimates and is therefore preferred over other methods (OECD, 2002a, p.33). The other methods such as emission factors and mass balance are recommended when direct monitoring is

too costly or difficult to apply. The US PRTR program, on the other hand, treats all methods equally and does not prescribe any specific method for use by reporting facilities.

25. Many sources lend themselves to direct monitoring. These sources are normally operated in a regular and consistent way (OECD, 1999, p. 7). Their emissions do not vary much with time and, therefore, direct measurements at periodic intervals can be made to determine average emissions. Sources of this type include large steam boilers at industrial facilities, smelters, blast furnaces and ovens at steel production facilities, and catalytic crackers at petroleum refineries.

26. Direct monitoring is particularly applicable to pollutants released into wastewater. Generally, wastewater is confined to a pipe or a similar system (OECD, 2002a, p.20; OECD, 1999, p.7). Flow meters are frequently installed at various points along the pipe in order to monitor flow conditions. Releases can be estimated by measuring the concentrations of target pollutants in wastewater flows and then multiplying them by the flow rates measured.

27. Direct monitoring can be expensive for air emissions if used on a routine basis. This is because direct monitoring requires staff to operate and maintain the instruments involved, complete quality assurance and control checks, and provide data management (OECD, 2002a, p.30; OECD, 1999, p.21). As a result, direct monitoring is not commonly used to derive air emission estimates for point sources.

28. An alternative to direct continuous monitoring is the use of composite sampling. This method can be almost as accurate as continuous monitoring.

29. Direct monitoring is a common practice used in land disposal management and, therefore, provides a convenient means for estimating releases to land. Land disposal is common to both solid and liquid waste materials that contain chemical pollutants (OECD, 2002a, p.20). Records on the amount of chemicals disposed of are collected and maintained on a routine and continuous basis. These records are normally required by the waste management regulations in most OECD member countries and can provide sufficient data for the purpose of emission estimation by direct monitoring.

2.3.2 – Mass Balance

30. Mass balance is based on the principle of mass conservation. The principle can be stated as what goes in must either come out in the form of a product or as a release, or be chemically changed to other compounds (OECD, 2002a, p.21; Environment Canada, 2002, p.45). Emissions from a system can be estimated by knowing the amount of a substance going into the system and the amount that is created or destroyed within the system. Any positive difference between the input and the net destruction (destruction minus creation) in the system represents a release. The general form of mass balance methods is described as follows:

$$\Sigma(\text{Output}) = \Sigma(\text{Input}) - \Sigma(\text{Consumption}) + \Sigma(\text{Generation})$$

31. Mass balance is often used for estimating releases to water. It is well suited to situations where releases to water are very complex and difficult to quantify with other methods (OECD, 2002a, p.22; OECD, 1999, p.15). The mass balance method for estimating releases to water can be expressed as follows:

$$R_{water} = R_{input} - (R_{react} - R_{gen} + R_{air} + R_{waste})$$

where

R_{water}: amount of chemical released to water

R_{input}: amount of chemical input into a process

R_{react}: amount of chemical that is reacted away in a process

R_{gen}: amount of chemical that is created in a process

R_{air}: amount of chemical released to air

R_{waste}: amount of chemical released in solid or liquid waste to land including quantities recycled or treated

32. Mass balance can also be used for estimating air emissions from facilities dealing with solvents. The amount of a solvent used as a raw material is often known and the air release can be determined by subtraction (OECD, 2002a, p.21; OECD, 1999, p.19). The use of the mass balance method also requires that the following quantities be known: 1) the amount of the solvent added to the product; 2) the amount released as a water pollutant; and 3) the amount in the waste disposed of, recycled or treated. This approach is suited to complex operations for estimating fugitive releases that result from many potential release points such as pumps, valves, flanges or monitoring ports. The equation used for the estimation is given as follows:

$$S_{air} = S_{input} - (S_{react} - S_{gen} + S_{prod} + S_{water} + S_{waste})$$

where

S_{air}: amount of solvent released to air

$S_{input:}$ amount of solvent input to a process

S_{react}: amount of solvent that is reacted away in a process

S_{gen}: amount of solvent generated in a process

S_{prod}: amount of solvent incorporated into product

S_{water}: amount of solvent released in wastewater

S_{waste}: amount of solvent released in solid or liquid waste to land, including quantities recycled or treated

33. Mass balance further offers an efficient means for estimating releases to land when used in conjunction with direct monitoring (OECD, 2002a, p.22; OECD, 1999, p.15). As with the application for aqueous releases and air emissions, the mass balance method is well suited to situations where good estimates are available for the fate of other chemicals used in a given process. The basic equation used to estimate releases to land is essentially the same as for water and air.

2.3.3 – Emission Factors

34. An emission factor is defined as a constant that relates the amount of emissions to an activity that results in the emissions (OECD, 2002a, p.24; OECD, 1999, p.11). Emission factors can be used to estimate releases from nearly any source that generates emissions with a strong linear dependence on the extent of

an activity. The emission estimation equation based on emission factors is expressed as follows (Environment Canada, 2002. p.46):

$E_x = BQ \times CEF_x$

or

$E_x = BQ \times EF_x \times (100 - CE_x)/100$

where

E_x: emission of contaminant, kg

BQ: activity rate or base quantity, base quantity unit

CEF_x: controlled emission factor of contaminant, kg/BQ unit

EF_x: uncontrolled emission factor of contaminant, kg/BQ unit

CE_x: overall emission control efficiency of contaminant, %

35. An emission factor can be expressed in almost any units. Such flexibility is attributed to the fact that emission-generating activities vary greatly in nature and can be measured in many different ways. Typically, emission factors are based on a reactant or process input, a product or process output, or land use (OECD, 2002a, p.23; OECD, 1999, p.11). They may also be based on populations, a feature that makes emission factors particularly useful for many diffuse sources.

36. The great majority of emission factors are derived from the results of emission tests. These tests have been conducted on samples chosen to represent typical sources within a defined source category (OECD, 1999, p.11). The underlying assumption used in applying emission factors is that untested sources, within a defined source category, have emission characteristics similar to those of tested ones.

37. Emission factors can be applied to essentially any pollutant or source. As a matter of fact, while emission factors may be derived using many different techniques, most of them are developed by taking the average measured emission rate during a representative time interval and relating it to the extent of the activity in question (OECD, 1999, p.9). When used for emission estimation, these emission factors can be applied to all other similar activities whether or not they are included in the categories tested.

38. Emission factors are widely used to estimate air emissions (UK Environment Agency, 2004. p.12). Several compilations of air emission factors are available, such as

- USEPA's AP-42
- USEPA's Factor Information Retrieval (FIRE) database
- USEPA's Locating and Estimating Documents
- Data for pulp and paper operations from the National Council of Paper Industry for Air and Water Stream Improvement (NCASI)
- Data for textile operations from German Environmental Protection Agency

39. Emission factors are often used to quantify releases to water when monitoring data is not available (OECD, 2002a, p.24). They are particularly useful for well-defined and regulated processes, such

as continuous chemical operations. As in the case for emission factors used to predict releases of air pollutants, emission factors for water pollutants provide accuracy for aggregate estimates that represent a large number of similar sources. Emission factors, however, do not reflect on variability in individual sources and change in effluent characteristics with time.

40. Emission factors are not commonly used to estimate releases to land (OECD, 2002a, p.25). Such releases are more frequently determined by direct monitoring, mass balance, or engineering calculations.

41. The primary limitation associated with the use of emission factors is their inability in addressing design and operation differences of emitting sources (OECD, 2002a, p.23; OECD, 1999, p.11). Estimation errors will likely to occur when an individual source is dealt with. For a large number of sources, however, errors associated with different operating conditions will likely be averaged out.

2.3.4 – Engineering Calculations

42. Engineering calculations are based on mathematical relationships between variables within a system. These relationships do not require the knowledge of the input or output of the system, but predict what is likely to happen to the input or output under specified conditions (OECD, 2002a, p.25). For example, while the mass balance method needs to consider the inflow and outflow of a storage tank in order to estimate releases from the tank, the engineering calculation method focuses on key parameters such as tank pressure, liquid vapour pressure, and relief valve conditions.

43. Engineering calculations are also referred to as calculation models since mathematical relationships used for engineering calculations are models of a source, facility, or process. Calculation models can range widely in terms of complexity and transparency (UK Environmental Agency, 2004, p.13; OECD, 2002a, p.25; OECD, 1999, p.16). Generally speaking, the more information known about the input and output of a system, the less knowledge is needed about internal processes, and vice versa. In addition, calculation models are less data intensive that the mass balance method.

44. A sound engineering knowledge is often required when engineering calculations are employed for emission estimation. This requires a good understanding of industrial processes, facility design features and physical and chemical laws (Environment Canada, 2002, p.46). The reliability of the outcome of engineering calculations depends on the complexity of a process in question and the level of understanding of its operations. The following principles should be followed when engineering calculations are applied:

- Review all data pertaining to a specific source and to an industrial sector in general;
- Use this data to provide gross approximations and refine them using sound engineering principles as data becomes available to provide more accurate estimates;
- Whenever possible, alternate methods of calculation should be conducted to cross-check each level of approximation; and
- Employ good record keeping by documenting all related information for further emission refinement when more accurate data becomes available.

45. The application of calculation models is widespread. Calculation models can provide information about releases to the environment from numerous sources including both industrial establishments and residential areas (OECD, 2002a, p.27). They can be applied for estimating releases from all environmental media.

46. Calculation models have found applications in estimating releases to water. Specifically, they are often used to estimate releases to surface and ground water from diffuse sources (OECD, 2002a, p.26).

They have also been developed for estimating aqueous releases from point sources such as industrial effluent.

47. Calculation models can be applied for estimating air emissions. In this case, air emissions are not only dependent upon an activity; they are also influenced by other external factors that are not related to the activity (UK Environmental Agency, 2004, p.13). For example, some sources of volatile organic pollutants are affected by temperature in addition to the extent of an activity.

48. Calculation models are also used for estimating releases to land (OECD, 1999, p.18). For example, the amount of sewage sludge produced from sewage treatment plants can be modeled to obtain estimates of releases to land. In a similar manner, the amount of biodegradable and non-biodegradable wastes can be modeled for household refuse landfilled. Models can also be used to predict the amount of solid waste produced by the livestock industry.

49. A key weakness of calculation models is similar to that associated with emission factors (OECD, 2002a, p.25). These models are sometimes inappropriately applied to sources that are different in terms of operations from those used for the model development. In other cases, specific information required by calculation models may not be readily available.

50. Engineering calculation can be automated through the development of software programs. Such programs offer efficiency and consistency. As an example, the USEPA has developed the WATER9 model to estimate air and water releases of individual pollutants from wastewater collection, storage, treatment and disposal facilities (OECD, 2002a, p.26). The software is able to evaluate an entire facility with multiple influent streams, different collection systems, and complex treatment configurations.

51. Indirect monitoring is a variation of engineering calculation. It supplies to calculation models measured values of certain parameters included in the models. Indirect monitoring can be applied in many cases for estimating industrial aqueous releases from point sources (UK Environmental Agency, 2004, p.14; OECD, 2002a, p.26; OECD, 1999, p.18). The amount and nature of water pollutants released are often related to one or more process parameters and the releases can be estimated with sufficient accuracy through the measurement of these parameters.

2.3.5 – Engineering Judgement

52. All the previous approaches described above are considered to be explicit models: the parameters and assumptions used to make a prediction for an emission can be explicitly stated. Often, however, emissions are estimated using more intuitive methods, using the experience and/or professional knowledge of the estimator.

53. Engineering judgement methods have potential pitfalls of error and inconsistencies, but the practical value in developing emission estimates quickly and economically should not be overlooked. As well, engineering judgement methods can lead to more complete methods that will improve the accuracy and validity of the data.

54. Another drawback to engineering judgement methods is that they are sometimes improperly applied to emission sources that are not operated like the source for which the original model was developed.

55. Areas of application for engineering judgement include both point sources (e.g., effects of landfill leachate on groundwater) and diffuse sources (e.g., pollutant release to surface and groundwater). There is, however, no ready way of characterizing the application of engineering judgement to different release media (UK Environment Agency, 2004).

3 – REVIEW OF ESD EMISSION ESTIMATION METHODS

3.1 – Emission Scenario Documents

56. An Emission Scenario Document (ESD) is defined by the OECD as a document that describes the sources, production processes, release pathways and use patterns with the aim of quantifying the emissions of a chemical (OECD, 2000, p.8; OECD web site at www.oecd.org accessed Jan.25, 2004). The emissions include releases to water, air, soil and/or solid waste from various stages of the chemical's lifecycle, i.e., 1) production; 2) formulation; 3) industrial use; 4) professional use; 5) private and consumer use; 6) service life of product/article; 7) recovery; and 8) waste disposal (incineration, landfill, etc.).

57. An ESD does not often in itself cover all relevant stages of the lifecycle of a chemical (OECD, 2000, p.8). Although an ESD by its definition should provide information about the chemical for all of its lifecycle stages concerned, some stages can be dealt with more easily under other industry sectors. As a result, these stages may not be included in the ESD in the question.

58. The purpose of an ESD is to facilitate the risk assessment of substances. It is used to provide emission estimates into various compartments of the environment where releases initially occur (OECD, 2000, p.8; OECD web site at www.oecd.org accessed Jan.25, 2004). These estimates provide the basis for subsequent estimation of the chemical concentration in the environment. An ESD, however, does not deal with the behaviour and fate of the substances in the environment after they are released.

59. An ESD has many uses where emissions of chemicals into the environment from their production, use and disposal need to be estimated. It can be used by regulatory agencies to make appropriate assessments on the risk of the chemicals to the environment and human health (OECD, 2000, p.9). It improves understanding and communication between the regulatory authority and the industry concerned. The regulatory authority can gain a detailed knowledge of the processes and use patterns in the industry area, while the industry can gain an understanding of the assessment process and how information is used in the assessment. An ESD is also a valuable tool not only for chemical producers to evaluate the potential impact of current and new products, but also for potential users of chemicals to compare alternatives. Furthermore, an ESD can be useful to PRTR's for emission estimation as well as to those involved in hazard assessment.

60. ESD's can be grouped in two ways: by manufacture and by application (OECD web site at www.oecd.org accessed Jan.25, 2004). The grouping by manufacture includes the following 16 industry categories:

1. Agricultural industry (e.g. pesticides, fertilizers)

2. Basic chemical industry (basic chemicals, e.g. solvents, pH-regulating agents including acids and alkalis)
3. Chemical industry (chemicals used in synthesis, e.g. intermediates including monomers, process regulators)
4. Electrical/electronic engineering industry (e.g. electrolytes, semiconductors, excluding galvanics, electroplating agents)
5. Fuel industry (e.g. gasoline, colouring agents, fuel additives, antiknock agents)
6. Leather processing industry (e.g. dyestuffs, tanning auxiliaries)
7. Metal extraction, refining and processing industry (e.g. heat transferring agents, electroplating agents)
8. Paints, lacquers and varnishes industry (e.g. solvents, viscosity adjusters, dyestuffs)

9. Paper, pulp and board industry (e.g. dyestuffs, toners)
10. Personal and domestic use (e.g. consumer products such as detergents including additives, cosmetics, non-agricultural pesticides for domestic use)
11. Photographic industry (e.g. antifogging agents, sensitizers)
12. Polymers industry (e.g. stabilizers, softeners, antistatic agents, dyestuffs)
13. Public domain (e.g. professional products used in public areas such as non-agricultural pesticides, cleaning agents)
14. Textile processing industry (e.g. dyestuffs, flame retardants)
15. Other
16. Unclassified

61. The grouping by application includes the following 56 use categories:

1. Absorbents and Adsorbents
2. Adhesive, binding agents
3. Aerosol propellants
4. Anti-condensation agents
5. Anti-freezing agents
6. Anti-set-off and anti-adhesive agents
7. Anti-static agents
8. Bleaching agents
9. Cleaning/washing agents and disinfectants
10. Colouring agents
11. Complexing agents
12. Conductive agents
13. Construction materials additives
14. Corrosion inhibitors
15. Cosmetics
16. Dust binding agents
17. Electroplating agents
18. Explosives
19. Fertilizers
20. Fillers
21. Fixing agents
22. Flame retardants and fire preventing agents
23. Flotation agents
24. Flux agents for casting
25. Foaming agents
26. Food/foodstuff additives
27. Fuel
28. Fuel additives
29. Heat transferring agents
30. Hydraulic fluids and additives
31. Impregnation agents
32. Insulating materials
33. Intermediates
34. Laboratory chemicals
35. Lubricants and additives
36. Non-agricultural pesticides
37. Odour agents
38. Oxidizing agents
39. pH-regulating agents

40. Pesticides
41. Pharmaceuticals
42. Photochemicals
43. Process regulators
44. Reducing agents
45. Reprographic agents
46. Semiconductors
47. Softeners
48. Solvents
49. Stabilizers
50. Surface-active agents
51. Tanning agents
52. Viscosity adjusters
53. Vulcanizing agents
54. Welding and soldering agents
55. Others
56. Unclassified

62. The development of ESD’s has been carried out primarily within OECD member countries. These ESD’s are industry specific and are intended to provide conservative estimates of chemical emissions into the environment (OECD web site at www.oecd.org accessed Jan.25, 2004). A Guidance Document on Emission Scenario Documents was published by the OECD in 2000 in order to assist in the preparation of ESD’s. In the European Union, ESD’s are developed by OECD's Task Force on Environmental Exposure Assessment. Many of these ESD’s are included in the Technical Guidance Document for EU Risk Assessment and others are published separately. In the U.S., EPA's Office of Pollution Prevention and Toxics is responsible for the development of ESD’s. The industry sectors covered by the existing ESD’s from OECD and USEPA are as follows:

1. Textile processing;
2. Pulp and paper;
3. Coatings;
4. Printing;
5. Leather processing;
6. Metal extraction and processing;
7. Metal plating;
8. Chemical manufacturing;
9. Bioprocessing;
10. Semiconductor manufacturing; and
11. Application of cleaning products.

3.2 – Approach to Emission Estimation

63. The approach to emission estimation used in ESD’s is outlined in the OECD's Guidance Document on Emission Scenario Documents (OECD, 2000). Although each ESD is specific to an industry or use category, there is a set of common features in the approach. The OECD requires that these features be included in all ESD’s developed in order to facilitate emission estimation.

64. The first feature common to the emission estimation approach is a scenario description (OECD, 2000, p.10). In case of an industry area, the description provides a picture of the industry structure, relationship between the various facilities involved, and the types of operations employed. For a use area, the description presents a profile on the types of products, use patterns, expected lifetimes, and recovery and reuse activities.

65. The second feature is a substance description (OECD, 2000, p.10). Substances may be referred to by their functional groups and illustrated with examples. Their uses and fate should be specified in each of its lifecycle stages. Where substances are used in products, their concentrations should be provided.

66. The third feature is a list of potential release points along with their respective release estimates (OECD, 2000, p.10). Ideally these estimates should be provided as factors related to the quantities used, processed, or manufactured so that they can be applied to different circumstances. Such factors may be dependent on substance properties such as vapour pressure and/or product properties such as surface area.

67. The fourth feature is the scale of operations employed in an industry area (OECD, 2000, p.11). The scale can be characterized by the quantities of substances or products used at various sites and the size distribution of these sites. It further includes the number of operation days and other process-related information such as water usage, ventilation rate, and use of on-site wastewater treatment.

68. The fifth feature is an account of emission control techniques (OECD, 2000, p.11). It provides a list of applicable emission control techniques for an industry area and describes the extent of their applications. Ideally these techniques are accounted for in emission estimation in the form of additional factors which are applied to base release estimates.

69. The sixth feature is the derivation of emission estimates through the use of all available data (OECD, 2000, p.12). If necessary, emission estimation equations may be developed to facilitate the calculation of emission rates for relevant release pathways. Calculation examples may also be provided on different scales, local and regional, where appropriate for a use area.

70. The emission estimates derived from ESD's are used in the estimation of concentrations in the environment (OECD, 2000, p.8). According to the level and purpose of the risk assessment carried out by OECD member countries, estimated concentration values can be classified into the following four types:

1. Values that likely exceed actual exposure ("bounding" or "worst-case estimates).
2. Values that are representative of the "high end" of actual exposures ("reasonable worst-case" estimates).
3. Values that are representative of "typical" exposures.
4. A complete set of actual exposure values.

71. The first three estimates are point estimates and can be used in risk quotient calculations (OECD, 2000, p.8). The last type, i.e., a complete set of actual exposure values, is represented as frequency distribution and can be incorporated into risk analysis. To date, the majority of ESD's have aimed at yielding the second type or "high end" ("reasonable worst-case") estimates. It is, however, possible to provide other types of estimates through the use of ESD's and emission estimation methods are believed to play a key role in providing such estimates.

3.3 – Differences and Similarities between PRTR and ESD Methods

72. There are a number of differences between emission estimation methods used in PRTR's and ESD's. Firstly, the purposes of the methods are different. The methods used in PRTR's are intended to provide a means for determining on-site releases of potentially harmful chemicals to air, water and land, and off-site transfers (OECD, 2001, p.12-20). The purpose of those used in ESD's, on the other hand, is to facilitate the environmental and health risk assessments of substances.

73. Secondly, the principal users of the methods are different. Emitting facilities are the principal users of the PRTR methods for the purpose of determining and reporting releases and transfers to their respective PRTR programs, while regulatory agencies are primarily involved with the use of the ESD

methods for the purpose of risk assessments. This difference, however, does not rule out any possible use of PRTR or ESD methods for other applications.

74. Thirdly, the scopes of the methods are different. This difference is reflected in substances and emission sources. A specific selection of substances is normally defined by a PRTR program for reporting and varies from country to country. Listed in Table 1 are the numbers of substances associated with the PRTR programs in Canada, the U.S., the U.K, and Australia. There is, however, no specific set of substances associated with ESD's and substances can be selected for risk assessments if they are of potential environmental and health concerns. Substances in the context of PRTR's and ESD's include both single chemical compounds and chemical categories.

Table 1 – Numbers of Substances Associated with PRTR Programs in Canada, U.S., U.K and Australia

Country	PRTR Program	Number of Substances
Canada	National Pollutant Release Inventory (NPRI)	323
U.S.	Toxics Release Inventory (TRI)	612
U.K.	Pollution Inventory (PI)	167
Australia	National Pollutant Inventory (NPI)	90

75. The methods used in ESD's are designed to deal with broader emissions than those used in PRTR's. The PRTR methods are normally focused on emissions from individual facilities, while the ESD methods are intended to determine emissions from both individual facilities and clusters of facilities. The latter can provide emission data on a given substance and leads to the determination of its exposure level on a local or regional basis.

76. There are also similarities between PRTR and ESD methods. Both PRTR and ESD methods are intended for estimating emissions from the same sources to three common environmental compartments, i.e., air, water and land. They share some common calculation fundamentals such as use of facility-specific and sector-wide data and application of engineering knowledge. Furthermore, accuracy and efficiency are two important factors to be considered in emission estimation and either PRTR or ESD methods must provide a reasonable trade-off to meet their respective objectives.

77. The primary method suggested for ESD's is based on emission factors (Wagner, 2003). It is similar to emission factors used in PRTR, but includes other parameters to account for duration of emission and reduction under specific conditions. The method is based on the use of fixation rate in estimating water emissions in the case of pulp and paper and textile ESD's and is, therefore, referred to as the fixation-based method in this study.

4 – EVALUATION OF PRTR METHODS USED BY PULP AND PAPER MILLS

4.1 – PRTR Emission Estimation

78. Only one PRTR program is found to have described emission estimation methods for pulp and paper mills. This is Australia's National Pollutant Inventory that provides a manual entitled "Emission Estimation Technique Manual for Pulp and Paper Manufacturing" (Environment Australia, 1998). The

manual covers various pulp and paper product manufacturing activities for the production of commodity grades of paper pulp, printing and writing papers, sanitary tissue, industrial-type papers, container board, and boxboard (Environment Australia, 1998, p.4). The primary materials used for the production are cellulose fibre from timber, and purchased or recycled fibres, as well as organic and inorganic additives.

4.1.1 – Environmental Releases

79. Environmental releases from pulp and paper mills are grouped into three categories in the Australian PRTR program: 1) air emissions; 2) water releases; and 3) land releases (Environment Australia, 1998, p.5). Summarized in Table 2 are common pollutants in air emissions and water releases along with their respective sources. Air emissions include fugitive emissions and point source emissions. The fugitive emissions originate from stockpiles, vats, open vessels, valves, flanges, equipment leaks, and material handling areas, while the point source emissions are releases from vents, stacks, carbon adsorption units, scrubbers, baghouses, and afterburners.

Table 2 – Common Pollutants in Air Emissions and Water Releases from Pulp and Paper Mills

Air Emissions	
Source	Pollutant
Kraft recovery furnace	Particulate matter (PM_{10})
Fly ash from wood waste and coal fired boilers	Particulate matter (PM_{10})
Sulphite mill operations	Sulphur oxides
Kraft pulping and recovery processes	Reduced sulphur gases
Chip digester and liquor evaporation	Volatile organic compounds
All combustion processes	Oxides of nitrogen, SO_x, CO, PM_{10}
Water Releases	
Water used in wood handling, debarking, and chip washing	Solids, BOD, colour
Chip digester and liquor evaporator condensate	Concentrated BOD, reduced sulphur compounds
White waters from pulp screening, thickening and cleaning	Large volumes of water with suspended solids, significant BOD
Bleach plant washer filtrates	BOD, colour, chlorinated organic compounds
Paper machine water flows	Solids, often precipitated for reuse
Fibre and liquor spills	Solids, BOD, colour

Source: Australia, 1998, p.5-6

80. Water releases are discharges to surface water (e.g., lakes, rivers, dams, and estuaries), coastal or marine water, and stormwater (Environment Australia, 1998, p.5). The Australian PRTR program does not require the discharge to sewers or tailings dam to be reported. Air pollution control equipment such as wet scrubbers is usually the primary source of wastewater.

81. Land releases include both solid and liquid waste materials destined for land disposal. They generally originate from surface impoundments of liquids and slurries and unintentional leaks and spills as far as the substances for reporting are concerned (Environment Australia, 1998, p.6). Other sources of land releases include storage and distribution of liquids and the use of pollution control agents.

4.1.2 – Emission Estimation Methods

82. There are four emission estimation methods prescribed in the Australian PRTR program (Environment Australia, 1998, p.4). These methods are: 1) direct measurement; 2) mass balance; 3) engineering calculations (fuel analysis); and 4) emission factors. One method or a mix of several methods

is allowed for use in estimating emissions. Any other method must be approved by the regional environmental authority before it can be used by a reporting facility.

83. Direct measurement is recommended for the determination of water releases in the Australian PRTR program (Environment Australia, 1998, p.6). In cases where direct measurement is not available, other methods are allowed.

84. Direct measurement is also commonly applied for estimating air emissions. Stack sampling can provide data on pollutant concentration and flow rate (Environment Australia, 1998, p.11-12). For example, hourly emissions of particulate matter (PM) can be estimated by multiplying the concentration by the flow rate using the following equations:

$$E_{PM} = C_{PM} \times Q_d \times 3600 \div 1000$$

$$C_{PM} = C_f \div V_{m,\,STP}$$

where

E_{PM}: hourly emissions of particulate matter, kg/hr

C_{PM}: concentration of particulate matter or gram loading (grams/dscm)

Q_d: stack gas volumetric flow rate, dscm

C_f: filter catch, grams

$V_{m,\,STP}$: metered volume of sample under standard temperature and pressure, dscm

85. Annual emissions can be calculated by multiplying the emission rate in kg/hr by the number of operating hours using the following equation (Environment Australia, 1998, p.22).

$$E_{tpy,x} = E_x \times OpHrs \div 1000$$

where

$E_{tpy,x}$: annual emissions of pollutant, tonnes/year

E_x: hourly emissions of pollutant, kg/hr

OpHrs: annual operating hours, hr/yr

86. Engineering calculations can be very complex (Reisman, 2005). To simplify these calculations the National Council of Paper Industry for Air and Water Stream Improvement (NCASI) has developed factors using direct and/or indirect monitoring for certain pollutants.

87. Fuel analysis is a variation of engineering calculations prescribed by the Australian PRTR program for pulp and paper mills. It can be used to predict emissions of sulphur dioxide, metals, and other pollutants based on the application of conservation laws if fuel rate is measured (Environment Australia, 1998, p.20). The basic equation for fuel analysis is given as follows:

$$E_x = Q_f \times \text{pollutant concentration in fuel} \times (MW_p \div MW_f)$$

where

E_x: emissions of pollutant

Q_f: fuel use, kg/hr

MW_p: molecular weight of pollutant emitted, kg/kgmol

MW_f: molecular weight of pollutant in fuel, kg/kgmol

88. When emission factors are used, the Australian PRTR program requires that their associated rating code be indicated (Environment Australia, 1998, p.10). The rating code is based on the work from the USEPA and European Environment Agency. The code provides a measure of uncertainty associated with the emission factor used and is divided into the following levels in a decreasing order of uncertainty:

A - Excellent
B - Above Average
C - Average
D - Below Average
E - Poor
U - Unrated

89. Emission factors are commonly expressed as the weight of a substance emitted per unit weight, volume, distance, or duration of an emitting activity (Environment Australia, 1998, p.13-14). For example, the emission factor for sulphur dioxide is given as kg of sulphur dioxide per tonne of air-dried unbleached pulp produced. Emission factors for pollutants associated with pulp and paper mills can be obtained from US, European, and Australian sources. The general equation for emission estimation based on emission factors is given as follows:

$$E = A \times T \times EF \times [1 - (ER/100)]$$

where

E: emissions
A: activity rate
T: time (or another variable)
EF: uncontrolled emission factor
ER: overall emission reduction efficiency

4.2 – ESD Emission Estimation

90. Several ESD’s are found to have addressed emission estimation for pulp and paper mills. These documents are listed below:

- European Commission (2003), "Harmonization of Environmental Emission Scenarios for Slimicides (Product Type 12),"Haskoning Nederland BV Environment, The Netherlands, 16 September 2003 (not reviewed yet).

- Tissier, C.; and V. Migne (2001), "Emission Scenario Document for Biocides Used in Paper Coating and Finishing – Supplement to the Methodology for Risk Evaluation of Biocides," Institut National de l'Environnement Industriel et des Risques, France, May 2001.

- European Commission (1996), "Technical Guidance Document in Support of Commission Directive 93/67/EEC on Risk Assessment for New Notified Substances and Commission Regulation (EC) No 1488/94 on Risk Assessment for Existing Substances," Part IV, Office for Official Publications of the European Communities, Luxembourg, 1996.

91. In estimating emissions from pulp and paper mills, an emission scenario is provided with various sets of input and output variables. These input and output variables are different in concept from those described for the mass balance method in PRTR's. They are parameters with values specified (input) and calculated (output), rather than flows entering and exiting a facility or process.

92. Input variables are grouped into five categories. The first category, denoted by S, consists of variables that must be specified in the emission estimation and there are neither default values for these variables nor methods providing their estimates (OECD, 2002b, p.4; Tissier and Migne, 2001, p.4). The second category, denoted by D, includes variables with standard defaults which can be modified by users. The third category, denoted by O, provides a group of variables with their values calculated which can, however, be overwritten by users with alternative data. The fourth category, denoted by P, pertains to variables with their values selected from a pick-list. The fifth category, denoted by C, refers to variables with their values provided as constants which cannot be changed by users.

93. Output variables are generally divided into two groups. The first group is a set of variables determined through intermediate calculations and the second group through end calculations (Tissier and Migne, 2001, p.4). Output variables from intermediate calculations are derived for use in other calculations, while those from end calculations are expected to present emission results. The general format of the emission estimation employed in ESD's for pulp and paper mills is summarized in Table 3.

Table 3 – General Format of Emission Estimation for Pulp and Paper Mills

Type	Variable	Symbol	Units	Default	Category (S, D, O, P, C)
Input	Definition of an input variable				
Output	Definition of an output variable				
Calculation	Equations for intermediate and end calculations				

94. A set of input and output variables commonly corresponds to an individual case and an emission scenario can consist of a number of such cases. Each case provides emission estimates for a specific type of operations and a specific release medium. Examples of emission estimation methods are provided in Table 4 for air emissions from drying sections of a paper mill (Tissier and Migne, 2001, p.16), Table 5 for water release from broke of a paper machine (Tissier and Migne, 2001, p.18), Table 6 for water releases from paper recycling (Tissier and Migne, 2001, p.18; European Commission, 1996, p.705), and Table 7 for water releases from paper making (European Commission, 1996, p.702).

95. The determination of input variables constitutes a significant portion of emission estimation. Input variable values can be derived from the data reported by individual facilities, statistical averages over many sites within a sector, facility operation data gathered through survey and site investigation, and literature data.

Table 4 – Estimation Method for Air Emissions from Paper Mill Drying Sections after Size-Pressing and Coating

Type	Variable	Symbol	Units	Default	Category
Input	Quantity of coated paper produced per day	Q_{paper}	t/d		P
	Quantity of active substance applied per ton of paper for each application step	Q_{active}	kg/t		S
	Evaporation rate	F_{evap}			S, P
	Decomposition rate during drying	F_{decomp}		0	S
Output	Local emission of active substance to air for one treatment step	$E_{local\text{-}air}$	kg/d		O
Calculation	$E_{local\text{-}air} = Q_{paper} \times Q_{active} \times F_{evap} \times (1 - F_{decomp})$				

Source: Tissier and Migne, 2001, p.16

Table 5 – Estimation Method for Water Releases from Broke of a Paper Machine

Type	Variable	Symbol	Units	Default	Category
Input	Quantity of coated paper produced per day	Q_{paper}	t/d		P
	Quantity of active substance applied per ton of paper	Q_{active}	kg/t		S
	Degree of closure of water system	$F_{closure}$			S, P
	Fraction of coated broke produced compared to overall produced	F_{broke}		0.2	S, D
	Fixation rate	F_{fix}		0	S, D
Output	Local emission of active substance to wastewater	$E_{local\text{-}water}$	kg/d		O
Calculation	$E_{local\text{-}water} = Q_{paper} \times Q_{active} \times F_{broke} \times (1 - F_{fix}) \times (1 - F_{closure})$				

Source: Tissier and Migne, 2001, p.18

Table 6 – Estimation Method for Water Releases from Paper Recycling

Type	Variable	Symbol	Units	Default	Category
Input	Relevant tonnage in EU for this application	T	t/yr		S
	Relevant tonnage in the region for this application	T_{reg}	t/yr		O
	Fraction of the region	F_{reg}		0.1	D
	Fraction of main source compared to overall produced	f		0.1	D
	Paper recycling rate	$F_{recycling}$		0.5	D, P
	Deinking yield	$F_{deinking}$		1	S, D
	Fraction decomposed during deinking	F_{decomp}		0	S
	Fraction removed from wastewater during preliminary on-site treatment	F_{pre}			S
	Number of working days	N_d	d/yr	320	D
	Total annual consumption of substance on paper	W_s	kg/yr		
	Removal rate in on-site primary treatment	P_a			
	Number of recycling sites	N_s			
Output	Local emission of active substance to wastewater	$E_{local\text{-}water}$	kg/d		O
	Emission of substance to wastewater from a site	E_{water}	kg/d		
Calculation	$E_{local\text{-}water} = F_{reg} \times T \times F_{recycling} \times f \times F_{deinking} \times (1\text{-}F_{pre}) \times (1\text{-}F_{decomp}) \times 1000/N_d$ $E_{water} = W_r \times R_{recycling} \times F_{deinking} \times (1 - P_a) / (N_d \times N_s)$				

Sources: Tissier and Migne, 2001, p.18 (for $E_{local\text{-}water}$); European Commission, 1996, p.705 (for E_{water}).

Table 7 – Estimation Method for Water Releases from Paper Making

Type	Variable	Symbol	Units	Default	Category
Input	Specific consumption of substance	W_s	kg/t		
	Quantity of paper produced per day	Q	t/d		
	Degree of fixation of substance	F	fraction		
	Degree of closure of water system	C	fraction		
	Concentration of substance in water	C_s	kg/m^3		
	Water consumption per tonne of paper produced	A_s	m^3/t		
Output	Water emission per day	$E_{local\text{-}water}$	kg/d		
Calculation	$E_{local\text{-}water} = W_s \times Q \times (1 - F) \times (1 - C)$ (for mass of substance per tonne of paper) or $E_{local\text{-}water} = C_s \times A_s \times Q \times (1 - F)$ (for concentration of substance in water)				

Source: European Commission, 1996, p.702

4.3 – Comparison between PRTR and ESD Methods

96. The equations used in ESD's to estimate emissions for pulp and paper mills suggest that the form of the estimation methods is similar to that of emission factors used in PRTR's. Based on this form, the emission of a pollutant is related to the extent of an activity through one or more fractional constants. These constants are equivalent to emission factors used in PRTR's. For example, the air emission from paper mill drying sections after size-pressing and coating ($E_{local\text{-}air}$) is related to two quantities, quantity of coated paper produced per day (Q_{paper}) and quantity of active substance applied per ton of paper (Q_{active}), as a measure of the extent of the drying sections through two fractional constants, Evaporation rate (F_{evap}) and Decomposition rate during drying (F_{decomp}):

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

97. Although similar, the form of the emission estimation method used in ESD's for pulp and paper is more complicated than that of emission factors used in PRTR's. This is reflected in the number of quantities used to measure the extent of an activity as well as the number of fractional constants used to relate the emission to the activity. In the case of PRTR's, a single quantity and a single emission factor (fractional constant) are commonly present in the emission estimation equation. The method used in ESD's, however, often employs two or more activity-related quantities and more than one fractional constant in an estimation equation.

98. The principle of the emission estimation method used in ESD's for pulp and paper is a simplified version of mass balance. It states that the quantity released equals the available quantity minus the quantity retained or decomposed. This simplification does not take into consideration chemical formation and chemical input from non-chemical sources such as raw materials.

99. The activity-related quantities and the fractional constants for linking the emission to the activity are extensively quantified in ESD's for pulp and paper mills. The values for these quantities and constants are often provided for different processes and operations and therefore enable more accurate emission estimates. The data in this aspect is more extensive than that provided in PRTR's. For example, different wastewater discharge rates have been gathered in ESD's for different paper products in the European Union and can be used to estimate water releases from a site (Tissier and Migne, 2001, p.11):

2,500-25,000 m^3/d for printing and writing paper
0-10,000 m^3/d for paperboard
2,000-10,000 m^3/d for tissue paper
1,000-30,000 m^3/d for specialty paper

100. Sources of emissions have been a common area for both PRTR's and ESD's to identify in order to capture all possible emissions in their respective estimation procedures. Water and air releases are well characterized in ESD's, but land releases appear to be lacking. It is also observed that the data on land releases is much less than that on water and air releases in the Australian PRTR manual for pulp and paper mills (Environment Australia, 1998). This may be due to the fact that pollutants of environmental concern are primarily associated with water and air releases for pulp and paper mills.

101. The emission estimation method used in ESD's is intended for a broader scope of emission estimation than those used in PRTR's. The focus of a PRTR is normally placed on individual facilities and the methods prescribed are used with a boundary defined around a single facility. The scope of emission estimation for the purpose of ESD's, however, includes not only individual facilities, but also a sector consisting of many facilities of the same nature. As a result, the method and data provided in ESD's

involve the use of many other variables which are not commonly found in PRTR's. Examples of these variables include the total number of sites and the total consumption of a chemical within a sector.

102. As far as risk assessments are concerned, emission factor and mass balance methods described in PRTR's can serve the purpose of ESD's, although their use has not been found as such. To date the majority of ESD's have aimed at yielding reasonable worst-case estimates. Since their form is similar to the method used in ESD's, emission factors are judged to be capable of providing similar estimates used for risk assessments, which have been the primary objective of ESD's. The accuracy of the mass balance method would, on the other hand, depend upon several factors such as facility conditions, type of pollutants, types of releases, etc. (Leisman, 2005). Since direct measurements involve significant effort for data gathering and engineering calculations may require in-depth process knowledge, the two methods may not be suitable for the purpose of risk assessment.

5 – EVALUATION OF PRTR METHODS USED BY TEXTILE MILLS

5.1 – PRTR Emission Estimation

103. There are two PRTR programs found to provide emission estimation methods for textile mills. These two programs are USEPA's Toxics Release Inventory and Australia's National Pollutant Inventory. Their respective emission estimation manuals are listed below:

> USEPA (2000), "Emergency Planning and Community Right-To-Know Act Section 313 Reporting Guidance for the Textile Processing Industry," USEPA, Office of Pollution Prevention and Toxics, Washington, DC, EPA745-B-00-008, May 2000.
>
> Environment Australia (1999), "Emission Estimation Technique Manual for Textile and Clothing Industry," National Pollutant Inventory, July 1999.

104. The USEPA's guidance covers a complete range of activities involved in the textile industry. These activities are grouped into the following four areas:

- Yarn formation: spinning of natural and synthetic raw materials, and texturizing of man-made filament fibres.
- Fabric formation: yarn warping and slashing, weaving, and knitting.
- Wet processing: pretreatment, dyeing, finishing, and printing.
- Product fabrication: fabric cutting, sewing, and final finishing.

105. The scope of the Australia's National Pollutant Inventory program is limited for textile mills. The Emission Estimation Technique Manual for Textile and Clothing Industry is primarily focused on weaving and knitting operations. The processes and pollutants associated with carpet manufacture are briefly discussed.

5.1.1 – Environmental Releases

106. Environmental releases from textile mills are grouped into three categories: 1) air emissions; 2) water releases; and 3) land releases. For textile wet processing, air emissions are commonly generated from desizing, scouring, and singeing operations (USEPA, 2000, p.4-44). Dusts emitted from printing and dyeing operations also contain various chemical pollutants. Volatilization during drying, heat setting and finishing is another source of air emissions. Non-process sources of air emissions include storage tanks and loading and unloading operations.

107. Spent process baths, solutions, and rinses are the primary liquid sources of water releases from textile wet processing (USEPA, 2000, p.4-44). They are generated from desizing, scouring, dyeing, and mercerizing operations. Pollutants typically found in textile industry wastewater include dyes, pigments, and salts. Other water releases include equipment cleaning wastewater, container cleaning wastewater, and used lubricants and other machine operating aids.

108. There are several forms of solid waste. Textile and fabric scrap or off-specification products may contain chemical pollutants of environmental concerns (USEPA, 2000, p.4-44). Pollutant-laden dusts, container residue and machine operating aids are common solid waste found at textile mills.

5.1.2 – Emission Estimation Methods

109. There are four emission estimation methods applicable to textile mills. These methods are: 1) direct measurement or monitoring; 2) mass balance; 3) engineering calculations; and 4) emission factors. Many sources of data exist for these methods, as summarized in Table 8 (USEPA, 2000, p.4-18). These data sources can be combined with site-specific knowledge to determine the best method for calculating each release.

Table 8 – Emission Estimation Methods and Their Associated Data Sources

Monitoring Data	**Mass Balance**
Air permits	Air emissions inventory
Continuous emission monitoring	Hazardous material inventory
Effluent limitations	Hazardous waste manifests
Hazardous waste analysis	MSDSs
Industrial hygiene monitoring data	Pollution prevention reports
NPDES permits	Spill event records
Outfall monitoring data	Supply and purchasing records
pH for acids and bases	
POTW pretreatment standards	
RCRA permit	
Stack monitoring data	
New Source Performance Standards	
Title V permit data	
Emission Factors	**Engineering Calculations**
AP-42 chemical specific emission factors	Facility non-chemical specific emission factors.
Facility or trade association derived chemical-	Henry's Law
specific emission factors	Raoult's Law
	SOCMI* or trade association non-chemical
	specific emission factors
	Solubilities
	Volatilization rates

*Synthetic Organic Chemicals Manufacturing Industry
Source: USEPA, 2000, p.4-18

110. Direct measurement is considered the most accurate method for emission estimation and may be used to estimate water release. Many jurisdictions require that pollutants in the wastewater discharged from textile mills be monitored and measured (USEPA, 2000, p.4-51; Environment Australia, 1999a, p.15). Once the pollutant concentration is known, emission rates can be obtained by multiplying the concentration by the volumetric flow rate of the discharge.

111. Direct monitoring via stack sampling is a preferred method for estimating point source air emissions (Australia, 1999a, p.16-23). It is considered a relatively accurate method for estimating air emissions from textile facilities. Collection and analysis of samples from facilities, however, can be expensive. For particulate matter, the direct monitoring method employs the following equations to determine the emission:

$$E_{PM} = Q_W \times C_{PM} \times 3.6 \times (1 - moist_R / 100) \times [273 / (273 + T)]$$

or

$$E_{PM} = C_{PM} \times Q_d \times 3.6 \times (273 / (273 + T)$$

where

$C_{PM} =$ $C_r / V_{m.STP}$

C_{PM}: concentration of particulate matter, g/m^3

C_r: filter catch, g

$V_{m.STP}$: metered volume of sample at standard temperature and pressure, m^3

E_{PM}: hourly emissions of particulate matter, kg/hr

Q_d: stack gas volumetric flow rate, m^3/s (dry)

T: gas sample temperature, K

Q_W: stack gas volumetric flow rate, m^3/s (wet)

$moist_R$: moisture content, %

112. In the U.S., mass balance combined with engineering calculations is commonly used for textile operations (USEPA, 2000, p.4-47). Data required for mass balance includes operational data such as batch recipes, inventory records, and production records. This data can help determine the quantity of a given chemical or chemical category used on site. Data included in material safety data sheets (MSDS) can also be used for mass balance. The knowledge of production processes and engineering calculations can then be used to determine the quantity of a chemical remaining on fabric and released to an environmental medium.

113. In Australia, the use of mass balance by textile mills is limited (Environment Australia, 1999a, p.23). The method appears to be straightforward, but requires facilities to consistently track material usage and waste generation. Errors associated with individual material tracking or other activities can often result in large deviations of total facility emissions. This is because emissions from specific materials are typically below 2 percent of their gross consumption and an error of 5 percent in any step of the tracking operation can skew emission estimates.

114. Engineering calculations can be used for estimating emissions from textile mills. The method is more complex and time consuming than the use of emission factors (Environment Australia, 1999a, p.24). Although it requires more detailed input data, the method of engineering calculations enables the determination of emission estimates based on facility-specific conditions. Computer models are also classified as engineering calculations and are available for estimating emissions from storage tanks, water and wastewater treatment, and other processes (USEPA, 2000, p.4-24).

115. Emission factors are the usual method for determining losses through fugitive emissions (Australia, 199a, p.12-21). They are commonly expressed as the weight of a substance emitted per unit weight, volume, distance, or duration of an emitting activity. The general form of this method is given as:

$$E_{kpyi} = (A \times OpHrs) \times EF_i \times (1 - CE_i/100)$$

where

E_{kpyi}: annual emissions of pollutant, kg/yr

A: activity rate, t/hr

OpHrs: operating hours, hr/yr

EF_i: uncontrolled emission factor of pollutant, kg/t

CE_i: overall control efficiency for pollutant, %

116. When emission factors are used, the Australian PRTR program requires that their associated rating code be indicated (Environment Australia, 1999a, p.24). The rating code is based on the work from the USEPA and European Environment Agency. The code provides a measure of uncertainty associated with the emission factor used and is divided into the following levels in a decreasing order of uncertainty:

A - Excellent
B - Above Average
C - Average
D - Below Average
E - Poor
U - Unrated

117. USEPA's publication *Compilation of Air Pollutant Emission Factors (AP-42)* is the most widely known and used source for emission factors (USEPA, 2000, p.4-22). It contains emission factors for both individual chemicals and chemical groups such as volatile organic compounds. Volume I of AP-42 contains information on over 200 stationary source categories, including process descriptions and potential sources of air emissions from these processes. Only chemical-specific emission factors are required to estimate emissions for textile mills.

5.2 – ESD Emission Estimation

118. Several ESD's are found to have addressed emission estimation for textile mills. These documents are listed below:

European Union (2001), "Emission Scenario Document – Textile Finishing Industry," May 2001.

OECD (2003), "OECD Emission Scenario Document on Textile Finishing Industry," Umweltbundesamt (UBA), Berlin, Germany, January 2003.

OECD (2002), "Emission Scenario Document on Textile Finishing Industry," Organisation for Economic Co-operation and Development, Environment Directorate, February 2002.

European Commission (1996), "Technical Guidance Document in Support of Commission Directive 93/67/EEC on Risk Assessment for New Notified Substances and Commission Regulation (EC) No 1488/94 on Risk Assessment for Existing Substances," Part IV, Office for Official Publications of the European Communities, Luxembourg, 1996.

119. The emission estimation method used in ESD's for textile mills is the same as that for pulp and paper mills discussed in Section 4.2 – ESD Emission Estimation (for pulp and paper mills). The method defines emission to an environmental medium as an output and a number of parameters as inputs used in an equation for the determination of the output (OECD, 2003; OECD, 2002b; European Union, 2001; European Commission, 1996). The general format of this method is presented in Table 9.

Table 9 – General Format of Emission Estimation for Textile Mills

Type	Variable	Symbol	Units	Default	Category (S, D, O, P, C)
Input	Definition of an input variable				
Output	Definition of an output variable				
Calculation	Equations for intermediate and end calculations				

120. Variables in an emission estimation equation are grouped into five categories. The first category, denoted by S, consists of variables that must be specified in the emission estimation and there are no default values for these variables or methods providing their estimates (OECD, 2003; OECD, 2002b). The second category, denoted by D, includes variables with standard defaults which can be modified by users. The third category, denoted by O, provides a group of variables with their values calculated which can, however, be overwritten by users with alternative data. The fourth category, denoted by P, pertains to variables with their values selected from a pick-list. The fifth category, denoted by C, refers to variables with their values provided as constants which cannot be changed by users. Output variables are always specified as O.

121. The method described above is used to estimate water emissions of pollutants from various operations. For the purpose of emission estimation, operations at textile mills are divided into 1) pre-treatment; 2) exhaust; and 3) padding, printing and coating (OECD, 2003; OECD, 2002b). Chemicals used are divided into basic chemicals, dyestuff, and auxiliary (preparation agents, sizing agents, softening agents, repellents, biocides, etc.). Summarized in Table 10, 11, and 12 are sets of variables and equations used for estimating water emissions from pretreatment, exhaust, and padding, printing and coating operations, respectively.

Table 10 – Estimation Method for Water Emissions of Preparation Agents, Sizing Agents, Biocides from Pretreatment Processes

Type	Variable	Symbol	Units	Default	Category
Input	Mass of textile processed per day	$Q_{textile}$	t/d		D
	Mass of auxiliary (preparation agents, sizing agents, biocides) per mass of fabric	$Q_{product}$	kg/t		D, S
	Content of active substance in preparation	$C_{substance}$		1	D, S
	Degree of fixation	$F_{fixation}$		0	D, S
Output	Local emission of substance per day to wastewater	$E_{local\text{-}water}$	kg/d		O
Calculation	$E_{local\text{-}water} = Q_{textile} \times Q_{product} \times C_{substance} \times (1 - F_{fixation})$				

Source: OECD, 2003, p.48; OECD, 2002b

Table 11 – Estimation Method for Water Emissions of Basic Chemicals, Dyestuff, Softening Agents, Repellents, and Biocides from Exhaust Processes

Type	Variable	Symbol	Units	Default	Category
Input	Mass of textile processed per day	$Q_{textile}$	t/d		D
	Fraction of fabric treated with auxiliary, basic chemical or dyestuff	$F_{product}$	-	0.3	D
	Mass of auxiliary, basic chemical or dyestuff preparation per mass of fabric	$Q_{product}$	kg/t		D, S
	Content of active substance in preparation of auxiliary, basic chemical or dyestuff	$C_{substance}$		1	D, S
	Degree of fixation	$F_{fixation}$	-		D, S
Output	Local emission of substance per day to wastewater	$E_{local\text{-}water}$	kg/d		O
Calculation	$E_{local\text{-}water} = Q_{textile} \times F_{product} \times Q_{product} \times C_{substance} \times (1 - F_{fixation})$				

Source: OECD, 2003, p.49; OECD, 2002b, p.22

Table 12 – Estimation Method for Water Emissions of Basic Chemicals, Dyestuff, Softening Agents, Repellents, and Biocides from Padding and Printing Processes

Type	Variable	Symbol	Units	Default	Category
Input	Mass of textile processed per day	$Q_{textile}$	t/d		D
	Fraction of fabric treated with auxiliary, basic chemical or dyestuff	$F_{product}$	-	0.3	D
	Mass of auxiliary, basic chemical or dyestuff preparation per mass of fabric	$Q_{product}$	kg/t		D, S
	Content of active substance in preparation of auxiliary, basic chemical or dyestuff	$C_{substance}$		1	D, S
	Degree of fixation	$F_{fixation}$	-		D, S
	Amount of Residual Liquor	$F_{residual}$			D, S
Output	Local emission of substance per day to wastewater	$E_{local\text{-}water}$	kg/d		O
Calculation	$E_{local\text{-}water} = Q_{textile} \times F_{product} \times Q_{product} \times C_{substance} \times (1 - F_{fixation}) + Q_{textile} \times F_{product} \times Q_{product} \times C_{substance} \times F_{residual}$				

Source: OECD, 2003, p.50; OECD, 2002b, p.24

122. The water release from a dyeing operation can also be estimated from the liquor ratio. The liquor ratio is defined as the ratio of mass of fabric to volume of dyebath (European Commission, 1996, p.719). The water release per day may be calculated by the equation:

$$E = W_1 \times W_2 \times (100 - F) / 100$$

where

W_1: mass of good processed per day, t/d

W_2: mass of substance used per mass of good, g/kg

F: degree of fixation, %

123. The principle of the emission estimation method used for estimating emissions to water is a simplified version of mass balance. It states that the quantity released equals the available quantity minus the quantity retained. This simplification does not take into consideration chemical formation and chemical input from non-chemical sources such as raw materials.

124. Emission factors are used to estimate air emissions from textile mills, as illustrated in Table 13. They are based on either pollutant or textile substrate (OECD, 2003, p.51). A substance emission factor is defined as the amount of a substance emitted per unit mass of auxiliary used under defined conditions. In Germany, the substance emission factor of a chemical is included in its Material Safety Data Sheets. A substrate emission factor is defined as the amount of a substance emitted per unit mass of textile processed under defined conditions.

Table 13 – Estimation Method for Air Emissions of Basic Chemicals, Dyestuff, Softening Agents, Repellents, and Biocides

Type	Variable	Symbol	Units	Default	Category
Input	Mass of textile processed per day	$Q_{textile}$	t/d		D
	Mass of auxiliary, basic chemical or dyestuff preparation per mass of fabric	$Q_{product}$	kg/t		D, S
	Fraction of fabric treated with auxiliary, basic chemical or dyestuff	$F_{product}$		0.3	D
	Substance emission factor of auxiliary, basic chemical or dyestuff	f_s	g/g		DS
Output	Local emission of substance per day to wastewater	$E_{local\text{-}air}$	kg/d		O
Calculation	$E_{local\text{-}air} = Q_{textile} \times Q_{product} \times F_{product} \times f_s$				

Source: OECD, 2003, p.50

125. Several parameters must be known in order to estimate air emissions by emission factors. For example, the concentration of an auxiliary in the finish applied and the liquor pick-up rate must be determined in order to estimate air emissions from finishing. The total air emissions from a mill can be obtained by adding up emissions from all individual sources.

5.3 – Comparison between PRTR and ESD Methods

126. Emission factors are found to be a method of choice for estimating air emissions in both PRTR's and ESD's for textile mills. Although direct monitoring is a preferred method for estimating point source air emissions as indicated in the Australia PRTR program, emission factors are usually used in case of fugitive air emissions (Australia, 1999a, p.12-23). In a similar manner, an ESD developed for textile facilities by the German Environmental Agency also suggests the use of emission factors for estimating air emissions from textile finishing operations (OECD, 2003, p.51).

127. There is a difference in using the method of emission factors for air emissions between PRTR's and ESD's. For the purpose of PRTR's, the most widely used source for emission factors is USEPA's publication *Compilation of Air Pollutant Emission Factors (AP-42)* (USEPA, 2000, p.4-22), while the ESD from the German Environmental Agency employs substance and textile substrate based emission factors developed specifically for the German textile industry. The emission factors from Germany can be found in a document entitled "Best Available Techniques in Installations of the Textile Industry" prepared by H. Schonberger and T. Schafer for the German Environmental Agency.

128. The emission estimation method used for estimating water releases in ESD's is found to have a similar form to that of emission factors described in PRTR's. The method provides various equations to estimate water releases from different operations. Each equation calculates the amount of a chemical pollutant released from a given operation based on the extent of the operation and the degree of the release. The extent of the operation is usually characterized by two or more quantities, while the degree of the release is accounted for by one fractional constant. This constant is equivalent to emission factors used in PRTR's. As an example, the following equation for estimating water releases from a dyeing operation illustrates the form used in ESD's where the degree of fixation ($F_{fixation}$) is considered to have the same role as an emission factor:

$$E_{local\text{-}water} = Q_{textile} \times F_{product} \times Q_{product} \times C_{substance} \times (1 - F_{fixation})$$

where

$E_{local\text{-}water}$: local emission of substance per day to wastewater

$Q_{textile}$: mass of textile processed per day (Qtextile)

$F_{product}$: fraction of fabric treated with auxiliary, basic chemical or dyestuff

$Q_{product}$: mass of auxiliary, basic chemical or dyestuff preparation per mass of fabric

$C_{substance}$: content of active substance in preparation of auxiliary, basic chemical or dyestuff

$F_{fixation}$: degree of fixation

129. Although similar, the form of the emission estimation method used in ESD's for textile mills is more complicated than that of emission factors used in PRTR's. This is reflected in the number of quantities used to measure the extent of an activity as well as the number of fractional constants used to relate the emission to the activity. An emission factor is merely a coefficient determined by testing, survey or modelling, while the fractional constant present in an estimation equation used in ESD's is a process parameter and often used in operation-related calculations. For example, the degree of fixation in the equation given above is defined as the amount of dyestuff exhausted to fabric and can be used to determine the amount required for dyeing a given quantity of fabric materials.

130. Sources of emissions are well identified in both PRTR's and ESD's. Emissions to air, water, and land are identified in the USEPA's PRTR guidance for textile facilities. Air and water emissions are further related to specific operations such as desizing, scouring, dyeing, finishing and printing. Water emissions are the primary focus of the OECD ESD's reviewed. They are grouped by operation type into pretreatment, exhaust, and finishing/printing as well by chemical type into basic chemicals, dyestuff, and auxiliaries. Emissions to land are not discussed in the ESD's.

131. The ESD's reviewed are found to have provided emission estimation equations for individual textile facilities only. In many other ESD's such as those for pulp and paper manufacture, the scope of emission estimation is extended to include a sector consisting of many facilities of the same nature. Such extension may be incorporated in future versions of ESD's for textile industry. This will make it necessary to introduce emission estimation equations for an entire sector and sector related parameters such as the total number of sites and the total consumption of a chemical within a sector.

132. As in the case of pulp and paper manufacture, emission factors and mass balance described in PRTR's can support the purpose of ESD's, i.e., the risk assessments for textile industry. Since their form is similar to the method used in ESD's, emission factors are judged to be able to provide reasonable worst-case estimates or similar estimates. The accuracy of the mass balance method would, on the other hand, depends upon several factors such as facility conditions, types of pollutants, and types of releases (Reisman, 2005). Since direct measurements involve significant effort for data gathering and engineering calculations may require in-depth process knowledge, the two methods may not be suitable for the purpose of risk assessment.

6 – SAMPLE EMISSION ESTIMATES BY PRTR AND ESD METHODS

133. Summarized in this section are seven emission estimation calculation examples with detailed calculations compiled in related appendices. In each example, the emission of a substance to wastewater is estimated by a PRTR method (mass balance or emission factor) and the ESD fixation-based method. The estimates from the two methods are compared and reasons for differences are discussed. The seven examples are

- Biocide Emission to Wastewater from Paper Mills
- Emission of Nonylphenol and Its Ethoxylates to Wastewater from Yarn Dyeing
- Chromium Emission to Wastewater from Textile Dyeing
- Surfactant Emission to Wastewater from Commercial Laundering
- Siloxane Emission to Wastewater from Textile Mills
- Siloxane Emission to Wastewater from Paper Mills
- Dye Emission to Wastewater from Paper Mills

134. Provided in Table 14 is a summary of the above seven examples. As an estimation basis, the throughput is assumed to be 100,000 tonne of paper produced per year for paper mills, 1,000 tonne of textile processed per year for textile mills, and 0.5 tonne of laundry per day in case of laundering.

Table 14 – Summary of Emission Estimation Calculation Examples

Sample No.	Description	PRTR Method	Emission to Wastewater (kg/d)		Discrepancy
			PRTR Method	ESD Fixation-based Method	
1	Biocide emitted from paper mill	mass balance	7.5	5.7	32%
2	Nonylphenol and its ethoxylates emitted from yarn dyeing	mass balance	15.4	11.4	26%
3	Chromium emitted from textile dyeing	emission factor	5.32	3.77	41%
4	Surfactant emitted from laundering	emission factor	1.1	0.6	83%
5	Siloxane emitted from textile mill	mass balance	4.4	4.4	0%
6	Siloxane emitted from paper mill	mass balance	0.063	0.054	14%
7	Dye emitted from paper mill	mass balance	104.3	85.7	22%

135. It is found during the preparation of calculation examples that emission factors for water releases are scarce. Published emission factors are primarily limited to air emissions. Although a wide range of data is available to the ESD fixation-based method, it has been prevented from comparing to the PRTR emission factor method in many cases due to the absence of aqueous emission factors.

6.1 – Biocide Emission to Wastewater from Paper Mills

136. Compared in Table 15 are the estimation results of the PRTR mass balance method with those of the ESD fixation-based method for biocide emission to wastewater from non-integrated paper mills. Detailed calculations can be found in Appendix 1. The results pertain to an active ingredient in a biocide used for paper preservation and the quantity of pulp used (100,000 tonne/yr) refers to the input excluding

the amount of broke recycled. The PRTR mass balance method yields a higher estimate than the ESD fixation-based method by 32%. In other words, the PRTR method is more conservative than the ESD method.

Table 15 – Biocide Emission to Wastewater from Paper Mills

Method	PRTR – Mass Balance	ESD – Fixation Based
Emission to Wastewater	7.5 kg/d	5.7 kg/d
Basis	Quantity of pulp = 100,000 tonne/yr Number of operation days = 350 d/yr	Quantity of pulp = 100,000 tonne/yr Number of operation days = 350 d/yr
Assumption	Biocide use rate = 2 kg/tonne Active ingredient concentration = 0.1 Biocide fixation rate = 0.8 Degree of water closure = 0.5 Broke recycle rate = 0.2	Biocide use rate = 2 kg/tonne Active ingredient concentration = 0.1 Biocide fixation rate = 0.8 Degree of water closure = 0.5

137. The higher estimate by the PRTR method results from the inclusion of both water and broke recycles in the analysis of the fate of biocide within a papermaking process. Although broke recycle at 20% is common at paper mills, only water recycle is considered in the ESD fixation-based method. The broke recycle adds a source for biocide emission through broke repulping, since a fraction of the biocide contained in broke is released upon re-introduction into the papermaking process. It should be noted that the biocide use rate at 2 kg/tonne is defined as kg of biocide added to one tonne of pulp without accounting for the returning biocide via water and broke recycles.

138. In the mass balance analysis, it becomes important to distinguish between the quantity of biocide added to the process (use rate) and the quantity contained in pulp suspension per unit mass of fibre. The two quantities are different when the papermaking process involves recycles (broke or water or both). This difference is, however, not recognized in the ESD method.

139. In the emission estimation with the PRTR and ESD methods, the following assumptions are made

- Biocide use is assumed at 2 kg/tonne based on the range of 0.1-4% on paper given by Tissier and Migne (2001).
- The concentration of an active ingredient in a biocide is assumed at 10% based on a calculation example provided by Tissier and Migne (2001).
- The biocide fixation rate is assumed at 0.8 as given by Tissier and Migne (2001).
- The broke recycle rate is assumed at 20% of paper production as suggested by Tissier and Migne (2001).
- The degree of water closure is understood as the ratio of water recycled to white water generated and assumed at 0.5 based on the range of 0.4-0.7 for fine paper mills (European Commission, 1996).

6.2 – Emission of Nonylphenol and Its Ethoxylates to Wastewater from Yarn Dyeing

140. Nonylphenol (NP) and its ethoxylates (NPEs) are a group of compounds used as surfactants in textile processing. In fibre and yarn production, they can be added to spin finishes which are used during fibre spinning operations to reduce the fibre-to-fibre and fibre-to-metal friction. It is expected that the amount applied will remain in the finished products.

141. A spin finish consists of several components (Slade, 1998, p.5; Fourné, 1999, p.622). Mineral oil derivatives, commonly referred to as lubricants, are the basis of spin finishes. Other components include emulsifiers, antistatic agents, anti-microbial compounds, cohesive agents, humectants, wetting agents, etc.

142. Yarn dyeing is also likely to involve the use of NP/NPEs. Surfactants are normally added to the dye bath to facilitate the dyeing process and may contain NP/NPEs. It is expected that the majority of the surfactants used is discharged along with the dye bath and the remaining portion is washed off the dyed goods during subsequent rinsing operations.

143. Presented in Table 16 are calculation results for NP/NPE emissions to wastewater from yarn dyeing. Detailed calculations can be found in Appendix 2. The emission sources include both surfactants used during yarn dyeing and spin finishes carried with raw materials. The PRTR's mass balance method took both sources into consideration, while the ESD fixation-based method ignores the source of raw materials. As a result, the ESD method underestimates the NP/NPE emissions to wastewater by 26% compared with the PRTR calculation.

Table 16 – Emission of Nonylphenol and Its Ethoxylates to Wastewater from Yarn Dyeing

Method	**PRTR – Mass Balance**	**ESD – Fixation Based**
Emission to Wastewater	15.4 kg/d	11.4 kg/d
Basis	Quantity of textile = 1,000 tonne/yr Number of operation days = 250 d/yr	Quantity of textile = 1,000 tonne/yr Number of operation days = 250 d/yr
Assumption	Use rate of surfactants = 11 kg/tonne yarn Fraction of NP/NPEs in surfactants = 0.26 Fixation rate of surfactants = 0 Spin finishes in yarn = 5 kg/tonne yarn Fraction of NP/NPEs in spin finishes = 0.20 Removal rate of spin finishes = 1	Use rate of surfactants = 11 kg/tonne yarn Fraction of NP/NPEs in surfactants = 0.26 Fixation rate of surfactants = 0

144. The calculations are based on the following assumptions:

- The amount of surfactants used in yarn dyeing was estimated at 11 kg/tonne goods dyed (Crechem, 2000).
- The proportion of NP/NPEs in surfactants for the Canadian wet processing sector was estimated at 0.26 (Crechem, 2000).
- The fixation rate of surfactants on goods is assumed at zero.
- The amount of spin finishes applied to fibre during fibre and yarn production is assumed at 5 kg per tonne of fibre/yarn. This is based on a number of studies cited by Slade (1998, p.25). In one study, the fibre-to-fibre and fibre-to-metal friction was found to decrease as the amount of spin finishes increased and reach a plateau at 0.5% by weight on fibre. In two other studies, a minimum of 0.15 to 0.20% by weight on fibre was found necessary for the formation of a mono-molecular film on fibre.
- The proportion of NP/NPEs in spin finishes is assumed to be 0.2 on average based on an industry survey (Crechem, 2004e).
- The removal rate of spin finishes from yarn is 100%.

6.3 – Chromium Emission to Wastewater from Textile Dyeing

145. Compared in Table 17 are the estimation results of the PRTR emission factor method with those of the ESD fixation-based method for total chromium emission to wastewater from textile dyeing. Detailed calculations can be found in Appendix 3. The PRTR emission factor method is found to yield a higher estimate than the ESD method by 41%. In other words, the PRTR method is more conservative than the ESD method.

Table 17 – Chromium Emission to Wastewater from Textile Dyeing

Method	PRTR – Emission Factor	ESD – Fixation Based
Emission to Wastewater	5.32 kg/d	3.77 kg/d
Basis	Quantity of textile = 1,000 tonne/yr Number of operation days = 250 d/yr	Quantity of textile = 1,000 tonne/yr Number of operation days = 250 d/yr
Assumption	Emission factor = 1.33 kg/tonne textile dyed (Environment Australia, 1999a).	Use level of dyes = 19.0 kg/tonne textile (Crechem, 2004a). Use level of dye auxiliaries = 44.3 kg/tonne textile (Crechem, 2004a). Chromium concentration in dyes = 0.02 (USEPA, 2000). Fixation rate for dyes = 0.85 (USEPA, 2000). Fixation rate for dye auxiliaries = 0 (Crechem, 2004a).

146. Chromium emission to wastewater results from the use of chromium-containing dyes and dye auxiliaries (USEPA, 2000). In the emission estimation calculations, the chromium concentration in dye auxiliaries is unknown and is assumed to be the same as that in dyes.

6.4 – Surfactant Emission to Wastewater from Commercial Laundering

147. Commercial laundering results in a wastewater discharge to sewers and detergents are the major source of contaminants. A medium sized laundering facility has a throughput of 60,000 pieces per week, which is equivalent to 15-25 tonnes per week (OECD, 2002c, p.70). Typical dosage of detergents ranges from 5 to 20 kg per tonne laundry.

148. Detergents are used to aid in soil removal and provide fabric softening, whitening, stiffening and disinfection (OECD, 2002c, p.67). They contain various components, as listed below along with their respective proportions:

- Surfactants (10-17%)
- Phosphates (5-25%)
- Alkalis (20-70%)
- Bleaching agents (0-45%)
- Optical brighteners (0.1-0.3%)
- Anti-redeposition (1-2%)
- Stabilisers (1-2%)
- Corrosion inhibitors (0-5%)

149. Surfactants most frequently used in detergents include linear alkyl benzene sulphonates, secondary alkyl sulphonates, alpha olefin sulphonates, and alcohol ethoxylates (OECD, 2002c, p.68).

Several surfactants are commonly combined into one formulation in order to achieve optimum performance at reasonable cost.

150. Compared in Table 18 are the estimation results of the PRTR emission factor method with those of the ESD fixation-based method for surfactant emission to wastewater from commercial laundering. Detailed calculations can be found in Appendix 4. The PRTR emission factor method is found to predict a higher emission than the ESD fixation-based method by 83%. In other word, the PRTR method yields a more conservative estimate than the ESD method.

Table 18 – Surfactant Emission to Wastewater from Commercial Laundering

Method	PRTR – Emission Factor	ESD – Fixation Based
Emission to Wastewater	1.1 kg/d	0.6 kg/d
Basis	Facility throughput = 0.5 tonne/d.	Facility throughput = 0.5 tonne/d.
Assumption	Per capita quantity of laundry = 5 kg/person-week.	Detergent dosage = 10 kg/tonne. Surfactant concentration = 12%. Fixation rate = 0.

151. The following assumptions are made in the estimation calculations with the PRTR and ESD methods:

- Facility throughput = 0.5 tonne/d (OECD, 2002c, p.71).
- Detergent dosage = 10 kg/tonne (OECD, 2002c, p.71).
- Surfactant concentration = 12% (OECD, 2002c, p.71).
- Fixation rate = 0.
- Per capita quantity of laundry = 5 kg/person-week.

6.5 – Siloxane Emission to Wastewater from Textile Mills

152. Presented in Table 19 are the estimates for siloxane emission to wastewater from textile finishing based on the PRTR mass balance and ESD fixation-based methods. The two methods yielded the same results because they both followed the same estimation principle although different procedures were used. The two methods become equivalent to each other only when an operation such as textile finishing does not involve recycle streams, multiple substance sources, and other complicated factors. Detailed calculations can be found in Appendix 5.

Table 19 – Siloxane Emission to Wastewater from Textile Finishing

Method	PRTR – Mass Balance	ESD – Fixation Based
Emission to Wastewater	4.4 kg/d	4.4 kg/d
Basis	Quantity of textile = 1,000 tonne/yr Number of operation days = 250 d/yr	Quantity of textile = 1,000 tonne/yr Number of operation days = 250 d/yr
Assumption	Fixation rate = 1.0 Fraction of residual finish liquor = 0.1 Siloxane pick-up = 10 kg/tonne Siloxane concentration = 10 kg/m^3	Fixation rate = 1.0 Fraction of residual finish liquor = 0.1 Siloxane pick-up = 10 kg/tonne Siloxane concentration = 10 kg/m^3

153. The siloxane estimated was amido polyether modified silicone fluid which was a notified substance in Australia (Department of Health and Ageing of Australia, 1992). It was manufactured in Japan and imported to Australia by Dow Corning Australia. Its formula was given as $C_3H_9SiO(C_2H_6SiO)_{400}(C_{29}H_{59}O_3N_2)_8SiC_3H_9$ with a molecular weight of 34,400 g/gmol. The substance was used as a textile softener to impart durable, wash resistant softness to fabrics.

154. Pad is a conventional textile finishing technique. It involves three steps commonly referred to as pad-dry-cure (Vail, 1983). In the first step, the fabric is immersed in an aqueous finish bath and then squeezed to remove excess liquor to assure even distribution of chemicals in the fabric. Padding is followed by drying which simply involves removal of water from the fabric. Drying and curing are often performed in one continuous process, while on the other hand, the dried fabric may be made into garments prior to curing. Depending upon the formulation used in the finish bath, chemical reactions with cellulose may take place during drying.

155. In general, the emission of a softener to wastewater from a textile finishing operation is considered to result from two sources: 1) the amount picked up by but not fixed onto textile; and 2) the amount in residual finish liquor discharged. The former is normally negligible since the fixation rate is 100% for a pad process, and the latter, therefore, becomes the principal source of the emission. The following assumptions were used in the estimation with both PRTR mass balance and ESD fixation-based methods:

- Fixation rate = 1.0 (Shafer, 2003)
- Fraction of residual finish liquor = 0.1 (Shafer, 2003)
- Siloxane picked up by textile per unit production = 10 kg/tonne textile finished (Department of Health and Ageing of Australia, 1992)
- Siloxane concentration in finish liquor = 10 kg/m^3 (Department of Health and Ageing of Australia, 1992)

6.6 – Siloxane Emission to Wastewater from Paper Mills

156. Presented in Table 20 are the estimates for siloxane emission to wastewater from coating operations at a paper mill based on the PRTR mass balance and ESD fixation-based methods. The PRTR method yielded a higher estimate than the ESD method, or in other words, the fixation-based calculation resulted in an underestimate by 14% compared to the mass balance analysis. Detailed calculations can be found in Appendix 6.

Table 20 – Siloxane Emission to Wastewater from Paper Coating

Method	PRTR – Mass Balance	ESD – Fixation Based
Emission to Wastewater	0.063 kg/d	0.054 kg/d
Basis	Paper production = 100,000 tonne/yr Number of operation days = 350 d/yr	Paper production = 100,000 tonne/yr Number of operation days = 350 d/yr
Assumption	Use level of paper coatings = 4.5 kg/tonne Fixation rate = 0.998 Mass fraction of siloxane in paper coatings = 0.0019 Broke generation rate = 20% of paper production Coated broke generation rate = 10% of paper production Rate of coatings removal from broke processing = 10%	Use level of paper coatings = 4.5 kg/tonne Fixation rate = 0.998 Mass fraction of siloxane in paper coatings = 0.0019 Broke generation rate = 20% of paper production Rate of coatings removal from broke processing = 10%

157. The siloxane estimated is a dimethylpolysiloxane fluid used as an antifoam additive for paper coatings (www.rhodia-silicones.com accessed May 10, 2004). The product is manufactured by Rhodia and marketed under the trade name of RHODORSIL 47V200. It is a linear polymer and functions as a mold release agent, lubricant or foam control agent.

158. Both PRTR and ESD methods recognize that the siloxane emission result from two sources: one is the loss occuring during the use of coatings and the other is the release from broke repulping. The two methods gave the same estimate for the amount lost during the use of coatings, but differed in the determination for the amount released from broke repulping. The PRTR method took into consideration the coatings both applied to paper surface and contained in paper fibre in the estimation of the amount released from broke repulping, while the ESD method only accounted for the coatings applied. The exclusion of the coatings contained in paper fibre from the estimation is believed to result in an underestimate from the ESD method.

6.7 – Dye Emission to Wastewater from Paper Mills

159. Presented in Table 21 are the estimates for dye emission to wastewater from a paper mill based on the PRTR mass balance and ESD fixation-based methods. The PRTR method yielded a higher estimate than the ESD method by 22%. In other words, the PRTR method is more conservative than the ESD method. Detailed calculations can be found in Appendix 7.

Table 21 – Dye Emission to Wastewater from Paper Mills

Method	PRTR – Mass Balance	ESD – Fixation Based
Emission to Wastewater	104.3 kg/d	85.7 kg/d
Basis	Quantity of pulp = 100,000 tonne/yr Number of operation days = 350 d/yr	Quantity of pulp = 100,000 tonne/yr Number of operation days = 350 d/yr
Assumption	Dye use rate = 10 kg/tonne Dye compound concentration in dye = 1 Dye fixation rate = 0.95 Degree of water closure = 0.4 Broke recycle rate = 0.2	Dye use rate = 10 kg/tonne Dye compound concentration in dye = 1 Dye fixation rate = 0.95 Degree of water closure = 0.4

160. The higher estimate by the PRTR method results from the inclusion of both water and broke recycles in the analysis of the fate of a dye compound within a papermaking process, whereas only water recycle is considered in the ESD method. The broke recycle adds a source for dye emission through broke repulping, since a fraction of the dyes contained in broke is released upon re-introduction into the papermaking process.

161. In the mass balance analysis, it becomes important to distinguish between the quantity of dye added to the process (use rate) and the quantity contained in pulp suspension per unit mass of fibre. The two quantities are different when the papermaking process involves recycles (broke or water or both). This difference is, however, not recognized in the ESD method.

7 – CONCLUSIONS

162. Common emission estimation methods found in PRTR's are as follows: direct monitoring or measurement, mass balance, emission factors, and engineering calculations. These methods are used in the PRTR programs of Canada, the US, Australia, and the UK. Engineering judgement, although identified by the OECD, is not included in the PRTR programs of Canada, Australia, and the UK, but may be considered under the category of engineering calculations in the US PRTR program. Types of engineering calculations include fuel analysis, indirect monitoring, computer models, etc.

163. Emission estimation methods found in ESD's are similar to emission factors. They employ various equations of the same form which links the amount of emissions to two groups of parameters. The first group provides a measure of the extent of an emitting operation and the second group consists of proportional coefficients to account for the fraction of chemicals emitted. These equations are used to estimate air and water emissions from pulp and paper mills and water emissions from textile mills. The method of emission factors is, in fact, used to determine air emissions from textile mills.

164. The basic approach to emission estimation is found similar between PRTR's and ESD's. This approach first identifies sources of emissions with their environmental media and then provides appropriate methods to estimate these emissions. Emissions to air, water, and land are identified in the PRTR guidance manuals from the US and Australia for textile and pulp and paper mills, while the emphasis of the ESD's reviewed is placed on air and water emissions. The intent of an emission estimation method provided in PRTR's is to determine emissions from individual facilities. On the other hand, the scope of the emission estimation described in ESD's is extended to include emission estimates from a sector consisting of many facilities.

165. Emission factors and mass balance are judged to be capable of supporting risk assessments intended by ESD's. Several calculation examples showed that the PRTR mass balance and emission factor methods yielded more conservative estimates than the ESD fixation-based method by up to 80%. The PRTR mass balance method was found to present a thorough analysis on parameters such as multiple substance sources and recycles which could impact emissions to wastewater. These parameters were apparently not accounted for in the ESD method, which might be the cause for higher emission estimates from the PRTR method.

166. It has been found that emission factors for water releases are scarce. Published emission factors are primarily limited to air emissions. Although a wide range of data is available to the ESD fixation-based

method, it has been prevented from comparing to the PRTR emission factor method in many cases due to the absence of aqueous emission factors.

REFERENCES

Ash, M.; and I. Ash (2001), Handbook of Paper and Pulp Chemicals, Synapse Information Resources Inc., Endicott, NY, USA, 2001.

Cai, Y.; M. T. Pailthorpe; and S. K. David (1999), "A New Method for Improving the Dyeability of Cotton with Reactive Dyes," Textile Research Journal 69, 440-446 (1999).

Canadian Textile Institute (www.textiles.ca), Tel: (613) 232-7195, Fax: (613) 232-8722

222 Somerset St. W., Suite 500, Ottawa, ON K2P 2G3, Environmental contact: Sophie Tourangeau, ext.108, Email: cti@textiles.ca.

Crechem Technologies Inc.(2004a), "Emission Scenario Document for Woven Fabric Dyeing and Finishing Mills," prepared for Environment Canada, Gatineau, Quebec, March 31, 2004a.

Crechem Technologies Inc.(2004b), "Emission Scenario Document for Kraft Pulp Mills," prepared for Environment Canada, Gatineau, Quebec, March 31, 2004b.

Crechem Technologies Inc.(2004c), "Emission Scenario Document for Recovered Paper Mills," prepared for Environment Canada, Gatineau, Quebec, March 31, 2004c.

Crechem Technologies Inc.(2004d), "Emission Scenario Document for Non-integrated Paper Mills," prepared for Environment Canada, Gatineau, Quebec, March 31, 2004d.

Crechem Technologies Inc. (2004e), "NPE-Containing Chemical Evaluation in the Textile Sizing Process and in Synthetic Fibre Manufacturing," prepared for Environment Canada, Environmental Protection Branch, Montreal, Quebec, March 2004.

Crechem Technologies Inc. (2000), "Background Study on Canadian Wet Processing Textile Mills Industry and Their Effluents," prepared for Environment Canada, Environmental Protection Branch, Montreal, Quebec, August 30, 2000.

Department of Health and Ageing of Australia (1992), "National Industrial Chemicals Notification and Assessment Scheme – Full Public Report: Amido Polyether Modified Silicone Fluid," File No.: NA/57, December 17, 1992, obtained from the web site of the Department of Health and Ageing, Australian Government, www.nicnas.gov.au, May 4, 2004.

Environment Australia (2003), "National Pollutant Inventory Guide," version 2.16 released October 17, 2003, Australian Government, Department of the Environment and Heritage, downloaded from http://www.npi.gov.au (accessed Jan.13, 2004).

Environment Australia (1999a), "Emission Estimation Technique Manual for Textile and Clothing Industry," National Pollutant Inventory, July 1999, downloaded from www.npi.gov.au (accessed Jan.13, 2004).

Environment Australia (1998), "Emission Estimation Technique Manual for Pulp and Paper Manufacturing," National Pollutant Inventory, August 1998, downloaded from www.npi.gov.au (accessed Jan.13, 2004).

Environment Canada (2004), "2003 Guide for Reporting to the National Pollutant Release Inventory," National Pollutant Release Inventory, Hull, Quebec, Canada, 2004, downloaded from www.ec.gc.ca/pdb/npri/npri_home_e.cfm (accessed Mar.15, 2004).

Environment Canada (2002), "Guide for Reporting to the National Pollutant Release Inventory 2002," National Pollutant Release Inventory, Hull, Quebec, Canada, 2002, downloaded from www.ec.gc.ca/pdb/npri/npri_home_e.cfm (accessed Jan.13, 2004).

Environment Canada (1998), "Survey of Wet Processing Textile Mills," 1997/98, Environmental Protection Branch, 105 McGill Street, 4th Floor, Montreal, Quebec H2Y 2E7.

European Commission (2003), "Harmonisation of Environmental Emission Scenarios for Slimicides (Product Type 12),"Haskoning Nederland BV Environment, The Netherlands, 16 September 2003.

European Commission (1999), "Integrated Pollution Prevention and Control (IPPC) – Draft Reference Document on Best Available Techniques in the Pulp and Paper Industry," August 1999.

European Commission (1996), "Technical Guidance Document in Support of Commission Directive 93/67/EEC on Risk Assessment for New Notified Substances and Commission Regulation (EC) No 1488/94 on Risk Assessment for Existing Substances," Part IV, Office for Official Publications of the European Communities, Luxembourg, 1996.

European Union (2001), "Emission Scenario Document – Textile Finishing Industry," May 2001.

Fourné, F., *Synthetic Fibers – Machines and Equipment, Manufacture, Properties: Handbook for Plant Engineering, Machine Design, and Operation*, Hanser Publishers, Munich, 1999.

Gray, C.; M. Dagemais; T. Evans; and Y. Dionne (2001), "Mass Balance of Silica at a Canadian Deinking Plant," Pulp & Paper Canada 102 (12), 107-110 (2001).

Macek, G. J., "Carbonless Copy Paper Manufacture and Recycling Operations Generic Scenario," U.S. Environmental Protection Agency, Chemical Engineering Branch, June 1991.

Netherlands Ministry of Health and Environmental Protection, *Handbook of Emission Factors - Part 1: Non-Industrial Sources*, The Hague, The Netherlands, 1980.

OECD (2003), "OECD Emission Scenario Document on Textile Finishing Industry," Umweltbundesamt (UBA), Berlin, Germany, January 2003.

OECD (2002a), "Resource Compendium of PRTR Release Estimation Techniques Part 1: Summary of Point Source Techniques," Organisation for Economic Co-operation and Development, Environment Directorate, Joint Meeting of the Chemicals Committee and the Working Party on Chemicals, Pesticides and Biotechnology, ENV/JM/MONO(2002)20, 31 July 2002, downloaded from http://www.oecd.org (accessed Jan.14, 2004).

OECD (2002b), "Emission Scenario Document on Textile Finishing Industry," Organisation for Economic Co-operation and Development, Environment Directorate, February 2002.

OECD (2002c), "Emission Scenario Document on Industrial Surfactants (Draft)," Organisation for Economic Co-operation and Development, Environment Directorate, February 2002.

OECD (2001), "Why Pollutant Release and Transfer Registers (PRTR's) Differ: A Review of National Programmes," OECD Series on Pollutant Release and Transfer Registers No.4, Organisation for Economic Co-operation and Development, Environment Directorate, Joint Meeting of the Chemicals Committee and the Working Party on Chemicals, Pesticides and Biotechnology, ENV/JM/MONO(2001)16, 6 December 2001, downloaded from http://www.oecd.org (accessed Jan.14, 2004).

OECD (2000), "Guidance Document on Emission Scenario Documents," OECD Series on Pollutant Release and Transfer Registers No.1, Organisation for Economic Co-operation and Development, Environment Directorate, Joint Meeting of the Chemicals Committee and the Working Party on Chemicals, Pesticides and Biotechnology, ENV/JM/MONO(2000)12, 18 August 2000, downloaded from http://www.oecd.org (accessed Jan.25, 2004).

OECD (1999), "Compendium of Estimation Methods to Quantify Releases to the Environment for Use in Pollutant Release and Transfer Registries," Organisation for Economic Co-operation and Development, September 22, 1999.

Reisman, L., email correspondence with the Task Force on Environmental Exposure Assessment, Organization for Economic Development and Cooperation, March 7, 2005.

Rucher, J. W.; and D. M. Guthrie (1997), "Reduction of Salt Requirements in Dyeing Cotton with Fiber Reactive Dyes, " in Book of Papers of 1997 International Conference & Exhibition, American Association of Textile Chemists and Colorists, September 28-October 1, 1997, Atlanta, Ga., USA, pp.329-336.

Shafer, T. (2003), "OECD Emission Scenario Document on Textile Finishing Industry (Draft)," Umweltbundesamt (UBA), Berlin, Germany, 24 January 2003.

Schramm, W.; and J. Jantschgi (1999), "Comparative Assessment of Textile Dyeing Technologies from a Preventive Environmental Protection Point of View," Journal of the Society of Dyers and Colourists 115, 130-135 (1999).

Slade, P. E., Handbook of Fiber Finish Technology, Marcel Dekker, New York, 1998.

Tissier, C.; and V. Migne (2001), "Emission Scenario Document for Biocides Used in Paper Coating and Finishing – Supplement to the Methodology for Risk Evaluation of Biocides," Institut National de l'Environnement Industriel et des Risques, France, May 2001, obtained from the web site of European Chemicals Bureau at http://ecb.jrc.it (accessed Jan.19, 2004).

USEPA (2002), "Profile of the Pulp and Paper Industry," 2nd ed., U.S. Environmental Protection Agency, Office of Compliance, Washington, DC, EPA/310-R-02-002, November 2002, obtained from www.epa.gov/compliance (accessed Jan.19, 2004).

USEPA (2001), "The Emergency Planning and Community Right-To-Know Act Section 313 Release and Other Waste Management Reporting Requirements," USEPA, Office of Environmental Information, Washington, DC, EPA260/K-01-001, February 2001, downloaded from http://www.epa.gov/tri (accessed Jan.14, 2004).

USEPA (2001b), “Generic Scenario for Formulation of Latex/Emulsion Coatings (Draft),” U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxicities, Washington, DC, September 28, 2001b.

USEPA (2000), "Emergency Planning and Community Right-To-Know Act Section 313 Reporting Guidance for the Textile Processing Industry," USEPA, Office of Pollution Prevention and Toxics, Washington, DC, EPA745-B-00-008, May 2000, downloaded from http://www.epa.gov/tri (accessed Jan.14, 2004).

USEPA (1996), "Best Management Practices for Pollution Prevention in the Textile Industry," EPA/625/R-96/004, U.S. Environmental Protection Agency, Office of Research and Development, Washington, DC, September 1996.

UK Environment Agency (2004), "Guidance on Completing the Pollution Inventory Reporting Form PI-2," Pollution Inventory, downloaded from the web site of UK Environment Agency at http://www.environment-agency.gov.uk (accessed Jan.14, 2004).

Vail, S. L., "Textile Finishing," in *Kirk-Othmer's Encyclopedia of Chemical Technology, Vol.22, 3rd ed.*, John Wiley & Sons, New York, 1983, pp.769-802.

Wagner, B., "Guidance for Writing an OECD Emission Scenario Document (ESD)," Document 6-1, Organization for Economic Development and Co-operation, Task Force on Environmental Exposure Assessment, September 2003.

APPENDIX 1 – BIOCIDE EMISSION TO WASTEWATER FROM PAPER MILLS

Compared in Table A.1 are the estimation results of the PRTR mass balance method with those of the ESD fixation-based method for biocide emission to wastewater from non-integrated paper mills. The results pertain to an active ingredient in a biocide used for paper preservation and the quantity of pulp used (100,000 tonne/yr) refers to the input excluding the amount of broke recycled. The PRTR mass balance method yields a higher estimate than the ESD fixation-based method by 32%. In other words, the PRTR method is more conservative than the ESD method.

Table A.1 – Emission of a Biocide Active Ingredient to Wastewater from Paper Mills

Method	PRTR – Mass Balance	ESD – Fixation Based
Emission to Wastewater	7.5 kg/d	5.7 kg/d
Basis	Quantity of pulp = 100,000 tonne/yr Number of operation days = 350 d/yr	Quantity of pulp = 100,000 tonne/yr Number of operation days = 350 d/yr
Assumption	Biocide use rate = 2 kg/tonne active ingredient concentration = 0.1 Biocide fixation rate = 0.8 Degree of water closure = 0.5 Broke recycle rate = 0.2	Biocide use rate = 2 kg/tonne Active ingredient concentration = 0.1 Biocide fixation rate = 0.8 Degree of water closure = 0.5

The higher estimate by the PRTR mass balance method results from the inclusion of both water and broke recycles in the analysis of the fate of a biocide active ingredient within a papermaking process. Although broke recycle at 20% is common at paper mills, only water recycle is considered in the ESD fixation-based method. The broke recycle adds a source for the emission through broke repulping, since a fraction of the biocide contained in broke is released upon re-introduction into the papermaking process. It should be noted that the biocide use rate at 2 kg/tonne is defined as kg of biocide added to one tonne of pulp without accounting for the returning biocide via water and broke recycles.

Listed below are various substances contained in biocides used for paper preservation (Tissier and Migne, 2001):

- Ascorbic acid and its salts
- Benzoic acid
- Sodium benzoate
- Formic acid
- Hydrobenzoic acid ethylester
- Gluteraldehyde
- 2-Bromo-2-nitropropandiole
- Thione
- Isothiazolinones
- Bromohydroxy-acetophenone
- Dodecylguanidine hydrochloride

In the emission estimation with the PRTR and ESD methods, the following assumptions are made

- Biocide use rate is assumed at 2 kg/tonne based on the range of 0.1-4% on paper given by Tissier and Migne (2001), i.e., $Q_{product}$ = 2 kg/tonne.

- The concentration of an active ingredient in a biocide is assumed at 10% based on a calculation example provided by Tissier and Migne (2001), i.e., $C_{substance} = 0.1$.

- The biocide fixation rate is assumed at 0.8 as given by Tissier and Migne (2001), i.e., $F_{fixation} = 0.8$.

- The broke recycle rate is assumed at 20% of paper production as suggested by Tissier and Migne (2001), i.e., $R_{broke} = 0.2$.

- The degree of water closure is understood as the ratio of water recycled to white water generated and assumed at 0.5 based on the range of 0.4-0.7 for fine paper mills (European Commission, 1996), i.e., $R_{water\text{-}recycle} = 0.5$.

PRTR Mass Balance Estimation

The PRTR mass balance method considers the impact of both water recycle and broke recycle on the biocide emission to wastewater. Shown in Figure A.1 is a simplified process scheme describing the mass balance on biocide around a non-integrated paper mill (European Commission, 1999). Dry fibre is prepared into pulp by mixing with water in the pulp stock preparation stage. The water used includes both fresh water and recycled water. Also added to this stage are the broke collected from the paper machine and the fibre recovered from white water clarification.

Biocide enters the papermaking process at the pulp stock preparation stage through several routes. The first route is the addition of biocide to mixing chests. The second route is the re-introduction of broke which contains the same fraction of biocide as the paper produced. The third route is the recycled water which contains unfixed biocide. The fourth and final route is the recovered fibre which contains adsorbed biocide.

Biocide leaves the papermaking process through the paper produced and the wastewater generated. The paper produced contains fixed biocide and the amount contained depends upon use rate and fixation rate. The unfixed biocide contained in the wastewater generated represents the release from the process.

In the mass balance analysis presented below, a number of assumptions are made:

- The quantity of dry fibre used equals the quantity of paper produced.

- The quantity of the recovered fibre from stock recovery and water clarification is negligible.

- Biocide does not undergo chemical transformation.

- Biocide does not volatilize.

- The water recycled and the wastewater generated have the same chemical composition as the white water generated.

The quantity of biocide per tonne of fibre in prepared pulp is an important parameter to the emission estimation. It is a function of biocide use rate, water recycle rate and broke generation rate. Such a function can be determined from the mass balance on biocide.

Biocide entering pulp stock preparation stage = Biocide exiting paper machine
i.e.,
Biocide added + Biocide carried in by broke +
Biocide carried in by water recycle + Biocide carried in by recovered fibre
= Biocide carried out by paper + Biocide carried out by broke +
Biocide carried out by white water

Considering that the quantity of the recovered fibre is negligible and the water recycle has the same composition as the white water, the above mass balance relation is translated into the following equations:

$$Q_{paper}Q_{product} + Q_{broke}D_{product}F_{fixation} + (Q_{paper} + Q_{broke})D_{product}(1 - F_{fixation})\frac{Q_{water-recycle}}{Q_{white-water}}$$
$$= Q_{paper}D_{product}F_{fixation} + Q_{broke}D_{product}F_{fixation} + (Q_{paper} + Q_{broke})D_{product}(1 - F_{fixation})$$

$$Q_{paper}Q_{product} + (Q_{paper} + Q_{broke})D_{product}(1 - F_{fixation})\frac{Q_{water-recycle}}{Q_{white-water}}$$
$$= Q_{paper}D_{product}F_{fixation} + (Q_{paper} + Q_{broke})D_{product}(1 - F_{fixation})$$

$$Q_{product} + (1 + \frac{Q_{broke}}{Q_{paper}})D_{product}(1 - F_{fixation})\frac{Q_{water-recycle}}{Q_{white-water}}$$
$$= D_{product}F_{fixation} + (1 + \frac{Q_{broke}}{Q_{paper}})D_{product}(1 - F_{fixation})$$

$$Q_{product} = D_{product}F_{fixation} + (1 + \frac{Q_{broke}}{Q_{paper}})D_{product}(1 - F_{fixation}) -$$
$$(1 + \frac{Q_{broke}}{Q_{paper}})D_{product}(1 - F_{fixation})\frac{Q_{water-recycle}}{Q_{white-water}}$$

$$Q_{product} = D_{product}[F_{fixation} + (1 + \frac{Q_{broke}}{Q_{paper}})(1 - F_{fixation})(1 - \frac{Q_{water-recycle}}{Q_{white-water}})]$$

$$Q_{product} = D_{product}[F_{fixation} + (1 + R_{broke})(1 - F_{fixation})(1 - R_{water-recycle})]$$

$$D_{product} = \frac{Q_{product}}{F_{fixation} + (1 + R_{broke})(1 - F_{fixation})(1 - R_{water-recycle})}$$

where

$D_{product}$: quantity of biocide per tonne of fibre in prepared pulp, kg/tonne
$Q_{product}$: biocide use rate, kg/tonne
$F_{fixation}$: biocide fixation rate, dimensionless
R_{broke}: broke recycle rate as a fraction of paper production, dimensionless
$R_{water-recycle}$: water recycle rate as a fraction of white water generation or degree of water closure, dimensionless
Q_{broke}: broke generation rate, tonne/d
$Q_{water-recycle}$: water recycle rate, tonne/d

$Q_{white\text{-}water}$: white water generation rate, tonne/d

The following values are used in the emission estimation for biocide:

annual paper production, Q_{paper} = 100,000 tonne/yr (assumption)
active ingredient concentration in biocide, $C_{substance}$ = 0.1 (Tissier and Migner, 2001)
biocide fixation rate, $F_{fixation}$ = 0.80 (Tissier and Migne, 2001)
annual operation days, $T_{operation}$ = 350 d/yr (assumption)
biocide use rate, $Q_{product}$ = 2 kg/tonne (Tissier and Migne, 2001)
broke recycle rate, R_{broke} = 0.2 (Tissier and Migne, 2001)
water recycle rate, $R_{water\text{-}recycle}$ = 0.5 (European Commission, 1996)

The quantity of biocide per tonne of fibre in prepared pulp is determined as

$$D_{product} = \frac{Q_{product}}{F_{fixation} + (1 + R_{broke})(1 - F_{fixation})(1 - R_{water-recycle})}$$

$$D_{product} = \frac{2\ kg/tonne}{0.8 + (1 + 0.2)(1 - 0.8)(1 - 0.5)}$$

$$D_{product} = \frac{2\ kg/tonne}{0.8 + 0.12}$$

$$D_{product} = 2.17\ kg/tonne$$

The amount of a biocide active ingredient added to the pulp stock preparation stage is determined as

Biocide active ingredient added to pulp stock preparation
= (paper production × biocide use rate × active ingredient concentration) ÷ annual operation days
= $(Q_{paper} \times Q_{product} \times C_{substance}) \div T_{operation}$
= (100,000 tonne/yr × 2 kg/tonne × 0.1) ÷ 350 d/yr
= 57.1 kg/d

The amount of a biocide active ingredient contained in paper is determined as

Biocide active ingredient contained in paper
= (paper production × quantity of biocide per tonne of fibre in prepared pulp × active ingredient concentration × fixation rate) ÷ annual operation days
= $(Q_{paper} \times D_{product} \times C_{substance} \times F_{fixation}) \div T_{operation}$
= (100,000 tonne/yr × 2.17 kg/tonne × 0.1 × 0.8) ÷ 350 d/yr
= 49.6 kg/d

The amount of a biocide active ingredient contained in broke is determined as

Biocide active ingredient contained in broke
= (broke recycle rate × paper production × quantity of biocide per tonne of fibre in prepared pulp × active ingredient concentration × fixation rate) ÷ annual operation days

= $(R_{broke} \times Q_{paper} \times D_{product} \times C_{substance} \times F_{fixation}) \div T_{operation}$
= (0.2 × 100,000 tonne/yr × 2.17 kg/tonne × 0.1 × 0.8) ÷ 350 d/yr
= 9.9 kg/d

The amount of a biocide active ingredient contained in water recycle is determined as

Biocide active ingredient contained in water recycle

= paper production × (1 + broke recycle rate) × quantity of biocide active ingredient per tonne of fibre in prepared pulp × active ingredient concentration × (1 – fixation rate) × water recycle rate ÷ annual operation days
= $Q_{paper} \times (1 + R_{broke}) \times D_{product} \times C_{substance} \times (1 - F_{fixation}) \times R_{water\text{-}recycle} \div T_{operation}$
= 100,000 tonne/yr × (1 + 0.2) × 2.17 kg/tonne × 0.1 × (1 – 0.8) × 0.5 ÷ 350 d/yr
= 7.4 kg/d

The amount of a biocide active ingredient exiting the pulp stock preparation stage
Biocide active ingredient exiting pulp stock preparation
= biocide active ingredient added to pulp stock preparation + biocide active ingredient contained in broke + biocide active ingredient contained in water recycle + biocide active ingredient contained in recovered fibre
= 57.1 kg/d + 9.9 kg/d + 7.4 kg/d + 0
= 74.4 kg/d

The amount of a biocide active ingredient contained in the white water collected from the paper machine is determined as
Biocide active ingredient contained in white water
= paper production × (1 + broke recycle rate) × quantity of biocide active ingredient per tonne of fibre in prepared pulp × active ingredient concentration × (1 – fixation rate) ÷ annual operation days
= $Q_{paper} \times (1 + R_{broke}) \times D_{product} \times C_{substance} \times (1 - F_{fixation}) \div T_{operation}$
= 100,000 tonne/yr × (1 + 0.2) × 2.17 kg/tonne × 0.1 × (1 – 0.8) ÷ 350 d/yr
= 14.9 kg/d

The amount of a biocide active ingredient emitted to wastewater is determined as
Biocide active ingredient emitted to wastewater
= biocide active ingredient contained in white paper × (1 – water recycle rate)
= 14.9 kg/d × $(1 - R_{water\text{-}recycle})$
= 14.9 kg/d × (1 – 0.5)
= 7.5 kg/d

The mass balance on biocide active ingredient is shown in Figure A.1.

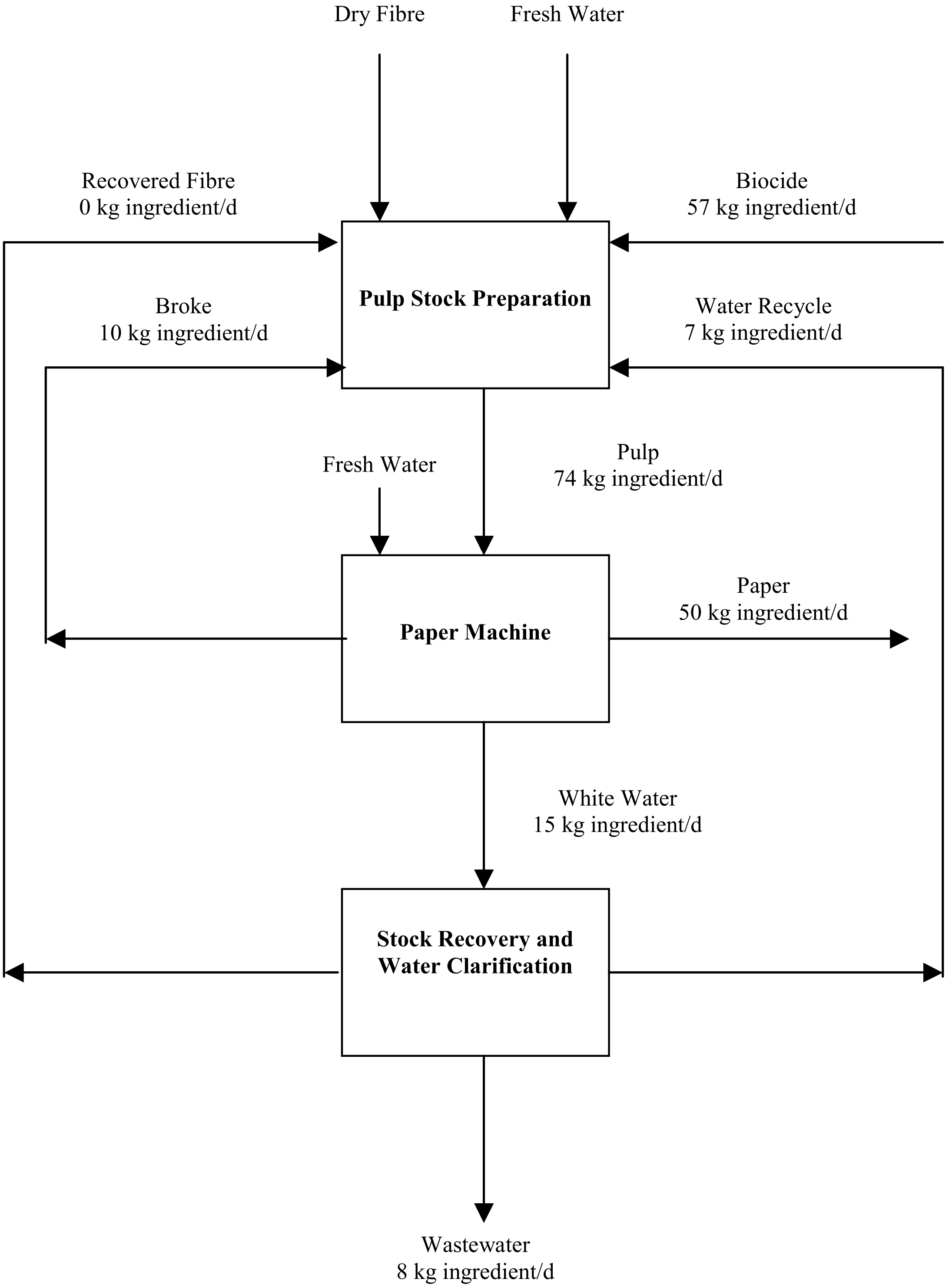

Figure A.1 – Mass Balance on Biocide Determined for Paper Mill by PRTR Method

ESD Fixation-Based Estimation

The ESD fixation-based method considers the impact of the degree of water closure, but not broke recycle, on the emission of a biocide active ingredient to wastewater (European Commission, 1996). The emission is estimated by the equation

$$E_{water} = \frac{Q_{paper} Q_{product} C_{substance} (1 - F_{fixation})(1 - R_{water-recycle})}{T_{operation}}$$

where

E_{water}: daily emission of biocide active ingredient to wastewater, kg/d
Q_{paper}: annual paper production, tonne/yr
$Q_{product}$: biocide use rate, kg/tonne
$C_{substance}$: active ingredient concentration in biocide, dimensionless
$F_{fixation}$: biocide fixation rate, dimensionless
$R_{water-recycle}$: water recycle rate or degree of water closure, dimensionless
$T_{operation}$: number of operation days per year, d/yr

The following values are used in the emission estimation for a biocide active ingredient:

Q_{paper} = 100,000 tonne/yr (assumption)
$Q_{product}$ = 2 kg/tonne (Tissier and Migne, 2001)
$C_{substance}$ = 0.1 (Tissier and Migne, 2001)
$F_{fixation}$ = 0.8 (Tissier and Migne, 2001)
$R_{water-recycle}$ = 0.5 (European Commission, 1996)
$T_{operation}$ = 350 d/yr (assumption)

The emission of a biocide active ingredient to wastewater is determined as

$$E_{water} = \frac{Q_{paper} Q_{product} C_{substance} (1 - F_{fixation})(1 - R_{water-recycle})}{T_{operation}}$$

$$= \frac{100{,}000\ tonne/yr \times 2\ kg/tonne \times 0.1 \times (1 - 0.8) \times (1 - 0.5)}{350\ d/yr}$$

$$= 5.7\ kg/d$$

The amount of a biocide active ingredient added to the pulp stock preparation stage is determined as

Biocide active ingredient added to pulp stock preparation
= (paper production × biocide use rate × active ingredient concentration) ÷ annual operation days
= ($Q_{paper} \times Q_{product} \times C_{substance}$) ÷ $T_{operation}$
= (100,000 tonne/yr × 2 kg/tonne × 0.1) ÷ 350 d/yr
= 57.1 kg/d

The amount of a biocide active ingredient contained in water recycle is determined as

Biocide active ingredient contained in water recycle
= paper production × biocide use rate × active ingredient concentration × (1 – fixation rate) × water recycle rate ÷ annual operation days
= $Q_{paper} \times Q_{product} \times C_{substance} \times (1 - F_{fixation}) \times R_{water-recycle} \div T_{operation}$

= 100,000 tonne/yr × 2 kg/tonne × 0.1 × (1 – 0.8) × 0.5 ÷ 350 d/yr
= 5.7 kg/d

The amount of a biocide active ingredient contained in the white water collected from the paper machine is determined as

Biocide active ingredient contained in white water
= paper production × biocide use rate × active ingredient concentration × (1 – fixation rate) ÷ annual operation days
= $Q_{paper} \times Q_{product} \times C_{substance} \times (1 - F_{fixation}) \div T_{operation}$
= 100,000 tonne/yr × 2 kg/tonne × 0.1 × (1 – 0.8) ÷ 350 d/yr
= 11.4 kg/d

The amount of a biocide active ingredient contained in paper is determined as

Biocide active ingredient contained in paper
= Biocide active ingredient added to pulp stock preparation – Biocide active ingredient emitted to wastewater
= 57.1 kg/d – 5.7 kg/d
= 51.4 kg/d

The mass balance on a biocide active ingredient is shown in Figure A.2.

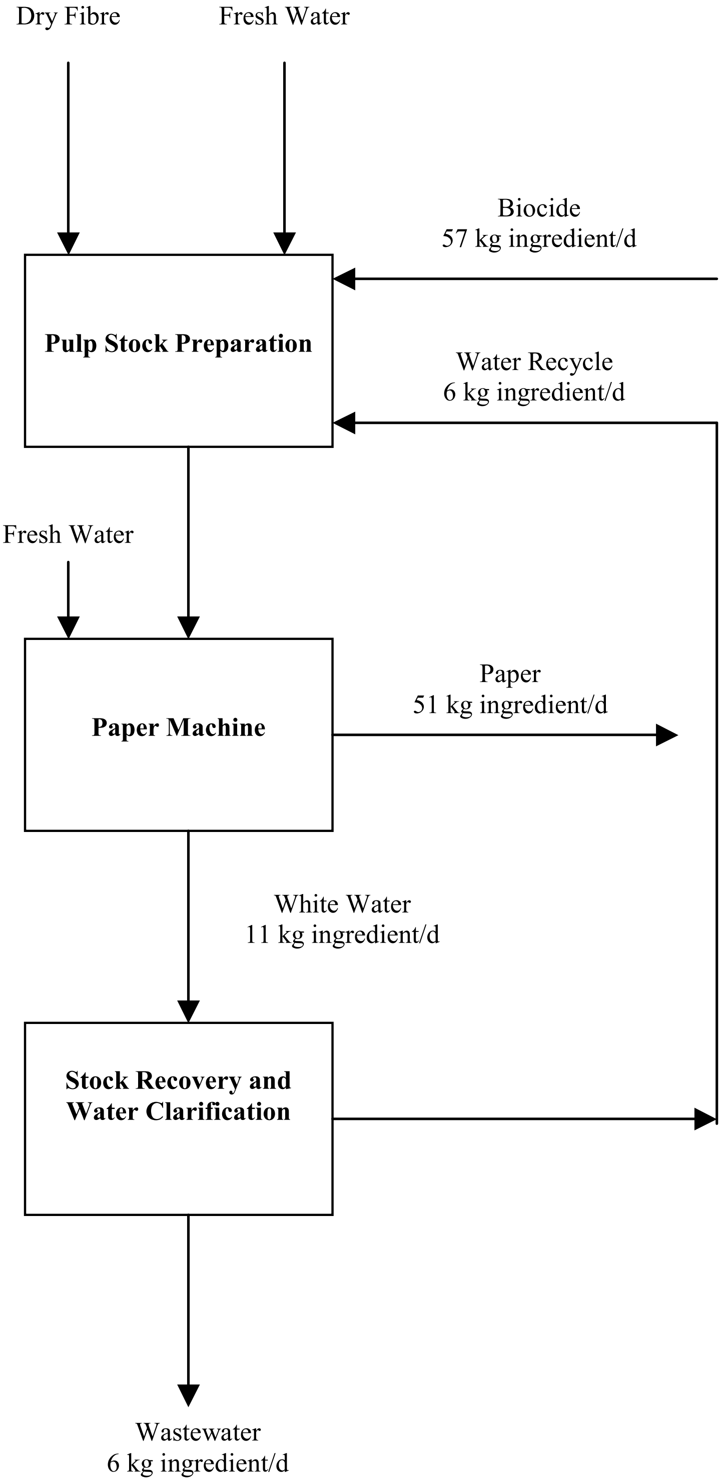

Figure A.2 – Mass Balance on Biocide Determined for Paper Mill by ESD Method

APPENDIX 2 – EMISSION OF NONYLPHENOL AND ITS ETHOXYLATES TO WASTEWATER FROM YARN DYEING

Nonylphenol (NP) and its ethoxylates (NPEs) are a group of compounds used as surfactants in textile processing. In fibre and yarn production, they can be added to spin finishes which are used during fibre spinning operations to reduce the fibre-to-fibre and fibre-to-metal friction. It is expected that the amount applied will remain in the finished products.

A spin finish consists of several components (Slade, 1998, p.5; Fourné, 1999, p.622). Mineral oil derivatives, commonly referred to as lubricants, are the basis of spin finishes. Other components include emulsifiers, antistatic agents, anti-microbial compounds, cohesive agents, humectants, wetting agents, etc.

Yarn dyeing is also likely to involve the use of NP/NPEs. Surfactants are normally added to a dye bath to facilitate the dyeing process and may contain NP/NPEs. It is expected that the majority of the surfactants used is discharged along with the dye bath and the remaining portion is washed off the dyed goods during subsequent rinsing operations.

The calculation example provided in this section illustrates that the emission of a substance to wastewater during an operation can originate from multiple sources which can only be thoroughly accounted for using the PRTR's mass balance method. The ESD fixation-based method, on the other hand, considers the chemical use only within an operation and does not recognize there might be other sources such as raw materials being processed.

Presented in Table A.2 are calculation results for NP/NPE emissions to wastewater from yarn dyeing. The emission sources include both surfactants used during yarn dyeing and spin finishes carried with raw materials. The PRTR's mass balance method took both sources into consideration, while the ESD fixation-based method ignores the source of raw materials. As a result, the ESD method yields an underestimate by 26%.

Table A.2 – Emission of Nonylphenol and Its Ethoxylates to Wastewater from Yarn Dyeing

Method	**PRTR – Mass Balance**	**ESD – Fixation Based**
Emission to Wastewater	15.4 kg/d	11.4 kg/d
Basis	Quantity of textile = 1,000 tonne/yr Number of operation days = 250 d/yr	Quantity of textile = 1,000 tonne/yr Number of operation days = 250 d/yr
Assumption	Use rate of surfactants = 11 kg/tonne yarn Fraction of NP/NPEs in surfactants = 0.26 Fixation rate of surfactants = 0 Spin finishes in yarn = 5 kg/tonne yarn Fraction of NP/NPEs in spin finishes = 0.20 Removal rate of spin finishes = 1	Use rate of surfactants = 11 kg/tonne yarn Fraction of NP/NPEs in surfactants = 0.26 Fixation rate of surfactants = 0

The calculations detailed below are based on the following assumptions:

- The amount of surfactants used in yarn dyeing was estimated at 11 kg/tonne goods dyed (Crechem, 2000).
- The proportion of NP/NPEs in surfactants for the Canadian wet processing sector was estimated at 0.26 (Crechem, 2000).
- The fixation rate of surfactants on goods is assumed at zero.
- The amount of spin finishes applied to fibre during fibre and yarn production is assumed at 5 kg per tonne of fibre/yarn. This is based on a number of studies cited by Slade (1998, p.25). In one study, the fibre-to-fibre and fibre-to-metal friction was found to decrease as the amount of spin finishes increased and reach a plateau at 0.5% by weight on fibre. In two other studies, a minimum of 0.15 to 0.20% by weight on fibre was found necessary for the formation of a mono-molecular film on fibre.
- The proportion of NP/NPEs in spin finishes is assumed to be 0.2 on average based on an industry survey (Crechem, 2004e).
- The removal rate of spin finishes from yarn is 100%.

PRTR Mass Balance Estimation

According to the mass balance principle, the NP/NPE emission to wastewater is the sum of two quantities, one originating from surfactants used in yarn dyeing and the other from spin finishes carried with yarn.

The quantity of NP/NPEs carried into the dyeing process by surfactants is determined as
= NP/NPEs in surfactants
= annual quantity of yarn dyed × quantity of surfactants added per unit mass of yarn × fraction of NP/NPEs in surfactants ÷ number of annual operation days
= 1000 tonne/yr × 11 kg/tonne × 0.26 ÷ 250 d/yr
= 11.4 kg/d

The quantity of NP/NPEs carried into the dyeing process by incoming yarn is determined as
= NP/NPEs in incoming yarn
= annual quantity of yarn dyed × quantity of spin finishes per unit mass of yarn × fraction of NP/NPEs in spin finishes ÷ number of annual operation days
= 1000 tonne/yr × 5 kg/tonne × 0.20 ÷ 250 d/yr
= 4.0 kg/d

The NP/NPE emission originating from surfactants used in yarn dyeing is determined as
NP/NPE emission originating from yarn dyeing
= NP/NPEs in surfactants × (1 – fixation rate)
= 11.4 kg/d × (1 – 0)
= 11.4 kg/d

The NP/NPE emission originating from spin finishes carried with incoming yarn is determined as
NP/NPE emission originating from incoming yarn

= NP/NPEs in incoming yarn × removal rate
= 4.0 kg/d × 1
= 4.0 kg/d

The sum of NP/NPE emissions originating from surfactants and incoming yarn is given as
NP/NPE emissions from yarn dyeing
= NP/NPE emission originating from surfactants + NP/NPE emission originating from incoming yarn
= 11.4 kg/d + 4.0 kg/d
= 15.4 kg/d

The quantity of NP/NPEs remaining in dyed yarn is determined as
NP/NPEs remaining in dyed yarn
= NP/NPEs in surfactants × fixation rate + NP/NPEs in incoming yarn × (1 – removal rate)
= 11.4 kg/d × 0 + 4.0 kg/d × (1 – 1)
= 0 kg/d

The mass balance on NP/NPE around the dyeing process is shown in Figure A.3.

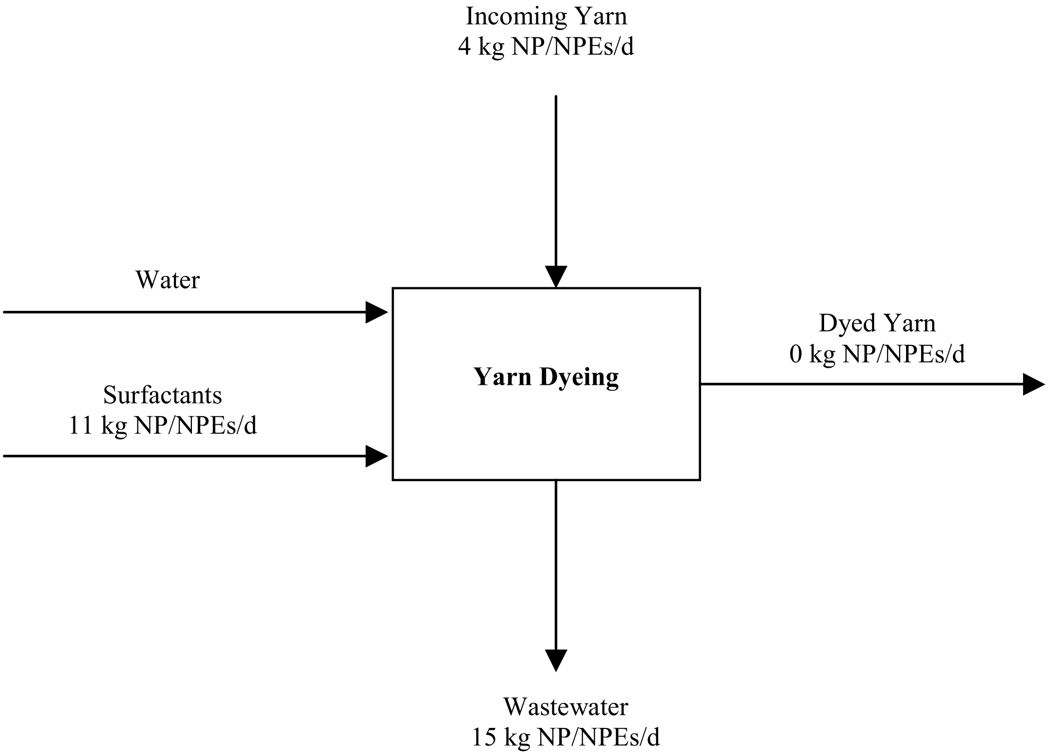

Figure A.3 – Mass Balance on NP/NPEs Determined for Yarn Dyeing by PRTR Method

ESD Fixation-Based Estimation

Using the ESD fixation-based method, the emission of NP/NPEs to wastewater is determined as follows.

NP/NPE emission to wastewater
= annual quantity of yarn dyed × quantity of surfactants added per unit mass of yarn × fraction of NP/NPEs in surfactants × (1 – fixation rate) ÷ number of annual operation days
= 1000 tonne/yr × 11 kg/tonne × 0.26 × (1 – 0) ÷ 250 d/yr = 11.4 kg/d

APPENDIX 3 – CHROMIUM EMISSION TO WASTEWATER FROM TEXTILE DYEING

Compared in Table A.3 are the estimation results of the PRTR emission factor method with those of the ESD fixation-based method for total chromium emission to wastewater from textile dyeing. Chromium emission to wastewater results from the use of chromium-containing dyes and dye auxiliaries (USEPA, 2000). The PRTR emission factor method is found to yield a higher estimate than the ESD method by 41%.

Table A.3 – Chromium Emission to Wastewater from Textile Dyeing

Method	PRTR – Emission Factor	ESD – Fixation Based
Emission to Wastewater	5.32 kg/d	3.77 kg/d
Basis	Quantity of textile = 1,000 tonne/yr Number of operation days = 250 d/yr	Quantity of textile = 1,000 tonne/yr Number of operation days = 250 d/yr
Assumption	Emission factor = 1.33 kg/tonne textile dyed (Environment Australia, 1999a).	Use level of dyes = 19.0 kg/tonne textile (Crechem, 2004a). Use level of dye auxiliaries = 44.3 kg/tonne textile (Crechem, 2004a). Chromium concentration in dyes = 0.02 (USEPA, 2000). Fixation rate for dyes = 0.85 (USEPA, 2000). Fixation rate for dye auxiliaries = 0 (Crechem, 2004a).

Emission estimation calculations for the total chromium emission to wastewater are detailed below. In the calculations, the data on the chromium concentration in dye auxiliaries is unknown and is assumed to be the same as that in dyes.

PRTR Emission Factor Estimation

Total chromium emission to wastewater from textile dyeing
= emission factor × quantity of textile dyed ÷ number of annual operation days
= 1.33 kg/tonne textile dyed × 1000 tonne/yr ÷ 250 d/yr
= 5.32 kg/d

ESD Fixation-Based Estimation

Total chromium emission to wastewater from textile dyeing
= quantity of textile dyed × dye use level × chromium concentration
× (1 – fixation rate) ÷ number of annual operation days +
quantity of textile dyed × use level of dye auxiliaries × chromium concentration
× (1 – fixation rate) ÷ number of annual operation days

= 1000 tonne/yr × 19.0 kg/tonne × 0.02 × (1 – 0.85) ÷ 250 d/yr +
1000 tonne/yr × 44.3 kg/tonne × 0.02 × (1 – 0) ÷ 250 d/yr
= 0.23 kg/d + 3.54 kg/d
= 3.77 kg/d

APPENDIX 4 – SURFACTANT EMISSION TO WASTEWATER FROM COMMERCIAL LAUNDERING

Commercial laundering results in a wastewater discharge to sewers and detergents are the major source of contaminants. A medium sized laundering facility has a throughput of 60,000 pieces per week, which is equivalent to 15-25 tonnes per week (OECD, 2002c, p.70). Typical dosage of detergents ranges from 5 to 20 kg per tonne laundry.

Detergents are used to aid in soil removal and provide fabric softening, whitening, stiffening and disinfection (OECD, 2002c, p.67). They contain various components, as listed below along with their respective proportions:

- Surfactants (10-17%)
- Phosphates (5-25%)
- Alkalis (20-70%)
- Bleaching agents (0-45%)
- Optical brighteners (0.1-0.3%)
- Anti-redeposition (1-2%)
- Stabilisers (1-2%)
- Corrosion inhibitors (0-5%)

Surfactants most frequently used in detergents include linear alkyl benzene sulphonates, secondary alkyl sulphonates, alpha olefin sulphonates, and alcohol ethoxylates (OECD, 2002c, p.68). Several surfactants are commonly combined into one formulation in order to achieve optimum performance at reasonable cost.

Compared in Table A.4 are the estimation results of the PRTR emission factor method with those of the ESD fixation-based method for surfactant emission to wastewater from commercial laundering. The PRTR emission factor method is found to predict a higher emission than the ESD fixation-based method by 83%. In other word, the PRTR method yields a more conservative estimate than the ESD method.

Table A.4 – Surfactant Emission to Wastewater from Commercial Laundering

Method	PRTR – Emission Factor	ESD – Fixation Based
Emission to Wastewater	1.1 kg/d	0.6 kg/d
Basis	Facility throughput = 0.5 tonne/d.	Facility throughput = 0.5 tonne/d.
Assumption	Per capita quantity of laundry = 5 kg/person-week.	Detergent dosage = 10 kg/tonne. Surfactant concentration = 12%. Fixation rate = 0.

The following assumptions are made in the estimation calculations with the PRTR and ESD methods:

- Facility throughput = 0.5 tonne/d (OECD, 2002c, p.71).
- Detergent dosage = 10 kg/tonne (OECD, 2002c, p.71).

- Surfactant concentration = 12% (OECD, 2002c, p.71).
- Fixation rate = 0.
- Per capita quantity of laundry = 5 kg/person-week.

<u>PRTR Emission Factor Estimation</u>

The PRTR emission factor method requires two parameters to be specified in calculating the emission of surfactants: 1) number of people using a laundering facility; 2) per capita surfactant emission factor. The number of people using a laundering facility can be estimated as

Number of people using a laundering facility
= facility throughput ÷ per capita quantity of laundry
= 0.5 tonne/d ÷ 5 kg/person-week
= 0.5 tonne/d × 1000 kg/tonne ÷ (5 kg/person-week ÷ 7 d/week)
= 700 persons/d

A surfactant emission factor for household detergents is found to be 1.5 g/person-d from an emission factor handbook published by The Netherlands' Ministry of Health and Environmental Protection (1985) and used as an approximation for the case of commercial laundering. The emission is therefore estimated to be

Surfactant emission to wastewater
= number of people using a facility × per capita surfactant emission factor
= 700 persons/d × 1.5 g/person-d
= 1050 g/d
= 1050 g/d ÷ 1000 g/kg
= 1.1 kg/d

<u>ESD Fixation-Based Estimation</u>

The emission of surfactants to wastewater from commercial laundering is determined as

Surfactant emission to wastewater
= facility throughput × detergent dosage × fraction of surfactants in detergents × (1 – fixation rate)
= 0.5 tonne/d × 10 kg/tonne × 0.12 × (1 – 0)
= 0.6 kg/d

APPENDIX 5 – SILOXANE EMISSION TO WASTEWATER FROM TEXTILE MILLS

Presented in Table A.5 are the estimates for siloxane emission to wastewater from textile finishing based on the PRTR mass balance and ESD fixation-based methods. The two methods yielded the same results because they both followed the same estimation principle although different procedures were used. The two methods become equivalent to each other only when an operation such as textile finishing does not involve recycle streams, multiple substance sources, and other complicating factors.

Table A.5 – Siloxane Emission to Wastewater from Textile Finishing

Method	PRTR – Mass Balance	ESD – Fixation Based
Emission to Wastewater	4.4 kg/d	4.4 kg/d
Basis	Quantity of textile = 1,000 tonne/yr Number of operation days = 250 d/yr	Quantity of textile = 1,000 tonne/yr Number of operation days = 250 d/yr
Assumption	Fixation rate = 1.0 Fraction of residual finish liquor = 0.1 Siloxane pick-up = 10 kg/tonne Siloxane concentration = 10 kg/m^3	Fixation rate = 1.0 Fraction of residual finish liquor = 0.1 Siloxane pick-up = 10 kg/tonne Siloxane concentration = 10 kg/m^3

The siloxane estimated was amido polyether modified silicone fluid, which was a notified substance in Australia (Department of Health and Ageing of Australia, 1992). It was manufactured in Japan and imported to Australia by Dow Corning Australia. Its formula was given as $C_3H_9SiO(C_2H_6SiO)_{400}(C_{29}H_{59}O_3N_2)_8SiC_3H_9$ with a molecular weight of 34,400 g/gmol.

The notified substance was used as a textile softener. It was imported to Australia as a pure compound and formulated as an emulsion before being sold to textile mills (Department of Health and Ageing of Australia, 1992). In textile finishing operations, the emulsion was added to a finish bath to give a siloxane concentration at 1-2% or 10-20 kg/m^3. The recommended maximum amount applied was 1% siloxane on weight of fabric or 10 kg siloxane/tonne textile finished.

A softener is used to impart durable, wash resistant softness to fabrics (Dow Corning, www.dowcorning.com). Application methods include pad and exhaustion for woven, knit, cotton, and polyester-cotton blend fabrics. The amount of siloxane required for optimum performance is typically in the neighbourhood of 0.75% on weight of fabric, but will vary depending upon the substrate.

A pad process is a conventional textile finishing technique. It involves three steps commonly referred to as pad-dry-cure (Vail, 1983). In the first step, the fabric is immersed in an aqueous finish bath and then squeezed to remove excess liquor to assure even distribution of chemicals in the fabric. The wet pickup usually varies from 60% to 100% on weight of fabric.

Padding is followed by drying which simply involves removal of water from the fabric (Vail, 1983). Drying and curing are often performed in one continuous process, while on the other hand, the dried fabric may be made into garments prior to curing. Depending upon the formulation used in the finish bath, chemical reactions with cellulose may take place during drying.

In textile finishing, more padding liquor is often prepared than needed for a few reasons (USEPA, 1996, p.206). Firstly, excessive liquor is mixed by operators to avoid having to make up a second batch to finish off a lot. Secondly, overmixing occurs when equipment is not designed to mix less than complete batches. Mix tanks, for example, commonly lack volume marking; therefore, the only way to make a mix properly is to make a full tank (normally 200 gallons). In addition, an extra volume is needed to compensate for the discard of residual liquor left in a finish trough. As a first approximation, residual liquor can be assumed at 10% of total liquor prepared (Shafer, 2003).

In general, the emission of a softener to wastewater from a textile finishing operation is considered to result from two sources: 1) the amount picked up by but not fixed onto textile; and 2) the amount in residual finish liquor discharged. The former is normally negligible since the fixation rate is 100% for a pad process, and the latter, therefore, becomes the principal source of the emission. In the estimation presented in this section, the following assumptions are used:

Fixation rate = 1.0
Fraction of residual finish liquor = 0.1
Siloxane picked up by textile per unit production = 10 kg/tonne textile finished
Siloxane concentration in finish liquor = 10 kg/m^3

PRTR Mass Balance Estimation

According to the mass balance principle, the siloxane emission can be estimated by

siloxane emission to wastewater = siloxane picked up by textile × (1 – fixation rate) + siloxane in residual finish liquor

Several values need to be obtained before the siloxane emission can be calculated. First of all, the siloxane quantity in total finish liquor prepared per unit production must be known and can be determined based on the mass balance around the finishing operation, as given below.

siloxane in total finish liquor per unit production = siloxane picked up by textile per unit production + siloxane in residual finish liquor per unit production

siloxane in total finish liquor per unit production – siloxane in residual finish liquor per unit production = siloxane picked up by textile per unit production

siloxane in total finish liquor per unit production × (1 – siloxane in residual finish liquor per unit production ÷ siloxane in total finish liquor per unit production) = siloxane picked up by textile per unit production

siloxane in total finish liquor per unit production × (1 – fraction of residual finish liquor) = siloxane picked up by textile per unit production

siloxane in total finish liquor per unit production = siloxane picked up by textile per unit production ÷ (1 – fraction of residual finish liquor)

The siloxane quantity in total finish liquor prepared per unit production is determined as
siloxane in total finish liquor per unit production

= siloxane picked up by textile per unit production ÷ (1 – fraction of residual finish liquor)
= 0.01 kg/kg textile finished ÷ (1 – 0.1)

= 0.0111 kg/kg textile finished
= 11.1 kg/tonne textile finished

The volume of total finish liquor prepared per unit production is determined as

total finish liquor per unit production
= siloxane in total finish liquor per unit production ÷ siloxane concentration
= 11.1 kg/tonne textile finished ÷ 10 kg/m^3
= 1.11 m^3/tonne textile finished

The volume of finish liquor picked up by textile per unit production is determined as

finish liquor picked up by textile per unit production
= total finish liquor prepared per unit production × (1 – fraction of residual finish liquor)
= 1.11 m^3/tonne textile finished × (1 – 0.1)
= 1.0 m^3/tonne textile finished

The volume of residual finish liquor discharged to wastewater per unit production is determined as

residual finish liquor per unit production
= total finish liquor per unit production × fraction of residual finish liquor
= 1.11 m^3/tonne textile finished × 0.1
= 0.11 m^3/tonne textile finished

The siloxane quantity picked up by textile per unit production is determined as
siloxane picked up by textile per unit production
= 0.01 kg/kg textile finished
= 10 kg/tonne textile finished

The siloxane quantity in residual finish liquor per unit production is determined as
siloxane in residual finish liquor per unit production
= residual finish liquor per unit production × siloxane concentration
= 0.11 m^3/tonne textile finished × 10 kg/m^3
= 1.1 kg/tonne textile finished

The siloxane emission to wastewater from textile finishing is determined as
siloxane emission to wastewater from textile finishing
= siloxane picked up by textile × (1 – fixation rate) + siloxane in residual finish liquor
= [siloxane picked up by textile per unit production × (1 – fixation rate) + siloxane in residual finish bath per unit production] × quantity of textile finished ÷ number of annual operation days
= [10 kg/tonne textile finished × (1 – 1) + 1.1 kg/tonne textile finished] × 1000 tonne/yr ÷ 250 d/yr
= 1.1 kg/tonne textile finished × 1000 tonne/yr ÷ 250 d/yr
= 4.4 kg/d

ESD Fixation-Based Estimation

The loss of paper coatings during carbonless paper manufacture was reported as 0.2% (Macek, 1991).

The release of paper coatings from broke to wastewater during reprocessing was assumed to be 10% if no data was available (Macek, 1991). Removal rates as high as 98% have been reported. The remainder of paper coatings is retained by the papermaking process and ends up in the paper produced.

The term "fixation rate" in the fixation-based method must be modified in order to account for the discharge of residual finish liquor to wastewater. The modified fixation rate is defined as the ratio of the amount of a substance fixed onto textile to the amount used in the preparation of finish liquor instead of the amount picked up by the textile.

The modified fixation rate can be determined as
modified fixation rate
= [siloxane in total finish liquor – siloxane in finish liquor picked up by textile × (1 – fixation rate) – siloxane in residual finish liquor] ÷ (siloxane in total finish liquor)
= [siloxane in total finish liquor – siloxane in finish liquor picked up by textile × (1 – 1) – siloxane in residual finish liquor] ÷ siloxane in total finish liquor
= (siloxane in total finish liquor – siloxane in residual finish liquor) ÷ siloxane in total finish liquor
= (1 – siloxane in residual finish liquor ÷ siloxane in total finish liquor)
= (1 – residual finish liquor ÷ total finish liquor)
= (1 – fraction of residual finish liquor)
= (1 – 0.1)
= 0.9

The volume of total finish liquor prepared per unit production was determined in the preceding calculation based on mass balance.

total finish liquor per unit production
= 1.11 m^3/tonne textile finished

The siloxane emission to wastewater from textile finishing is given as
siloxane emission to wastewater from textile finishing
= quantity of textile finished × total finish liquor per unit production × siloxane concentration × (1 – modified fixation rate) ÷ number of annual operation days
= 1000 tonne/yr × 1.11 m^3/tonne textile finished × 10 kg/m^3 × (1 – 0.9) ÷ 250 d/yr
= 4.4 kg/d

APPENDIX 6 – SILOXANE EMISSION TO WASTEWATER FROM PAPER MILLS

Presented in Table A.6 are the estimates for siloxane emission to wastewater from coating operations at a paper mill based on the PRTR mass balance and ESD fixation-based methods. The PRTR method yielded a higher estimate than the ESD method by 17%.

Table A.6 – Siloxane Emission to Wastewater from Paper Coating

Method	PRTR – Mass Balance	ESD – Fixation Based
Emission to Wastewater	0.063 kg/d	0.054 kg/d
Basis	Paper production = 100,000 tonne/yr Number of operation days = 350 d/yr	Paper production = 100,000 tonne/yr Number of operation days = 350 d/yr
Assumption	Use level of paper coatings = 4.5 kg/tonne Fixation rate = 0.998 Mass fraction of siloxane in paper coatings = 0.0019 Broke generation rate = 20% of paper production Coated broke generation rate = 10% of paper production Rate of coatings removal from broke processing = 10%	Use level of paper coatings = 4.5 kg/tonne Fixation rate = 0.998 Mass fraction of siloxane in paper coatings = 0.0019 Broke generation rate = 20% of paper production Rate of coatings removal from broke processing = 10%

The siloxane estimated is a dimethylpolysiloxane fluid used as an antifoam additive for paper coatings (www.rhodia-silicones.com accessed May 10, 2004). The product is manufactured by Rhodia and marketed under the trade name of RHODORSIL 47V200. It is a linear polymer and functions as a mold release agent, lubricant or foam control agent.

Both PRTR and ESD methods recognize that the siloxane emission results from two sources: one is the loss occurring during the use of coatings and the other is the release from broke repulping. The two methods gave the same estimate for the amount lost during the use of coatings, but differed in the determination for the amount released from broke repulping. The PRTR method took into consideration the coatings both applied to paper surface and contained in paper fibre in the estimation of the amount released from broke repulping, while the ESD method only accounted for the coatings applied. The exclusion of the coatings contained in paper fibre from the estimation is believed to result in an underestimate from the ESD method.

The release of coatings to wastewater originates from spent coating liquid and wash water generated from the cleaning of coating equipment (Tissier and Migne, 2001). The spent coating liquid can be undiluted surplus coatings from coating kitchen and coater station and contains 50-70% solids, while the solids content in the wash water from equipment cleaning is typically 2-4%. The loss of coatings has been assumed at 0.2% of the coatings used for the manufacture of carbonless copy paper if no facility data is available (Macek, 1991).

The amount of broke generated during papermaking is usually 5-20% of paper production, but can be as high as 50% (Tissier and Migne, 2001). An amount of 20% has been suggested as a default value for emission estimation, although a much lower value at 4% has been used by USEPA (Macek, 1991). Broke is generally collected and re-introduced to the papermaking process.

Broke can be coated and uncoated, depending upon where it is generated during the papermaking process. To yield a conservative emission estimate for coatings, all broke generated should be assumed to be coated. This assumption would result in the maximum possible amount of coatings released from broke repulping. The amount of coatings released from broke processing has been reported as 10% and the reminder is retained by fibre (Macek, 1991).

The mass fraction of the siloxane in paper coatings can be estimated from similar cases. In the case of latex/emulsion coatings formulated for architectural applications, defoamers are used as additives at 0.19% by weight (USEPA, 2001b). This value can be used as an approximation for the siloxane in paper coatings.

The quantity of surface coatings applied to paper is estimated from the data reported by European Commission for newsprint (1996). The reported quantity ranged from 0.1% to 0.8% on paper and an average of 0.45% is assumed.

As a summary, the following values are used in the estimation of siloxane emissions:

Paper production = 100,000 tonne/yr (assumption)
Use rate of coatings = 4.5 kg/tonne (European Commission, 1996)
Mass fraction of siloxane in coatings = 0.0019 (USEPA, 2001b)
Number of operation days per year = 350 d/yr (assumption)
Fixation rate of coatings = 0.998 (Macek, 1991)
Broke generation rate = 0.2 (Tissier and Migne, 2001)
Coated broke generation rate = 0.2 (assumption)
Coatings retained by fibre during broke processing = 0.9 (Macek, 1991)

PRTR Mass Balance Estimation

An estimation equation is derived from a mass balance analysis on coatings and used to determine the siloxane emission from paper coating to wastewater.

$$E_{water} = \frac{Q_{paper} Q_{product} C_{substance}}{T_{operation}} \{(1 - F_{fixation}) + R_{broke-coated}[1 - \frac{F_{retention} F_{fixation}}{1 + R_{broke}(1 - F_{retention})}]\}$$

where

E_{water}: siloxane emission from coating operation to wastewater, kg/d
Q_{paper}: annual paper production, tonne/yr
$Q_{product}$: use rate of coatings, kg/tonne
$C_{substance}$: fraction of siloxane in coatings, dimensionless
$T_{operation}$: number of operation days per year, d/yr
$F_{fixation}$: fixation rate of coatings, dimensionless
R_{broke}: broke generation rate as a fraction of paper production, dimensionless
$R_{broke\text{-}coated}$: coated broke generation rate as a fraction of paper production, dimensionless
$F_{retention}$: fraction of coatings retained by fibre during broke repulping, dimensionless

The following values are used in the emission estimation:

Q_{paper} = 100,000 tonne/yr (assumption)
$Q_{product}$ = 0.45% = 4.5 kg/tonne (European Commission, 1996)
$C_{substance}$ = 0.19% = 0.0019 (USEPA, 2001b)
$T_{operation}$ = 350 d/yr (assumption)
$F_{fixation}$ = 1 – process loss rate = 1 – 0.2% = 0.998 (Macek, 1991)
R_{broke} = 0.2 (Tissier and Migne, 2001)
$R_{broke-coated}$ = 0.2 (assumption)
$F_{retention}$ = 1 – fraction of coatings removed during broke processing
= 1 – 0.1 = 0.9 (Macek, 1991)

Shown in Figure A.4 is a process scheme describing the mass balance on siloxane around a non-integrated paper mill. Dry fibre is prepared into pulp by mixing with water in the pulp stock preparation stage. Recycled broke is added to this stage at the same time.

Coated paper is produced through a sequence of operations. These operations include wet-end operation, dry-end operation (drying and surface sizing), coating, calendering, and finishing (Tissier and Migne, 2001). Each operation except finishing results in the generation of both broke and wastewater.

Broke can be divided into two types: coated and uncoated. Coated broke is generated from the coating and calendering operations, and uncoated broke from the wet- and dry-end operations. Both types of broke are collected and repulped in the pulp stock preparation stage.

In the mass balance analysis presented below, a number of assumptions are made:

- The quantity of dry fibre used equals the quantity of paper produced.
- Siloxane in paper coatings does not undergo chemical transformation.
- Siloxane in paper coatings does not volatilize.

The coatings released to wastewater can be determined from the overall mass balance as follows

Coatings released to wastewater
= Coatings prepared for coating – Coatings carried with paper

or

$$F_{product-released} = F_{product-used} - F_{product-carried}$$

where

$F_{product-released}$: quantity of coatings released to wastewater, kg/yr
$F_{product-used}$: quantity of coatings prepared for coating, kg/yr
$F_{product-carried}$: quantity of coatings carried with paper, kg/yr

The coatings prepared for coating is determined by multiplying the use rate of coatings by the quantity of paper coated

$$F_{product-used} = Q_{paper}(1 + R_{broke-coated})Q_{product}$$

The amount of siloxane used in the coating process is determined as

Siloxane used in coating process

= paper production × (1 + broke recycle rate) × coatings use rate × siloxane concentration ÷ annual operation days

$= Q_{paper} \times (1 + R_{broke}) \times Q_{product} \times C_{substance} \div T_{operation}$
= 100,000 tonne/yr × (1 + 0.2) × 4.5 kg/tonne × 0.0019 ÷ 350 d/yr
= 2.9 kg/d

The coatings carried with paper consist of two parts: one is the quantity coated on paper surface and the other is the quantity contained in paper fibre, i.e.,

$$F_{product-carried} = F_{product-coated} + F_{product-contained}$$

where

$F_{product\text{-}carried}$: quantity of coatings carried with paper, kg/yr
$F_{product\text{-}coated}$: quantity of coatings coated on paper surface, kg/yr
$F_{product\text{-}contained}$: quantity of coatings contained in paper fibre, kg/yr

The quantity coated can be calculated as

$$F_{product-coated} = Q_{paper} Q_{product} F_{fixation}$$

The quantity of siloxane on paper surface is determined as

Siloxane on paper surface
= paper production × coatings use rate × siloxane concentration × fixation rate ÷ annual operation days

$= Q_{paper} \times Q_{product} \times C_{substance} \times F_{fixation} \div T_{operation}$
= 100,000 tonne/yr × 4.5 kg/tonne × 0.0019 × 0.998 ÷ 350 d/yr
= 2.4 kg/d

The coatings contained in paper fibre results from the fact that part of coatings carried with broke is retained by fibre during broke repulping. Their quantity is determined as

$$F_{product-contained} = Q_{paper} C_{product-contained}$$

where

$C_{product\text{-}contained}$: amount of coatings contained in fibre, kg/tonne

The amount of coatings contained in fibre can be determined from the mass balance on coatings around the pulp stock preparation stage as follows:

Total fibre exiting pulping stage × Fraction of coatings contained in fibre
= Coatings contained in uncoated broke × Fraction of coatings retained by fibre +
Coatings contained in coated broke × Fraction of coatings retained by fibre +
Coatings coated on broke × Fraction of coatings retained by fibre

or

$$Q_{paper}(1+R_{broke})C_{product-contained}$$
$$= Q_{paper}R_{broke-uncoated}C_{product-contained}F_{retention} +$$
$$Q_{paper}R_{broke-coated}C_{product-contained}F_{retention} + Q_{paper}R_{broke-coated}Q_{product}F_{fixation}F_{retention}$$

$$(1+R_{broke})C_{product-contained}$$
$$= R_{broke-uncoated}C_{product-contained}F_{retention} +$$
$$R_{broke-coated}C_{product-contained}F_{retention} + R_{broke-coated}Q_{product}F_{fixation}F_{retention}$$

$$C_{product-contained}(1+R_{broke} - R_{broke-uncoated}F_{retention} - R_{broke-coated}F_{retention}) =$$
$$R_{broke-coated}Q_{product}F_{fixation}F_{retention}$$

$$C_{product-contained}(1+R_{broke} - R_{broke}F_{retention}) = R_{broke-coated}Q_{product}F_{fixation}F_{retention}$$

$$C_{product-contained} = \frac{R_{broke-coated}Q_{product}F_{fixation}F_{retention}}{1+R_{broke} - R_{broke}F_{retention}}$$

The amount of coatings contained in fibre is determined as

$$C_{product-contained} = \frac{R_{broke-coated}Q_{product}F_{fixation}F_{retention}}{1+R_{broke} - R_{broke}F_{retention}}$$

$$= \frac{0.2 \times 4.5\ kg/tonne \times 0.998 \times 0.9}{1+0.2-0.2\times 0.9}$$

$$= \frac{0.808\ kg/tonne}{1.02}$$

$$= 0.792\ kg/tonne$$

The quantity of coatings contained in paper is, therefore, given as

$$F_{product-contained} = Q_{paper}C_{product-contained}$$

$$= Q_{paper}\frac{R_{broke-coated}Q_{product}F_{fixation}F_{retention}}{1+R_{broke} - R_{broke}F_{retention}}$$

The quantity of siloxane contained in paper fibre is determined as

Siloxane in paper fibre

= paper production × quantity of coatings in paper fibre × siloxane concentration ÷ fixation rate ÷ annual operation days

$= Q_{paper} \times C_{product\text{-}contained} \times C_{substance} \div T_{operation}$

= 100,000 tonne/yr × 0.792 kg/tonne × 0.0019 ÷ 350 d/yr

= 0.43 kg/d

The quantity of coatings carried with paper is further determined as

$$F_{product-carried} = F_{product-coated} + F_{product-contained}$$

$$= Q_{paper} Q_{product} F_{fixation} + Q_{paper} \frac{R_{broke-coated} Q_{product} F_{fixation} F_{retention}}{1 + R_{broke} - R_{broke} F_{retention}}$$

$$= Q_{paper} Q_{product} F_{fixation} (1 + \frac{R_{broke-coated} F_{retention}}{1 + R_{broke} - R_{broke} F_{retention}})$$

The quantity of siloxane carried with paper is determined as

Siloxane carried with paper
= siloxane on paper surface + siloxane in paper fibre
= 2.4 kg/d + 0.43 kg/d
= 2.8 kg/d

The quantity of siloxane contained in broke is determined as

Siloxane contained in broke
= paper production × broke generation rate × quantity of coatings in fibre × siloxane concentration × retention rate ÷ annual operation days

$= Q_{paper} \times R_{broke} \times C_{product\text{-}contained} \times C_{substance} \times F_{retention} \div T_{operation}$
= 100,000 tonne/yr × 0.2 × 0.792 kg/tonne × 0.0019 × 0.9 ÷ 350 d/yr
= 0.077 kg/d

The quantity of coatings released to wastewater is then given as

$$F_{product-released} = F_{product-used} - F_{product-carried}$$

$$= Q_{paper} (1 + R_{broke-coated}) Q_{product} - Q_{paper} Q_{product} F_{fixation} [1 + \frac{R_{broke-coated} F_{retention}}{1 + R_{broke} (1 - F_{retention})}]$$

$$= Q_{paper} Q_{product} (1 + R_{broke-coated} - F_{fixation} - \frac{R_{broke-coated} F_{retention} F_{fixation}}{1 + R_{broke} - R_{broke} F_{retention}})$$

$$= Q_{paper} Q_{product} \{(1 - F_{fixation}) + R_{broke-coated} [1 - \frac{F_{retention} F_{fixation}}{1 + R_{broke} (1 - F_{retention})}]\}$$

$$= Q_{paper} Q_{product} (1 - F_{fixation}) + Q_{paper} Q_{product} R_{broke-coated} [1 - \frac{F_{retention} F_{fixation}}{1 + R_{broke} (1 - F_{retention})}]$$

$$F_{product-released} = Q_{paper} Q_{product} (1 - F_{fixation}) + Q_{paper} Q_{product} R_{broke-coated} [1 - \frac{F_{retention} F_{fixation}}{1 + R_{broke} (1 - F_{retention})}]$$

The first term of the above equation represents the amount of coatings lost to wastewater from coating operation, while the secondary term accounts for the amount released to wastewater during broke repulping.

The daily emission of siloxane to wastewater can be obtained as

$$E_{water} = \frac{F_{product-released} C_{substance}}{T_{operation}}$$

$$= \frac{C_{substance}}{T_{operation}} \{Q_{paper} Q_{product} (1 - F_{fixation}) + Q_{paper} Q_{product} R_{broke-coated} [1 - \frac{F_{retention} F_{fixation}}{1 + R_{broke} (1 - F_{retention})}]\}$$

$$= \frac{Q_{paper} Q_{product} C_{substance}}{T_{operation}} \{(1 - F_{fixation}) + R_{broke-coated} [1 - \frac{F_{retention} F_{fixation}}{1 + R_{broke} (1 - F_{retention})}]\}$$

$$E_{water} = \frac{Q_{paper} Q_{product} C_{substance}}{T_{operation}} \{(1 - F_{fixation}) + R_{broke-coated} [1 - \frac{F_{retention} F_{fixation}}{1 + R_{broke} (1 - F_{retention})}]\}$$

$$= \frac{100{,}000\ tonne/yr \times 4.5\ kg/tonne \times 0.0019}{350\ d/yr} \times \{(1 - 0.998) + 0.2 \times [1 - \frac{0.9 \times 0.998}{1 + 0.2 \times (1 - 0.9)}]\}$$

$$= 2.44\ kg/d \times (0.002 + 0.2 \times (1 - 0.8806)$$

$$= 2.44\ kg/d \times 0.02588$$

$$= 0.063\ kg/d$$

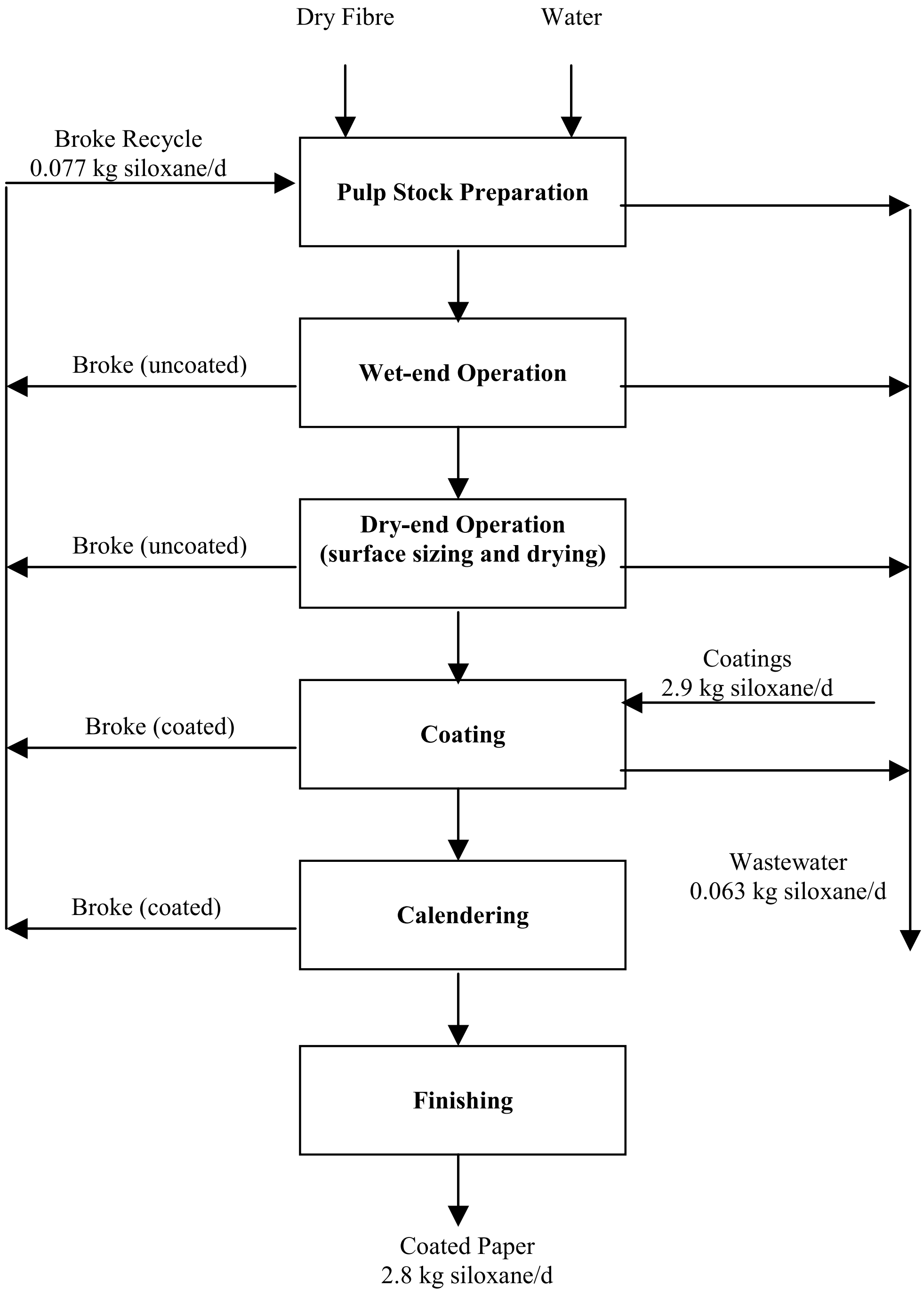

Figure A.4 – Mass Balance on Siloxane Determined for Paper Mill by PRTR Method

ESD Fixation-Based Estimation

The emission of coatings to wastewater from paper coating has been considered to result from two sources: 1) loss from coating operation; and 2) removal from broke processing (Macek, 1991). The siloxane emission can be estimated by the equation

$$E_{water} = \frac{Q_{paper} Q_{product} C_{substance} (1 - F_{fixation}) + Q_{paper} R_{broke} Q_{product} C_{substance} F_{fixation} F_{removal}}{T_{operation}}$$

or

$$E_{water} = \frac{Q_{paper} Q_{product} C_{substance} (1 - F_{fixation} + R_{broke} F_{fixation} F_{removal})}{T_{operation}}$$

where

E_{water}:	daily emission of siloxane from paper coating to wastewater, kg/d
Q_{paper}:	annual paper production, tonne/yr
$Q_{product}$:	use rate of coatings, kg/tonne
$C_{substance}$:	fraction of siloxane in coatings, dimensionless
$F_{fixation}$:	fixation rate of coatings, dimensionless
R_{broke}:	broke generation rate as a fraction of paper production, dimensionless
$F_{removal}$:	rate of coatings removal from broke processing as a fraction of total coatings contained in broke, dimensionless
$T_{operation}$:	number of operation days per year, d/yr

The following values are used in the estimation of the siloxane emission:

Q_{paper} = 100,000 tonne/yr (assumption)
$Q_{product}$ = 0.45% = 4.5 kg/tonne (European Commission, 1996)
$C_{substance}$ = 0.19% = 0.0019 (USEPA, 2001b)
$F_{fixation}$ = 1 – process loss rate = 1 – 0.2% = 0.998 (Macek, 1991)
R_{broke} = 0.2 (Tissier and Migne, 2001)
$F_{removal}$ = 0.1 (Macek, 1991)
$T_{operation}$ = 350 d/yr (assumption)

The siloxane emission to wastewater from paper coating is estimated as

$$E_{water} = \frac{Q_{paper} Q_{product} C_{substance} (1 - F_{fixation} + R_{broke} F_{fixation} F_{removal})}{T_{operation}}$$

$$= \frac{100{,}000\ tonne/yr \times 4.5\ kg/tonne \times 0.0019 \times (1 - 0.998 + 0.2 \times 0.998 \times 0.1)}{350\ d/yr}$$

$$= \frac{855\ kg/yr \times 0.02196}{350\ d/yr}$$

$$= 0.054\ kg/d$$

APPENDIX 7 – DYE EMISSION TO WASTEWATER FROM PAPER MILLS

Presented in Table A.7 are the estimates for dye emission to wastewater from a paper mill based on the PRTR mass balance and ESD fixation-based methods. The PRTR method yielded a higher estimate than the ESD method by 22%. In other words, the PRTR method is more conservative than the ESD method.

Table A.7 – Dye Emission to Wastewater from Paper Mills

Method	PRTR – Mass Balance	ESD – Fixation Based
Emission to Wastewater	104.3 kg/d	85.7 kg/d
Basis	Quantity of pulp = 100,000 tonne/yr Number of operation days = 350 d/yr	Quantity of pulp = 100,000 tonne/yr Number of operation days = 350 d/yr
Assumption	Dye use rate = 10 kg/tonne Dye compound concentration in dye = 1 Dye fixation rate = 0.95 Degree of water closure = 0.4 Broke recycle rate = 0.2	Dye use rate = 10 kg/tonne Dye compound concentration in dye = 1 Dye fixation rate = 0.95 Degree of water closure = 0.4

The higher estimate by the PRTR method results from the inclusion of both water and broke recycles in the analysis of the fate of a dye compound within a papermaking process, whereas only water recycle is considered in the ESD method. The broke recycle adds a source for dye emission through broke repulping, since a fraction of the dyes contained in broke is released upon re-introduction into the papermaking process.

The use rate of dyes depends upon the shade required in the production of printing and writing paper and of tissue paper. It can range from 0.005% by weight for very pale shade up to 10% for very dark shade and black (European Commission, 1996). The rate in the range of 0.01-1.0% is, however, normal.

The fixation rate of dyes varies with the type used, the substrate applied to, and the use of fixation agents. It ranges from a low of 40% up to a high of 99% (European Commission, 1996). Use of fixation agents generally result in a significant increase in fixation rates. Summarized in Table A.8 are fixation rates of four different dyes commonly used in paper production (European Commission, 1996).

Table A.8 – Fixation Rates of Paper Dyes

Type of Dye	Substrate	Fixation Rate	
		Range	Average
Anionic direct	Bleached and unbleached	79-90%	80% or up to 98% with fixing agents or alum
Cationic direct	All types	90-99%	95%
Basic	Bleached pulp	50-70%	60%
	Mechanical pulp	60-80%	70% or up to 95% with anionic fixation
Acid	Sized packaging paper	40-60% or 80-90% with cationic fixation	50% or 85% with cationic fixation

Source: European Commission, 1996

The degree of water closure varies depending upon the type of paper produced. It can range from a low of 40% for printing and writing paper to a high of 95% for paperboard (European Commission, 1996). Summarized in Table A.9 are estimates of water consumption and closure for four different types of paper.

Table A.9 – Estimates of Water Consumption and Closure

Type of Paper	Water Consumption (m^3/tonne)	Water Closure (%)
Printing and writing	40-75	40-70
Tissue	57	40-70
Newsprint	24-35	65-85
Packaging and board	2-20	>95

Source: European Commission, 1996

The amount of broke generated during papermaking is usually 5-20% of paper production, but can be as high as 50% (Tissier and Migne, 2001). An amount of 20% has been suggested as a default value for emission estimation, although a much lower value at 4% has been used by USEPA (Macek, 1991). Broke is generally collected and re-introduced to the papermaking process.

As a summary, the following values are selected for the estimation of dye emissions:

Paper production = 100,000 tonne/yr (assumption)
Dye use rate = 10 kg/tonne (European Commission, 1996)
Fraction of a dye compound in dye = 1 (assumption)
Dye fixation rate = 0.95 (cationic dye) (European Commission, 1996)
Number of operation days per year = 350 d/yr (assumption)
Broke generation rate = 0.2 (Tissier and Migne, 2001)
Rate of water recycle (water closure) = 0.4 (European Commission, 1996)

PRTR Mass Balance Estimation

The PRTR mass balance method considers the impact of both water recycle and broke recycle on the emission of a dye compound to wastewater. Shown in Figure A.5 is a simplified process scheme describing the mass balance on dyes around a non-integrated paper mill (European Commission, 1999). Dry fibre is prepared into pulp by mixing with water in the pulp stock preparation stage. The water used includes both fresh water and recycled water. Also added to this stage are the broke collected from the paper machine and the fibre recovered from white water clarification.

Dyes enter the papermaking process at the pulp stock preparation stage through several routes. The first route is the addition of fresh dyes to mixing chests. The second route is the re-introduction of broke which contains the same fraction of dyes as the paper produced. The third route is the recycled water which contains unfixed dyes. The fourth and final route is the recovered fibre which contains adsorbed dyes.

Dyes leave the papermaking process through the paper produced and the wastewater generated. The paper produced contains fixed dyes and the amount contained depends upon the shade required. The dyes contained in the wastewater generated represent the release from the process.

In the mass balance analysis presented below, a number of assumptions are made:

- The quantity of dry fibre used equals the quantity of paper produced.
- The quantity of the recovered fibre from stock recovery and water clarification is negligible.
- Dyes do not undergo chemical transformation.
- Dyes do not volatilize.
- The water recycled and the wastewater generated have the same chemical composition as the white water generated.

The quantity of dye per tonne of fibre in prepared pulp is an important parameter to the emission estimation. It is a function of dye use rate, water recycle rate and broke generation rate. Such a function can be determined from the mass balance on dyes.

Dyes entering pulp stock preparation stage = Dyes exiting paper machine

i.e.,

Dyes added + Dyes carried in by broke +
Dyes carried in by water recycle + Dyes carried in by recovered fibre
= Dyes carried out by paper + Dyes carried out by broke +
Dyes carried out by white water

Considering that the quantity of the recovered fibre is negligible and the water recycle has the same composition as the white water, the above mass balance relation is translated into the following equations:

$$Q_{paper}Q_{product} + Q_{broke}D_{product}F_{fixation} + (Q_{paper} + Q_{broke})D_{product}(1 - F_{fixation})\frac{Q_{water-recycle}}{Q_{white-water}}$$
$$= Q_{paper}D_{product}F_{fixation} + Q_{broke}D_{product}F_{fixation} + (Q_{paper} + Q_{broke})D_{product}(1 - F_{fixation})$$

$$Q_{paper}Q_{product} + (Q_{paper} + Q_{broke})D_{product}(1 - F_{fixation})\frac{Q_{water-recycle}}{Q_{white-water}}$$
$$= Q_{paper}D_{product}F_{fixation} + (Q_{paper} + Q_{broke})D_{product}(1 - F_{fixation})$$

$$Q_{product} + (1 + \frac{Q_{broke}}{Q_{paper}})D_{product}(1 - F_{fixation})\frac{Q_{water-recycle}}{Q_{white-water}}$$
$$= D_{product}F_{fixation} + (1 + \frac{Q_{broke}}{Q_{paper}})D_{product}(1 - F_{fixation})$$

$$Q_{product} = D_{product} F_{fixation} + (1 + \frac{Q_{broke}}{Q_{paper}}) D_{product} (1 - F_{fixation}) -$$

$$(1 + \frac{Q_{broke}}{Q_{paper}}) D_{product} (1 - F_{fixation}) \frac{Q_{water-recycle}}{Q_{white-water}}$$

$$Q_{product} = D_{product} [F_{fixation} + (1 + \frac{Q_{broke}}{Q_{paper}})(1 - F_{fixation})(1 - \frac{Q_{water-recycle}}{Q_{white-water}})]$$

$$Q_{product} = D_{product} [F_{fixation} + (1 + R_{broke})(1 - F_{fixation})(1 - R_{water-recycle})]$$

$$D_{product} = \frac{Q_{product}}{F_{fixation} + (1 + R_{broke})(1 - F_{fixation})(1 - R_{water-recycle})}$$

where

$D_{product}$: Quantity of dye per tonne of fibre in prepared pulp, kg/tonne
$Q_{product}$: dye use rate, kg/tonne
$F_{fixation}$: dye fixation rate, dimensionless
R_{broke}: broke recycle rate as a fraction of paper production, dimensionless
$R_{water\text{-}recycle}$: water recycle rate as a fraction of white water generation or degree of water closure, dimensionless
Q_{broke}: broke generation rate, tonne/d
$Q_{water\text{-}recycle}$: water recycle rate, tonne/d
$Q_{white\text{-}water}$: white water generation rate, tonne/d

The following values are used in the emission estimation for a dye compound:

annual paper production, Q_{paper} = 100,000 tonne/yr (assumption)
dye concentration, $C_{substance}$ = 1 (assumption)
dye fixation rate, $F_{fixation}$ = 0.95 (European Commission, 1996)
annual operation days, $T_{operation}$ = 350 d/yr (assumption)
dye use rate, $Q_{product}$ = 10 kg/tonne (European Commission, 1996)
broke recycle rate, R_{broke} = 0.2 (Tissier and Migne, 2001)
water recycle rate, $R_{water\text{-}recycle}$ = 0.4 (European Commission, 1996)

The quantity of dye per tonne of fibre in prepared pulp is determined as

$$D_{product} = \frac{Q_{product}}{F_{fixation} + (1 + R_{broke})(1 - F_{fixation})(1 - R_{water-recycle})}$$

$$D_{product} = \frac{10\ kg/tonne}{0.95 + (1 + 0.2)(1 - 0.95)(1 - 0.4)}$$

$$D_{product} = \frac{10\ kg/tonne}{0.95 + 0.036}$$

$$D_{product} = 10.14\ kg / tonne$$

The amount of dye added to the pulp stock preparation stage is determined as

Dye added to pulp stock preparation
= (paper production × dye use rate × dye concentration) ÷ annual operation days
= $(Q_{paper} \times Q_{product} \times C_{substance}) \div T_{operation}$
= (100,000 tonne/yr × 10 kg/tonne × 1) ÷ 350 d/yr
= 2,857.1 kg/d

The amount of dye contained in paper is determined as

Dye contained in paper
= (paper production × quantity of dye per tonne of fibre in prepared pulp × dye concentration × fixation rate) ÷ annual operation days
= $(Q_{paper} \times D_{product} \times C_{substance} \times F_{fixation}) \div T_{operation}$
= (100,000 tonne/yr × 10.14 kg/tonne × 1 × 0.95) ÷ 350 d/yr
= 2,752.3 kg/d

The amount of dye contained in broke is determined as

Dye contained in broke
= (broke recycle rate × paper production × quantity of dye per tonne of fibre in prepared pulp × dye concentration × fixation rate) ÷ annual operation days

= $(R_{broke} \times Q_{paper} \times D_{product} \times C_{substance} \times F_{fixation}) \div T_{operation}$
= (0.2 × 100,000 tonne/yr × 10.14 kg/tonne × 1 × 0.95) ÷ 350 d/yr
= 550.5 kg/d

The amount of dye contained in water recycle is determined as

Dye contained in water recycle
= paper production × (1 + broke recycle rate) × quantity of dye per tonne of fibre in prepared pulp × dye concentration × (1 – fixation rate) × water recycle rate ÷ annual operation days
= $Q_{paper} \times (1 + R_{broke}) \times D_{product} \times C_{substance} \times (1 - F_{fixation}) \times R_{water\text{-}recycle} \div T_{operation}$
= 100,000 tonne/yr × (1 + 0.2) × 10.14 kg/tonne × 1 × (1 – 0.95) × 0.4 ÷ 350 d/yr
= 69.5 kg/d

The amount of dye exiting the pulp stock preparation stage

Dye exiting pulp stock preparation
= dye added to pulp stock preparation + dye contained in broke + dye contained in water recycle + dye contained in recovered fibre
= 2,857.1 kg/d + 550.5 kg/d + 69.5 kg/d + 0
= 3,477.1 kg/d

The amount of dye contained in the white water collected from the paper machine is determined as

Dye contained in white water
= paper production × (1 + broke recycle rate) × quantity of dye per tonne of fibre in prepared pulp × dye concentration × (1 – fixation rate) ÷ annual operation days
= $Q_{paper} \times (1 + R_{broke}) \times D_{product} \times C_{substance} \times (1 - F_{fixation}) \div T_{operation}$
= 100,000 tonne/yr × (1 + 0.2) × 10.14 kg/tonne × 1 × (1 – 0.95) ÷ 350 d/yr
= 173.8 kg/d

The amount of dye emitted to wastewater is determined as

Dye emitted to wastewater
= dye contained in white paper × (1 – water recycle rate)
= 173.8 kg/d × $(1 - R_{\text{water-recycle}})$
= 173.8 kg/d × (1 – 0.4)
= 104.3 kg/d

The mass balance on dye is shown in Figure A.5.

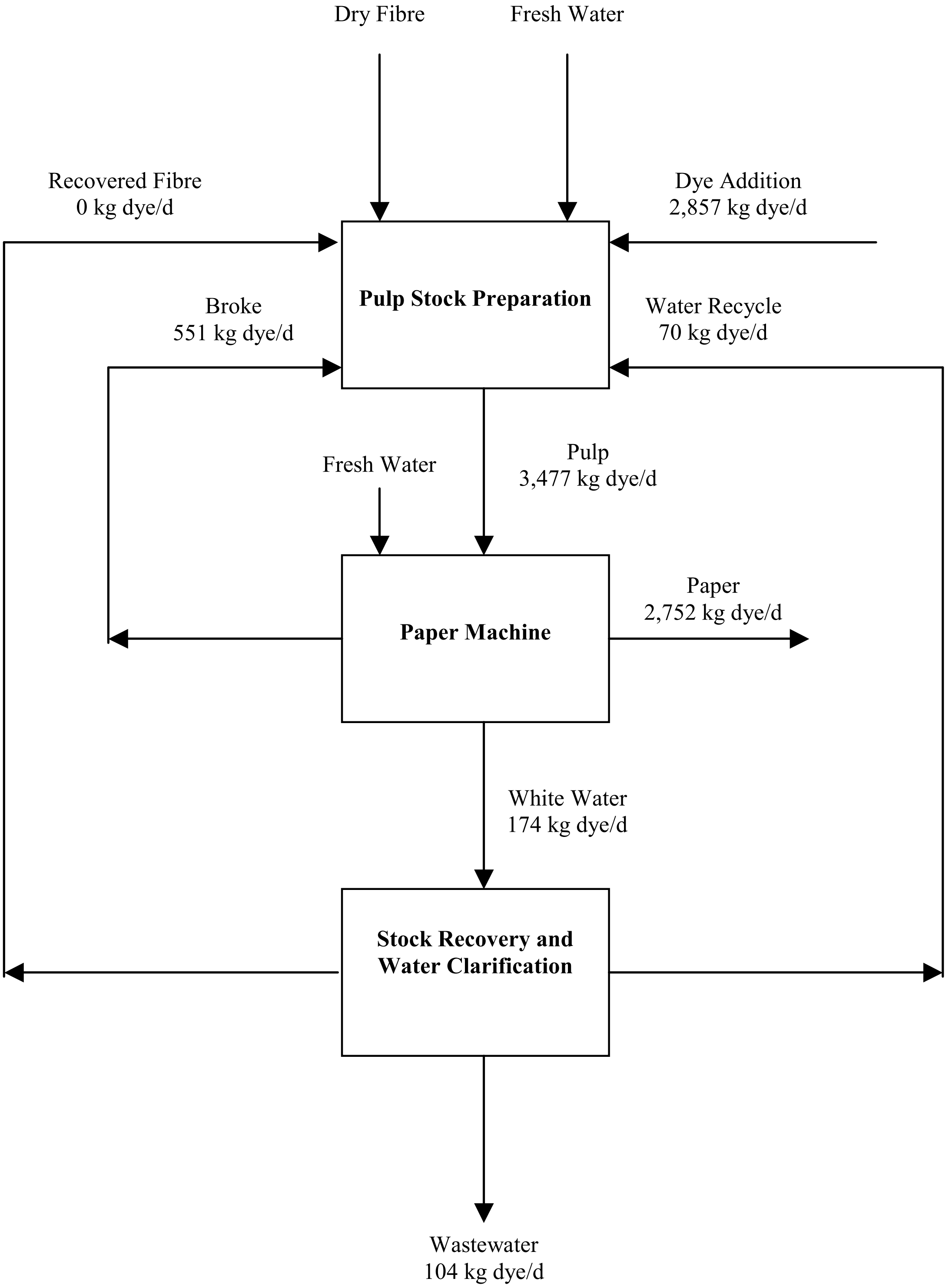

Figure A.5 – Mass Balance on Dye Determined for Paper Mill by PRTR Method

ESD Fixation-Based Estimation

The ESD fixation-based method considers the impact of the degree of water closure, but not broke recycle, on the emission of a dye compound to wastewater (European Commission, 1996). The emission is estimated by the equation

$$E_{water} = \frac{Q_{paper} Q_{product} C_{substance} (1 - F_{fixation})(1 - R_{water-recycle})}{T_{operation}}$$

where

E_{water}:	daily emission of a dye compound to wastewater, kg/d
Q_{paper}:	annual paper production, tonne/yr
$Q_{product}$:	dye use rate, kg/tonne
$C_{substance}$:	fraction of a dye compound in dye, dimensionless
$F_{fixation}$:	dye fixation rate, dimensionless
$R_{water-recycle}$:	water recycle rate or degree of water closure, dimensionless
$T_{operation}$:	number of operation days per year, d/yr

The following values are used in the estimation of the dye emission:

Q_{paper} = 100,000 tonne/yr (assumption)
$Q_{product}$ = 10 kg/tonne (European Commission, 1996)
$C_{substance}$ = 1 (assumption)
$F_{fixation}$ = 0.95 (European Commission, 1996)
$R_{water-recycle}$ = 0.4 (European Commission, 1996)
$T_{operation}$ = 350 d/yr (assumption)

The dye emission to wastewater is determined as

$$E_{water} = \frac{Q_{paper} Q_{product} C_{substance} (1 - F_{fixation})(1 - R_{water-recycle})}{T_{operation}}$$

$$= \frac{100{,}000\ tonne/yr \times 10\ kg/tonne \times 1 \times (1 - 0.95)(1 - 0.40)}{350\ d/yr}$$

$$= 85.7\ kg/d$$

The amount of dye added to the pulp stock preparation stage is determined as

Dye added to pulp stock preparation
= (paper production × dye use rate × dye concentration) ÷ annual operation days
= ($Q_{paper} \times Q_{product} \times C_{substance}$) ÷ $T_{operation}$
= (100,000 tonne/yr × 10 kg/tonne × 1) ÷ 350 d/yr
= 2,857.1 kg/d

The amount of dye contained in water recycle is determined as

Dye contained in water recycle
= paper production × dye use rate × dye concentration × (1 – fixation rate) × water recycle rate ÷ annual operation days
= $Q_{paper} \times Q_{product} \times C_{substance} \times (1 - F_{fixation}) \times R_{water-recycle} \div T_{operation}$
= 100,000 tonne/yr × 10 kg/tonne × 1 × (1 – 0.95) × 0.4 ÷ 350 d/yr

= 57.1 kg/d

The amount of dye contained in the white water collected from the paper machine is determined as

Dye contained in white water
= paper production × dye use rate × dye concentration × (1 – fixation rate) ÷ annual operation days
= $Q_{paper} \times Q_{product} \times C_{substance} \times (1 - F_{fixation}) \div T_{operation}$
= 100,000 tonne/yr × 10 kg/tonne × 1 × (1 – 0.95) ÷ 350 d/yr
= 142.9 kg/d

The amount of dye contained in paper is determined as

Dye contained in paper
= Dye added to pulp stock preparation – Dye emitted to wastewater
= 2,857.1 kg/d – 85.7 kg/d
= 2,771.4 kg/d

The mass balance on dye is shown in Figure A.6.

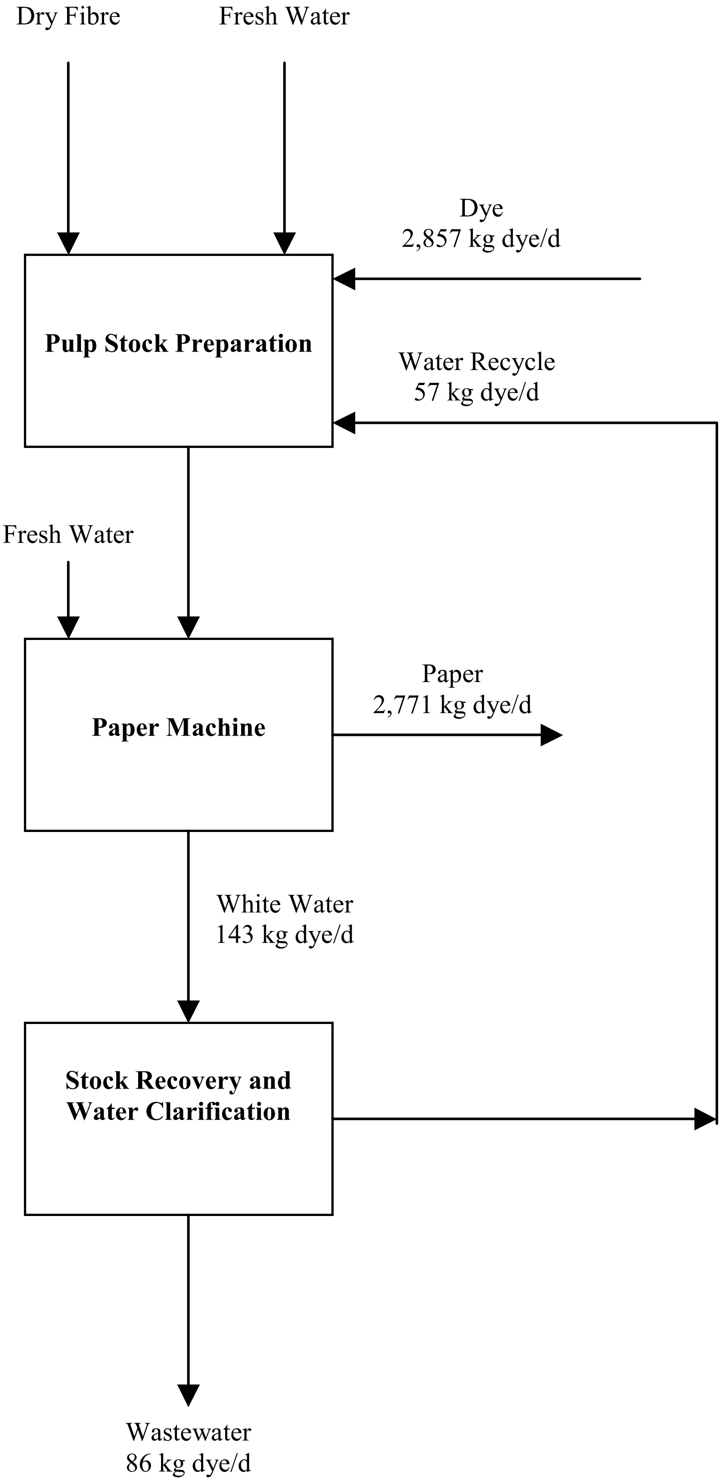

Figure A.6 – Mass Balance on Dye Determined for Paper Mill by ESD Method